酸素過剰な条件下で使用可能な窒素酸化物の選択的還元触媒に関する研究

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［研究成果概要］

１．研究目的

種々の燃焼装置から発生するNOxの低減にはこれまで触媒を用いる排気ガス処理が実施されてきたが，より高い燃焼効率を得る技術として注目されている希薄燃焼方式の排ガス，例えばガスタービンやディーゼルエンジン，希薄燃焼ガソリンエンジンの排ガス中には酸素が過剰に存在するため，これまでの排ガス浄化方式では現実的に困難である。従って，新たな触媒プロセスの開発が望まれてきた。そこで，排気ガス中に微量含まれる未燃炭化水素を還元剤とし，酸素過剰雰囲気下におけるNOx還元反応に高活性・高選択性な触媒の探索，及び反応機構の解明を主な目的とした。本反応では還元剤である炭化水素と酸素の反応（燃焼）を抑制し，還元剤を選択的にNOxと反応させ，効率よくNOxを除去する触媒の開発が不可欠である。このため高度な分子識別能を有する触媒が要求される。本研究は三次元かご状構造をもつゼオライトに着目し特異的な高選択性を示す触媒を設計することを特色としている。

２．研究成果

プロピレンによるNO選択還元反応に対して高活性を示す触媒の探索を行った結果，ゼオライト骨格中に鉄を取り込んだ鉄シリケートが３００℃という低温で本反応に対し高い活性を示すことを見い出した。ディーゼルエンジン等の排ガスの温度は２００－４００℃

であり，このような低温で高活性を示す触媒が有効となる。また，非定常状態法の反応解析から，鉄シリケート上でのNO還元反応の第一ステップは触媒表面上へのプロピレンの吸着であり，吸着した炭化水素とNOから生成した含窒素中間体が分解する過程で窒素を生成する反応機構を提唱した。

鉄シリケート触媒はプロピレンを還元剤とした場合高いNO除去活性を示すが，炭化水素の燃焼活性も高いため，特に高温域では炭化水素と酸素の燃焼反応が優先してNO転化率が低下する。従って，高転化率を示す反応温度域が比較的狭いという欠点がある。本反応系で高いNO除去率を達成するためには炭化水素を酸素よりもNOと選択的に反応させる必要がある。そこで次にこのような選択性の高い触媒について検討を行った。

NO還元反応の選択性の向上を目的として，種々の金属カチオン交換ゼオライトについて，NO還元反応に対する選択性を検討した。これまでの研究でC_3H_8及びC_2H_4を還元剤に用いた場合，Gaイオン交換ゼオライトではNOと炭化水素との反応が極めて高選択的に進むことを見い出した。また，Ga以外にもIn及びZnが比較的高い選択性を有することを示した。これらの交換カチオンはNOxセンサーに使用されていること及び種々のアルキル錯体を容易に生成することが知られていることから，本触媒の高選択性が高いNOx（特にNO_2）と炭化水素の吸着能に起因すると考察した。

また，CH_4による選択還元はこれまで困難とされてきた。しかし都市ガス（天然ガス）を燃料としたガスエンジン・コジェネレーションシステムの排ガスでは未燃炭化水素が主にCH_4であり，CH_4による還元に有効な触媒の開発が期待されている。

Al_2O_3はC_3H_8によるNO還元反応に対して高選択性を示すことが知られているが，CH_4では燃焼反応が優先し，NO還元反応の選択性は極めて低い。これに対し我々はCH_4によるNO還元反応に対してGaおよびInイオン交換ゼオライトが高活性を示し，NO還元の選択性が極めて高いことを見いだした。そこで次にGaおよびInイオン交換ゼオライトの高選択的挙動と反応機構について考察し，高選択性触媒の設計の指針とすることを目的とした。

本触媒系の高選択性がGaとゼオライトの酸点の共存により発現すること及びNO_2が本反応を促進することを明らかにしており，NO酸化によるNO_2の生成にゼオライトの酸性が関与していることを示した。

また、GaおよびInの役割はNOのNO_2への酸化を促進することではなく，NO_2とCH_4の反応の促進であり，本反応の高選択性はゼオライトにイオン交換されたGaおよびIn上でNO_2とCH_4の反応が選択的に進行することに起因すると考えられる。

また，Ga-ZSM-5上でのNO-CH_4-O_2反応において生成するCOおよびCO_2について検討した。反応初期にN_2とCOがほぼ1:1で生成し，CO_2はほとんど生成せず，反応の一次生成物はCOであることがわかった。反応するNOxとCH_4の比がNOx:CH_4=2:1であること，NO_2と

CH_4の反応により本反応が進行することから，本反応は

$$NO_2 + CH_4 + NO = N_2 + CO + 2H_2O$$

の化学量論式で示される。

また，In-ZSM-5でもNO-CH_4-O_2反応では高SV条件下ではCOが選択的に生成し、NO_2-CH_4反応では一次生成物がCO_2であることからGa-,およびIn-ZSM-5は本質的に反応機構は同じであると考えられる。

以上の結果より，次の反応機構が導かれる。すなわちNOが酸化されてNO_2を生成し，NO_2とCH_4の反応により生成した反応中間体がNOとの反応によりN_2を生成する。

$$NO + 1/2O_2 = NO_2 \quad .....(1)$$

$$NO_2 + CH_4 = [X](\text{反応中間体}) + mH_2O \quad ....(2)$$

$$[X] + NO = N_2 + CO + nH_2O \quad ....(3)$$

また本反応では共存水蒸気による反応の阻害が深刻な問題となるが，In-ZSM-5触媒は水蒸気存在下でも比較的高い活性を示すことを見いだしており，今後の展開が期待できる。

発表論文

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Selective Reduction of NO with Propane on Gallium Ion-exchanged Zeolites

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The reduction of NO with propane in the presence of excess oxygen was investigated using gallium ion-exchanged zeolite catalysts, among which ferrierite(Ga-ferrierite) and ZSM-5(Ga-ZSM-5) showed high activity in a wide range of reaction temperature.

The removal of nitrogen oxides(NOx) is a serious environmental problem. Iwamoto et al.[1] reported that copper ion-exchanged ZSM-5(Cu-ZSM-5) showed high catalytic activity for the reduction of NO with hydrocarbons in the presence of oxygen. This study has induced many researches on the application of zeolite-based catalysts to the reduction of NO with hydrocarbons.[2—4] Cu-ZSM-5 is the most efficient catalyst for this reaction among the catalysts which have been reported. However, it is very difficult to accomplish high selectivity for conversion of NO to N_2 on Cu-ZSM-5 if excess oxygen is present, like in diesel or gas turbine exhaust. It is due to the high ability of Cu-ZSM-5 to oxidize hydrocarbons in oxygen-rich atmosphere, resulting in the restriction of the selectivity for this conversion. Therefore, it has been expected for the practical performance to develop the catalyst having less selectivity for oxidation of hydrocarbons even under oxygen-rich conditions. In our experimental studies, it was found that gallium ion-exchanged zeolites showed high activity and selectivity for the reaction of NO with propane even in high oxygen concentration.

Parent zeolites, ZSM-5(molar SiO_2/Al_2O_3 ratio, 23.3), mordenite(19.3), ferrierite(17.8), and Y(14.5) were supplied by Tosoh Corporation. Gallium ion-exchanged

Table 1. Catalytic activities of various ion-exchanged ZSM-5

Catalysts a)	Conv. of NO to N_2 / % [C_3H_8 to CO_X / %]			
	300 °C	400 °C	500 °C	600 °C
Ga-ZSM-5 (79)	71.9 [29.5]	91.1 [53.8]	87.2 [91.9]	85.9 [97.6]
Al-ZSM-5 (53)	62.8 [28.1]	85.0 [55.4]	74.8 [73.1]	43.4 [90.0]
Zn-ZSM-5 (97)	18.1 [7.1]	45.3 [18.6]	93.0 [88.0]	56.5 [96.0]
In-ZSM-5 (65)	76.0 [30.9]	85.8 [99.9]	53.8 [100]	57.7 [100]
Sn-ZSM-5 (104)	54.8 [23.8]	43.0 [47.0]	25.9 [69.7]	16.4 [97.1]
H-ZSM-5 (100)	69.6 [38.5]	86.6 [72.2]	73.2 [86.5]	
Cu-ZSM-5 (111)	60.5 [92.1]	46.1 [100]	46.9 [100]	45.2 [100]

a) Catalysts have been called cation-type of zeolite (degree of ion exchange / %).

zeolites were prepared by the ion-exchange of the ammonium form zeolites using aqueous solutions of $Ga(NO_3)_3 \cdot 9H_2O$ at 95 °C for 24 h, followed by calcination at 500 °C. Copper ion-exchanged ZSM-5, as a reference catalyst, was prepared according to the method reported by Iwamoto et al.5) ZSM-5 catalysts exchanged with other cations were prepared using nitrate or chloride solutions.

The measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 1000 ppm propane was fed on to 0.5 g catalyst at a rate of 100 $cm^3 \cdot$(STP) min^{-1}. After reaching steady-state, effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO.

Table 1 summarizes the activities of various ion-exchanged ZSM-5 catalysts. Ga-ZSM-5 showed high activity in a wide range of reaction temperature(300 - 600 °C). It should be noted that the conversion level of propane was lower on Ga-ZSM-5 than on Cu-ZSM-5, particularly in the low temperature region, although the conversion of NO on Ga-ZSM-5 was higher than on Cu-ZSM-5. Propane was almost completely consumed on Cu-ZSM-5 above 400 °C because of the high ability of this catalyst for the oxidation of propane. The high oxidation ability would rather limit the reaction of NO to N_2 in the presence of excess oxygen. The ability of Ga-ZSM-5 catalyst for the oxidation of propane was moderate, so that high

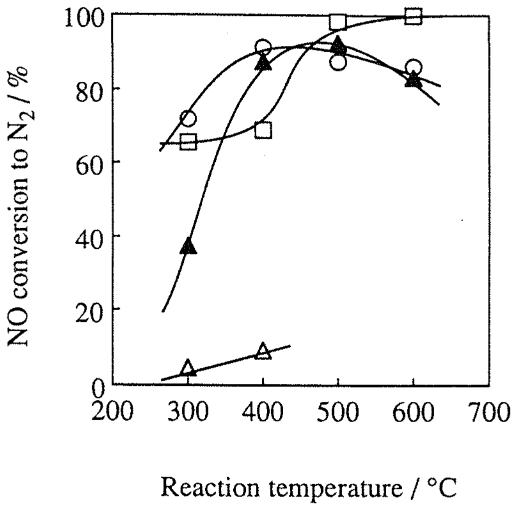

Fig.1. Variation in the catalytic activities of various gallium ion-exchanged zeolites as a function of reaction temperature. Catalysts:
○, Ga-ZSM-5(79); ▲, Ga-mordenite(106);
□, Ga-ferrierite(91); △, Ga-USY(103).

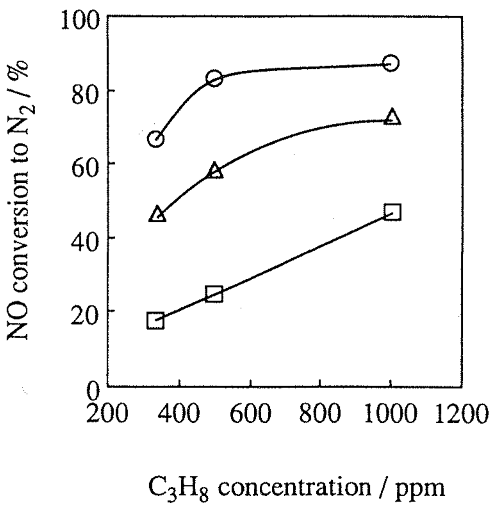

Fig.2. Selective reduction of NO as a function of C_3H_8 concentration over Ga-ZSM-5, H-ZSM-5, and Cu-ZSM-5. Catalysts: ○, Ga-ZSM-5(79);
△, H-ZSM-5(100); □, Cu-ZSM-5(111).
Reaction temperature, 500°C.

efficiency was attained for the reaction of propane with NO. Although Zn-ZSM-5 showed high activity at 500 °C, the activity was not high in the other temperature region.

The difference in the catalytic effects between gallium cation and proton on the catalytic activities of ZSM-5 are characteristic at higher reaction temperature than 500 °C. Ga-ZSM-5 was more active for the reduction of NO than H-ZSM-5 above 500 °C, although no remarkable difference was observed in the temperature range 300 - 400 °C.

Figure 1 compares the catalytic activities of various zeolites exchanged with gallium cations. The activity depended on the type of zeolites. Ga-ZSM-5 and Ga-ferrierite were highly active among these catalysts at all temperatures, and NO was completely reduced to N_2 above 500 °C on Ga-ferrierite under these reaction conditions. Although Ga-mordenite showed relatively high activity above 400 °C, the activity was poor below this temperature. Ga-Y showed low activity at these temperatures.

The difference in the catalytic performance of Ga-ZSM-5, H-ZSM-5, and Cu-ZSM-5 became more remarkable, when the concentration of propane in the reactant mixture was smaller. Figure 2 shows the effect of propane concentration on the conversion of NO to N_2 at 500 °C. Propane was completely consumed on all these catalysts when the concentration of propane was smaller than 500 ppm. The conversion of NO on Cu-ZSM-5 remarkably decreased and less than 20% conversion was shown when the concentration of propane was lowered to 333 ppm. On the contrary, 67% conversion of NO was maintained on Ga-ZSM-5 under the same reaction conditions, although almost the same amount of propane was converted on both of these catalysts. The conversion of NO was lower on H-ZSM-5 than on Ga-ZSM-5 under all these conditions.

From these results, it is shown that Ga-ZSM-5 shows high activity and selectivity for the reduction of NO with propane, even in the presence of excess oxygen and in the wide range of temperatures(300 - 600 °C). No such catalysts showing high activity under these conditions have been reported. Although it has been reported that Cu-ZSM-5 shows high activity for this reaction at low temperatures and high SV, the working temperature range of Cu-ZSM-5 is somewhat limited due to its low selectivity for the reduction of NO with hydrocarbon compared with Ga-ZSM-5. High selectivity of Al_2O_3 catalyst for NO-hydrocarbon reaction has been reported,6) while its activity is smaller than Ga-ZSM-5 catalyst.

Although further studies are required to understand the effect of gallium on the catalytic activity, it is concluded in this study that NO can more effectively be reduced into nitrogen on gallium ion-exchanged zeolites with smaller amounts of propane than on Cu-ZSM-5 and on proton type zeolites, and that gallium ion-exchanged zeolites have high possibility for the practical use under excess oxygen condition.

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Gallium ion-exchanged zeolite as a selective catalyst for reduction of nitric oxide with hydrocarbons under oxygen-rich conditions

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Selective reduction of nitric oxide with propane in the presence of excess oxygen was investigated using gallium ion-exchanged zeolite catalysts. Gallium ion-exchanged ferrierite (Ga-ferrierite) showed extremely high selectivity for this reaction under oxygen-rich conditions (10%). The molar ratio of reacted NO to consumed C_3H_8 was found to be near 3 on Ga-ferrierite.

Keywords: Nitric oxide; selective reduction; propane; gallium; zeolite

1. Introduction

Emission of nitrogen oxides (NOx) from combustion exhaust stream has attracted much attention. It had widely been accepted that selective catalytic reduction (SCR) in oxidizing atmosphere is only possible with ammonia, and hydrocarbons are ineffective for this reaction. Although ammonia SCR process is now practically applied to stationary sources, this process is unsuitable for small scale exhaust. Recently, Iwamoto et al. [1] reported that selective reduction of NO with hydrocarbons proceeds on copper ion-exchanged ZSM-5 (Cu-ZSM-5) in the presence of oxygen. Their study has induced many researches on the application of zeolite-based catalysts to the reduction of NO with hydrocarbons [2–4]. Although Cu-ZSM-5 is the most efficient catalyst for this reaction among the catalysts which have ever been reported, the selectivity for NO–hydrocarbon reaction is insufficient, due to the high ability of Cu-ZSM-5 to oxidize hydrocarbons in oxygen-rich atmosphere. Therefore, it has been expected for the practical performance to develop the catalyst having high

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selectivity for NO–hydrocarbon reaction even under oxygen-rich conditions like in ammonia SCR process. High catalytic selectivity of Al_2O_3 [5] and H-form zeolites [2] for NO–hydrocarbon reaction has been reported by Hamada et al., while their activities are not enough under high GHSV condition. In our previous experimental studies, it was found that gallium ion-exchanged zeolites show high activity and selectivity for the reduction of NO with C_3H_8 even in high oxygen concentration [6]. In this study, we have found that Ga-ferrierite shows extremely high selectivity and the molar ratio of reacted NO to consumed C_2H_8 is near 3. Such a catalyst showing higher selectivity than Ga-ferrierite has never been reported.

2. Experimental

Zeolites used in this study, ZSM-5 (molar SiO_2/Al_2O_3 ratio, 23.3), mordenite (19.3), ferrierite (17.8), and ultra stable Y (14.5) were supplied by Tosoh Corporation. Gallium ion-exchanged zeolites were prepared by ion-exchange of ammonium form zeolites using aqueous solutions of $Ga(NO_3)_3 \cdot 9H_2O$ at 95°C for 24 h, followed by calcination at 500°C. The concentration of Ga cations in the solutions was adjusted to the level that the ratio of dissolved gallium ions to Al cations is one third (100% ion-exchange level as Ga^{3+}). Copper ion-exchanged ZSM-5, as a reference catalyst, was prepared according to the method reported by Iwamoto et al. [7]. The zeolites will be abbreviated, for instance, to Ga-ZSM-5 (100) etc. The values in parentheses represent the level of cation exchange.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 1000 ppm C_3H_8 was fed to 0.5 g catalyst at a rate of 100 cm^3(STP) min^{-1} unless otherwise specified. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence detection of NO. The catalytic activity was evaluated by the level of NO conversion to N_2.

3. Results and discussion

Fig. 1 compares NO conversion on Cu-, H- and Ga-ZSM-5 as a function of reaction temperature. Ga-ZSM-5 showed higher catalytic activity than Cu-ZSM-5 in the temperature range of 300–600°C under these reaction conditions. C_3H_8 was almost completely consumed on Cu-ZSM-5 above 400°C because of the high ability of this catalyst for the oxidation of C_3H_8. The high oxidation ability would rather limit the reaction of NO to N_2 in the presence of excess oxygen.

The difference in the catalytic performance between gallium and proton type ZSM-5 are characteristic at higher reaction temperature than 500°C. Ga-ZSM-5

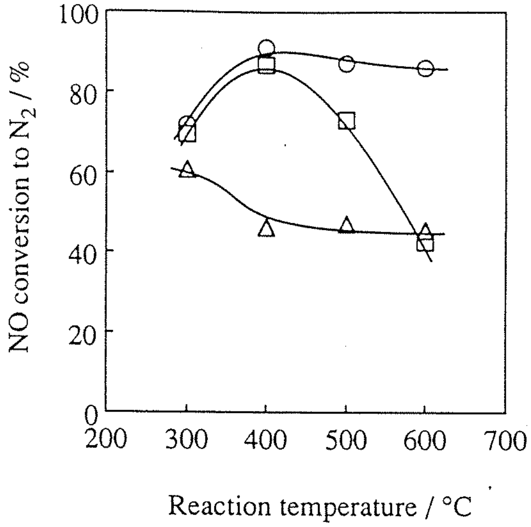

Fig. 1. Variation in the catalytic activities of various ion-exchanged ZSM-5 as a function of reaction temperature. Catalysts: (□) H-ZSM-5(100); (△) Cu-ZSM-5 (111); (○) Ga-ZSM-5 (79). NO, 1000 ppm; C_3H_8, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

was more active for this reaction than H-ZSM-5 above 500°C, although no remarkable difference was observed in the temperature range 300–400°C.

Fig. 2 shows the relationships between NO conversion and C_3H_8 conversion on these cation-exchanged ZSM-5 catalysts. The selectivity for NO-hydrocarbon

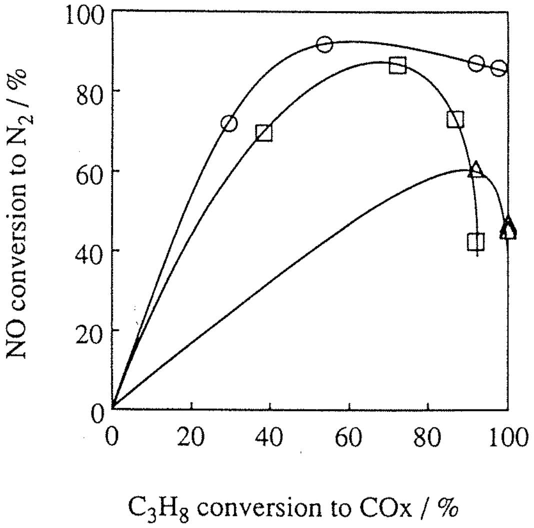

Fig. 2. Relationships between NO conversion and C_3H_8 conversion on various ion-exchanged ZSM-5. Catalysts: (□) H-ZSM-5 (100); (△) Cu-ZSM-5 (111); (○) Ga-ZSM-5 (79). NO, 1000 ppm; C_3H_8, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g; reaction temperature, 300–600°C.

Table 1
Catalytic activities of H-form and gallium ion-exchanged zeolites

Catalyst	NO conversion to N_2 (%) [C_3H_8 conversion to COx (%)]			
	300°C	400°C	500°C	600°C
Ga-ZSM-5 (79)	71.9 [29.5]	91.1 [53.8]	87.2 [91.9]	85.9 [97.6]
Ga-ferrierite (91)	65.5 [21.8]	69.1 [22.4]	98.5 [40.0]	100 [76.1]
Ga-mordenite (106)	37.5 [12.0]	87.4 [34.8]	92.4 [86.2]	83.3 [97.7]
Ga-USY (103)	4.7 [1.2]	9.4 [3.1]	13.0 [13.9]	17.4 [46.5]
H-ZSM-5	69.6 [38.5]	86.6 [72.2]	73.2 [86.5]	42.7 [92.1]
H-ferrierite	64.6 [22.6]	72.7 [24.2]	52.3 [24.4]	58.2 [47.8]
H-mordenite	28.9 [11.0]	74.0 [40.8]	72.7 [70.5]	40.6 [99.9]

Reaction conditions: NO, 1000 ppm, C_3H_8, 1000 ppm, O_2, 10%, total flow rate, 100 cm^3 min^{-1}, catalyst weight, 0.5 g.

reaction against hydrocarbon–O_2 reaction varied quite differently among these catalysts particularly at high temperature. The ratio of NO conversion to C_2H_8 conversion is a measure of selectivity, and the selective catalyst provides larger ratio. Ga-ZSM-5 was remarkably selective among these catalysts particularly at high temperatures.

Table 1 shows the effect of the kind of zeolite on the catalytic activity for NO reduction. The catalytic activity and selectivity for NO reduction varied with the kind of zeolite. Fig. 3 summarizes the results of these Ga- and H-zeolites. It must be noted that gallium ion-exchanged zeolites were more selective than

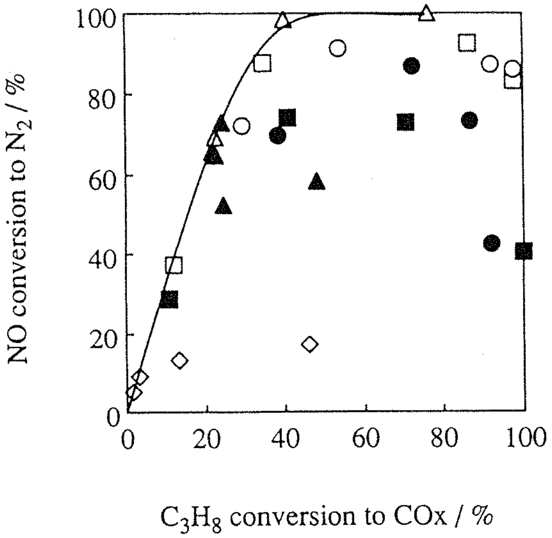

Fig. 3. Relationships between NO conversion and C_3H_8 conversion on Ga- and H-zeolites. Catalysts: (○) Ga-ZSM-5 (79); (●) H-ZSM-5; (△) Ga-ferrierite (91); (▲) H-ferrierite; (□) Ga-mordenite (103); (■) H-mordenite; (◇) Ga-USY (106). NO, 1000 ppm; C_3H_8, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g; reaction temperature, 300–600°C.

proton-type zeolites, irrespective of the kind of zeolite. Ga-ferrierite was most selective among these catalysts.

Fig. 4 shows the ratio in conversion of NO to that of C_3H_8 to COx on various catalysts at 500°C. The selectivity of Ga- and H-ZSM-5 lowered with increasing C_3H_8 concentration, due to increasing the contribution of combustion reaction. On the contrary, C_3H_8 reacted selectively with NO, and the reaction with O_2 hardly proceeded even under oxygen-rich conditions on Ga-ferrierite. The selectivity of Cu-ZSM-5 was extremely low under these reaction conditions. The limiting molar ratio of reacted NO to consumed C_3H_8 on Ga-ferrierite and Ga-ZSM-5 is near 3. This ratio corresponds to the following stoichiometry:

$$3NO + C_3H_8 + kO_2 = \tfrac{3}{2}N_2 + mCO + nCO_2 + 4H_2O, \quad k = \tfrac{1}{2}(m + 2n + 1). \tag{1}$$

According to this stoichiometry, 1000 ppm NO completely reduced to N_2 with 333 ppm C_3H_8 (33.3% C_3H_8 conversion under the present conditions). No catalyst showed higher selectivity than this ratio.

Although further studies are required to understand the effect of gallium on the catalytic activity, it is concluded in this study that NO can more effectively be reduced into nitrogen on gallium ion-exchanged zeolites with smaller amounts of C_3H_8 than on Cu-ZSM-5 and on H-form zeolites. The molar ratio of reacted NO to consumed C_3H_8 is near 3 on gallium ion-exchanged zeolites. Ga-ferrierite is the most selective catalyst which has ever been reported. It is thus

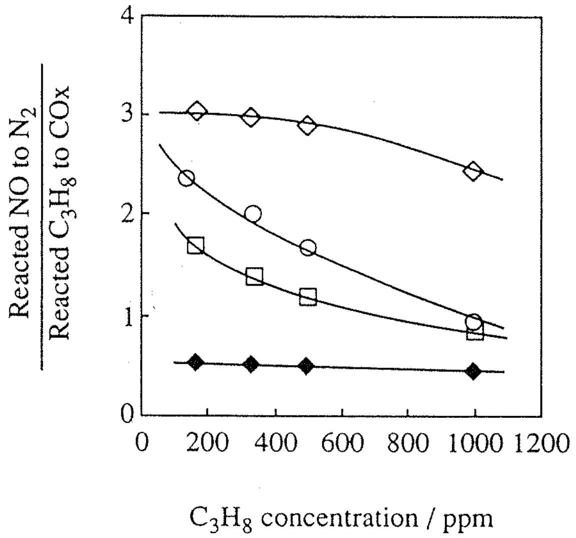

Fig. 4. Ratio in reacted NO to reacted C_3H_8 on various ion-exchanged zeolites. Catalysts: (○) Ga/H-ZSM-5 (79); (◇) Ga/H-ferrierite (91); (△) H-ZSM-5; (◆) Cu-ZSM-5 (111). NO, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g; reaction temperature, 500°C.

concluded that gallium ion-exchanged zeolites are strong candidates for practical removal of NO, alternatively for ammonia SCR process.

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Selective catalytic reduction of nitric oxide by ethene on gallium ion-exchanged ZSM-5 under oxygen-rich conditions

applied catalysis
Letter

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Abstract

Selective reduction of nitric oxide by ethene in the presence of excess oxygen was investigated using a gallium ion-exchanged ZSM-5 catalyst. Ga-ZSM-5 showed high activity in a wide range of reaction temperatures. In addition, Ga-ZSM-5 showed extremely high selectivity for this reaction under oxygen-rich conditions (10%). The limiting molar ratio of reacted NO to consumed ethylene was found to be 2. High catalytic activity was maintained even under high space velocity at 500°C on Ga-ZSM-5.

Keywords: ethene; gallium; nitric oxide; selective reduction; ZSM-5

INTRODUCTION

The reduction of nitrogen oxides (NO_x) to molecular nitrogen is a significant task for environmental chemistry. A selective catalytic reduction (SCR) process with ammonia in an oxidizing atmosphere can be carried out over oxide catalysts such as V_2O_5–TiO_2 and this process has been used for the practical removal of NO_x from stationary sources [1]. It had been accepted that this SCR process in an oxidizing atmosphere is only possible when using ammonia as a reducing reagent, and that hydrocarbons are ineffective for this reaction. A new type of catalytic reduction of NO with hydrocarbons has been reported using Cu-ZSM-5 [2], Fe-silicate [3], and Ce-ZSM-5 [4], of which the selectivities for the NO–hydrocarbon reaction are insufficient due to their high ability to oxidize the hydrocarbons in oxygen-rich conditions. Therefore, it has

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been necessary from a practical point of view to develop a catalyst having less selectivity for the oxidation of hydrocarbons even under oxygen-rich conditions. High catalytic selectivity of Al_2O_3 and H-form zeolites for the NO–hydrocarbon reaction has been reported by Hamada and coworkers [5,6], while their activities are small under high space velocity conditions. In our previous experimental studies, it was found that gallium ion-exchanged zeolites show high activity and selectivity for the reaction of NO with propane even under high oxygen partial pressures [7]. Recently, it was also found that the limiting molar ratio of reacted NO to consumed propane is near to 3 [8]. No catalyst showing a higher selectivity than gallium ion-exchanged zeolites have ever been reported.

On the other hand, it has been reported that the catalytic performance is greatly affected by the kind of hydrocarbons used [1]. It has been suggested that for practical purposes ethylene is a better reducing reagent than propane when used in the diesel engine, because ethylene is a major component in the diesel exhaust stream. In this study, we report that a highly selective reduction of NO by ethylene proceeded on gallium ion-exchanged ZSM-5 and that its high activity was maintained even under a high space velocity.

EXPERIMENTAL

Na-ZSM-5 having a molar SiO_2/Al_2O_3 ratio of 23.3 was supplied by the Tosoh Corporation. Gallium ion-exchanged ZSM-5 (Ga-ZSM-5(92)) was prepared by the ion-exchange of ammonium form ZSM-5 using an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$ at 95°C for 24 h, followed by calcination at 500°C. Copper ion-exchanged ZSM-5 (Cu-ZSM-5(111)), as a reference catalyst, was prepared according to the method reported by Iwamoto et al. [9]. Values in parentheses for the expression of the catalysts represent the level of cation exchange determined by ICP.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 167–1000 ppm ethylene was fed to 0.05–0.5 g catalyst at a rate of 100–200 cm^3 (STP)$\cdot min^{-1}$. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence detection of NO_x. The catalytic activity was evaluated by the level of NO conversion to nitrogen.

RESULTS AND DISCUSSION

As we have already reported [7,8], the reaction of NO by propane proceeds on Ga-ZSM-5 selectively in an oxygen-rich atmosphere, according to the following stoichiometry:

$$3NO + C_3H_8 + kO_2 = 3/2N_2 + mCO + nCO_2 + 4H_2O \qquad (1)$$

where $k=1/2(m+2n+1)$, $m+n=3$. As is shown in Fig. 1, NO conversion increased with increasing concentration of ethylene. Furthermore, NO conversion reached 90% when the ethylene concentration was 500 ppm. Thus it was perceived that NO reduction proceeded with an extremely high selectivity. However, NO conversion was limited by the ethylene concentration, and the limiting molar ratio of reacted NO to consumed ethylene was 2. In addition, the selectivity for CO increased with increasing space velocity, showing that CO_2 was formed by the secondary reaction of CO and O_2. Therefore it is concluded that the limiting stoichiometry of this reaction with ethylene is as shown in eqn. (2):

$$2NO+C_2H_4+kO_2=N_2+mCO+nCO_2+2H_2O \qquad (2)$$

where $k=1/2(m+2n)$, $m+n=2$. When the concentration of ethylene was 1000 ppm, the selectivity was lowered because excessive ethylene was consumed with the combustion reaction with oxygen. However, NO was almost exclusively reduced to nitrogen.

It is known that the reaction proceeds in a one-to-one molar ratio of ammonia to NO_x in the NH_3-SCR process [10]. Ga-ZSM-5 shows a high selectivity for the reduction of NO by ethylene as in the NH_3-SCR process. From these results, it was revealed that the Ga-ZSM-5 exhibits a high selectivity not only for ethylene but also for propane.

Fig. 2 compares the catalytic activities of H-, Cu-, and Ga-ZSM-5. The maximum conversion of NO was expected to be 50% from eqn. (2) under the above reaction conditions (dotted line in Fig. 2). Ga-ZSM-5 showed a high activity in a wide range of reaction temperatures (300–600°C), and NO conversion reached 50% above 400°C. Ethylene was almost completely consumed to CO and CO_2 on all of these catalysts under these reaction conditions. The

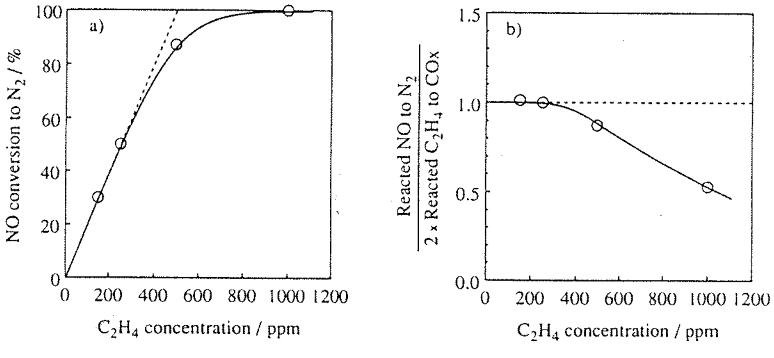

Fig. 1. NO reduction on Ga-ZSM-5(92) as a function of ethylene concentration. Reaction conditions: NO, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g; reaction temperature, 500°C.

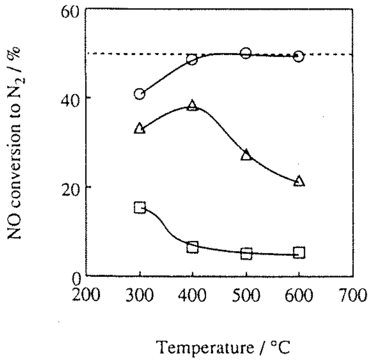

Fig. 2. Variation in NO conversion on Ga-, H-, and Cu-ZSM-5 as a function of reaction temperature. Catalysts: (○) Ga-ZSM-5(92); (△) H-ZSM-5(100); (□) Cu-ZSM-5(111). Reaction conditions: NO, 1000 ppm; C_2H_4, 250 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

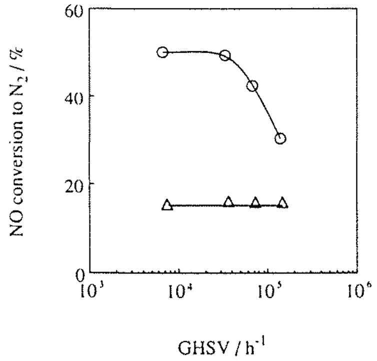

Fig. 3. Correlation between NO conversion and space velocity. Catalyst: (○) Ga-ZSM-5(92) reaction temperature, 500°C; (△) Cu-ZSM-5(111) reaction temperature, 300°C. Reaction conditions: NO, 1000 ppm; C_2H_4, 250 ppm; O_2, 10%; total flow-rate, 100-200 $cm^3 \cdot min^{-1}$; catalyst weight, 0.05-0.5 g.

C_2H_4–O_2 reaction proceeded preferentially at higher temperatures on Cu-ZSM-5 and H-ZSM-5.

It has been reported that the reaction of NO with hydrocarbon is greatly affected by the oxygen concentration on the Cu-ZSM-5 or noble metal catalysts. In contrast, the activity of Ga-ZSM-5 is not affected by oxygen in the concentration range 2–10%, while this reaction did not proceed in the absence of oxygen. Therefore, although oxygen is a necessary component for this reaction, it never inhibits the NO (or NO_2)–C_2H_4 reaction on Ga-ZSM-5. These results show that Ga-ZSM-5 possesses an extremely high selectivity for the reduction of NO by ethylene, even in the presence of excess oxygen and in a wide range of reaction temperatures. Catalysts showing such a high activity under these conditions have never previously been reported.

Not only a high selectivity, but also a high activity is required under high space velocity for the practical removal of NO_x from diesel exhaust. Fig. 3 shows the effect of space velocity on NO conversion over Ga-ZSM-5 and Cu-ZSM-5. Ga-ZSM-5 showed a high activity even under high space velocity, for instance GHSV=144 000 h^{-1}. Although it has been reported that Cu-ZSM-5 shows a high activity for this reaction at low temperatures and a high space velocity [1], NO conversion on this catalyst is limited due to its low selectivity for the reduction of NO by hydrocarbon compared with Ga-ZSM-5 under these reaction conditions. A high selectivity of an alumina catalyst for the NO–hydrocarbon reaction has also been reported [6], but its activity is less than the Ga-ZSM-5 catalyst at high space velocity.

CONCLUSION

From this study we conclude that the selective catalytic reduction of NO by ethylene proceeds on Ga-ZSM-5, and that its selectivity is extremely high as is the NO–NH_3 reaction in the practical NH_3-SCR process, even in an oxygen-rich atmosphere. As Ga-ZSM-5 shows a high activity under a relatively high space velocity, this catalyst shows a practical potential for the removal of NO_x under oxygen-rich conditions. Further studies on the effect of the presence of steam on catalytic activity, the role of gallium, and the reaction mechanism are now in progress.

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Selective Reduction of Nitrogen Monoxide with Methane or Ethane on Gallium Ion-exchanged ZSM-5 in Oxygen-rich Atmosphere

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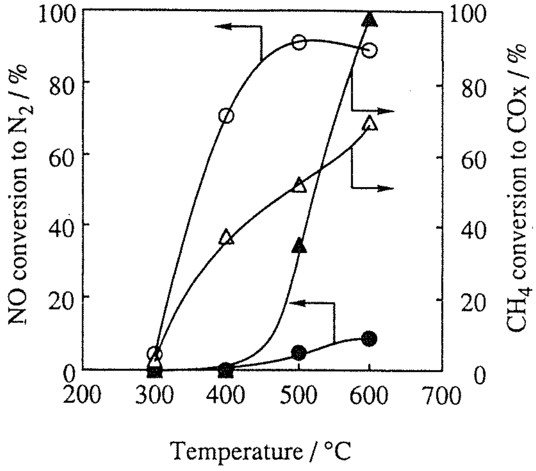
Selective reduction of nitric oxide with methane or ethane in the presence of excess oxygen was investigated using a gallium ion-exchanged ZSM-5 zeolite catalyst(Ga-ZSM-5). Ga-ZSM-5 was highly active and selective for NO reduction above 400 °C. The limiting molar ratios of reacted NO to consumed carbon in C_2H_6 and CH_4 at 500 °C were found to be 1.5 and 2, respectively.

The reduction of nitrogen oxides(NOx) to molecular nitrogen is an important task for environmental chemistry. A new type of catalytic reduction of NO with hydrocarbons has been reported using various cation-exchanged zeolites,[1 - 4] metallosilicates,[5, 6] Al_2O_3,[7, 8] and SiO_2-Al_2O_3.[9] It was shown in our previous work[10] that gallium ion-exchanged zeolites were active, and were most selective for reduction of NO with C_3H_8 among these catalysts.

It has been reported by Iwamoto and co-workers[11] that NO was reduced by C_2 or higher olefins and that H_2 and CO were ineffective for this reaction on Cu-ZSM-5. Hamada et al.[12] have studied the catalytic activity of Al_2O_3 for reduction of NO with various hydrocarbons. They reported that NO was hardly reduced when CH_4 and benzene were used as reductants. Therefore, it has been considered that CH_4 and C_2H_6 are rather inactive for reduction of NO.

In this study, we have found that Ga-ZSM-5 shows high catalytic activity and extremely high selectivity for reduction of NO with CH_4 or C_2H_6. It was also found that the molar ratios of reacted NO to consumed carbon in CH_4 and C_2H_6 were 2 and 1.5, respectively.



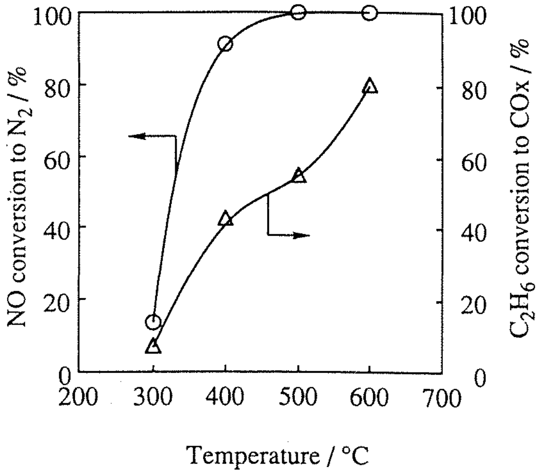


Fig.1. Variation in NO conversion and CH_4 conversion on Ga-ZSM-5(open symbol) and Al_2O_3(solid symbol) as a function of reaction temperature.
○ ●, NO conversion to N_2;
△ ▲, CH_4 conversion to COx.
NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

Fig.2. Variation in NO conversion and C_2H_6 conversion on Ga-ZSM-5 as a function of reaction temperature.
○, NO conversion to N_2;
△, C_2H_6 conversion to COx.
NO, 1000 ppm; C_2H_6, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

Na form ZSM-5 having a molar SiO_2/Al_2O_3 ratio of 23.3 was supplied by Tosoh Corporation. Gallium ion-exchanged ZSM-5(Ga-ZSM-5(92)) was prepared by ion-exchange of ammonium form ZSM-5 using an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$ at 95 °C for 24 h, followed by calcination at 500 °C. The solution was adjusted to give a concentration of gallium cations equal to one third of Al(100% ion-exchange level as Ga^{3+}). The value in parenthesis represents the level of gallium exchange. Alumina, as a reference catalyst, was obtained from Catalysts & Chemical Ind. Co.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 150 - 1000 ppm CH_4 or C_2H_6 was fed on to 0.5 g catalyst at a rate of 100 cm^3(STP)$\cdot min^{-1}$. After reaching steady-state, effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO and NO_2. The catalytic activity was evaluated by the level of NO conversion to N_2.

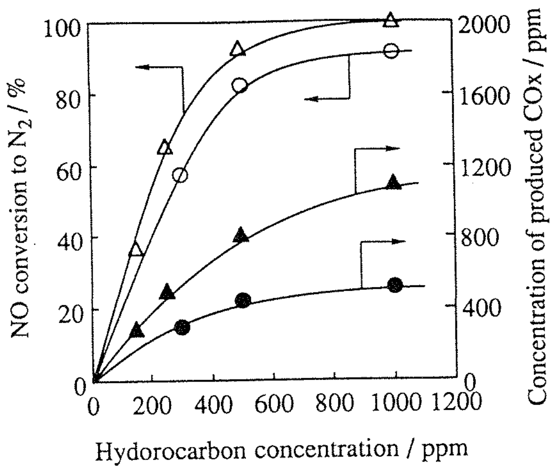


Fig.3. Variation in NO conversion(open symbol) and concentration of produced COx(solid symbol) of Ga-ZSM-5 as a function of hydorocarbon concentration.
Hydorocarbons: CH_4(○, ●); C_2H_6(△, ▲).
NO, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.
Reaction temperature, 500 °C.

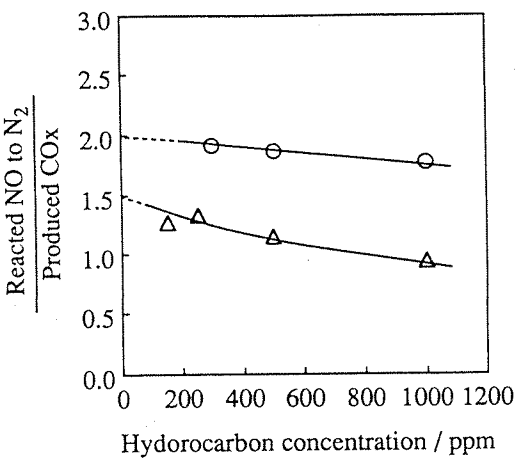


Fig.4. Ratio of reacted NO to produced COx on Ga-ZSM-5.
Hydrocarbons: ○, CH_4; △, C_2H_6.
NO, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.
Reaction temperature, 500 °C.

Figure 1 shows the temperature dependence of the catalytic activity of Ga-ZSM-5 for NO reduction with CH_4 in comparison with Al_2O_3. NO was hardly reduced to N_2 at 300 °C on Ga-ZSM-5. The level of NO conversion, however, increased with increasing reaction temperature, and finally 90% NO was reduced above 500 °C. Hamada and co-workers reported[12)] that reduction of NO with CH_4 slightly proceeded on Al_2O_3 catalyst only when reaction temperature was higher than 500 °C. As shown in this figure, the catalytic activity of Al_2O_3 was extremely low compared with that of Ga-ZSM-5. On Al_2O_3 catalyst, CH_4 was mainly consumed by reaction with O_2, resulting in the low level of NO conversion. In contrast, NO was selectively reduced to N_2 on Ga-ZSM-5.

The results of reduction of NO with C_2H_6 on Ga-ZSM-5 were shown in Fig.2. The levels of NO conversion with C_2H_6 were comparable or a little higher than those with CH_4 on this catalyst.

Figure 3 shows the effect of hydrocarbon concentration on the catalytic activity of Ga-ZSM-5 at 500 °C. NO conversion increased with increasing concentration of CH_4 and C_2H_6.

It should be noted that Ga-ZSM-5 showed high catalytic activity for reduction of NO even in the presence of small amounts of CH_4 and C_2H_6. It was shown in our previous work$^{13)}$ that gallium ion-exchanged zeolites showed high activity and selectivity for the reduction of NO with C_3H_8, and that the limiting molar ratio of reacted NO to produced COx was near unity.

Figure 4 shows the relationship between the molar ratio of reacted NO to produced COx and the concentration of reductants. The limiting molar ratio of reacted NO to consumed carbon in C_2H_6 and CH_4 was 1.5, and 2, respectively. These ratios were almost independent of the concentration of hydrocarbons. Reduction of NO with CH_4 and C_2H_6 proceeded predominantly on Ga-ZSM-5, and CH_4 and C_2H_6 were hardly consumed by the reaction with O_2.

We conclude from these results that reduction of NO proceeds on Ga-ZSM-5 even when CH_4 and C_2H_6 are used as reductants, and CH_4 was an effective reductant for selective reduction of NO.

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Selective reduction of nitric oxide by methane on H-form zeolite catalysts in oxygen-rich atmosphere

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Selective reduction of NO by CH_4 in the presence of excess oxygen was investigated using H-form zeolite catalysts. H-ZSM-5, H-ferrierite, and H-mordenite showed high catalytic activity and selectivity. On the contrary, H-USY and Al_2O_3 were not effective for this reaction. Both NO–CH_4 and O_2–CH_4 reaction hardly proceeded on H-ZSM-5. Higher NO_x conversion was obtained in the NO_2–O_2–CH_4 and NO_2–CH_4 systems than in the NO–O_2–CH_4 system under high GHSV condition. It seemed that NO_2 plays an important role for selective reduction of NO by CH_4 on H-form zeolites.

Keywords: Nitric oxide; selective reduction; methane; zeolite

1. Introduction

Recently, selective catalytic reduction of NO by hydrocarbons in oxygen-rich atmosphere has attracted considerable attention as a new type of reaction alternative for the traditional NH_3-SCR process. This reaction has been reported to proceed on various cation-exchanged zeolites [1–5], metallosilicates [6,7], Al_2O_3 [8,9] and SiO_2–Al_2O_3[10].

Iwamoto et al. [11] and Hamada et al. [12] have studied the reduction of NO by various hydrocarbons in the presence of oxygen on Cu-ZSM-5 and Al_2O_3 catalysts, respectively. They have classified reductants into two groups, selective (C_2H_4, C_3H_6, C_3H_8, C_4H_8), and non-selective (H_2, CO, CH_4, C_2H_6) reductants for NO reduction in the presence of O_2 [13]. The CH_4–O_2 reaction proceeded predominantly and the NO–CH_4 reaction hardly proceeded on Cu-ZSM-5 and Al_2O_3. It has been accepted that CH_4 is not effective for selective reduction.

However, hydrocarbon in the exhaust from a gas-cogeneration system is mainly CH_4. Therefore, it is expected to develop a catalyst which is active for selective reduction of NO by CH_4 in oxygen-rich atmosphere. Recently, Li and Armor [14]

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have reported that selective reduction by CH_4 proceeds on Co-ZSM-5. In our previous study, we have also found that Ga-ZSM-5 shows high catalytic activity and extremely high selectivity for reduction of NO by CH_4 or C_2H_6 [15]. We have recently found that various H-form zeolite catalysts are also active and fairly selective for this reaction. In this paper, we will report the catalytic properties of H-form zeolites and the role of O_2 for selective reduction of NO by CH_4.

2. Experimental

Zeolites used in this study were ZSM-5 (molar SiO_2/Al_2O_3 ratio, 23.3), mordenite (19.9), ferrierite (17.8), and USY (14.5), supplied by Tosoh Corporation. Alumina, as a reference catalyst, was obtained from Catalysts & Chemical Ind. Co.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO (or NO_2), 10% O_2, and 1000 ppm CH_4 was fed to 0.1–0.5 g catalyst at a rate of 100 cm^3(STP) min^{-1}. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence detection of NO_x. The catalytic activity was evaluated by the level of NO conversion to N_2.

3. Results and discussion

Fig. 1 shows the temperature dependence of catalytic activities of various H-form zeolites and Al_2O_3 for NO reduction by CH_4. Among these catalysts, H-ZSM-5 showed the highest activity at 500°C. H-USY was inactive under these

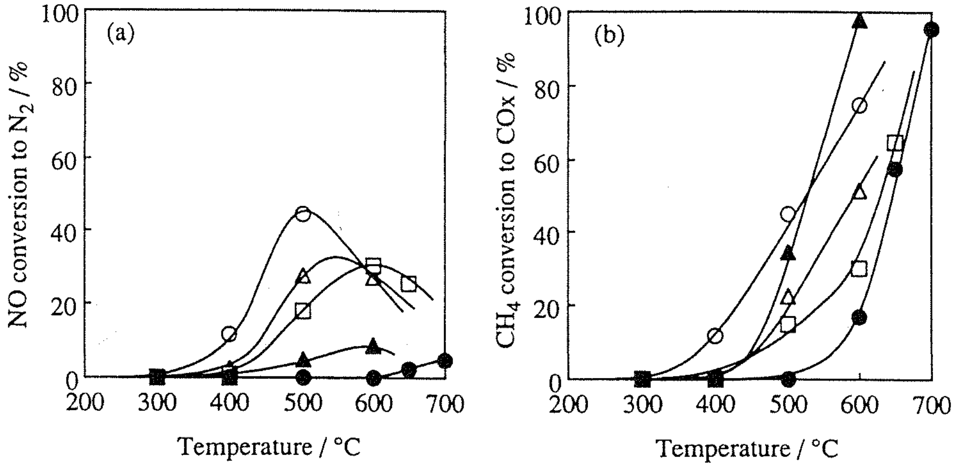

Fig. 1. Variation in NO conversion (a) and CH_4 conversion (b) on various zeolites as a function of reaction temperature. (○) H-ZSM-5; (△) H-mordenite; (□) H-ferrierite; (●) H-USY; (▲)Al_2O_3. NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

reaction conditions, and its activity was similar to that of Al_2O_3. The CH_4–O_2 reaction was predominant and NO reduction hardly proceeded on these catalysts.

The ratio of NO conversion to CH_4 conversion is a measure of selectivity. As shown in fig. 2, H-ferrierite was most selective and the order of the selectivity for this reaction on these zeolites was as follows:

H-ferrierite > H-mordenite > H-ZSM-5 >> H-2USY.

H-ferrierite exhibited the lowest activity for the CH_4–O_2 reaction, resulting in high selectivity for NO reduction. Although a high selectivity of Al_2O_3 catalyst for NO reduction by C_3H_8 has been reported [2], the selectivity for NO reduction by CH_4 was extremely low. On the contrary, NO was selectively reduced on H-ZSM-5, H-mordenite, and H-ferrierite.

It has been reported by Hamada and co-workers [2] that the acidity of catalysts is one of the important factors which control the catalytic activity for selective reduction of NO. Fig. 3 shows NH_3-TPD spectra of various zeolites used in this study. H-USY showed very small acidity with weak acid strength, suggesting that the low catalytic activity of H-USY is probably due to its poor acidity.

Fig. 4 shows the catalytic activities of H-ZSM-5 for conversions of NO to N_2 and CH_4 to CO_x in various reaction temperatures. The NO–CH_4 reaction hardly proceeded at all temperatures in the absence of O_2, showing that NO reduction was promoted by O_2. Furthermore, CH_4 oxidation did not proceed below 500°C in the absence of NO. Since NO reduction occurred under the conditions where the CH_4–O_2 reaction did not proceed, NO_2 should be concerned in selective reduction. All the zeolite catalysts used in this study were inactive for reduction of NO with CH_4 in the absence of O_2 and for oxidation of CH_4 in the absence of NO. It has also

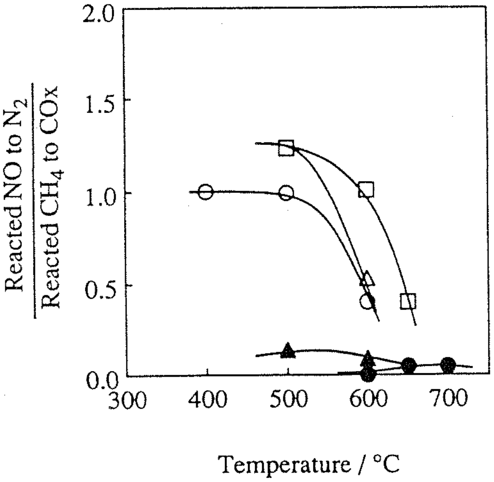

Fig. 2. Relationships between the ratio of reacted NO to consumed CH_4 and reaction temperature. (○) H-ZSM-5; (△) H-mordenite; (□) H-ferrierite; (●) H-USY; (▲) Al_2O_3. NO, 1000 ppm; CH_4, 1000 ppm; O_2 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

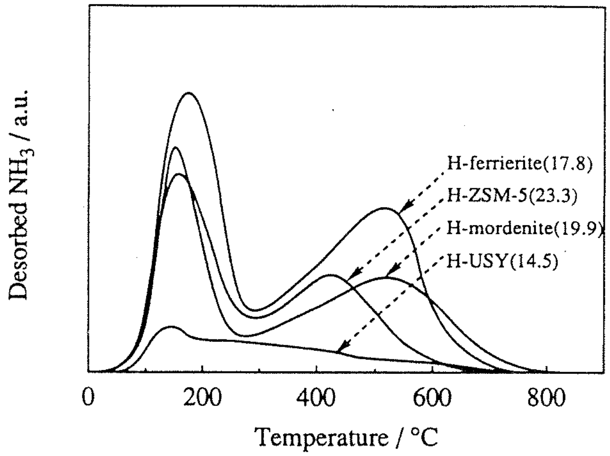

Fig. 3. NH_3-TPD spectra of various zeolites.

been reported by Hamada and co-workers [16] that selective reduction of NO with C_3H_8 on Al_2O_3 and H-form zeolites proceeds via NO_2–C_3H_8 reaction and that high selectivity was attributable to NO_2–C_3H_8 reaction and poor activity of these catalysts for C_3H_8 oxidation by O_2.

In fig. 5, we compare the level of NO_x conversion to N_2 as a function of reciprocal GHSV. Higher NO_x conversion was obvious in the NO_2–O_2–CH_4 and NO_2–CH_4 systems than in the NO–O_2–CH_4 system in high GHSV condition. In the latter system, NO conversion seems to show an induction period. These results

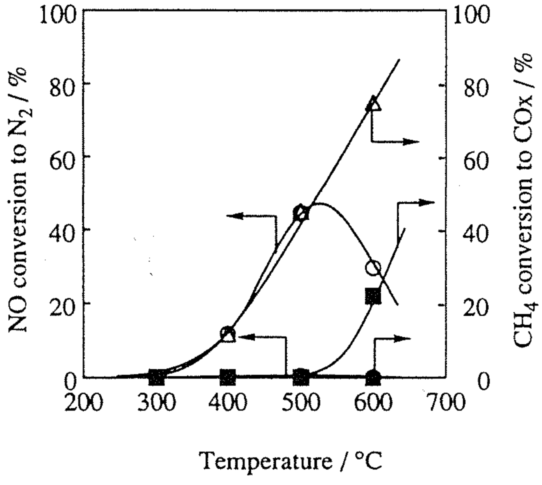

Fig. 4. Variation in NO conversion and CH_4 conversion on H-ZSM-5 as a function of reaction temperature. (○) NO conversion in NO–CH_4–O_2 reaction; (△) CH_4 conversion in NO–CH_4–O_2 reaction; (●) NO conversion in NO–CH_4 reaction; (▲) CH_4 conversion in NO–CH_4 reaction; (■) CH_4 conversion in CH_4–O_2 reaction.

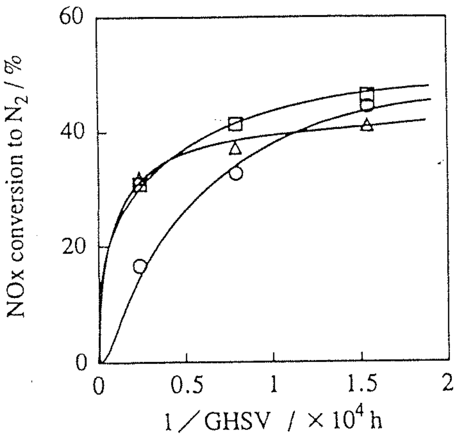

Fig. 5. Relationships between NO_x conversion and GHSV on H-ZSM-5. (○) NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; (△) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2 0%; (□) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.1–0.5 g; reaction temperature, 500 °C.

lead us to deduce that the first step is NO oxidation to NO_2, which further reacts with CH_4 to give N_2, CO_x, and H_2O, similarly to the reduction of NO_x by C_3H_8 on H-form zeolites [16].

We conclude from these results that reduction of NO proceeds on various H-form zeolites even when CH_4 is used as reductant, and CH_4 can be an effective reductant for selective reduction of NO, and that NO_2 plays an important role in the selective reduction of NO by CH_4.

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1B7　ゼオライト触媒上でのメタンによるＮＯ選択還元

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ゼオライト触媒上でのCH_4によるNO還元反応について検討を行った。Gaイオン交換ゼオライトは本反応に対し高活性，高選択性を示した。また，プロトン型ゼオライト上でも本反応は進行し，比較的高い活性と選択性を示すことが明らかとなった。これらの触媒上での反応機構について検討を行い，NO選択還元に対するGaの効果について検討した。酸素が存在しない場合にはNOとCH_4の反応は全く起こらないこと，及びNOが存在しない場合にはCH_4の燃焼反応も起こらないことから本反応にはNO_2が重要な役割をしていることが示された。また，Ga/Al_2O_3,及びGa_2O_3では選択性が低いことから，本反応にはゼオライトにイオン交換されたGaカチオンが有効であると考えられ，NO_xと炭化水素の両者が配位不飽和なGa上に吸着し，反応するためと考察した。また，プロトン型ゼオライトでは，ルイス酸が配位不飽和なGaと同様の働きをすると推測した。

［討論したい事項］①固体酸性の影響　②活性サイト・反応機構

1．緒言

酸素過剰雰囲気下での炭化水素類を還元剤としたNOの選択的還元反応が注目されている。Cu-ZSM-5触媒を用いた炭化水素によるNOの還元反応が岩本ら1)により報告されて以来，ゼオライト系触媒を中心として検討がなされ種々の触媒で本反応が進行することが明らかとなった2-5)。しかし，これらの触媒ではまだ高酸素濃度下で炭化水素と酸素との反応が優先し，NOの還元の選択性は十分に高くない。また，プロトン型ゼオライト3)，$Al_2O_3$4)等の固体酸触媒は本反応に対して比較的高い選択性を有することがこれまでに報告されているが，高GHSV条件下では活性が低い。

我々は種々の金属イオンで交換したゼオライトについてNOの炭化水素による還元を検討したところ，C_3H_6及びC_2H_4を還元剤に用いるとGaイオン交換ゼオライトが高いNO転化率を示し，酸素過剰雰囲気下においてもNOと炭化水素の反応が高選択的に進行することを見いだした5)。また，Gaイオン交換ゼオライトはこれまでに報告された触媒に比べて極めて広い温度範囲で高い活性を示すことを明らかにした。

一方，還元剤となる炭化水素種の効果に関しては岩本と浜田が，銅イオン交換ゼオライト及びAl_2O_3について選択的な還元剤（C_2H_4，C_3H_6，C_3H_8，C_4H_8）と非選択的な還元剤（CH_4，C_2H_6，CO，H_2）とに分類している。CH_4による選択還元はこれまで困難とされてきが，都市ガス（天然ガス）を燃料としたガスエンジン・コジェネレーションシステムの排ガスでは未燃炭化水素が主にCH_4であり，CH_4による還元に有効な触媒の開発が期待されている。

我々はCH_4によるNO還元反応に対して，Gaイオン交換ゼオライトが極めて高い活性を示し，NOの還元が極めて選択的に起こることを見いだした6)。また，プロトン型ゼオライト上でも本反応は進行し，比較的高い活性と選択性を示すことが明らかとなった。本研究ではGaイオン交換ゼオライトの高選択性及び反応機構について考察した。

2．実験

ゼオライトへのガリウムの担持は，硝酸ガリウム水溶液を用い，イオン交換法により行った。硝酸アンモニウム水溶液にてNH_4^+型としたゼオライトを硝酸ガリウム水溶液中にて95℃24時間攪拌し調製した。ゼオライトとしてはZSM-5，ferrierite，mordenite，USY(以上，東ソー製)について検討した。各々のSiO_2/Al_2O_3比は23.3，17.8，19.3，14.5である。触媒中のGa^{3+}イオン交換率(％)はICPにより求め，Ga/H-ZSM-5(92)のように示した。またAl_2O_3（触媒化成 ACP-1）及びGa_2O_3(三津和化学薬品)は500℃で焼成して用いた。

反応は常圧固定床流通式反応装置を用い，反応温度300－700°C，NO濃度1000ppm，O_2濃度は10％で行ったまた，CH_4濃度は100－1000ppm，空間速度は7200－72000h^{-1}(全流量100$cm^3\cdot min^{-1}$,触媒重量0.05－0.5g)の範囲で変化させた。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。なお，活性はすべてNOのN_2への転化率で評価した。

3．結果と考察

3．1　Gaイオン交換ゼオライトの高選択性

Ga-ZSM-5，H-ZSM-5，及びAl_2O_3上でのCH_4によるNO還元反応の結果を図１及び図２に示す。Al_2O_3はC_3H_8によるNO還元反応に対して比較的高い選択性を示すことが知られているが4)，CH_4では燃焼反応が優先し，NO還元反応の選択性は極めて低い。しかし，Gaイオン交換ゼオライトを用いるとCH_4でもNO選択還元が可能となる

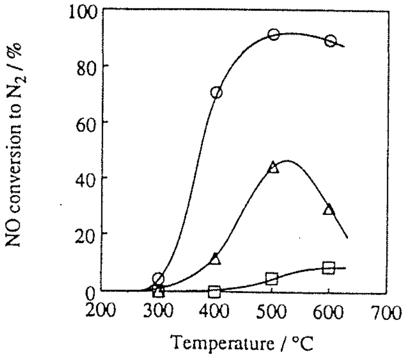

Fig.1. Reduction of NO by CH_4 on various catalysts:
○, Ga/H-ZSM-5(92); △, H-ZSM-5; □, Al_2O_3.
NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.5g.

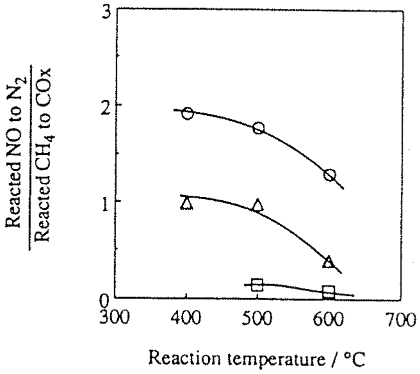

Fig.2. Selectivity expressed by the ratio of reacted NO to consumed CH_4 as a function of temperature.
○, Ga/H-ZSM-5(92); △, H-ZSM-5; □, Al_2O_3.
NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.5g.

Ga-ZSM-5は400℃以上の温度域で高いNO転化率を示し，NO還元反応の選択性も極めて高い。Ga-ZSM-5上での反応のNO還元の選択性は，

$$2NO + CH_4 + kO_2 = N_2 + CO_x + 2H_2O \quad .....(1)$$

の化学量論で示される。また，プロトン型ゼオライト上でもCH_4によるNO還元反応が比較的高い選択性で進行する。本反応条件下ではGa-ZSM-5では反応したNOとCH_4の比は$NO:CH_4=2:1$であるのに対し，H-ZSM-5上ではほぼ$NO:CH_4=1:1$となる。すなわちGaの存在によりNO還元の選択性が向上していることがわかる。そこで次にGaイオン交換による高選択性発現の要因について検討した。

3．2　NO選択還元反応に対するGaの効果

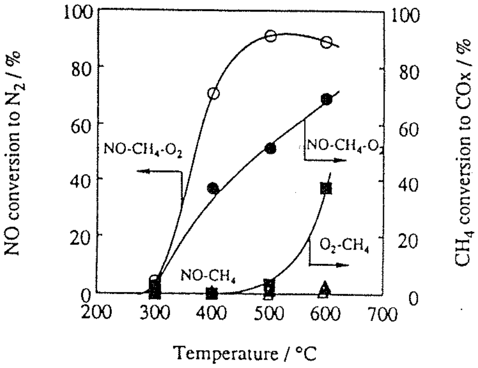

Fig.3. Catalytic activities of Ga/H-ZSM-5(92) in NO-CH_4-C (○, ●), NO-CH_4(△, ▲), and CH_4-O_2(■) reaction.
NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.5g.

図3に示すように，酸素が存在しない場合NOとCH_4の反応は全く起こらないことから，本反応には酸素の存在が不可欠であることがわかる。また，500℃以下ではCH_4の燃焼はほとんど進行しない。これらのことから本反応にはNOと酸素から生成したNO_2が関与すると考えられる。NO_2の本反応への関与に関してはすでに浜田ら[8]の報告がある。浜田らはAl_2O_3上でのC_3H_8によるNO還 反応について検討し，NO_2が本反応の反応中間体であ という報告をしている。

そこでGa-ZSM-5及びH-ZSM-5についてNO_2の反応性 ついて検討した。図4にGa-ZSM-5上でのNO-CH_4-O_2，NO_2-CH_4-O_2，及びNO_2-CH_4反応の結果を示した。高GHS 条件下ではNO_2系に比べてNO系の方がN_2への転化率が いことがわかる。また，NO_2系では酸素が存在しなく もこの条件下では差異が見られなかった。また図5に すように，Ga-ZSM-5上でのNO還元反応の選択性はC 濃度を変化させてもほぼ一定の値を示した。従ってGa ZSM-5上ではCH_4の燃焼反応が起こっておらず，NO還元

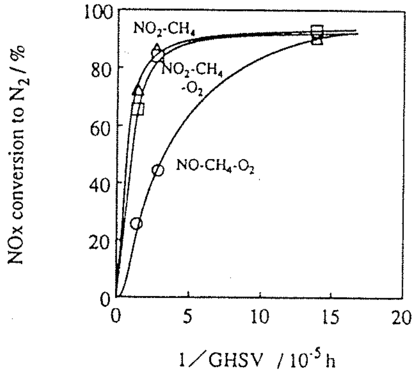

Fig.4. Relationships between NOx conversion and GHSV on Ga/H-ZSM-5(92).
○, NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%;
△, NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 0%;
□, NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10%;
total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.05-0.5g; temperature, 500°C.

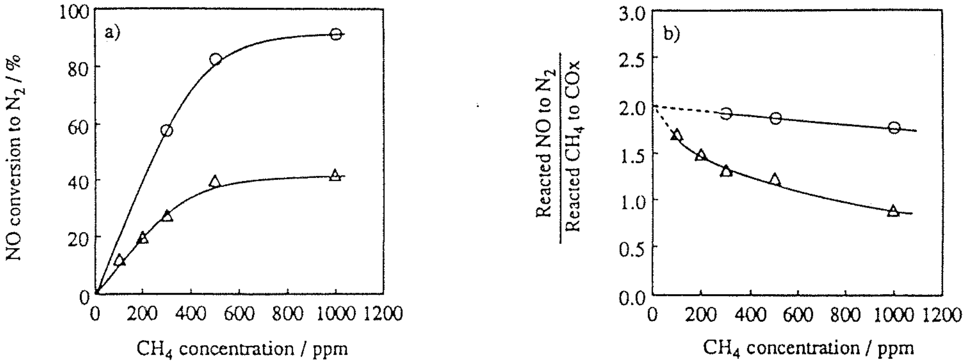

Fig.5. NO reduction on Ga/H-ZSM-5(○) and H-ZSM-5(△) as a function of CH_4 concentration. NO, 1000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.5g; temperature, 500°C.

反応が選択的に進行すると考えられる。これに対してH-ZSM-5上ではCH_4濃度の増加とともにNO還元反応の選択性が低下し，H-ZSM-5上ではCH_4の燃焼反応も起こっていることがわかる。またH-ZSM-5上でも同様に，高GHSV条件下ではNO_2系の方がN_2への転化率が高かった。これらのことから，本反応の第一ステップはNOの酸化によるNO_2の生成と考えられる。

つぎに種々のゼオライト上でのCH_4によるNO還元反応及びNO_2生成反応について検討を行った。図６に示すように種々のプロトン型ゼオライト上でNO還元反応が進行した。低酸性のAl_2O_3及びUSYではN_2はほとんど生成せずNOの酸化反応もほとんど起こらなかった（表１）。従って，本反応にはゼオライトの固体酸性が関与していると考えられる。また，NO_2-CH_4-O_2反応に対してもAl_2O_3及びH-USYの活性は低く，これらの触媒上ではNOの酸化だけでなくNO_2とCH_4の反応に必要な活性点も少ないと考えられる。

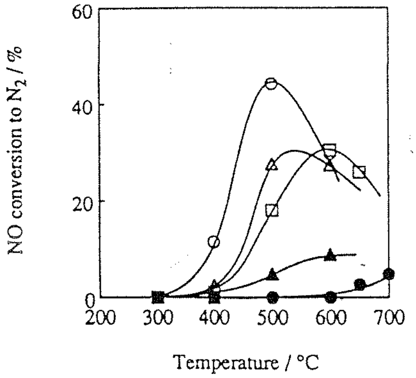

Fig.6. Reduction of NO by CH_4 on various H-form zeolites and Al_2O_3.
○, H-ZSM-5; △, H-mordenite; □, H-ferrierite; ●, H-USY; ▲, Al_2O_3.
NO, 1000ppm; CH_4, 1000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.5g.

また，Ga-ZSM-5はH-ZSM-5と比較してNO酸化に低活性である。しかし，NOのN_2への転化率はGa-ZSM-5の方がはるかに高い。以前報告したように[6)]，NH_3-TPDから求めたGa-ZSM-5の酸量及び酸強度はH-ZSM-5に比べて減少している。これらのことからNOのNO_2への酸化にはゼオライトの酸性が寄与しており，Gaの効果はNO_2への酸化を促進することではなく，NO_2とCH_4の反応の促進にあると考えられる。

Table 1. Catalytic activities for the oxidation of NO to NO_2.

Catalyst	Conversion of NO to NO_2 / %				
	300°C	400°C	500°C	600°C	700°C
none	6	6	5	6	6
H-ZSM-5	76	56	27	14	9
H-mordenite	34	44	25	14	9
H-ferrierite	87	55	26	14	9
H-USY	6	7	6	8	9
Al_2O_3	7	8	9	11	8
Ga-ZSM-5	67	55	27	14	9

Reaction conditions: NO, 1000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

３．３　NO選択還元の活性サイト

次に本反応に有効なGaの状態について考察する。図７に示すように，Al_2O_3にGa_2O_3を担持した場合には高い選択性は得られなかった。また，Ga_2O_3単味の場合も同様にNO還元反応の選択性は低い。このことからゼオライトにイオン交換することがGaの高い選択性の発現に有効であると考えられる。ゼオライトにイオン交換されたGaカチオンはGa_2O_3に比べて，配位不飽和度が高く，NO_xや炭化水素が容易に吸着すると考えられる。

感度が高いNO_xセンサー材料にGaが使われていること[9)]，及びGaは種々のアルキル錯体を容易に生成することがよく知られていること[10)]から，ゼオライトにイオ

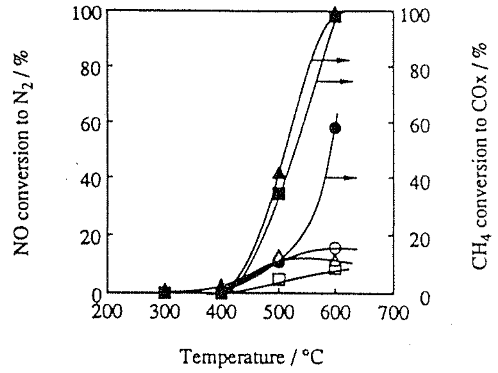

Fig.7. Catalytic activities of Ga_2O_3(○, ●), Ga/Al_2O_3(△, ▲), and Al_2O_3(□, ■), for NO conversion (open symbol) and CH_4 conversion (solid symbol).
NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.5g.

ン交換されたGa上でNO_xと炭化水素が効率よく反応するために高い選択性が達成されるものと考えられる。またプロトン型ゼオライト上でもNO還元反応が選択的に進行することからプロトン型では脱水により生成したルイス酸が配位不飽和なGaと同様の働きをすると推測される。

4. 結論

Gaイオン交換ゼオライトはCH_4によるNO還元反応に対して高い選択性を示した。NOとNO_2の反応性の比較の結果から，本反応はNO_2の生成を経て進行すると考えられ，Gaイオン交換ゼオライトの高選択性はゼオライトにイオン交換された配位不飽和な同一Gaサイトに吸着したNO_xとメタンが反応するためと考察した。

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Selective Reduction of NO by Methane on Zeolite Catalysts

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Selective reduction of NO by CH_4 on zeolite catalysts has been studied. Ga-ZSM-5 showed high catalytic activity and extremely high selectivity for NO reduction by CH_4. It was also found that this reaction was moderately promoted even by H-form zeolites. NO-CH_4 reaction hardly proceeded in the absence of O_2, showing that O_2 is a necessary component for NO reduction. Furthermore, CH_4-O_2 reaction also did not take place below 500℃ in the absence of NO. In a comparison with the results on NO_2-CH_4-O_2 reaction, it is deduced that NO_2 should be concerned in the selective reduction. The selectivity was low when Al_2O_3 was used as a support of gallium oxide, and the selectivity of unsupported Ga_2O_3 was likewise low. From these results, it is considered that ion-exchange onto zeolite is needed to attain high selectivity of gallium. The high selectivity of gallium cations in ZSM-5 can be attributed to their high affinity to NOx and alkyl species. We thus deduce that extremely high selectivity of gallium ion-exchanged ZSM-5 is achieved by efficient coordination of NOx and hydrocarbon species at the same unsaturated gallium cation in zeolite. On the other hand, it is suggested that this reaction also proceeds on Lewis acid site on H-form zeolites.

Key-words: selective reduction, nitric oxide, methane, gallium, zeolite

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Characterization of Fe-silicates and their catalytic properties for the selective reduction of nitric oxide by hydrocarbons

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Abstract

H-form Fe-silicate (H-Fe-silicate) catalysts having various Si/Fe molar ratios were synthesized and used for the reduction of NO by hydrocarbons. The results of the chemical analyses, NH_3-TPD, X-ray photoelectron spectroscopy (XPS) and TPR, showed that the non-framework iron content increased with increasing content of iron. Olefins (C_3H_6 and C_2H_4) were more effective reducing agents than parafins (C_3H_8, C_2H_6). The active temperature region for NO reduction by C_3H_6 became lower with increasing iron content in the Fe-silicates, while both the number of acid sites and the NO conversion to N_2 was approximately constant independent of the iron content. Therefore, the iron incorporated in zeolite framework provided acid sites that controlled the catalytic activity for selective reduction.

Key words: Fe-silicate; Nitric oxide; Selective reduction; Propene

1. Introduction

The emission of nitrogen oxides (NO_x) is a serious environmental problem. Iwamoto *et al.* [1] and Held *et al.* [2] reported that copper ion-exchanged ZSM-5 is an effective catalyst for the reduction of NO by hydrocarbons, even in oxidizing atmospheres. This reaction has been reported to proceed on various cation-exchanged zeolites [3–6], H-form zeolites [7], metallosilicates [8,9], Al_2O_3 [10,11] and SiO_2–Al_2O_3 [12].

In our previous study, we found that H-form metallosilicates showed catalytic activities for the reduction of NO by C_3H_6, and that H-Fe-silicate was, among various metallosilicates, the most active and stable catalyst for this reaction [8]. Inui *et al.* [9] also reported that Fe-silicate was, among various metallosilicates, the most suitable catalyst for this reaction because of its high redox capacity. In order to modify the catalytic performance of zeolites, substitution of Al by other elements has been investigated, and various types of metallosilicates have been synthesized [13–15]. As Fe-silicate is known as an effective catalyst for the conversion of methanol into light olefins [16], the chemical and physical properties of Fe-silicate have been studied extensively [17–20]. In these studies, the role of iron species, particularly in NO reduction, has not been wholly elucidated.

In the present study, we examined the catalytic performance of Fe-silicates having three different Si/Fe molar ratios (25, 50 and 80) and investigated the effect of the iron contents on the NO reduction by C_3H_6.

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2. *Experimental*

2.1. *Catalyst preparation*

Fe-silicates were synthesized according to the rapid crystallization method reported by Inui and co-workers [21,22]. Water glass (29 wt.-% SiO_2, 9 wt.-% Na_2O) and $FeCl_3 \cdot 6H_2O$ were used as the sources of silicon and iron, respectively. Tetrapropylammonium bromide (TPAB) was used as the template molecule. The mixture was heated in a stainless-steel autoclave from room temperature to 433 K at a constant heating rate of 1.5 K min^{-1}, and then to 483 K at a constant heating rate of 12 K h^{-1}. Synthesized metallosilicates were thus converted into the H-form by the ion-exchange method using a 1 *M* NH_4NO_3 solution, followed by calcination at 813 K. Such samples will be abbreviated as Fe-silicate (*X*), in which the value in parentheses will represent the molar ratio of silicon to iron.

In order to examine the effect of non-framework iron, Fe-silicate (25) was treated with a 0.1*M* HCl aqueous solution as follows: 5 g of H-Fe-silicate (25) were added to a 1*M* HCl solution, which was stirred for 2 h. The sample was filtered and washed with distilled water. The sample was abbreviated as Fe-silicate (25-HCl).

Iron ion-exchanged ZSM-5 (Fe-ZSM-5), as a reference for XPS and TPR measurements, was prepared by ion-exchanging the ammonium form of ZSM-5 (SiO_2/Al_2O_3 molar ratio of 23.3, supplied by Tosoh) using an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$.

2.2. *Catalyst characterization*

The X-ray diffraction (XRD) patterns of the catalysts were measured by means of a Rigaku RAD 1-C with CuKα radiation (nickel filter). The chemical compositions of synthesized Fe-silicates were determined by inductively coupled argon plasma atomic emission spectrometry (ICP) (Nippon Jarrell-Ash).

XPS was carried out with a JPS-9000MC system (JEOL) with Mgkα radiation at 150 W. The residual gas pressure in the spectrometer chamber during data acquisition was less than $5 \cdot 10^{-7}$ Pa. The measurements were performed in the following sequence: Fe_{2p}, O_{1s}, C_{1s} and Si_{2p}. The spectrometer was calibrated using pure Au 4f spectra, 7/2 (83.8 eV) and 5/2 (87.5 eV). A binding energy of 103.3 eV for Si_{2p} was used as internal reference. The intensity of various XPS bands was determined using linear background subtraction and integration of peak areas. The following equation was employed to evaluate the surface Si/Fe ratio:

$$\frac{\mathrm{Si}}{\mathrm{Fe}} = \frac{n(\mathrm{Si})}{n(\mathrm{Fe})} \cdot \frac{\sigma(\mathrm{Si})}{\sigma(\mathrm{Fe})} \cdot \frac{\lambda(\mathrm{Si})}{\lambda(\mathrm{Fe})} \cdot \frac{S(\mathrm{Si})}{S(\mathrm{Fe})}$$

where n, σ, λ and S denote the normalized peak area, the effective ionization cross-section, the escape depth of the photoelectrons and an analyzer transmission function. The λ values calculated by Penn [23] and cross-sections calculated by Scofield [24] were employed here. Periodic checks were performed to avoid drift due to charging; instrumental instability was not affected by peak positions. Previous to the XPS measurements, all samples were pretreated in air for 1 h at 773 K. Each sample was pressed into a disk-shape form and put on an aluminium sample holder.

TPR measurements were performed using hydrogen diluted in nitrogen (5% H_2) with a temperature increment of 10 K min^{-1}. The acidity of Fe-silicates was measured by NH_3-TPD. The sample was pretreated at 773 K in air for 30 min, and then 200 Torr NH_3 was adsorbed at 373 K for 30 min and degassed at 373 K for 30 min. The desorption of NH_3 at a constant heating rate of 10 K min^{-1} was monitored by a TCD detector.

2.3. *Selective reduction of NO on Fe-silicate catalysts*

Measurements of the catalytic activity were conducted by a fixed-bed flow reactor. A mixture of 1000 ppm of NO, 0–10% O_2, 300–1000 ppm of hydrocarbon and the balance helium was fed to 0.5 g of catalyst at a rate of 100 cm^3 (STP) min^{-1}. Effluent gases were analyzed by gas chromatography (GC): a Shimadzu GC-8AIT (TCD) for CO and CO_2, a Shimadzu GC-8APF (flame ionization detection) for hydrocarbons and a Shimadzu CLM107 NO_x analyzer for chemiluminescence detection of NO_x. The catalytic activity was determined by the level of NO into N_2 conversion.

3. Results and discussion

3.1. Synthesis and characterization of Fe-silicates

The X-ray diffraction patterns of all Fe-silicates were similar to that of H-ZSM-5, indicating that these metallosilicates had a pentasil pore-opening structure. The chemical compositions of synthesized Na-form Fe-silicates determined by ICP and XPS measurements are given in Table 1. Si/Fe atomic ratios determined by XPS were higher than those determined by ICP, showing that the distribution of iron in these Fe-silicates was not uniform. For Fe-silicates having Si/Fe molar ratios of 50 and 80, the amount of Na^+ was in accordance with that of iron, showing that iron is mostly incorporated in the framework. In contrast, the amount of sodium was smaller than that of iron in the case of Fe-silicate (25).

Fig. 1 shows the NH_3-TPD spectra of these Fe-silicates. The amount of desorbed NH_3 was not in accordance with the iron content. There was no appreciable difference in the acid amount between Fe-silicates having Si/Fe molar ratios of 25 and 50. It has been reported that considerable amounts of extra-framework elements exist in metallosilicates having Si/M molar ratios smaller than *ca.* 40, at which the ion-exchange capacity is saturated [25–27]. This agrees with the fact that considerable amounts of non-framework iron exist in Fe-silicate (25). As shown in Table 1, the iron content in this Fe-silicate decreased by HCl treatment, showing that non-framework iron was dissolved in the solution. There was no distinct difference in the NH_3-TPD spectra of parent Fe-silicate (25) and the HCl-treated sample.

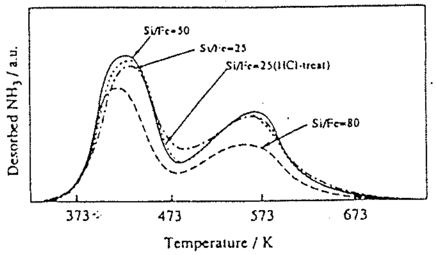

Fig. 1. NH_3-TPD spectra of various Fe-silicates.

These conclusions were also supported by the results of XPS and TPR. Fig. 2 shows the XPS spectra of Fe-silicates. The $Fe_{2p3/2}$ peak from these Fe-silicates appeared at a higher binding energy than that of Fe-ZSM-5 or Fe_2O_3–H-ZSM-5 (physical mixture, shown in Table 2). Therefore, most iron atoms are considered to be strongly combined to framework oxygen and to be incorporated in the zeolite framework. The shoulder peak of $Fe_{2p3/2}$ at 711 eV shifted to a lower binding energy with increasing iron content in the Fe-silicates. As shown in Table 2, the FWHM of these Fe-silicates increased with increasing iron content, showing that iron atoms exist in various states on high-iron-content Fe-silicates. On the other hand, Fe-silicate (25-HCl) showed a higher binding energy of $Fe_{2p3/2}$ than untreated Fe-silicate (25),

Table 1
Chemical compositions of Fe-silicates

Si/Fe (raw materials)	Si/Fe (XPS)	Si/Fe (ICP)	Na (ICP) (10^{-4} mol/g)	Fe (ICP) (10^{-4} mol/g)	Si (ICP) (10^{-2} mol/g)	Surface area (m^2/g)
Fe-silicate						
25	39.8	23.6	2.64	6.10	1.44	339
50	74.9	48.9	2.93	3.11	1.52	303
80	124.5	80.2	2.00	1.92	1.54	373
HCl-treated Fe-silicate						
25	71.5	47.8	–	3.14	1.50	–

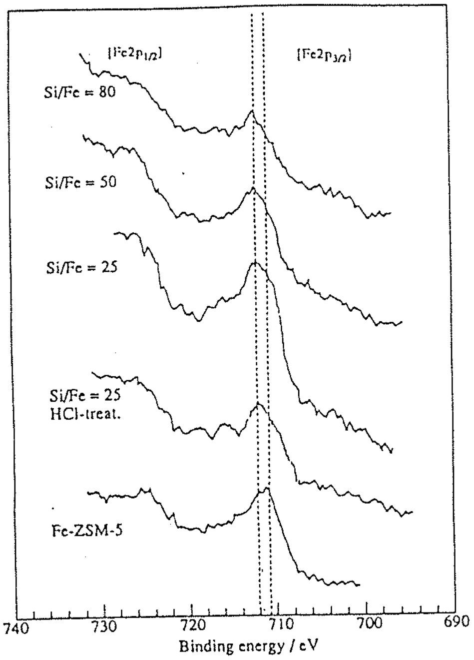

Fig. 2. XPS profiles for H-Fe-silicates and iron ion-exchanged ZSM-5.

and the FWHM decreased during treatment. From these results, we deduced that the amount of non-framework iron, such as Fe_2O_3 or Fe_3O_4, which gives a lower-binding-energy peak than framework iron, increases with increasing iron content.

Fig. 3 shows the results of the TPR experiments. Fe/H-ZSM-5 gave only a single peak, corresponding to Fe at non-framework sites, at 673 K under these conditions. On the other hand, Fe-silicates provided two additional peaks at higher temperatures. These peaks should correspond to the reduction of iron incorporated in the zeolite framework [20]. These results show that the amount of non-framework iron increases with increasing iron content in the Fe-silicates. As the peak position of Fe/H-ZSM-5 and that of Fe-silicate at lower temperature were almost the same, it is also possible that some non-framework iron exists on cation-exchange sites.

3.2. Selective reduction of NO by C_3H_6 on Fe-silicates

In our previous study [8], we found that H-Fe-silicate is a highly active and stable catalyst for the reduction of NO by C_3H_6 at 573 K. The first step of this reaction is the adsorption of C_3H_6; carbonaceous materials on the catalyst are probably involved in this reaction. Fig. 4 shows the temperature dependence of the NO conversion by various reducing gases on H-Fe-silicate (50). The level of NO conversion markedly depended on the kind of reducing gas. CO and H_2 were not effective for this reaction; they were preferentially consumed by the reaction with O_2. The reduction of NO proceeded when hydrocarbons were used as reductants, and the reduction reactivity decreased in the following order: $C_3H_6 > C_2H_4 > C_3H_8 >> C_2H_6 > CH_4$. This figure shows clearly that olefins are more effective than paraffins.

The catalytic activity of H-Fe-silicate gradually decreased and finally diminished at 473 K when C_3H_6 was used as a reducing agent, although a stable catalytic activity was obtained at temperatures higher than 573 K. As the decreased catalytic activity at 473 K was regenerated by calcination at 773 K with an evolution of CO_2, deposition of excess carbonaceous materials should be a cause of catalyst deactivation. Above 573 K, H-Fe-silicate showed enough ability to remove carbonaceous materials by combustion under high oxygen concentration conditions, resulting in the steady catalytic state activity. The H-ZSM-5 catalyst exhibited a stable activity above 748 K under the same reaction conditions [8]. As H-ZSM-5 is less active for combustion than H-Fe-silicate, higher temperatures are required to attain a stable activity. The decrease in NO conversion in the high-temperature region shown in Fig. 4 is not attributable to catalyst deactivation, as this level of NO conversion could be reproduced when the reaction temperature was lowered. In the $NO–C_3H_6–O_2$ reaction, C_3H_6 is consumed by both NO reduction and combustion. The consumption

Table 2
Binding energy and FWHM values of various components for Fe-silicates and Fe-ZSM-5[a]

Catalyst	$Fe2p_{3/2}$		O1s		Si2p	
	BE[b] (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
Fe-silicate						
Si/Fe = 80	712.1	3.2	532.8	2.1	103.3	2.1
Si/Fe = 50	712.5	4.3	532.8	2.2	103.3	2.1
Si/Fe = 25	711.8	5.2	532.8	2.2	103.3	2.2
Si/Fe = 25(HCl)	712.4	4.5	532.8	1.9	103.3	1.9
Fe-ZSM-5	711.4	4.6	532.8	2.0	103.3	1.9
Fe_2O_3/H-ZSM-5	710.9	3.1	532.8	2.2	103.3	2.1
Fe	706.9[c]					
FeO	709.6[c]					
Fe_3O_4	710.8[c]					
Fe_2O_3	710.9[c]					
α-FeOOH	711.8[c]					
γ-FeOOH	711.3[c]					

[a] A Mg X-ray source, operated at 15 kV and 10 mA, was used for excitation.
[b] Referenced to Si2p = 103.3 eV.
[c] Data from '*Handbook of X-ray photoelectron spectroscopy*' (JEOL).

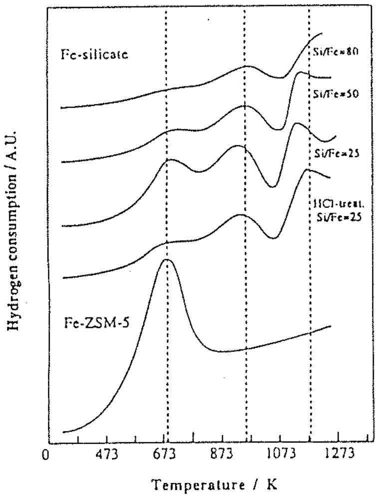

Fig. 3. TPR profiles for H-Fe-silicates and iron ion-exchanged ZSM-5.

of C_3H_6 by combustion causes the decrease in NO conversion at high reaction temperatures.

The effect of O_2 concentration on the catalytic activity of H-Fe-silicate (50) for NO reduction at 573 K is shown in Fig. 5. The reaction hardly proceeded in the absence of O_2. The activity increased with increasing O_2 concentration and reached a maximum at an O_2 concentration of 1%, although the catalytic activity decreased with time on stream. In contrast, the catalytic activity was stable against deactivation in the presence of excess O_2, although the activity slightly decreased with increasing O_2 concentration. Thus, it is important to control the combustion activity to attain high and stable catalytic activity for NO reduction.

Fig. 6 shows the temperature dependence of the catalytic activities of various H-Fe-silicates for NO reduction by C_3H_6. The working temperature region became lower with increasing iron content. Both NO conversion and C_3H_6 conversion in the low-temperature region increased with increasing iron content. Therefore the high steady-state activity of H-Fe-silicate (25) at low temperatures should be due to its high ability of C_3H_6 combustion. Excess carbonaceous materials formed in the NO–C_3H_6–O_2 reaction due to the high reactivity of C_3H_6 should be eliminated on H-Fe-silicate, resulting in a stable activity against deactivation.

Fig. 7 shows the relationship between NO conversion and the amount of CO_x produced on

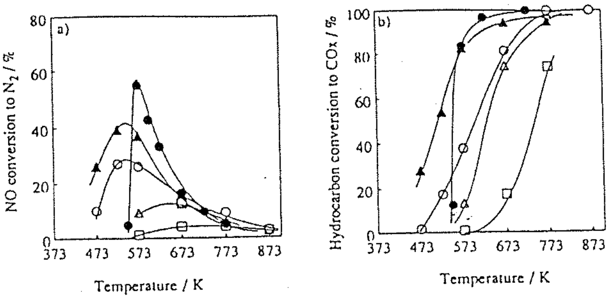

Fig. 4. Effect of reducing gases on the catalytic activity of Fe-silicate (50). Reducing gases, 1000 ppm: (○) C_3H_8, (●) C_3H_6, (△) C_2H_6, (▲) C_2H_4, (□) CH_4; NO, 1000 ppm; O_2, 10%; total flow-rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

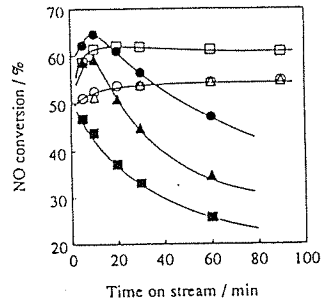

Fig. 5. Effect of O_2 concentration on the catalytic activity of H-Fe-silicate (50). O_2 concentrations: (○) 20%, (△) 10%, (□) 5%, (●) 1%, (▲) 0.5%, (■) 0.2%.

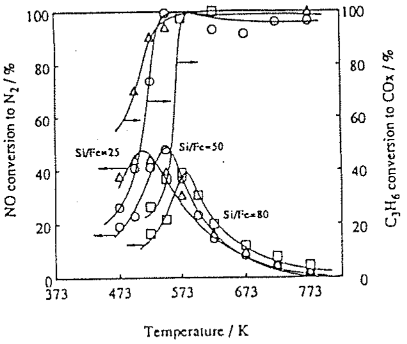

Fig. 6. Catalytic activity of H-Fe-silicates as a function of reaction temperature. NO, 1000 ppm; C_3H_6, 320 ppm; O_2, 10%; total flow-rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g. Catalysts: (△) Si/Fe = 25, (○) Si/Fe = 50, (□) Si/Fe = 80.

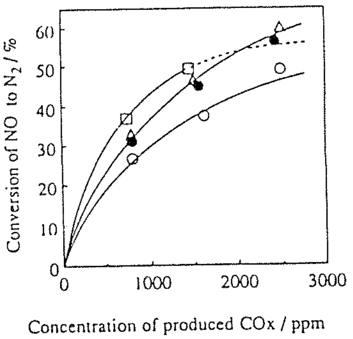

Fig. 7. Relationships between NO conversion and concentration of produced CO_x on various H-Fe-silicates. Reaction temperature, 673 K; NO, 1000 ppm; O_2, 10%; C_3H_6, 300, 500 and 1000 ppm; total flow-rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g. Catalysts: (□) Si/Fe = 80, (△) Si/Fe = 50, (○) Si/Fe = 25, (●) Si/Fe = 25 (HCl-treated).

various H-Fe-silicates at 573 K. The C_3H_6 concentration was varied from 300 to 1000 ppm. The selectivity for the NO–hydrocarbon reaction against the hydrocarbon–O_2 reaction varied among these catalysts. The ratio of NO conversion to the amount of CO_x produced is a measure of selectivity, and the more-selective catalysts provide larger ratios [28]. The selectivity of H-Fe-silicate (25), having a high Fe content, was lower than those of H-Fe-silicate (50) and H-Fe-silicate (80). Although H-Fe-silicate (80) showed the highest activity and selectivity among these Fe-silicates at 573 K, excess carbonaceous materials were deposited and NO conversion decreased with time on stream and finally diminished when the C_3H_6 concentration was higher than 500 ppm. On the other hand, NO conversion on H-Fe-silicate (25) increased by HCl treatment under these reaction conditions. Therefore, we deduced that the existence of non-framework iron increases the catalytic activity for C_3H_6 combustion at 573 K, which leads to lowering the working temperature region, as shown in Fig. 8.

Although the working temperature region shifted by HCl treatment, there was no difference in the level of maximum conversion between H-Fe-silicate (25) and H-Fe-silicate (25-HCl). The maximum conversion decreased in the following order: Fe-silicate (50) > Fe-silicate (25) = Fe-silicate (25-HCl) > > Fe-silicate (80). The order is in accordance with the number of acid sites.

Hamada *et al.* [7] reported that the acidity of the catalyst is one of the important factors controlling the catalytic activity for selective NO reduction. In order to examine the effect of acidity on selective reduction, Fe-silicate (50) was ion-exchanged with various alkali cations. Fig. 9 shows the NH_3-TPD spectra of these cation-exchanged Fe-silicates. The amount of acid varied with the kind of alkali cations.

As shown in Fig. 10, NO conversion and the amount of desorbed NH_3, determined by integration of TPD peaks, showed a good relation for these Fe-silicates. In addition, there was no distinct difference in the selectivity for NO reduction on these Fe-silicates. These observations show that the catalytic activity of Fe-silicate catalysts depends mainly on the surface acidity.

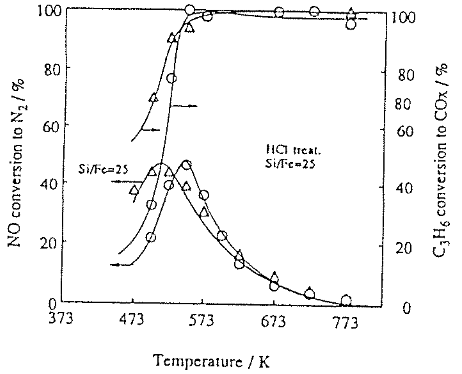

Fig. 8. Effect of HCl treatment on the catalytic activity pattern of H-Fe-silicate. NO, 1000 ppm; C_3H_6, 320 ppm; O_2, 10%; total flow-rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g. Catalysts: (△) Si/Fe = 25, (○) HCl treated Si/Fe = 25.

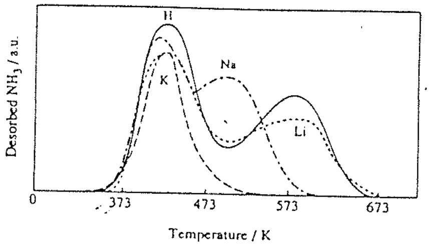

Fig. 9. NH_3-TPD spectra for Fe-silicate (50) exchanged by various cations.

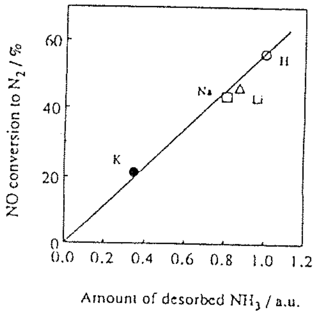

Fig. 10. Relationships between NO conversion and the acidity on Fe-silicate (50) exchanged by various cations. Exchanged cations: (○) H, (△) Li, (□) Na, (●) K. NO, 1000 ppm; C_3H_6, 1000 ppm; O_2, 10%; total flow-rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g. Reaction temperature, 573 K.

4. Conclusion

This study showed that non-framework iron increased with increasing iron content, particularly in Fe-silicate having a Si/Fe ratio of 25. The working temperature region for NO reduction by C_3H_6 became lower with increasing iron content of the Fe-silicates, while NO conversion into N_2

was approximately constant, independent of the iron content. Therefore, we can conclude that the existence of non-framework iron leads to the lowering the working temperature region. On the other hand, the catalytic activity depends mainly on the number of acid sites, namely the number of iron atoms incorporated in the framework. Consequently, it is important to control both the acidity of the catalyst and the combustion activity to attain a high and stable activity for NO reduction by hydrocarbons.

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トピックス

NO_x除去触媒の最近の進歩

1. はじめに

近年，地球環境問題がクローズアップされ，窒素酸化物（NO_x）による大気汚染の問題が深刻化している．燃焼装置から発生するNO_xの低減法として現在，ガソリンエンジンの排ガスには三元触媒法が，大型ボイラーの排ガスにはアンモニア選択還元（SCR）法が実用化されている．しかし高い燃焼効率を得る希薄燃焼排ガス，例えばガスタービンやディーゼルエンジン，希薄燃焼ガソリンエンジンの排ガス中には多量の酸素が含まれるため，非選択的還元法である三元触媒法は適用できない．また有毒なアンモニアを取り扱うSCR法の適用も技術的に限界があり，これらの排ガスの浄化は従来の触媒方式では現実的に困難である．従って，新たな触媒プロセスの開発が望まれてきた．これまで酸素過剰雰囲気下でNOの選択的還元剤としてはNH_3だけが利用されてきたが，炭化水素も選択的還元剤となり得ることが明らかにされ，新しいNO_x除去プロセスへの展開が注目されている．本稿ではこの新しいNO_x還元反応に関する最近の研究動向について解説する．

2. 炭化水素によるNO選択還元

一般に環境関連反応がそうであるように，本還元反応においても以下に示すように，通常の触媒反応に比べて過酷な反応条件のため触媒の開発が困難となる．

（1）目的反応物であるNO_xが低濃度（ppmオーダー）
（2）高反応ガス流速のための低滞留時間
（3）共存ガス（O_2，H_2O，SO_2等）による反応の阻害
（4）反応条件（温度，ガス組成，ガス流速）の大幅な変動

通常の触媒反応では触媒の特性に合わせて反応条件を設定し得るが，本反応系では排気ガスの条件にあった触媒を開発する必要がある．

NOの除去反応としてはN_2とO_2への直接分解が還元剤を必要とせず最も理想的な反応であり，種々の触媒が検討されてきた．岩本ら[1]はCu/ZSM-5が高活性を示すことを報告したが，酸素による反応の阻害が大きいことが実用化を困難にしている．

このような背景の中で岩本ら[2]によりCu/ZSM-5が炭化水素によるNO還元反応に活性であることが報告されて以来，ゼオライト系触媒を中心として種々の触媒が検討され，数種の触媒上で本反応が進行することが明らかとなった[8~10]．またこの反応は直接分解とは逆に酸素の存在が不可欠であり，酸素により反応が促進されることを特徴としている．

表1　炭化水素によるNO選択還元触媒の分類

遷移金属	
Cu-, Co-, Zn-, Ag-, Fe- ZSM-5 (Iwamoto et al.)	
Cu-silicate (Inui et al.)	Fe-silicate (Kikuchi et al.)
Fe-cluster/HY (Mochida et al.)	Fe-mordenite (Iwamoto et al.)
Metal oxides (Co_3O_4, Fe_2O_3, TiO_2, ZrO_2, etc.) (Hamada et al.)	
Perovskite($La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O_3$) (Kagawa, Teraoka et al.)	
Cu-SAPO-34(Takita, Ishihara et al.)	
Co-mordenite (Tokyo Gas Co.)	
Perovskite/Ti-mordenite (Sakai Chemical)	
Pt/Al_2O_3 (Hamada et al.)	Pt/H-zeolites (Arai et al.)
Pt/B_2O_3-SiO_2-Al_2O_3 (Sumitomo Metal Nining)	
Pd-ZSM-5 (Misono et al.)	Co/Al_2O_3 (Hamada et al.)
酸型	
H-ZSM-5, Al_2O_3, (Hamada et al.)	
Ga-, In-ZSM-5 (Yogo, Kikuchi et al.)	Ce-ZSM-5 (Misono et al.)
Mixed oxide(SiO_2-ZnO,TiO_2-ZnO) (Hamada et al.)	
Super acid(SO_4-ZrO_2, SO_4-TiO_2) (Hamada et al.)	

表1にこれまでに報告された触媒の主なものを示した．これらの触媒の活性点についてはまだ十分には解明されていないが，（以下に述べる）反応機構との関連で，遷移金属型と酸型に分類した．一部の触媒では遷移金属と酸の両機能を有する複合型といえる触媒もあるが，ここでは一応遷移金属を含む触媒ではその作用を重視して遷移金属型とした．

我々はこれまでにFe-silicateがC_3H_6を還元剤として用いた場合，300℃という低温で高活性を示すことを見いだしている[3]．これら遷移金属型触媒は一般に活性が高いが，高酸素濃度下では炭化水素と酸素との反応が優先し，NOの還元に対する選択性は十分に高くなく，選択性を向上させる方策が必要である．ここで言う選択性とはCO及びCO_2へと消費された炭化水素がNO還元に使われた割合のことを示している．この割合の高いものほど高選択的であると言える．

一方，H型ゼオライト[4]，Al_2O_3[5]等に代表される酸型触媒は本反応に対して比較的高い選択性を有することが報告されているが，これらの触媒は活性が低く高GHSV条件下ではNO転化率が低い．

そこで我々は遷移金属では還元剤の酸化活性が高すぎるので，典型元素カチオンのルイス酸性に着目し，種々のカチオンをイオン交換担持したゼオライトの活性・選択性について検討した．その結果Gaイオン交換ZSM-5やフェリエライトがC_3H_8，C_2H_4，C_2H_6及びCH_4を還元剤とするNO還元反応に対して高い活性を示し，か

つ酸素過剰雰囲気下においてもNOと炭化水素の反応が高選択的に進行することを見いだした6,7)．同様に本反応に対して高選択性を示す触媒として，御園生ら10)はC_3H_6を還元剤とした場合にCeイオン交換ゼオライトを報告している．

本反応系は，炭化水素の燃焼との競争反応であり，また特に酸型触媒では炭化水素の分解による炭素析出も問題となる．従って，触媒によって炭化水素種の効果が異なり，その影響が大となることが予想される．これまで岩本らと浜田らにより，それぞれCu/ZSM-5とAl_2O_3について還元剤炭化水素種の効果が詳細に検討されている．その結果によると，両触媒系においてC_2H_4，C_3H_6，C_3H_8，C_4H_8等の低級炭化水素が有効であること11)，アルコール類も還元剤となり得ること12)が明らかにされている．一方，炭化水素でもCH_4，C_2H_6，あるいは一般的還元剤であるCO，H_2はNOとの反応性が低く，選択的還元剤とはならないとされてきた．

しかし最近になってCH_4によるNO還元反応に対して，Co13)，Mn14)，Ni14)，Ga7)，In15)，Pd16)等のイオンで交換したZSM-5が高い活性を示し，選択的反応が可能となることが見いだされてきている．また，種々のプロトン型ゼオライトでも本反応が進行し，比較的高い活性と選択性を示すことも明らかとなった17)．特にGaおよびIn/ZSM-5上では極めて高選択的にNO還元が進行し，NOとCH_4が2:1で反応する．この触媒上での反応の化学量論は以下の式で示される．

$$2NO + CH_4 + (x/2)O_2 \longrightarrow N_2 + CO_x + 2H_2O \qquad (1)$$

CH_4による選択還元はこれまで困難と考えられ，あまり顧みられていなかったが，都市ガス(天然ガス)を燃料としたガスエンジン・コジェネレーション・システムの排ガスでは未燃炭化水素が主にCH_4であり，その処理プロセスへの適用が期待されている．また，CH_4はあらゆる燃焼排ガスに含まれるので，これを還元剤とすることが可能な触媒の開発は有用である．

3. NO選択還元反応機構

炭化水素によるNOの還元反応機構に関しては種々の説が提案されており18〜25)，現在活発に議論がなされている．研究者によって触媒，反応条件，あるいは還元剤の種類が異なっているが，これまでに報告されている反応機構に現れる中間体から，反応の第一段階は次の2つに大別される．

(1) 炭化水素と酸素の反応による部分酸化中間体の生成

(2) NOと酸素の反応によるNO_2中間体の生成

遷移金属触媒の反応機構としては，岩本ら20)がCu/ZSM-5上でのC_2H_4によるNO還元反応について検討し，C_2H_4酸化活性発現温度とNO還元活性発現温度が一致することから，炭化水素が酸素により活性化されて生成する部分酸化中間体がNOと反応する説を提唱している．これに対し，プロトン型ZSM-5やAl_2O_3等の燃焼活性の低い触媒では，酸性が本反応に対応しており，NOと酸素の反応により生成したNO_2が炭化水素と反応して還元反応が進行する説21)が提案されている．

また，いずれの反応機構についても，上記中間体からC, N, O, (H)を含む中間体が生成し，その中間体を経て最終的に窒素分子が生成するとの考え方が最近確立されつつある．岩本ら22)は部分酸化中間体とNOから生成したイソシアネート(-NCO)からN_2が生成することをIR測定の結果をもとに提案している．我々23)は過渡応答法の結果から，Fe-silicate上でC_3H_6とNOより生成した含窒素中間体中の窒素原子と気相のNO_xの窒素原子とから窒素分子が生成する機構を提案している．また御園生ら24)はCe/ZSM-5上でニトロ，ニトリト化合物が吸着種として存在することをIRにより観測しており，含窒素化合物の分解によりNO還元が進行することを示唆している．

以下には，最も単純な炭化水素であるCH_4による還元反応に選択的なGa/ZSM-5触媒について，その作用機構について少し詳しく述べる25)．図1に示すように，酸素が存在しない場合NOとCH_4の反応は全く起こらないことから，本反応には酸素の存在が不可欠であることがわかる．また，500℃以下ではCH_4の燃焼はほとんど進行せず，酸素によるCH_4の活性化が初期段階とは考えにくい．これらのことから本反応にはNOと酸素から生成したNO_2が関与すると考えられる．

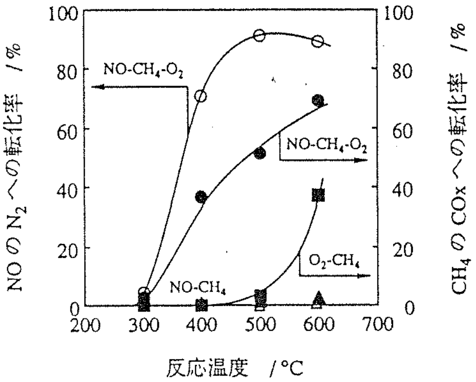

図1　Ga/H-ZSM-5(92)上でのNO，CH_4，及びO_2の反応

NO-CH_4-O_2(○, ●)，NO-CH_4(△, ▲)，CH_4-O_2(■)．NO, 1000 ppm；CH_4, 1000 ppm；O_2, 10 %；流速, 100 $cm^3 \cdot min^{-1}$；触媒重量, 0.5 g.

そこでGa/ZSM-5上でのNOとNO_2の反応性について比較すると，図2に示すように高GHSV条件下ではNO_2系に比べてNO系の方がN_2への転化率が低いことがわかる．また，NO_2系では酸素が存在しなくてもこの条件下では差異がみられなかった．したがって酸素の役割はNOの酸化によるNO_2の生成であり，本反応系での第一段階はNO_2の生成といえる．また，NOのNO_2への酸化活性はゼオライトの固体酸性とよい相関があり，NO_2の生成に対するゼオライト酸点の関与が明らかである．また，NO_2-CH_4反応に対する活性はGa交換率に伴い増加することから，本触媒上での反応は以下に示すよう

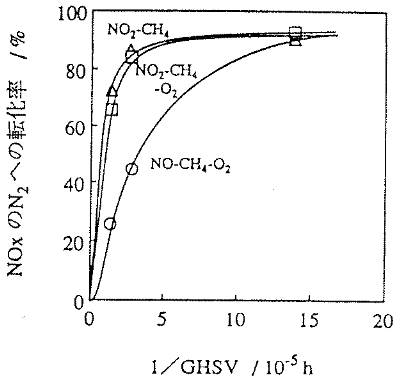

図 2　NO_x 転化率の空間速度依存性

○，NO，1000 ppm；CH_4，1000 ppm；O_2，10％；
△，NO_2，1000 ppm；CH_4，1000 ppm；O_2，0％；
□，NO_2，1000 ppm；CH_4，1000 ppm；O_2，10％；
流速，100 $cm^3 \cdot min^{-1}$；触媒重量，0.05－0.5 g；
反応温度，500℃；触媒，Ga/H-ZSM-5(92).

に2段階で進行すると考えられる.

$$NO + O_2 \longrightarrow NO_2 \text{（ゼオライト酸点上）} \quad (2)$$

$$NO_2 + CH_4 \longrightarrow N_2 + CO_x + H_2O \text{（Ga上）} \quad (3)$$

また本研究にはGaをイオン交換したZSM-5が高活性を示し，Al_2O_3に担持した場合やGa_2O_3単独酸化物では活性も選択性も低い．これは，Al_2O_3に担持されたGa_2O_3等に比べてGaカチオンの配位不飽和度が大きいためと考えられる．

以上Ga/ZSM-5上でのCH_4との反応機構について述べてきたが，Ga/ZSM-5のように酸型に分類される触媒は，炭化水素と酸素の反応性は低く，NO_2と炭化水素が効率的に反応する活性点を有するため高い選択性を達成し得るものと考えられる．これに対し遷移金属型では炭化水素の酸素との反応性が高く，部分酸化中間体を生成し易いと思われる．従って，NO選択還元触媒の設計においては，以下の3つの反応性を考慮することが重要と考えられる．

（1）NOと酸素の反応性
（2）炭化水素と酸素の反応性
（3）NO_2と炭化水素の反応性

（1）は主に触媒に依存し，（2）と（3）はこれに加えて炭化水素種の影響も大きい．以上をまとめると次のScheme 1のようになる．

(1)遷移金属型

$$C_mH_n + O_2 \longrightarrow C_xH_y(O) \xrightarrow{NO} N_2 + CO_x + H_2O$$

(2)酸型

$$NO + 1/2O_2 \longrightarrow NO_2$$

$$C_mH_n + NO_2 \longrightarrow N_2 + CO_x + H_2O$$

Scheme 1　炭化水素によるNO選択還元反応

なお，乾ら[26]は以上に述べた反応機構とは全く異なり，炭化水素により還元された触媒表面上でNOが分解するという微視的連続反応機構を提案している．

4.　今後の課題

以上述べてきたように，最近の研究により炭化水素によるNO_xの選択還元に活性を示す触媒系が数多く見いだされ，現在も活発に研究が展開されている．実用化に向けて以下に示すような課題が解決されねばならない．

（1）共存ガス，特にH_2O，SO_2による触媒活性の低下
（2）触媒作動温度域の拡大
（3）還元剤の効率的利用（選択性の向上）
（4）耐久性（活性成分及び担体の耐熱性・耐振動性）の向上

炭化水素還元剤の問題に限っても以下の点が指摘できる．例えば還元剤には主に低級炭化水素が用いられており，未燃の炭化水素を還元剤として利用することが考えられている．しかし，遷移金属または貴金属系の触媒では選択性が低く高いNO_x除去率を得るためには燃料を一部排ガスに加えることも考えなければならない．あるいはメタノール等のアルコール類を還元剤として添加することも検討されているが，これらは燃料消費率の低下を招き実用上は好ましくない[27]．従ってより選択性の高い触媒の開発が実用上不可欠である．

また，実排ガス中には還元剤となる炭化水素の成分が幅広く存在し，単一成分のみが存在するのではない．他の炭化水素による影響（例えば炭素析出）等も考慮しなければならない．従って，実排ガス中に含まれる炭化水素を考慮して，その排ガス処理に適した触媒の開発が必要である．

このように実用化へはまだ問題があるが，岩本らがCu/ZSM-5で炭化水素による選択還元を報告したのが1990年であり，まだこの触媒系の研究は始まったばかりであるといえる．しかし，大気汚染の問題は年々深刻化しておりその解決は緊急を要する．今後さらに研究が展開し実用触媒が開発されることを期待する．

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二酸化炭素の固体酸素への固定触媒

化石燃料の燃焼によって生成したCO_2を有用物質に変換する研究，技術開発が活発に行われている．筆者らは化石燃料，特に水素含有率の高いメタンを用いてCO_2の固体炭素への固定について検討してきた．理想的な反応は（1）である．

$$\mathrm{CO_2 + CH_4 \longrightarrow 2C + 2H_2O} \qquad (1)$$

例えば石炭の燃焼反応（2）と組み合わせると，

$$\begin{array}{ll} \mathrm{C + O_2 \longrightarrow CO_2} & (2) \\ \mathrm{CO_2 + CH_4 \longrightarrow 2C + 2H_2O} & (1) \\ \hline \mathrm{CH_4 + O_2 \longrightarrow C + 2H_2O} & (3) \end{array}$$

全反応は（3）となり，メタンの中の水素の燃焼のみを利用したことになる．

メタンは容易に固体炭素と水素とに分解することが出来るので，先ずCO_2のH_2による固体炭素合成触媒について検討した．

1.　CO_2の水素化による固体炭素への還元

一般に水素化反応では第Ⅷ族の金属が優れた触媒活性を有することが知られている．しかし，これらの金属は水素化能が非常に高いので，H_2を用いたCO_2の還元では，すでに多くの報告があるように高い選択率でCH_4などの炭化水素が生成する[1, 2]．そこで水素化能の比較的低い種々の金属酸化物または複合酸化物を触媒に用い，CO_2のH_2による接触還元反応を試みた[3, 4]．　Fig. 1 にWO_3触媒上のCO_2-H_2反応の結果を示した．CO_2のCへの還元反応は 300℃から進行し，500℃以上では反応温度の上昇とともにCへの転化率は増加した．一方，副生成物であるCOは 400℃から生成し始め，500℃以上ではCより生成速度は大きくなり，主生成物となっている．Table 1 に炭素への転化率が最も高くなった温度における種々の酸化物触媒での反応の結果を示した．Ⅱb，Ⅲa〜Ⅷ族の単独および複合酸化物ではいずれもCO_2のH_2による接触還元反応は進行したが，無触媒およびⅢb〜Ⅴb族の金属酸化物では反応はまったく進行しなかった．CuおよびCoを含む触媒では少量のCH_4の生成が認められたものの，大部分の触媒でCO_2はCOおよびCへ転化することがわかる．WO_3から$La_{0.9}Sr_{0.1}CoO_3$までの触媒ではいずれも高いCO_2転化率が得られるが，COの選択率が高い．しかし，WO_3，Y_2O_3，ZnOおよび$LaFe_{0.9}Cu_{0.1}O_3$では炭素への選択率が比較的高い．とくにWO_3では反応温度がやや高いものの，Cの収率は検討した触媒の中では最も高く，27.6％に達している．

Fig. 2 の 700℃におけるWO_3触媒によるCO_2の接触還元反応の反応時間依存性をみると，COの収率は反応時間によってほとんど変化しないが，CO_2転化率と炭素の

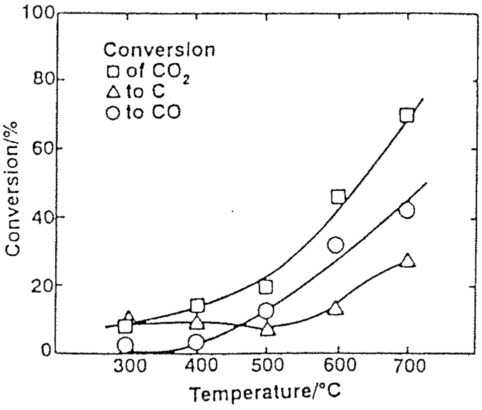

Fig. 1　CO_2-H_2 reaction over WO_3.
($CO_2 : H_2 : N_2 = 1 : 2 : 5$, W/F = 10 g·h/mol)

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Selective catalytic reduction of nitrogen monoxide by methane on zeolite catalysts in an oxygen-rich atmosphere

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Abstract

Selective reduction of NO by CH_4 on zeolite catalysts has been studied. After an investigation of the catalytic features of various cation-exchanged zeolites, we found that Ga-ZSM-5 and In-ZSM-5 were highly active and selective for NO reduction by CH_4. We also showed that this reaction was moderately promoted even by H-form ZSM-5, mordenite, and ferrierite. From the catalytic performance of Ga- and In-ZSM-5 in NO–CH_4–O_2, NO_2–CH_4–O_2, and NO–O_2 reactions, it is concluded that the selective reduction of NO on these catalysts proceeds in two stages: (1) NO is oxidized to NO_2 on zeolite acid sites, (2) NO_2 and CH_4 react on gallium or indium sites. The highly selective features of Ga and In in the zeolite for the NO_2–CH_4 reaction seem to be attributed to the coordinatively unsaturated nature of these sites which adsorb both of these reactants on the same site. Effect of water vapor on NO conversion was also investigated. It was found that Ga-ZSM-5 was strongly inhibited by steam, while In-ZSM-5 was fairly active even in the presence of 10% steam.

1. Introduction

The reduction of nitrogen oxides (NO_x) to molecular nitrogen is an important task for environmental chemistry. Recently, selective catalytic reduction (SCR) of NO by hydrocarbons in an oxygen-rich atmosphere has attracted considerable attention as a new type of reaction alternative for the traditional NH_3-SCR process. This reaction was reported to proceed on various cation-exchanged zeolites [1–5], metallosilicates [6,7], Al_2O_3 [8,9], and SiO_2–Al_2O_3 [10], when C_2H_4 or higher hydrocarbons were used as reductant. These studies showed that oxygen was a necessary component for this reaction system. It was shown in our previous work [5,11] that gallium ion-exchanged ZSM-5 and ferrierite were

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active for the reduction of NO by C_3H_8 and C_2H_4, and these catalysts were the most selective among the above-mentioned catalysts.

Iwamoto et al. [12] and Hamada et al. [13] have studied the effect of hydrocarbon species for this reaction on Cu-ZSM-5 and Al_2O_3 catalysts, respectively. They classified the reductants into two groups, one is selective (C_2H_4, C_3H_6, C_3H_8, C_4H_8), and the other is non-selective (CH_4, C_2H_6) [14]. For example, on Cu-ZSM-5 and Al_2O_3, being active for selective reduction of NO in a NO–O_2–C_2H_4 system, CH_4 and C_2H_6 were predominantly consumed by combustion and the NO–CH_4 or NO–C_2H_6 reaction hardly occurred. Therefore, it has been proposed by them that CH_4 and C_2H_6 are rather inactive for reduction of NO on these catalysts. They have also described that H_2 and CO are not effective reductants.

It would be very useful if the selective reduction of NO was possible by use of methane as reductant, since methane is found in every combustion exhaust, particularly from a gas-cogeneration system. Therefore, several recent research studies have tried to develop a catalyst which is active for selective reduction by CH_4. Li and Armor [15] reported that the selective reduction proceeded on Co-ZSM-5. In our previous study [16], we showed that Ga-ZSM-5 was highly active and selective for reduction of NO by CH_4 or C_2H_6. It was also found that the molar ratios of reacted NO molecules to consumed carbon atom in CH_4 and C_2H_6 were 2 and 1.5, respectively. Furthermore, it was reported that reduction of NO by CH_4 proceeded on Mn- [17], Ni- [17], Pd- [18], and In-ZSM-5 [19]. Therefore, CH_4 is a candidate effective reductant for the selective reduction of NO, if an appropriate catalyst is chosen.

We have recently found that various H-form zeolite catalysts are also active and fairly selective for this reaction [20]. In this paper, we describe the catalytic properties of Ga-, In- and H-form zeolites for the selective reduction of NO by CH_4, the reaction mechanism, and the effect of water vapor.

2. Experimental

Zeolites used in this study were ZSM-5 (molar SiO_2/Al_2O_3 ratio, 23.3), mordenite (19.9), ferrierite (17.8), and USY (14.5), supplied by the Tosoh Corporation. Gallium and indium ion-exchanged ZSM-5 were prepared by ion-exchange of ammonium form ZSM-5 using aqueous solutions of nitrate at 95°C for 24 h, followed by calcination at 500°C. The chemical composition of the catalysts was determined by means of inductively coupled plasma (ICP) atomic emission spectroscopy. The degree of the ion-exchange level was calculated assuming that the oxidation numbers were 3 for Ga and In, and 2 for Co. These catalysts will be abbreviated, for example, as Ga-ZSM-5 (92), where the value in parentheses represents the level of gallium exchange. Alumina, as a reference catalyst, was obtained from Catalysts and Chemical Ind. Co.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO (or NO_2), 10% O_2, 150–2000 ppm CH_4, and He (balance) was fed to 0.05–0.5 g catalyst at a rate of 100 cm^3(STP) $\cdot$ min^{-1}. Effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO and NO_2. The catalytic activity was evaluated by the level of NO conversion to N_2, after reaching steady-state.

3. Results and discussion

3.1. Selective reduction of NO by CH_4 on gallium and indium ion-exchanged zeolites

Fig. 1 compares the catalytic activities of various zeolites exchanged with gallium. The activity depended on the type of zeolite. Ga-ZSM-5 was the most highly active of the catalysts in the studied temperature range and reaction conditions. Although Ga-mordenite and Ga-ferrierite were highly active above 500°C, their activity was poor below this temperature. Ga-USY was the least active at these temperatures.

The ratio of NO conversion to CH_4 conversion is a measure of selectivity. The selectivity for NO reduction is defined by the following equation.

$$\text{Selectivity} = (\text{number of reacted NO to } N_2) / (\text{number of reacted } CH_4 \text{ to CO and } CO_2) \qquad (1)$$

The selectivity of these catalysts for NO reduction is shown in Fig. 2. The selectivity was 2 below 500°C.

The stoichiometry of the reaction on Ga-ZSM-5 can be written as in the following equation:

$$2NO + CH_4 + (x/2)O_2 \rightarrow N_2 + CO_x + 2H_2O \qquad (2)$$

The decrease in the selectivity above 500°C is attributed to combustion of CH_4, which became remarkable at this temperature.

Fig. 3 shows the temperature dependence of catalytic activities of Ga-ZSM-5, In-ZSM-5, H-ZSM-5, and Al_2O_3. In-ZSM-5 showed higher NO conversion at lower temperature than Ga-ZSM-5. The largest NO conversion on In-ZSM-5 was obtained at 400°C, while it was 500°C on Ga-ZSM-5. Although the selectivity for NO reduction on In-ZSM-5 was slightly lower than that on Ga-ZSM-5 at 500°C, NO was selectively reduced to N_2 at 400°C

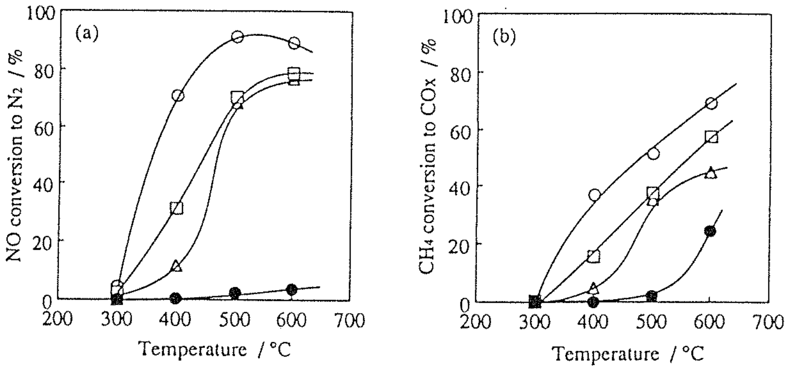

Fig. 1. Variation in NO conversion (a) and CH_4 conversion (b) on various catalysts as a function of reaction temperature. (○) Ga/H-ZSM-5 (92); (△) Ga/H-ferrierite (91); (□) Ga/H-mordenite (103); (●) Ga/H-USY (106). NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

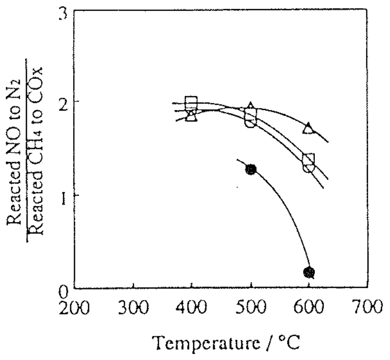

Fig. 2. Selectivity expressed by the ratio of reacted NO to consumed CH_4 as a function of reaction temperature. (○) Ga/H-ZSM-5 (92); (△) Ga/H-ferrierite (91); (□) Ga/H-mordenite (103); (●) Ga/H-USY (106). NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

and below, as shown in Fig. 4. H-ZSM-5 was also active for this reaction, while it was less selective than Ga-ZSM-5. The catalytic activity and selectivity of Al_2O_3 were extremely low compared with Ga-, In-, and H-ZSM-5. Although it was shown that Al_2O_3 exhibits high selectivity for NO reduction by C_3H_8 [13], CH_4 was preferentially consumed by combustion and the selectivity was extremely low as shown in Fig. 4.

Both NO conversion and the selectivity for NO reduction were low when Al_2O_3-supported Ga_2O_3 was used as catalyst, and the selectivity of unsupported Ga_2O_3 was likewise low as shown in Fig. 5. From these results, it can be concluded that ion-exchange onto zeolite is required to accomplish high selectivity of gallium. Gallium cations are known as an NO_x sensor material, which increases the sensitivity of ZnO thin film sensor to NO_x [21], and

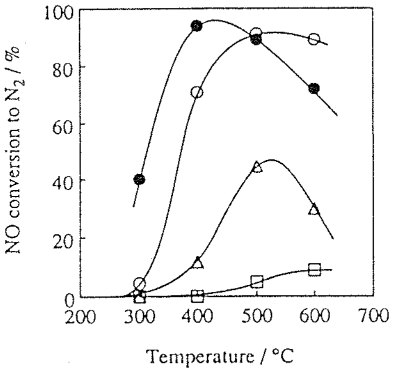

Fig. 3. Reduction of NO by CH_4 on various catalysts: (○) Ga/H-ZSM-5 (92); (△) H-ZSM-5; (□) Al_2O_3; (●) In/H-ZSM-5 (86). NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

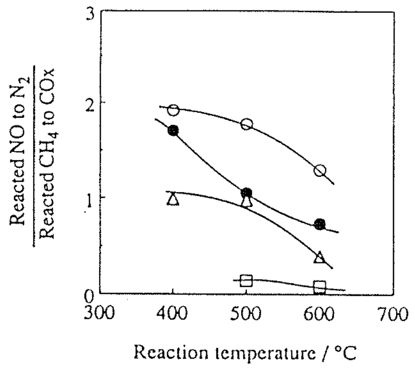

Fig. 4. Selectivity expressed by the ratio of reacted NO to consumed CH_4 as a function of reaction temperature. (○) Ga/H-ZSM-5 (92); (△) H-ZSM-5; (□) Al_2O_3; (●) In/H-ZSM-5 (86). NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

also acts as the coordination center for alkyl groups in organogallium compounds. Therefore, the high selectivity of gallium cations in ZSM-5 seems to be attributed to their high affinity to NO_x and alkyl species, and to efficient coordination of NO_x and hydrocarbon species at the same unsaturated gallium cation sites.

Fig. 6a shows the effect of hydrocarbon concentration on the catalytic activity of Ga-ZSM-5 at 500°C in comparison with H-ZSM-5. NO conversion increased with increasing concentration of CH_4. It is noted that Ga-ZSM-5 showed high catalytic activity even with a very small concentration of CH_4. The relationship between the molar ratio of reacted NO to produced CO_x and the concentration of CH_4 is shown in Fig. 6b. The limiting molar ratio of reacted NO to consumed CH_4 was 2. This ratio was almost independent of the concentration of CH_4 on Ga-ZSM-5, although the ratio decreased with increasing concentration of

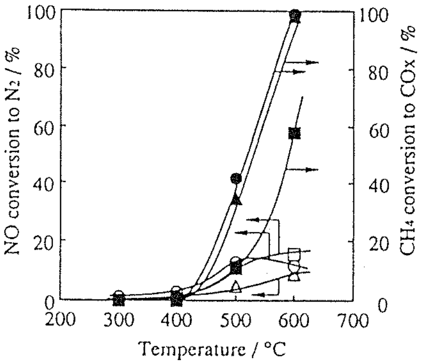

Fig. 5. Catalytic activities of Ga_2O_3 (□,■), Ga/Al_2O_3 (○,●), and Al_2O_3 (△,▲), for NO conversion (open symbol) and CH_4 conversion (solid symbol). NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

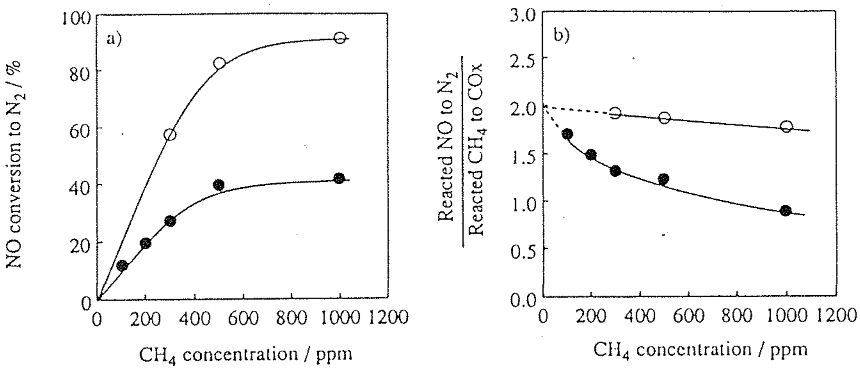

Fig. 6. NO reduction on Ga/H-ZSM-5 (○) and H-ZSM-5 (●) as a function of CH_4 concentration. NO, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g; temperature, 500°C.

H-ZSM-5. Reduction of NO by CH_4 proceeded predominantly on Ga-ZSM-5, and CH_4 was hardly consumed by the reaction with O_2. It is suggested that the contribution of CH_4 oxidation became more pronounced with increasing concentration of CH_4 on H-ZSM-5 leading to a decrease in selectivity for NO reduction.

3.2. Selective reduction of NO by CH_4 on H-form zeolites

Fig. 7 shows the temperature dependence of catalytic activities of various H-form zeolites for NO reduction by CH_4. Of these catalysts, H-ZSM-5 showed the highest activity at 500°C. H-USY was inactive under these reaction conditions, and its activity was comparable to that of Al_2O_3. The CH_4–O_2 reaction was predominant and NO reduction hardly took place

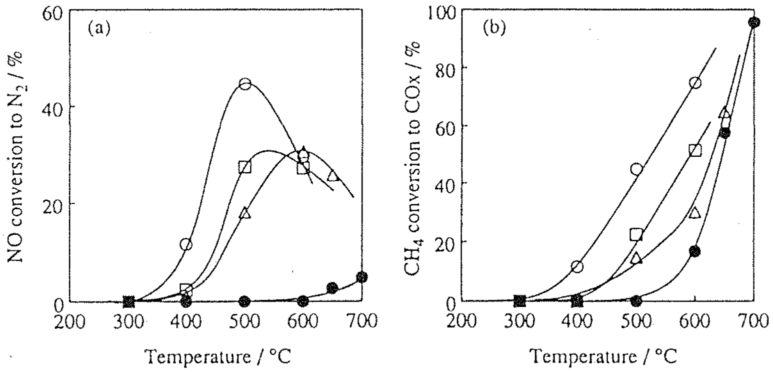

Fig. 7. Variation in NO conversion (a) and CH_4 conversion (b) on various zeolites as a function of reaction temperature. (○) H-ZSM-5; (□) H-mordenite; (△) H-ferrierite; (●) H-USY. NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

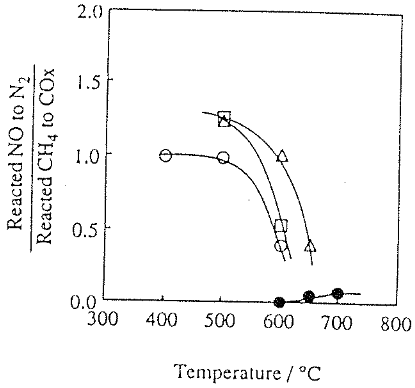

Fig. 8. Relationships between the ratio of reacted NO to consumed CH_4 and reaction temperature. (○) H-ZSM-5; (□) H-mordenite; (△) H-ferrierite; (●) H-USY. NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

on these catalysts. As shown in Fig. 8, H-ferrierite was the most selective and the decreasing order of selectivity for this reaction was as follows:

$$\mathrm{H-ferrierite > H-mordenite > H-ZSM-5 \gg H-USY}$$

H-ferrierite exhibited the least activity for the CH_4–O_2 reaction, resulting in high selectivity for NO reduction.

It has been reported by Hamada and co-workers [2] that the acidity of catalysts is one of the important factor controlling the catalytic activity for selective reduction of NO by C_3H_8. Fig. 9 shows NH_3-TPD spectra of various zeolites used in this study. H-USY showed very little acidity with weak acid strength, suggesting that the low catalytic activity of H-USY is probably due to its poor acidity.

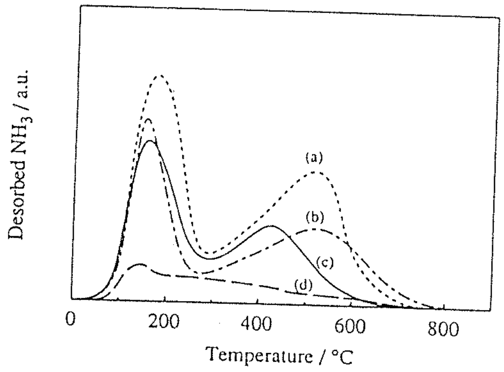

Fig. 9. NH_3-TPD spectra of various zeolites. (a) H-ferrierite; (b) H-mordenite; (c) H-ZSM-5; (d) H-USY.

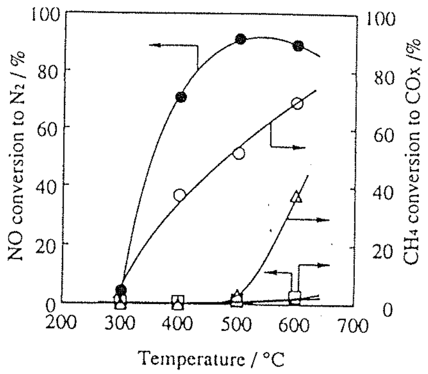

Fig. 10. Catalytic activities of Ga/H-ZSM-5 (92) in $NO-CH_4-O_2$ (●,○) $NO-CH_4$ (■,□), and CH_4-O_2 (△) reaction. NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

The decreasing order of selectivity for NO reduction on gallium ion-exchanged zeolites and that on H-form zeolites were same, and this order was found to be related to the acidity of the zeolites. We will describe the role of the acidity for this reaction connected with the reaction mechanism below.

3.3. Reaction mechanism for the selective reduction of NO by CH_4 on Ga- and In-ZSM-5

Several reaction mechanisms have been proposed for the reduction of NO with hydrocarbons [7,22–24]. The mechanism may vary from one type of catalyst to another, or it may depend on the kind of hydrocarbons used as reductant as well as the reaction conditions. We shall discuss the reaction mechanism of selective reduction by CH_4 on Ga- and In-ZSM-5 below.

Fig. 10 shows NO conversion to N_2 and CH_4 conversion to CO_x on Ga-ZSM-5 at various reaction temperatures. The $NO-CH_4$ reaction hardly took place, in the temperature range studied, in the absence of O_2, showing that NO reduction was promoted by O_2. Furthermore, oxidation of CH_4 did not take place below 500°C in the absence of NO. Not only Ga-ZSM-5 but all of the zeolite catalysts used in this study were inactive for the reduction of NO by CH_4 in the absence of O_2 and for the oxidation of CH_4 in the absence of NO.

Since NO reduction occurred under the conditions where CH_4 could not be activated solely by O_2, NO_2 is involved in the selective reduction. This conclusion is in accordance with the observation by Hamada and co-workers [22] for the selective reduction of NO by C_3H_8 on Al_2O_3 and H-form zeolites. They claimed that the $NO-C_3H_8$ reaction proceeded via a $NO_2-C_3H_8$ reaction and that the high selectivity is attributable to a $NO_2-C_3H_8$ reaction and to the poor activity of these catalysts for C_3H_8 oxidation by O_2.

In Fig. 11, we compare the level of NO or NO_2 conversion to N_2 as a function of reciprocal GHSV. A higher NO_2 conversion was obvious in the $NO_2-O_2-CH_4$ and NO_2-CH_4 systems than in the $NO-O_2-CH_4$ system at high GHSV. In the latter system, NO conversion to N_2 showed an induction period. Furthermore, there was no appreciable difference in the level

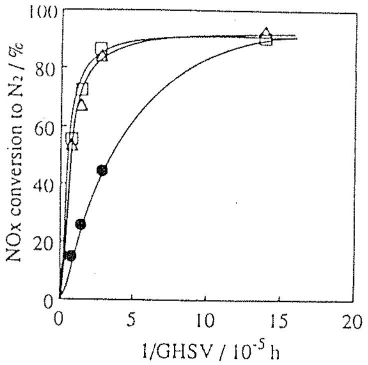

Fig. 11. Relationships between NO_x conversion and GHSV on Ga/H-ZSM-5 (92). (●) NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%. (□) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 0%. (△) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10%. Total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.05–0.5 g; temperature, 500°C.

of NO_2 conversion between the NO_2–CH_4 and the NO_2–O_2–CH_4 systems. Therefore, the predominant reaction of oxygen under these conditions should be the formation of NO_2. Namely, it seems that the first step is NO oxidation to NO_2, which further reacts with CH_4 to give N_2, CO_x, and H_2O.

As shown above, the acidity of the catalysts is correlated to the catalytic activity and selectivity for this reaction. Fig. 12 shows the effect of the proton exchange level on the catalytic activity on H/Na-ZSM-5. Na-ZSM-5 was completely inactive for NO oxidation. NO conversion increased with increasing proton exchange level. A similar correlation was observed for the case of the H/Na/Ga system. Therefore, it is reasonable to consider that the zeolitic acid sites are involved in NO oxidation to NO_2. Additionally, NO conversion

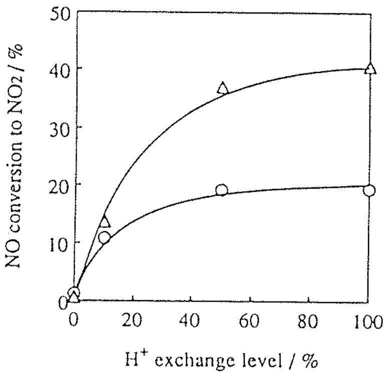

Fig. 12. Effect of H^+ exchange level on the catalytic activity for NO oxidation to NO_2 on H/Na-ZSM-5. NO, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.1 g. Temperature: (○) 500°C; (△) 400°C.

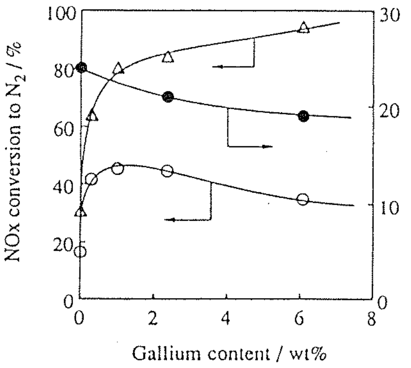

Fig. 13. Catalytic activity of Ga/H-ZSM-5 as a function of gallium content. (○) NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%. (△) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10%. (●) NO, 1000 ppm; O_2, 10%. Total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.1 g; temperature, 500°C.

to NO_2 on H-ZSM-5 at 400°C increased from 30% to 35% under these reaction conditions when increasing the pretreatment temperature from 500°C to 800°C. It is, thus, assumed that oxygen is adsorbed on Lewis acid sites and is activated by the electrostatic polarization caused by the zeolite framework [25], and that the gas phase NO molecule attacks the activated oxygen to form NO_2.

Therefore, we deduce that the selective reduction of NO by CH_4 on Ga-ZSM-5 proceeds according to the following two stages:

$$NO + O_2 \rightarrow NO_2 \text{ [on zeolite acid sites]} \quad (3)$$

$$NO_2 + CH_4 \rightarrow N_2 + CO_x + H_2O \text{ [on gallium (or indium) sites]} \quad (4)$$

These reaction sequences are in accordance with the effect of the gallium content on the activities of Ga/H-ZSM-5 catalysts, as shown in Fig. 13. The catalytic activity for NO oxidation decreased and the level of NO_2 conversion in the NO_2–CH_4 system increased with increasing gallium content. On the other hand, the level of NO conversion in the NO–O_2–CH_4 system gave a maximum around 1 wt.-% gallium. It is obvious that the effect of gallium is not the promotion of NO oxidation, but the promotion of the NO_2–CH_4 reaction. As In/H-ZSM-5 showed a similar performance to Ga/H-ZSM-5, the same reaction mechanism probably operates on these catalysts.

It is noted that Ga/Al_2O_3 and Ga_2O_3 were not active for the reduction of NO_2 by CH_4 in the NO_2–CH_4–O_2 system. It means that active sites for the NO_2–CH_4 reaction hardly exist on these catalysts. The state of gallium exchanged into zeolite should be very different from that on gallium oxides. The former should exist in a coordinatively unsaturated state compared with the latter [26]. It is thought that the zeolite framework is effective in making it possible for a gallium site to adsorb both NO_2 and hydrocarbon species which further react efficiently on the same site.

NO_2 is reduced by CH_4 to N_2, being accompanied by the formation of CO and/or CO_2. It is interesting to observe whether carbon monoxide or carbon dioxide is formed first. Fig.

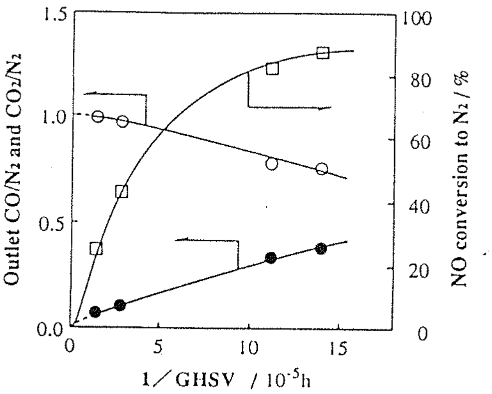

Fig. 14. NO conversion to N_2 (□) and the ratio of produced CO to N_2 (○) and CO_2 to N_2 (●) in a NO–CH_4–O_2 system on Ga/H-ZSM-5 (101). NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.05–0.5 g; temperature, 500°C.

14 shows that CO was selectively formed on Ga-ZSM-5 in the initial stage of the reaction, and that the selectivity for CO decreased with increasing conversion of NO. Therefore, on this catalyst, CO is the primary product of the reduction of NO. CO_2 might be formed by the secondary reaction of CO with O_2 or NO_2. At high GHSV conditions, the molar ratio of produced CO to produced N_2 was unity on Ga-ZSM-5. A similar result was reported on Cu-ZSM-5 [27], where a considerable amount of CO was produced with N_2 in the temperature-programmed reaction of NO and C_3H_6. The stoichiometry for the initial production of CO in NO reduction can be written as follows:

$$NO_2 + CH_4 + NO \rightarrow N_2 + CO + 2H_2O \qquad (5)$$

As mentioned above, reduction of NO proceeds via the NO_2–CH_4 reaction, and one additional NO molecule may participate in the formation of CO as shown in Eq. (5). However, it was found that CO_2 was the primary product in the NO_2–CH_4 reaction and that the molar ratio of produced CO_2 to produced N_2 was unity at high GHSV conditions. Therefore, the stoichiometry for the NO_2–CH_4 reaction can be written as follows:

$$NO_2 + CH_4 + NO_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad (6)$$

We propose that the reaction mechanism for NO reduction by CH_4 on Ga-ZSM-5 is as follows: NO_2 oxidized on zeolite acid sites activates CH_4 and forms a reaction intermediate. Successively, the intermediate reacts with the gas phase NO molecule to produce N_2 and CO. CO_2 might be formed the reaction (10) or (11).

$$NO + 1/2O_2 \rightarrow NO_2 \qquad (7)$$

$$NO_2 + CH_4 \rightarrow [X] \text{ (a reaction intermediate)} + nH_2O \qquad (8)$$

$$[X] + NO \rightarrow N_2 + CO + mH_2O \qquad (9)$$

$$[X] + NO_2 \rightarrow N_2 + CO_2 + mH_2O \qquad (10)$$

$$CO + O_2 \text{ (or } NO_2) \rightarrow CO_2 \qquad (11)$$

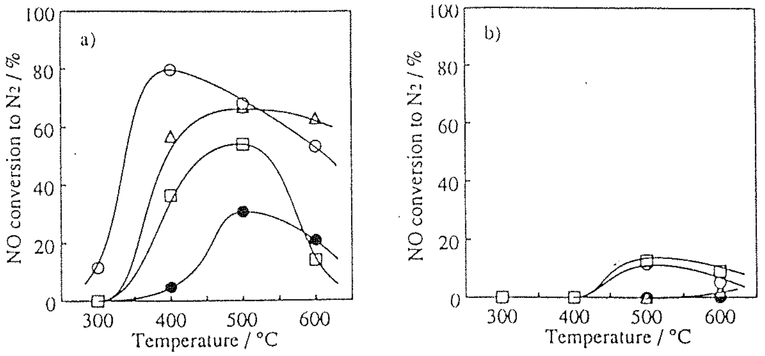

Fig. 15. Effect of water addition on the catalytic activities of various ion-exchanged ZSM-5 for reduction of NO by CH_4. (a) NO, 1000 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 0%. (b) NO, 1000 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 10%. Total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.25 g. (○) In/H-ZSM-5 (92); (△) Ga/H-ZSM-5 (96); (□) Co/H-ZSM-5 (65); (●) H-ZSM-5.

This reaction mechanism has been proved by the transient response study [28]: after reaching steady-state, the reactant was switched to NO gas in He balance. An equimolar mixture of N_2 and CO was formed.

In contrast to Ga-ZSM-5, it was found that In-ZSM-5 yielded CO_2 selectively. As the selectivity for CO also increased with increasing GHSV on this catalyst, it is thought that the reaction mechanism on In-ZSM-5 is similar to that on Ga-ZSM-5.

3.4. Effect of water vapor on the selective reduction of NO by CH_4

As previously mentioned, the high selectivity of Ga-ZSM-5 is attributed to coordinatively unsaturated gallium cations having a high affinity to NO_x and hydrocarbon species. Therefore, the effect of water vapor seems significant, since the Lewis acidity is responsible for this reaction. Fig. 15 shows the effect of water vapor on NO conversion on Ga-, In-, Co-, and H-ZSM-5 catalysts. NO conversion significantly decreased when 10% water vapor was added to the reactant feed. All these catalysts, particularly, Ga-ZSM-5 and H-ZSM-5 were very sensitive to H_2O. For H-ZSM-5, Lewis acid sites were poisoned by water vapor. On the other hand, Co- and In-ZSM-5 moderately reduced NO even in the presence of water vapor, although the effect of water vapor was also significant.

The poisoning of the catalytic activity of Ga- and In-ZSM-5 was, however, completely reversible: it was restored when steam was removed from the reactant mixture. Probably, H_2O is preferentially adsorbed on the unsaturated gallium or aluminum sites and inhibits the adsorption of NO_x and/or hydrocarbon species.

In contrast to the NO–CH_4–O_2 system, the effect of water vapor on NO_2 conversion on In-ZSM-5 was relatively unimportant in the NO_2–CH_4–O_2 system as shown in Fig. 16. NO_2 conversion on the other catalysts was almost the same as in the NO–CH_4–O_2 system. From these results, it is deduced that the effect of water vapor for the NO_2–CH_4 reaction (Reaction (4)) on indium sites is relatively unimportant, although the NO oxidation reaction (Reac-

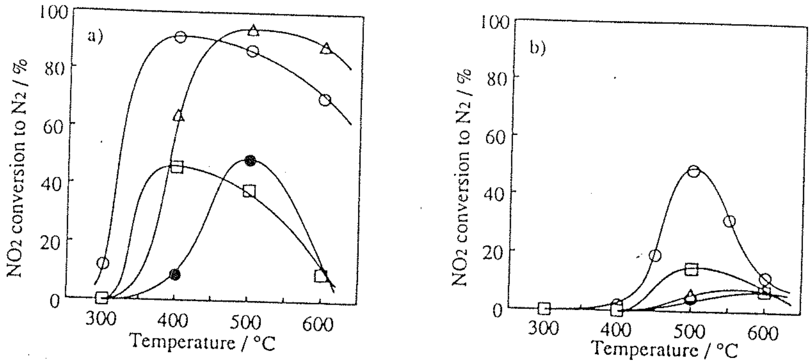

Fig. 16. Effect of water addition on the catalytic activities of various ion-exchanged ZSM-5 for reduction of NO_2 by CH_4. (a) NO_2, 1000 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 0%. (b) NO_2, 1000 ppm; CH_4, 2000 ppm; O_2, 10%; H_2O, 10%. Total flow-rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.25 g. (○) In/H-ZSM-5 (92); (△) Ga/H-ZSM-5 (96); (□) Co/H-ZSM-5 (65); (■) H-ZSM-5.

tion (3)) is strongly affected by H_2O. Although further studies are required to understand the higher durability of In-ZSM-5 for steam than Ga-ZSM-5, the affinity of H_2O to indium cations is probably smaller than to gallium cation.

4. Conclusions

We conclude from these results that the reduction of NO proceeds selectively on Ga- and In-ZSM-5 even when CH_4 is used as a reductant, and CH_4 can be an effective reductant for the selective reduction of NO. Selective reduction on these catalysts proceeds in two stages: (1) NO is oxidized to NO_2 on zeolite acid sites, (2) NO_2 and CH_4 react on gallium or indium sites. The effect of water vapor on these reactions was significant. It was found, however, that the effect was completely reversible and that In-ZSM-5 was moderately active even in the presence of a high concentration of water vapor.

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1A7 GaおよびInイオン交換ゼオライト上でのメタンによるNO選択還元反応機構

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GaおよびInイオン交換ゼオライト触媒上でのCH_4によるNO還元反応機構について検討を行い，NO選択還元に対するGaおよびInの効果について検討した。種々の反応の結果からNO還元反応は①NOの酸化によるNO_2の生成，および②NO_2とCH_4による反応，の2段階で進行することが明らかとなった。H/Na-ZSM-5のH^+交換率とともにNO酸化活性が増加することから，反応①にはゼオライト酸点が関与すると考えられる。GaおよびInのイオン交換によりNO酸化活性は低下するが，NO還元活性は増加することから，GaおよびInの役割は反応②の促進であると考えられる。またこれらの触媒がNO_xとCH_4の反応に極めて高選択的であることに着目して，反応の化学量論および過渡応答法による解析から，本反応に対してNO_2とCH_4により生成した反応中間体が気相のNO（またはNO_2）と反応し，N_2とCO（またはCO_2）を生成する反応機構を提唱した。

［討論したい事項］①GaおよびInの役割　②NO選択還元反応機構

1．緒言

これまでに酸素過剰雰囲気下での炭化水素によるNO選択還元反応に対して活性を示す触媒が数多く報告されてきた$^{1-5)}$。また，これまでに反応機構もいくつか提唱され，部分酸化中間体，およびNO_2中間体に大別される$^{6-12)}$。しかし，反応機構に関しては未解明な点が多く，詳細は明らかになっていない。

我々はこれまでに，GaおよびInイオン交換ゼオライトが酸素過剰雰囲気下でのCH_4によるNO還元反応に対して高活性，高選択性を示し，反応するNO_xとCH_4の比が$NO_x:CH_4=2:1$であることを見いだした$^{13)}$。また本反応の第一段階はNOの酸化によるNO_2の生成であり，反応性の高いNO_2とCH_4の反応により反応が進行することを報告している$^{14)}$。本報告では，本触媒系の高選択的な特性を利用してNO選択還元の反応機構および反応に有効な活性点について検討した。

2．実験

ゼオライトへのガリウムおよびインジウムの担持は，硝酸塩水溶液を用い，イオン交換法により行った。硝酸アンモニウム水溶液にてNH_4^+型としたゼオライトを硝酸ガリウムまたは硝酸インジウム水溶液中にて95℃24時間攪拌し調製した。ゼオライトは東ソー製のZSM-5(SiO_2/Al_2O_3比は23.3)を用いた。触媒中のGa^{3+}およびIn^{3+}イオン交換率（%）はICPにより求め，Ga-ZSM-5(101)のように示した。

反応は常圧固定床流通式反応装置を用い，反応温度300－600°C，NO濃度1000－2000ppm，O_2濃度は5-10%で行った。また，CH_4濃度は1000ppm，空間速度は7200－72000h^{-1}（全流量100$cm^3\cdot min^{-1}$，触媒重量0.05－0.5g）の範囲で変化させた。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。なお，活性はすべてNOのN_2への転化率で評価した。

また過渡応答実験には4方コックにて反応ガス組成を切り換えられるように2つの反応ガスラインを備えた装置を用い，2連8方コックにて生成ガスをサンプリングし，TCDを用いて分析を行なった。

3．結果と考察

3．1　Ga，Inイオン交換ゼオライトの高選択性

すでに報告したようにGa-ZSM-5は400℃以上の温度域でCH_4によるNO還元反応に高活性を示し，選択性も極めて高い。またGa-ZSM-5上では反応するNO_xとCH_4の比が $NO_x/CH_4 \leqq 2$ であり

$$2NO + CH_4 + kO_2 = N_2 + CO_x + 2H_2O \quad .....(1)$$

の化学量論で示される$^{13)}$。

また，Gaと同族元素であるIn-ZSM-5はGa-ZSM-5よりもNO還元の選択性は若干低下するが，低温で活性を示し，かつ生成するCO_xはほとんどがCO_2であった（図1）。これは図2に示すようにIn-ZSM-5はGa-ZSM-5と比較してCOのCO_2への酸化活性が非常に高いためCO_2が選択的に生成するものと考えられる。

3．2　NO選択還元反応に対するGaおよびInの役割

Ga-，In-ZSM-5ともに酸素が存在しない場合NOとCH_4の反応は起こらないことから，本反応には酸素の存在が不可欠である。また，500℃以下ではCH_4の燃焼はほとんど進行しない。従って本反応にはNOと酸素から生成したNO_2が関与すると考えられる。Ga-およびIn-ZSM-5上での$NO-CH_4-O_2$，$NO_2-CH_4-O_2$，及びNO_2-CH_4反応の結

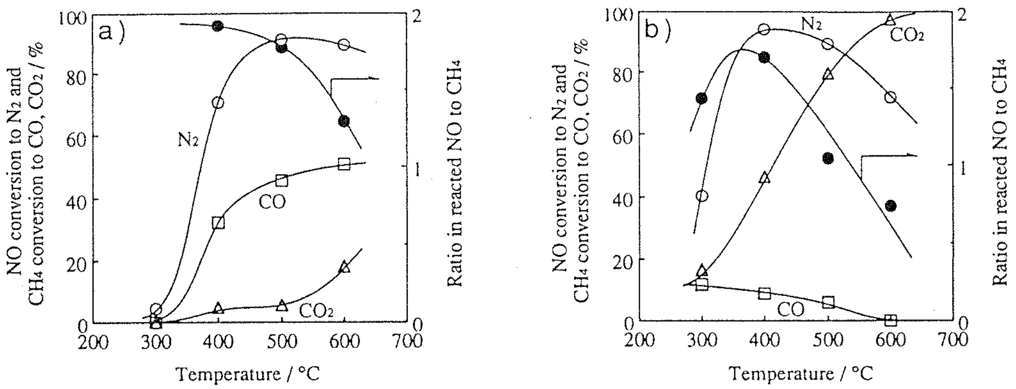


Fig.1. NO conversion to N_2 and CH_4 conversion to CO, CO_2 and ratio in reacted NO to CH_4 on: a), Ga-ZSM-5(92); b), In/H-ZSM-5(86) as a function of reaction temperature. ○, N_2; □, CO; △, CO_2; ●, ratio to reacted NO to CH_4; NO, 1000 ppm; CH_4 1000 ppm; O_2, 10 %; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

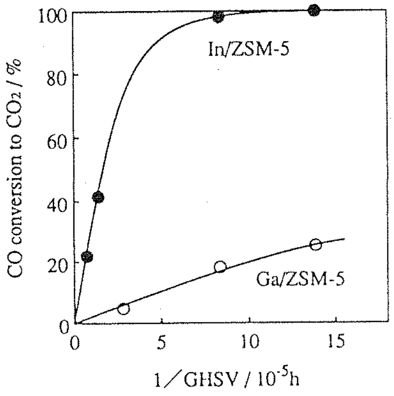


Fig.2. Oxidation of CO to CO_2 by O_2.
CO, 1000ppm; O_2, 10%; ○, Ga-ZSM-5(101); ●, In-ZSM-5(95); total flow rate, 100$cm^3 \cdot min^{-1}$; catalyst weight, 0.025-0.5g; reaction temperature; 500°C (Ga/ZSM-5); 400°C (In/ZSM-5).

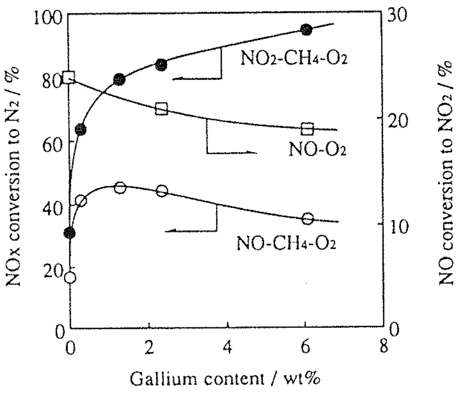


Fig.3. Catalytic activity of Ga-ZSM-5(92) as a function of Gallium content.
○ : NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10 %;
● : NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10 %;
□ : NO, 1000 ppm; O_2, 10 % ;
total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.1g; reaction temperature, 500 °C.

果を比較すると，高GHSV条件下ではNO_2系に比べてNO系の方がN_2への転化率が低く，NO_2系では酸素が存在しなくても同程度の活性を示すことから，本反応にはNO_2の生成が不可欠であり酸素の役割はNO_2の生成にあると考えられる。

次にGaおよびInの役割について検討を行った。図3に示すようにGa担持量の増加とともにH-ZSM-5と比較してNO酸化活性は減少したが，NO_2-CH_4反応でのNO_2転化率は増大した。またNO-CH_4-O_2反応では交換率50％で転化率は最大となり，過剰の添加により転化率は低下した。In-ZSM-5でも同様の結果となった。従って，GaおよびInの役割はNOのNO_2への酸化を促進することではなく，NO_2とCH_4の反応の促進であり，本反応の高選択性はゼオライトにイオン交換されたGaおよびIn上でNO_2とCH_4の反応が選択的に進行するためと考えられる。Ga-ZSM-5はCH_4を解離吸着させることができるとの報告があることから[14]，GaあるいはIn上でCH_4の解離が促進されNO_2と容易に反応すると考えられる。

従って，これらのことからGaおよびIn-ZSM-5上でのNO選択還元反応は以下のように二段階で反応が進行すると考えられる。

$NO + O_2 = NO_2$ （ゼオライト酸点上） .....(2)
$NO_2 + CH_4 = N_2 + CO_x + H_2O$ (Ga or Inサイト上) .....(3)

3．3 NO選択還元反応機構

Ga-ZSM-5上でのNO-CH_4-O_2反応において生成するCOおよびCO_2について検討した（図4）。反応初期にN_2とCOがほぼ1:1で生成し，CO_2はほとんど生成せず，反応の一次生成物はCOであることがわかった。反応するNO_xとCH_4の比がNO_x:CH_4=2:1であること，NO_2とCH_4の反応により本反応が進行することから，本反応は

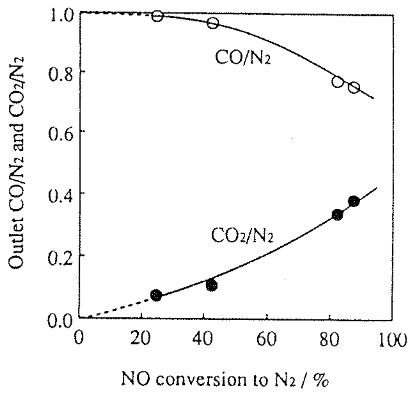


Fig.4. Ratio of produced CO to N_2(○) and CO_2 to N_2(●) as a function of NO conversion to N_2 in NO - CH_4 - O_2 system. NO, 1000ppm; CH_4, 1000ppm; O_2, 10%; total flow rate, $100 cm^3 \cdot min^{-1}$; catalyst weight, 0.05-0.5g; reaction temperature, 500°C; catalyst, Ga-ZSM-5(101).

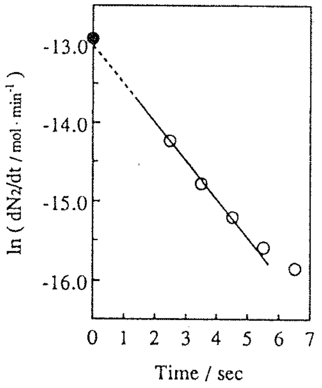


Fig.6. Relationship between ln(dN_2/dt) and reaction time. Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5%; Reaction (B): NO, 2000ppm; total flow rate, $100 cm^3 \cdot min^{-1}$; catalyst weight, 0.2g; reaction temperature, 500°C; catalyst, Ga-ZSM-5(101).

$$\mathrm{NO_2 + CH_4 + NO = N_2 + CO + 2H_2O} \quad .....(4)$$

の化学量論式で示される。

そこで次に過渡応答法により反応機構を検討した。図5に示すように，反応が定常に達した後に反応ガスをO_2あるいはHeに切り換えてもN_2は生成しなかったが，NOに切り換えるとN_2が生成した。また，図6に示すようにこの時のN_2生成速度の対数と反応時間に直線関係があり，外挿値は定常時のN_2生成速度にほぼ一致した。このことからN_2生成反応は中間体濃度について一次であり，N_2は中間体とNOの反応により生成するものと考えられる。またこの時，NOを導入するとN_2とほぼ同量のCOが生成し，CO_2はほとんど生成しなかった（図７）。

また同様にNO_2系の反応についても生成するCO，CO_2について検討した（図８）。NO_2転化率を零に外挿すると，NO系とは逆にCO_2とN_2が1:1で生成し，COはほとんど生成しなかった。このことからNO_2系では反応の一次生成物がCO_2であり，(5)式に示すように，化学量論的にはCH_4と2分子のNO_2の反応によりN_2とCO_2を生成するものと考えられる。

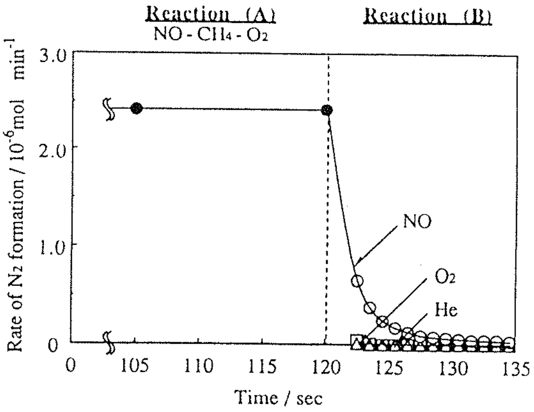


Fig.5. Effect of reactant components on N_2 formation. Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5% (●); Reaction (B): NO, 2000ppm (○); O_2, 5% (□); He only, (△); total flow rate, $100 cm^3 \cdot min^{-1}$; catalyst weight, 0.2g; reaction temperature, 500°C; catalyst, Ga-ZSM-5(101).

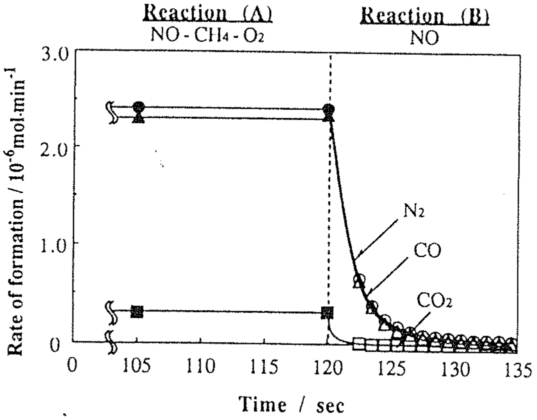


Fig.7. Transient response of the rate of N_2(○,●), CO(△,▲) and CO_2(□,■) formation when reactant component was changed. Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5%; Reaction (B): NO, 2000ppm; total flow rate, $100 cm^3 \cdot min^{-1}$; catalyst weight, 0.2g; reaction temperature, 500°C; catalyst, Ga-ZSM-5(101).

$$\mathrm{NO_2 + CH_4 + NO_2 = N_2 + CO_2 + 2H_2O} \quad .....(5)$$

また，In-ZSM-5でもNO-CH_4-O_2反応では高SV条件下ではCOが選択的に生成し、NO_2-CH_4反応では一次生成物がCO_2であることからGa-，およびIn-ZSM-5は本質的に反応機構は同じであると考えられる。

以上の結果より次の反応機構を提唱する(Scheme 1)

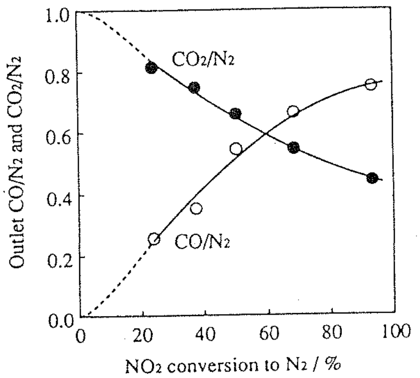


Fig.8. Ratio of produced CO to N_2(○) and CO_2 to N_2(●) as a function of NO_2 conversion to N_2 in NO_2 - CH_4 system on Ga-ZSM-5(101).
NO_2, 1000ppm; CH_4, 1000ppm; total flow rate, $100 cm^3 \cdot min^{-1}$; catalyst weight, 0.005-0.5g; reaction temperature; 500°C;

すなわちNOが酸化されてNO_2を生成し，NO_2とCH_4の反応により生成した反応中間体がNOもしくはNO_2との反応によりN_2を生成する。

$NO + 1/2 O_2 = NO_2$ ..... (6)
$NO_2 + CH_4 = [X]$（反応中間体）$+ mH_2O$ ..... (7)
$[X] + NO = N_2 + CO + nH_2O$ ..... (8)
$[X] + NO_2 = N_2 + CO_2 + nH_2O$ ..... (9)
$CO + O_2 (or\ NO_2) = CO_2$ ..... (10)

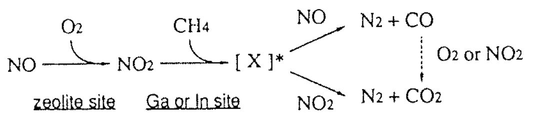
また，化学量論から本反応の中間体の組成は，中間体が生成する過程で生成するH_2O分子数により

①m=0の場合
　$2H + {}^*CH_2NO_2$（ニトロ、ニトリト化合物型）
②m=1の場合
　${}^*CH_2NO$（ニトロソ化合物型）
③m=2の場合
　${}^*CN$（シアノ基）

と示され，これらのいずれかが吸着しているものと考えられる。

4. 結論

GaおよびInイオン交換ZSM-5上でのCH_4によるNO還元反応はNO_2を経由して反応が進行し，以下に示すスキームで進行すると結論した。また，GaおよびInの役割はNO_2とCH_4の反応の促進であると考えられる。



Scheme 1. Mechanism of NO redution by CH_4 on Ga and In-ZSM-5.

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Mechanism of Selective Catalytic Reduction of Nitric Oxide by Methane on Ga and In Ion-exchanged Zeolite Catalysts

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Mechanism of selective catalytic reduction of nitric oxide by methane on Ga and In ion-exchanged zeolite catalysts was studied. Ga- and In-ZSM-5 were found catalytically active for selective reduction of NO by CH_4 in the presence of excess oxygen. The overall reaction proceeded in two stages: 1) NO is oxidized to NO_2, 2) NO_2 reacts with CH_4 to give N_2, CO_x, and H_2O. The mechanism of the latter stage was investigated in detail by means of transient response method. It was shown that NO_2 reacts with CH_4 to yield nitrogen-containing intermediate, which further reacts with NO_x to give N_2, CO_x, and H_2O.

Key-words: selective reduction, nitric oxide, methane, gallium, indium, zeolite

Reaction Mechanism of Selective Reduction of Nitric Oxide by Methane on Ga- and In-ZSM-5 Catalysts

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Ga- and In-ZSM-5 catalysts were found to be active and extremely selective for reduction of NO by CH_4 in the presence of oxygen. The overall reaction proceeded in two stages : 1) NO is oxidized to NO_2, 2) NO_2 reacts with CH_4 to give N_2, CO or CO_2, and H_2O. The mechanism of the latter stage was investigated in detail by means of the transient response method. It was shown that NO_2 reacts with CH_4 to yield nitrogen-containing intermediate, which further reacts either with NO to give N_2, CO, and H_2O, or with NO_2 to give N_2, CO_2, and H_2O.

1. INTRODUCTION

The reduction of nitrogen oxides(NO_x) to molecular nitrogen is an important subject for environmental chemistry. Selective catalytic reduction(SCR) of NO by hydrocarbon in oxygen-rich atmosphere has recently attracted considerable attention as a new type of reaction alternative for the conventional NH_3-SCR process. This reaction was first reported to proceed on Cu-ZSM-5 [1,2]. Several types of catalysts have been proposed as alternatives for Cu-ZSM-5, for instance, various cation-exchanged zeolites [3 - 6], metallosilicates [7, 8], Al_2O_3 [9, 10], and SiO_2-Al_2O_3 [11], when the reactant is C_2H_4 or higher hydrocarbons.

Several reaction mechanisms have also been proposed, and they could be classified into the following three groups:

(1) Oxidation of NO to reactive NO_2 which reacts with hydrocarbon [12, 13].
(2) Oxidative conversion of hydrocarbon forming some kinds of intermediate reacting with NO_x (e.g. isocyanate, radical, oxygen-containing compound, etc.) [9, 14-16]
(3) Composed of oxidation and reduction of catalyst surface by NO and hydrocarbon, respectively. Redox mechanism [17].

The mechanism may vary from one type of catalyst to another, or it may depend on the kind of hydrocarbons used as reductant as well as the reaction conditions.

It is very attractive if selective reduction of NO is possible by use of methane as reductant, since methane is found in every combustion exhaust, particularly from town gas or natural gas burning systems, where methane is a sole reductant. Therefore, several recent works have been intended to develop a catalyst being active for the selective reduction by CH_4. Li and Armor [18] first reported that the selective reduction proceeded on Co-ZSM-5. In our previous study [19], we showed that Ga-ZSM-5 was highly active and selective for reduction of NO by CH_4

or C_2H_6 which were not reactive on Cu-ZSM-5 or other zeolite catalysts. In addition to these catalysts, recent studies have shown that Mn- [20], Ni- [20], Pd- [21], H- [22] and In-ZSM-5 [23] are active for reduction of NO by CH_4. Nowadays it is recognized that CH_4 would be a candidate of effective reductants for selective reduction of NO, if a proper catalyst would be chosen.

In this paper, we discuss the reaction mechanism of selective reduction of NO by CH_4 on Ga- and In-ZSM-5 and their catalytic properties.

2. EXPERIMENTAL

Ga- and In-ZSM-5 catalysts used in this study were prepared by ion-exchange of ammonium form ZSM-5(molar SiO_2/Al_2O_3 ratio, 23.3 , Tosoh Corp.) using an aqueous solution of Ga or In nitrate at 95 °C for 24 h, followed by calcination at 500 °C. The degree of ion exchange level will be expressed assuming that the oxidation number of Ga and In cations is +3. These catalysts will be abbreviated such as Ga-ZSM-5(92), where the value in parenthesis represents the level of gallium exchange.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ~ 2000 ppm NO(or NO_2), 5 ~10% O_2, 1000 ppm CH_4, and He(balance) was fed to 0.005 ~ 0.5 g catalyst at a rate of 100 $cm^3(STP)\cdot min^{-1}$. Effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO and NO_2. The catalytic activity was evaluated by the level of NO conversion to N_2, after reaching a steady-state.

Transient response experiments were conducted using a fixed-bed flow reactor which was equipped with 2 lines of reactant gas stream, which could be switched by use of a 4-way valve to change immediately one reactant gas composition to another. The first reaction run before switching the reactant gas will be called "reaction (A)" and the latter run "reaction (B)".

3. RESULTS AND DISCUSSION

3-1. Selective Performance on Ga- and In-ZSM-5 Catalysts for NO reduction by CH_4

Figure 1 shows the temperature dependence of catalytic activities of Ga -and In-ZSM-5. In-ZSM-5 showed higher NO conversion at lower temperature than Ga-ZSM-5. The highest NO conversion on In-ZSM-5 was observed at 400 °C, while that on Ga-ZSM-5 was 500 °C. The ratio of NO conversion to CH_4 conversion is a measure of selectivity. The selectivity for NO reduction is defined by the following equation:

$$\text{Selectivity} = (\text{reacted NO molecules to } N_2) / (\text{reacted } CH_4 \text{ molecule to CO and } CO_2) \qquad (1)$$

The selectivity was smaller than 2 on both of these catalysts. The selectivity of In-ZSM-5 was slightly lower than that of Ga-ZSM-5, on which NO was selectively reduced to N_2 at 400 °C. In our previous work, we have shown that the limiting (highest) selectivity of Ga-ZSM-5 at 500 °C was 2 [19]. Therefore, the stoichiometry of the reaction on Ga-, and In-ZSM-5 can be written as in the following equation:

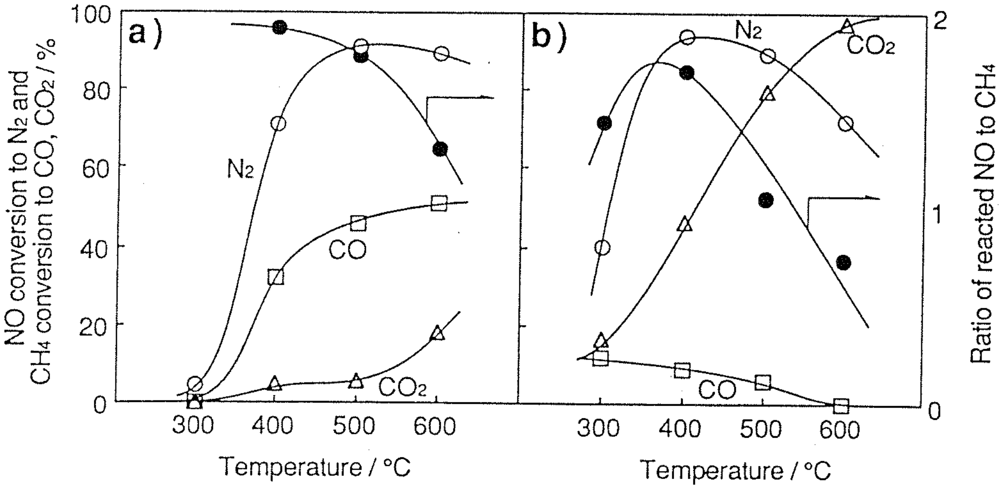


Fig.1. NO conversion to N_2, CH_4 conversion to CO, CO_2 and the ratio of reacted NO to CH_4 on: a), Ga-ZSM-5(92); b), In/H-ZSM-5(86) as a function of reaction temperature. ○, N_2; □, CO; △, CO_2; ●, ratio of reacted NO to CH_4; NO, 1000 ppm; CH_4 1000 ppm; O_2, 10 %; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

$$2NO + CH_4 + kO_2 \rightarrow N_2 + CO_x + 2H_2O \qquad (2)$$

The decrease in selectivity above 500 °C is attributed to combustion of CH_4, which became remarkable at this temperature even in the absence of NO.

$NO\text{-}CH_4\text{-}O_2$ reaction yields N_2 with CO and/or CO_2. As shown in Fig. 1, CO was selectively formed on Ga-ZSM-5, while CH_4 was almost completely oxidized to CO_2 on In-ZSM-5. Figure 2 shows that CO was selectively formed on Ga-ZSM-5 at the initial stage of reaction, and that the selectivity for CO decreased with increasing conversion of NO. Therefore, on this catalyst, CO is the primary product of the reduction of NO, and CO_2 is formed by the secondary reaction between CO and O_2 or NO_2. Thus, the stoichiometric equation for the initial production of CO on Ga-ZSM-5 can be written as follows:

$$NO_2 + CH_4 + NO \rightarrow N_2 + CO + 2H_2O \qquad (3)$$

In contrast to Ga-ZSM-5, CO_2 rather than CO was formed on In-ZSM-5 with N_2. The selectivity for CO, however, also increased with decreasing NO conversion. At higher GHSV conditions, the molar ratio of produced CO to produced N_2 approached to unity on both of these catalysts. As shown in Fig.3, In-ZSM-5 showed remarkably high catalytic activity for CO oxidation reaction to CO_2 compared with Ga-ZSM-5. The difference in the formation of CO or CO_2, observed for Ga- and In-ZSM-5, should be attributed to CO oxidation activity. Accordingly, it is deduced that CO_2 is the secondary product from CO and consequently the reaction mechanism is common for both of these catalyst.

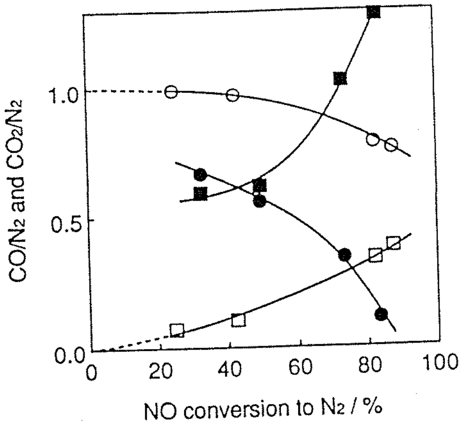


Fig.2. Ratio of produced CO to N_2(○, ●) and CO_2 to N_2(□, ■) as a function of NO conversion to N_2 in NO - CH_4 - O_2 system on Ga-ZSM-5(101)(○, □) and In-ZSM-5(95) (●, ■).
NO, 1000ppm; CH_4, 1000ppm; O_2, 10%;
total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.05-0.5g;
reaction temperature, 500°C(Ga), 400°C(In).

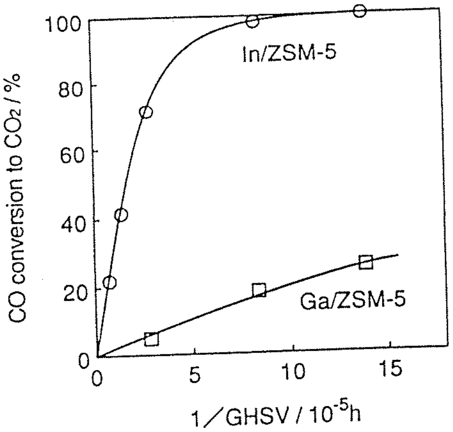
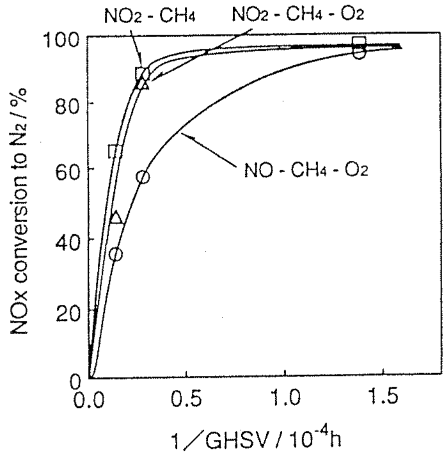


Fig.3. Oxidation of CO to CO_2 by O_2 on Ga-ZSM-5(101) (□)and In-ZSM-5(95) (○).
CO, 1000ppm; O_2, 10%;
total flow rate, $100cm^3 \cdot min^{-1}$;
catalyst weight, 0.025-0.5g;
reaction temperature, 500°C(Ga), 400°C(In).

3-2. Mechanism of NO reduction by CH_4

In Fig.4, we compare the extent of NO or NO_2 conversion to N_2 on In-ZSM-5 as a function of reciprocal GHSV. Higher NO_2 conversion was obvious for the NO_2-O_2-CH_4 and NO_2-CH_4 systems than for the NO-O_2-CH_4 system at high GHSV. As NO-CH_4 reaction hardly proceeded in the absence of O_2 and CH_4-O_2 reaction was not noticeable below 400°C in the absence of NO, it is evident that the presence of O_2 and formation of NO_2 are necessary component for this selective reduction. Furthermore, there was no appreciable difference in the level of NO_2 conversion between NO_2-CH_4 and NO_2-O_2-CH_4 systems. Similar results were obtained with Ga-ZSM-5 [24]. Therefore, it seems that the first step is NO oxidation to NO_2, which further reacts with CH_4 to give N_2, CO_x, and H_2O.

As NO_2 formation is an important step for NO reduction, we next studied on the active sites on these catalysts for this reaction. Figure 5 shows the effect of proton exchange level on the catalytic activity of H/Na-ZSM-5. Na-ZSM-5 was inactive for this reaction and NO oxidation increased with increasing proton exchange level. Homogeneous (non-catalytic) NO oxidation gave only about 6% NO conversion to NO_2; therefore, Na-ZSM-5 was completely inactive. A similar correlation was observed for the case of H/Na/Ga-ZSM-5. Therefore, it is reasonable to consider that the zeolitic acid sites are concerned in NO oxidation to NO_2. Additionally, NO conversion to NO_2 on H-ZSM-5 at 400 °C increased from 30% to 35% under these reaction conditions with increasing pretreatment temperature from 500 °C to 800 °C. It is, thus, deduced that oxygen is adsorbed on Lewis acid sites and activated by the electrostatic polarization caused by zeolite framework [25], and that gas phase NO molecule should attack the activated oxygen to form NO_2.



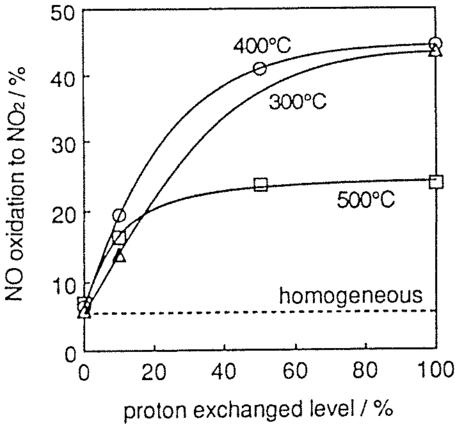


Fig.4. NOx conversion on In-ZSM-5 as a function of reciprocal GHSV.
○: NO, 1000ppm; CH_4, 1000ppm; O_2, 10%;
△: NO_2, 1000ppm; CH_4, 1000ppm; O_2, 10%;
□: NO_2, 1000ppm; CH_4, 1000ppm; O_2, 0%;
total flow rate, 50-100 $cm^3 \cdot min^{-1}$;
catalyst weight, 0.025-0.5g.

Fig.5. Effect of proton exchanged level on the catalytic activities of H/Na-ZSM-5 for NO oxidation to NO_2.
□, 500°C; ○, 400°C; △, 300°C;
NO, 1000ppm; O_2, 10%;
total flow rate, 100 $cm^3 \cdot min^{-1}$;
catalyst weight, 0.1 g.

Accordingly, we assume that the selective reduction of NO by CH_4 on Ga-, and In-ZSM-5 would proceed in the following sequence:

$NO + O_2 \rightarrow NO_2$ [on zeolite acid sites] (4)

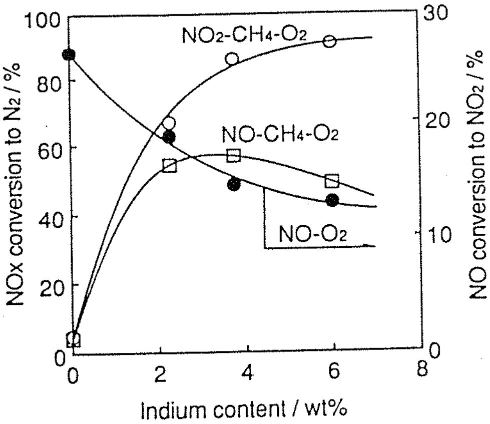
$NO_2 + CH_4 \rightarrow N_2 + CO_x + H_2O$ [on Ga (or In) sites] (5)

The sequence of these reactions is in accordance with the results observed for the effect of indium content on the activities of In/H-ZSM-5 catalysts, as shown in Fig.6. The catalytic activity for NO oxidation decreased and the level of NO_2 conversion in NO_2-CH_4 system increased with increasing indium content. On the other hand, the level of NO conversion in NO-O_2-CH_4 system, which required both of these reactions, gave a maximum around 4 wt% indium. It is thus obvious that the effect of indium is not the promotion of NO oxidation, but the promotion of the NO_2-CH_4 reaction. As Ga/H-ZSM-5 showed a similar performance to In/H-ZSM-5, the same reaction sequence should be operating on these catalysts [24].

As mentioned above, reduction of NO proceeds via NO_2-CH_4 reaction, and one additional NO molecule may participate in the formation of CO as shown in the equation (3). On the other hand, it was found that CO_2 was the primary product in NO_2-CH_4 reaction and that the molar ratio of produced CO_2 to produced N_2 became unity on extrapolation of NO_2 conversion to zero, as shown in Fig.7. Therefore, the stoichiometry for NO_2-CH_4 reaction can be written as follows:

$$2NO_2 + CH_4 \rightarrow N_2 + CO_2 + 2H_2O \quad (6)$$

These results lead us to a supposition of a reaction mechanism for NO reduction by



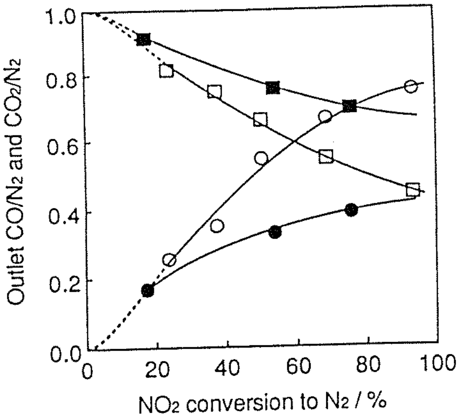


Fig.6. The effect of Indium content on catalytic activity at 400°C.
□: NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10 %;
○: NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10 %;
●: NO, 1000 ppm; O_2, 10 % ;
total flow rate, 100 $cm^3 \cdot min^{-1}$;
catalyst weight, 0.1g;

Fig.7. Ratio of produced CO to N_2(○, ●) and CO_2 to N_2(□, ■) as a function of NO_2 conversion to N_2 in NO_2 - CH_4 system on Ga-ZSM-5(101) (○, □) and In-ZSM-5(95) (●, ■).
NO_2, 1000ppm; CH_4, 1000ppm;
total flow rate, $100 cm^3 \cdot min^{-1}$;
catalyst weight, 0.005-0.5g;
reaction temperature, 500°C(Ga), 400°C(In).

CH_4 on Ga-ZSM-5 and In-ZSM-5: NO_2 formed on zeolite active sites activates CH_4 and yield a reaction intermediate. Successively, the intermediate reacts with gas phase NO and NO_2 molecules to produce N_2 with CO or N_2 with CO_2, respectively. CO_2 might also be formed by reaction (10) and/or (11).

$$NO + 1/2O_2 \rightarrow NO_2 \tag{7}$$
$$NO_2 + CH_4 \rightarrow [X] \text{ (reaction intermediate) } + nH_2O \tag{8}$$
$$[X] + NO \rightarrow N_2 + CO + mH_2O \tag{9}$$
$$[X] + NO_2 \rightarrow N_2 + CO_2 + mH_2O \tag{10}$$
$$CO + O_2(\text{or } NO_2) \rightarrow CO_2 \tag{11}$$

This reaction mechanism was verified by a transient response study: After N_2 formation in NO-CH_4-O_2 reaction reached a steady state[reaction (A)], the reactant gas stream was switched to various different components[reaction (B)] to observe the difference in N_2 formation rate. Typical results are shown in Fig.8. When the mixture of O_2 and He or only He was introduced in reaction (B), N_2 was not formed at all. On the other hand, when NO in He alone was introduced, N_2 was produced. The logarithm of N_2 formation rate and reaction time in reaction (B) showed a linear relationship. When N_2 formation rate was extrapolated to the moment of switching the reactant component, the rate coincided with the steady state N_2 formation rate of reaction (A).

Figure 9 shows the rates of N_2, CO, CO_2 formation in the steady state NO-CH_4-O_2 reaction [reaction (A)] and in the case when the NO-CH_4-O_2 mixture was

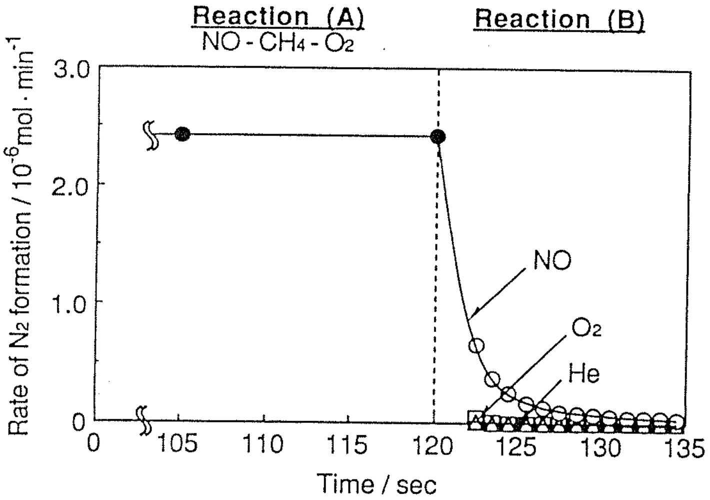


Fig.8. Transient response experiments to observe the effect of gas phase component on N_2 formation in reaction (B).
Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5% (●);
Reaction (B): NO, 2000ppm (○); O_2, 5% (□); He alone, (△);
total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.2g;
reaction temperature, 500°C; catalyst, Ga-ZSM-5(101).

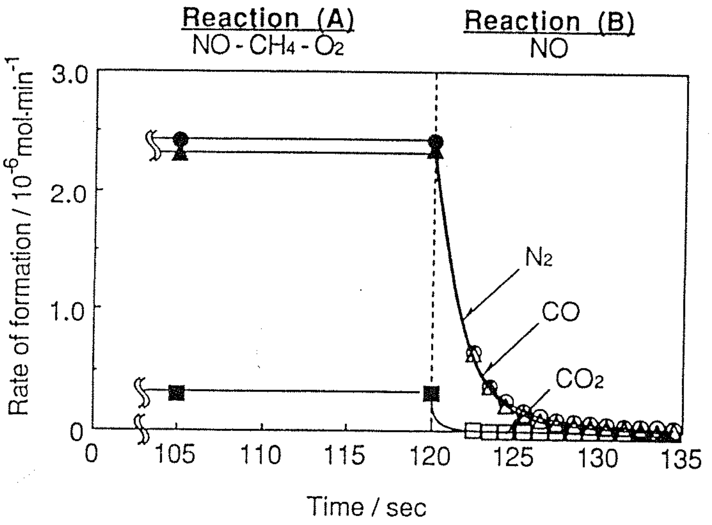
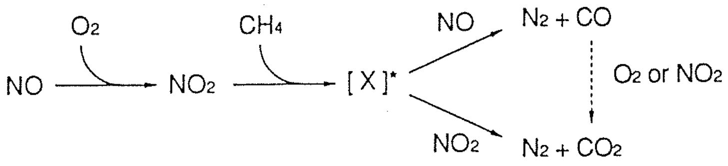


Fig.9. Transient response of the formation rate of N_2(○,●), CO(△,▲) and CO_2(□,■).
Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5%;
Reaction (B): NO, 2000ppm;
total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.2g;
reaction temperature, 500°C; catalyst, Ga-ZSM-5(101).

switched to NO [reaction (B)]. The formation of N_2 was accompanied by that of the same amount of CO, with negligible formation of CO_2. On the other hand, when NO_2 was admitted in stead of NO in reaction (B), N_2 and CO_2 were formed in an equimolar ratio. The results obtained in the transient response study show that N_2 is formed by the reaction between surface intermediate (X) and gas phase NO or NO_2 molecule, as shown in scheme 1.



Scheme 1. Proposed mechanism of NO reduction by CH_4 on Ga and In-ZSM-5.

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Chapter XX

Mechanism of Selective Catalytic Reduction of Nitric Oxide by Propene on Fe-Silicate in Oxygen-Rich Atmosphere: A Transient Response Study

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The reaction mechanism of NO reduction by C_3H_6 on Fe-silicate catalyst was investigated by means of a transient response method. From the reaction analysis, we propose a mechanism in which the first step of NO reduction is the adsorption of C_3H_6 on the catalyst surface, and a nitrogen-containing organic intermediate is generated from the adsorbed C_3H_6 and NO. A nitrogen molecule is produced in a process where the intermediate(carbonaceous material containing nitrogen) is decomposed by the reaction with another NO(or NO_2) molecule in the gas phase.

The reduction of nitrogen oxides(NOx) to molecular nitrogen is an important task for environmental chemistry. Recently, selective catalytic reduction(SCR) of NO by hydrocarbons in an oxygen-rich atmosphere has attracted considerable attention as a new type of reaction alternative for traditional NH_3-SCR process. This reaction was reported to proceed on various cation-exchanged zeolites (*1 - 5*), metallosilicates (*6, 7*), Al_2O_3 (*8, 9*), and SiO_2-Al_2O_3 (*10*), when C_2H_4 or higher hydrocarbons were used as reductant. These studies showed that oxygen was a necessary component for this reaction system.

We have reported that Fe-silicate exhibited high catalytic activity for this reaction at a relatively low temperature when C_3H_6 is used as a reducing agent. We also showed that the carbonaceous material deposited on the catalyst surface was involved in this reaction (*6*). As for this type of selective reduction, several mechanisms have been proposed:

(1) Reaction between NO_2 and hydrocarbon (*11, 12*).
(2) Participation of an intermediate such as isocyanate, radicals, or oxygen-containing compound (*13-16*).
(3) Redox mechanism consisting of alternative oxidation and reduction of catalyst surface by NO and hydrocarbon (*17- 19*).

The mechanism, however, may vary from one type of catalyst to another, or it may depend on the kind of hydrocarbons used as reductant as well as the reaction conditions. In this study, we studied the reaction mechanism on Fe-silicate catalyst using a technique of transient response method.

Experimental

Catalyst Preparation Fe-silicate(Si/Fe = 50, molecular ratio) used in this study was synthesized according to the rapid crystallization method reported by Inui et al.(*20*). Water glass(29wt% SiO_2, 9wt% Na_2O) and $FeCl_3 \cdot 6H_2O$ were used as the sources of silicon and iron, respectively. Tetrapropylammonium bromide (TPAB) was used as the template molecule. The mixture was heated in a stainless steel autoclave from room temperature to 433 K at a constant heating rate of 1.5 $K \cdot min^{-1}$, and then up to 483 K at a constant heating rate of 12 $K \cdot h^{-1}$.

The X-ray diffraction patterns of the synthesized Fe-silicate was similar to that of H-ZSM-5, indicating that the Fe-silicate had a pentasil pore-opening structure. Chemical compositions of synthesized Na-form Fe-silicate were determined by inductively coupled argon plasma atomic emission spectrometer (ICP) (*21*). The amount of sodium ion was in accordance with that of iron, showing that iron is mostly incorporated in the framework. Thus, the synthesized Fe-silicate was converted into H-form by the ion-exchange method using 1 M-NH_4NO_3 solution (353K for 1h, 5 times), followed by calcination at 813 K for 3 h. Sodium was hardly detected after this ion-exchange.

Transient response study A mixture of 1000 - 2000 ppm of NO, 500 - 1000 ppm C_3H_6, and 10% O_2 was fed to 0.5 g of catalyst at a rate of 100 $cm^3 \cdot min^{-1}$. Effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO and NO_2. The catalytic activity was evaluated by the level of NO conversion to N_2.

Transient response experiments were conducted using a fixed-bed reactor which was equipped with 2 lines of reactant stream, which could be switched by use of a 4-way valve to change immediately one reactant gas composition to another. All dead volume was minimized. Effluent gases were stored in a multiposition 8-way loop valve, and analyzed in turn by means of on line gas chromatography. The first reaction run before switching the reactant gas will be called "Reaction A" and the latter run "Reaction B".

During Reaction A, the concentration of C_3H_6, CO_x, and NO_x in the outlet gas were measured by means of gas chromatography and chemiluminescence detection of NO_x, respectively. The amounts of adsorbed C_3H_6 and NO_x on the catalyst were calculated from the material balance of reactant and product. After switching the reactant components for various types (Reaction B), the variation in the behavior in N_2 formation were compared.

Results and Discussion

Effect of Reducing gases on NO reduction As shown in our previous study (*1*), H-Fe-silicate is a highly active and stable catalyst for the reduction of NO with C_3H_6 at 573 K, and the first step of this reaction is considered to be the adsorption of C_3H_6, followed by the formation of carbonaceous material on the catalyst.

Table 1 summarizes the temperature dependence of NO conversion with various reducing gases on H-Fe-silicate. The level of NO conversion markedly depended on the kind of reducing gases. CO and H_2 were not effective for this reaction, and they were preferentially consumed by the reaction with O_2. Reduction of NO proceeded when hydrocarbons were used as reductants, and the reduction reactivity decreased in the following order:

$$C_3H_6 > C_2H_4 > C_3H_8 >> C_2H_6 > CH_4.$$

Table I . Effect of reducing gases on the catalytic activity of Fe-silicate.

	NO conversion to N_2(Hydrocarbon conversion to COx) / %			
Temperature / K	473	573	673	773
CH_4	-	1.33(1.00)	4.04(17.3)	4.22(74.0)
C_2H_4	25.9(28.2)	36.6(82.2)	15.5(94.6)	5.82(94.6)
C_2H_6	-	9.36(13.1)	12.5(74.3)	5.85(98.3)
C_3H_6	-	54.6(83.4)	16.5(100)	5.15(100)
C_3H_8	10.1(1.5)	26.1(37.7)	12.9(81.3)	9.20(100)

Reducing gases, 1000 ppm (C_3H_8, C_3H_6, C_2H_6, C_2H_4, CH_4);
NO, 1000 ppm; O_2 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

Mechanism of NO reduction by Propene We studied the reaction mechanism of NO reduction by C_3H_6 on Fe-silicate catalyst by means of transient response method in the following manner. First, the reaction was carried out using a mixture of NO, C_3H_6, and O_2 at 573 K (Reaction A). After the N_2 formation rate reached the steady-state, the reactant mixture was switched for various components.

Figure 1 shows the variation in the behavior of N_2 formation when the components of the reactant mixture in Reaction B were switched for various types. When only NO or O_2 in He alone was introduced, or when a mixture of C_3H_6 and O_2 was introduced, N_2 was hardly produced. On the other hand, when a mixture of NO and O_2 was introduced, a large amount of N_2 was produced.

Carbonaceous material was deposited on the catalyst surface simultaneously *(6)* with the formation of N_2 and COx in Reaction A (Figure 2) . After a mixture of NO and O_2 was introduced(Reaction B), COx was produced simultaneously with the formation of N_2. However, the formation of N_2 decreased gradually and completely terminated after 60 min with no more formation of CO_x. From these results, it is suggested that carbonaceous material deposited on the catalyst surface plays an important role in this reaction and that the first step of the reaction is the adsorption of C_3H_6 on the catalyst surface.

As shown in Fig.3-(a), when the reactant component was switched from the mixture of NO, C_3H_6, and O_2 into the mixture of NO and O_2, the ln(N_2 formation rate) and reaction time at early stage in Reaction B have a linear relationship. In addition to this, when N_2 formation rate is extrapolated to the moment of switching the reaction component, the rate coincides with the steady state N_2 formation rate of Reaction A. Therefore, from these results, it can be concluded that N_2 is produced by the reaction between an intermediate and NO + O_2, and first order reaction with respect to the concentration of reaction intermediate.

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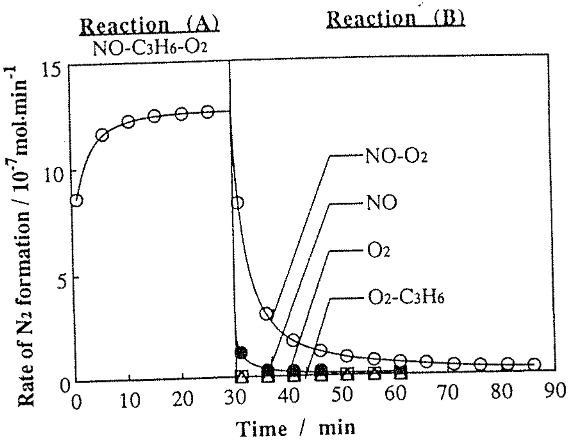


Fig.1 Effect of reactant components on NO reduction to N_2.
Reaction A: C_3H_6, 1000 ppm; NO, 1000 ppm; O_2, 10%.
Reaction B: ○: NO, 1000 ppm; O_2, 10%.
△: O_2, 10%; C_3H_6, 1000 ppm .
□: O_2, 10%. ●: NO, 1000 ppm.

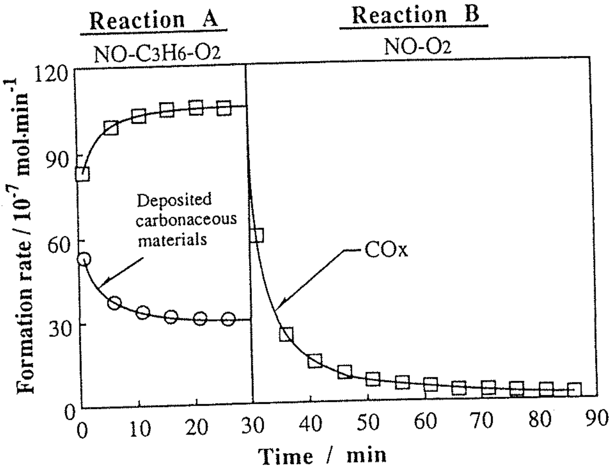


Fig.2 Time-on-stream variation in the formation rate of carbonaceous material and COx.
Reaction A: C_3H_6, 1000 ppm; NO, 1000 ppm; O_2, 10%.
Reaction B: NO, 1000 ppm; O_2, 10%.

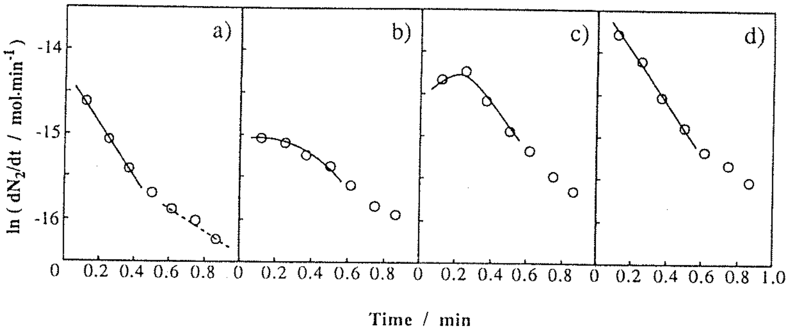


Fig.3 Relationship between ln(dN_2/dt) and reaction time
when reactant components was changed.
Reaction A: (a): NO, 2000 ppm; C_3H_6, 1000 ppm; O_2, 10%.
(b): C_3H_6, 1000 ppm, O_2 10%. (c): C_3H_6, 1000 ppm;
(d): NO, 2000 ppm; C_3H_6, 1000 ppm.
Reaction B: NO, 2000 ppm; O_2, 10%;

In order to obtain further insight into the carbonaceous material, the effects of the reactant components of Reaction A on the behavior of N_2 formation in Reaction B were studied.

First, when the mixture of C_3H_6 and O_2 in He was introduced in Reaction A, the rate of N_2 formation in Reaction B was smaller than that of the steady-state reaction (Figure 3-(b)). Therefore, the carbonaceous material formed by the reaction between C_3H_6 and O_2 also promotes the reaction. However, the reactive intermediate could not be formed. Probably, the carbonaceous material formed by the reaction between C_3H_6 and O_2 should also contribute to N_2 formation at later stage of the Reaction B (shown in Fig.3-(a): dotted line), however, this is not the main pathway of NO reduction.

Second, when only C_3H_6 in He was introduced in Reaction A, the rate of N_2 formation in Reaction B was almost the same as with the C_3H_6, NO, O_2 mixture. However, the induction period was observed at an early stage (Figure 3-(c)). Therefore, adsorption of C_3H_6 on the catalyst surface should be the first step of this reaction. However, the C_3H_6 adsorbed on the catalyst could not form the reactive intermediate.

Finally, when a mixture of NO and C_3H_6 was introduced in Reaction A, the rate of N_2 formation in Reaction B was the same as during steady-state reaction. Therefore, coexistence of NO and C_3H_6 is necessary to form the reaction intermediate.

Figure 4-(a) shows the variation in the formation rate of the deposited carbonaceous material in Reaction A, determined by the material balance, whereas Fig.4-(b) shows the variation in the formation rate of N_2.

After one of the gas mixtures of NO + C_3H_6 + O_2, C_3H_6 + O_2, NO + C_3H_6, C_3H_6 was fed for 30 minutes, followed by the deposition of carbonaceous material on the catalyst, the reactant gas was switched to NO and O_2. The amount of the deposited carbonaceous materials decreased in the order:

$$NO + C_3H_6 + O_2 > C_3H_6 + O_2 > NO + C_3H_6 \approx C_3H_6$$

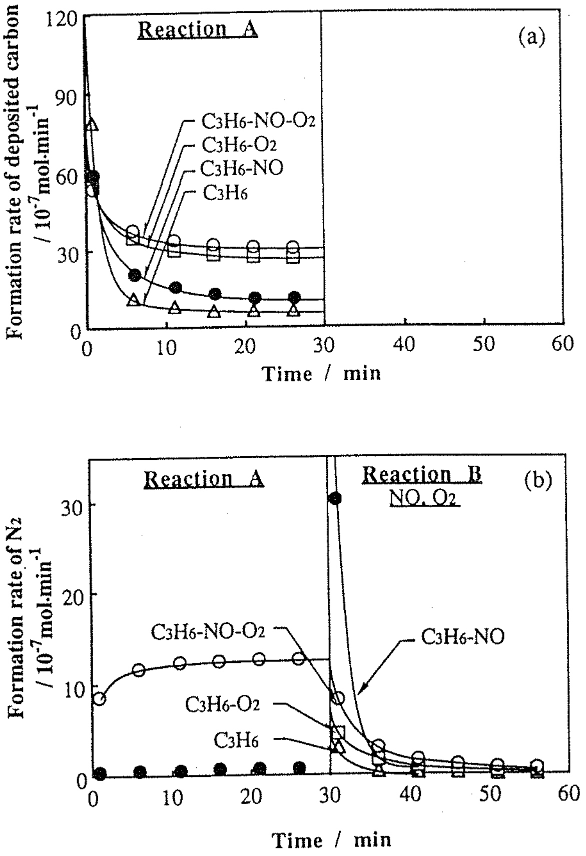


Fig.4 Effect of reactant components on the formation of carbonaceous materials and N_2.
Reaction A: ○: C_3H_6, 1000 ppm; NO, 1000 ppm; O_2, 10%.
□: C_3H_6, 1000 ppm; O_2, 10%.
△: C_3H_6, 1000 ppm.
●: C_3H_6, 1000 ppm; NO, 1000 ppm.
Reaction B: NO, 1000 ppm; O_2, 10%.

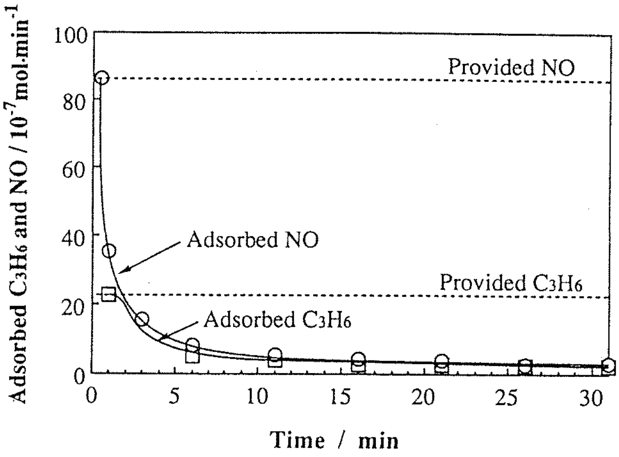


Fig.5 Time-on-stream variation in the rate of adsorbed C_3H_6 and NO in NO-C_3H_6 reaction.
○, adsorbed NO; □, adsorbed C_3H_6.

In the case of NO + C_3H_6 treatment, N_2 formation started immediately after switching feed stream to NO + O_2 in spite of small amount of deposited carbonaceous material. The carbonaceous material deposited upon treatment with C_3H_6 + NO is extremely reactive, showing that carbonaceous species effective for NO reduction is probably produced by the coexistence of C_3H_6 and NO.

Also when reactant components were switched in the order of NO → C_3H_6 → NO+O_2, or C_3H_6 → NO → NO+O_2, the behavior of N_2 formation was almost same with the order of C_3H_6 → NO+O_2 in this reaction conditions.

As shown in Fig.5, when a mixture of NO and C_3H_6 was introduced in Reaction A, both NO and C_3H_6 were adsorbed on the catalyst surface, and the adsorbed molar ratio of NO to C_3H_6 was unity.

From the results that the coexistence of C_3H_6 and NO was necessary to form the reactive intermediate, the intermediate is suggested to be produced by the reaction between the unstable carbon species such as radical or π-aryl and NO. Thus, it is suggested that NO reduction proceeds via decomposition of the nitrogen containing organic compounds.

Figure 6 shows the effect of the amount of reaction intermediate on N_2 formation in Reaction B. The reaction time in Reaction A was varied from 0.5 min to 30 min in order to change the amount of reactive intermediate. At 0.5 min and 1 min, the N_2 formation rate in Reaction B was same. On the other hand, when NO and C_3H_6 were introduced for 30 min in Reaction A, a limit on N_2 formation was observed in the

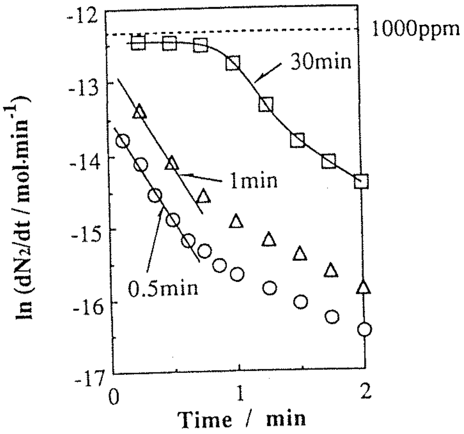


Fig.6 Effect of the amount of carbonaceous material formed from C_3H_6 and NO on the rate of N_2 formation.
Reaction A: C_3H_6, 2000 ppm; NO, 500 ppm.
Reaction time: ○, 0.5 min; △, 1 min; □, 30 min.
Reaction B: NO, 1000 ppm; O_2, 10%.

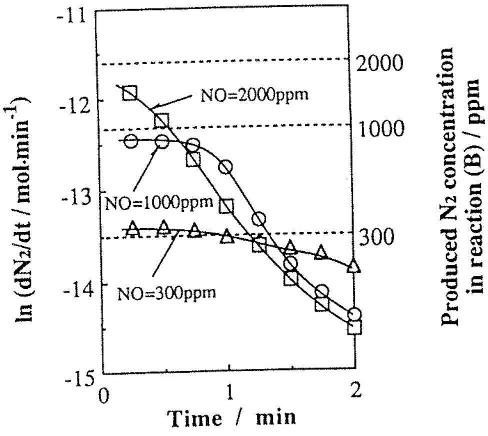


Fig.7 Effect of NO concentration in reaction (B) on the rate of N_2 formation.
Reaction A: C_3H_6, 2000 ppm; NO, 500 ppm. Reaction time, 30 min.
Reaction B: ○: NO, 300 ppm; O_2, 10%.
□: NO, 1000 ppm; O_2, 10%.
△: NO, 2000 ppm; O_2, 10%.

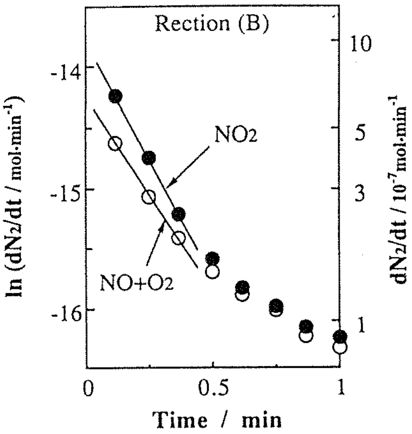
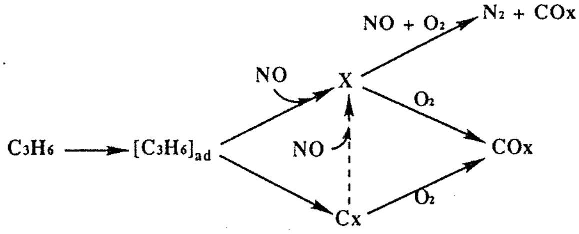


Fig.8 Effect of NO_2 on the rate of N_2 formation in reaction (B).
Reaction A: NO, 2000 ppm; C_3H_6, 500 ppm; O_2, 10 %; 0.5 min
Reaction B:○; NO, 1000 ppm; O_2, 10 %
●; NO_2, 1000 ppm



Scheme 1 Proposed reaction mechanism of NO reduction on Fe-silicate catalyst.

early stage in Reaction B. As shown in Fig.7, N_2 formation in Reaction B was limited by the NO concentration in Reaction B. For instance, when 1000 ppm of NO was introduced, the maximum N_2 produced was 1000 ppm. Therefore, N_2 should be produced by the reaction between a nitrogen-containing reaction intermediate and a gas phase NO(or NO_2) molecule.

As mentioned above, the coexistence of NO and O_2 was necessary to produce N_2 in Reaction B. It has been reported that NO_2 plays an important role in NO reduction by hydrocarbons (*12, 22*). Therefore, the effect of NO_2 on N_2 formation rate in Reaction B was studied. As shown in Figure 8, when NO_2 in He alone was introduced in Reaction B, N_2 formation rate was greater than when NO and O_2 mixture was introduced. This suggests that NO_2 plays an important role in the decomposition of the nitrogen-containing organic compound.

Conclusion

From these results, we propose a reaction mechanism in which the first step of NO reduction is the adsorption of C_3H_6 on the catalyst surface, and a nitrogen-containing organic intermediate is formed by the reaction between the adsorbed C_3H_6 and NO (Scheme 1). A nitrogen molecule seems to be produced in a process where the carbonaceous material containing nitrogen (intermediate) is decomposed by the reaction with another NO(or NO_2) molecule in the gas phase.

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口頭発表

Ga担持ゼオライト触媒を用いたNOの選択的還元反応

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1．緒言

ディーゼルエンジン，リーンバーンガソリンエンジンの排ガス中に含まれるNOxの低減に関して、Cu-ZSM-5 1)をはじめとするゼオライト系触媒が注目されている。しかし、高酸素濃度下では炭化水素と酸素との反応が優先し、選択的なNOの還元が困難となることがある。そこで、我々はGaをはじめとする炭化水素の酸化能が比較的小さい金属をイオン交換法により担持したゼオライトについて検討を行った。還元剤としてC_3H_8を用いた場合、Ga担持ゼオライトが高酸素濃度(10%)において高いNO還元活性を示すことを見いだした2)。本報では、特にGa担持ゼオライトの触媒特性について検討を行った。

2．実験操作

ゼオライトへの金属の担持は、硝酸塩(Ga，Al，Zn)あるいは塩化物(Ti，In，Sn)を用い、イオン交換法により行った。また、Cu-ZSM-5は岩本ら3)の方法に従い、酢酸塩水溶液によるイオン交換法により調製した。ゼオライトはZSM-5の他にferrierite，mordenite，USY(以上、東ソー製)について検討した。各々のSiO_2/Al_2O_3比は23.3，17.8，19.3，14.5である。調製した触媒のイオン交換率(%)はICPにより求め、( )内に記した。

反応は常圧固定床流通式反応装置を用いて、反応温度300-600°C，NO濃度1000ppmで行った。また、C_3H_8濃度は167-1000ppm，O_2濃度は2-10%，GHSVは12000-60000h^{-1}の範囲で変化させた。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。なお、活性はすべてN_2への転化率で評価した。

3．結果と考察

表1に種々の金属担持ZSM-5を用いたNO還元反応の結果を示した。Al，Ti-ZSM-5は反応温度300-500°CでH-ZSM-5とほぼ同程度

Table 1　Catalytic activities of various ion-exchanged ZSM-5.

Catalyst	Conv. of NO to N_2 / % [C_3H_8 to CO_X / %]			
	300°C	400°C	500°C	600°C
Ga-ZSM-5 (79)	71.9 [29.5]	91.1 [53.8]	87.2 [91.9]	85.9 [97.6]
Al-ZSM-5 (53)	62.8 [28.1]	85.0 [55.4]	74.8 [73.1]	43.4 [90.0]
Ti-ZSM-5 (11)	60.2 [27.5]	85.3 [56.5]	72.7 [66.2]	37.3 [86.3]
Zn-ZSM-5 (97)	18.1 [7.1]	45.3 [18.6]	93.0 [88.0]	56.5 [96.0]
In-ZSM-5 (65)	76.0 [30.9]	85.8 [99.9]	53.8 [100]	57.7 [100]
Sn-ZSM-5 (104)	54.8 [23.8]	43.0 [47.0]	25.9 [69.7]	16.4 [97.1]
H-ZSM-5 (100)	69.6 [38.5]	86.6 [72.2]	73.2 [86.5]	
Cu-ZSM-5 (111)	60.5 [92.1]	46.1 [100]	46.9 [100]	45.2 [100]

Reaction conditions: NO, 1000ppm; C_3H_8, 1000ppm; O_2, 10%; GHSV 12000h^{-1}.

Table 2　Catalytic activities of gallium ion-exchanged zeolites.

Catalyst	Conv. of NO to N_2 / % [C_3H_8 to CO_X / %]			
	300°C	400°C	500°C	600°C
Ga-ferrierite (91)	65.5 [21.8]	69.1 [22.4]	98.5 [40.0]	100 [76.1]
Ga-mordenite(106)	37.5 [12.0]	87.4 [34.8]	92.4 [86.2]	83.3 [97.7]
Ga-USY (103)	4.7 [0.9]	9.4 [3.1]		
H-ferrierite (100)	64.6 [22.6]	72.7 [24.2]	52.3 [24.4]	
H-mordenite (100)	28.9 [11.0]	74.0 [40.8]	72.7 [70.5]	

Reaction conditions: NO, 1000ppm; C_3H_8, 1000ppm; O_2, 10%; GHSV 12000h^{-1}.

の転化率を示した。また、Zn-ZSM-5は500°C、In-ZSM-5は300-400°Cの範囲で高い転化率を示したが、その他の反応温度範囲での転化率は低かった。これに対して、Ga-ZSM-5は500°C以上でも高い転化率を示し、広い温度範囲でNOの還元反応に有効な触媒であることがわかった。

表2に、種々のゼオライトにGaを担持し活性の比較を行った結果を示した。500-600°Cの範囲でferrieriteは特に高い転化率を示した。mordeniteも高温域では高い転化率を示したが、300°Cでは著しく低下した。また、USYの活性は他のゼオライトに比べて著しく低かった。以上から、ZSM-5の他にferrieriteが広い反応温度域

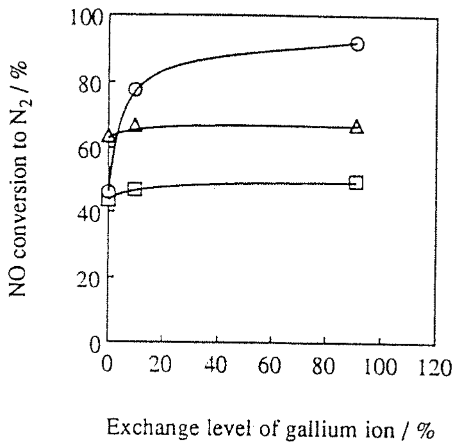

Fig.1. Dependence of the catalytic activity of Ga-ferrerite on the exchange level of gallium ion.
Reaction temperature; □, 300°C; Δ, 400°C; ○, 500°C.
NO, 1000ppm; C_3H_8, 500ppm; O_2, 10%; GHSV, 12000h^{-1}.

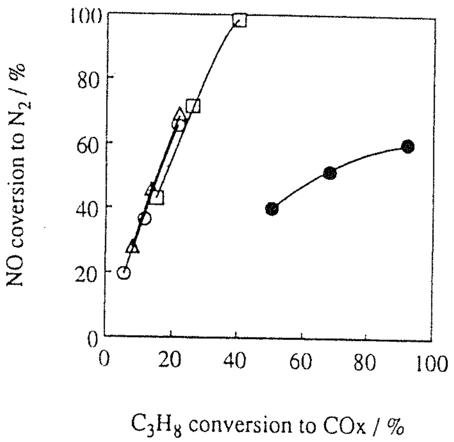

Fig.2. Selective reduction of NO as a function of C_3H_8 conversion to COx over Ga-ferrierite(91).
Reaction temperature: ○, 300°C; Δ, 400°C; □, 500°C; ●, 300°C(over Cu-ZSM-5(111)).
NO, 1000ppm; C_3H_8, 1000ppm; O_2, 10%; GHSV, 12000-60000h^{-1}.

でNO還元反応に対して有効であることが示された。また、Ga担持ゼオライトをH型と比較すると反応温度300-400°Cではほぼ同程度の活性を示し、500-600°CではGa担持ゼオライトの方が高いNO還元活性を示した。

図1に、ferrieriteへのGa担持量とNO転化率の関係について示した。反応温度500°Cにおいて、少量(交換率10%)のGaの担持によりNO転化率が著しく向上することがわかる。300-400°Cの反応温度域ではGa担持による変化は見られなかった。

Ga-ferrieriteおよびCu-ZSM-5で反応(GHSV, 12000-60000h^{-1})を行った時のC_3H_8の消費量に対するNO転化率を図2に示した。Cu-ZSM-5と比較して、Ga-ferrieriteではNOの還元反応の選択性が高いことがわかる。

図3に、Ga-ferrieriteを用いたときのC_3H_8の濃度に対するNO転化率の変化ついて示した。C_3H_8濃度を減少させるとNO転化率も減少したが、C_3H_8濃度が167ppmと少量の場合でも50%程度のNO転化率を維持し、C_3H_8が選択的にNOと反応していることが示された。

図4に、NO転化率のO_2濃度依存性について示した。低O_2濃度域では微量のCH_4等が副生したものの、O_2濃度が2-10%の間ではN_2

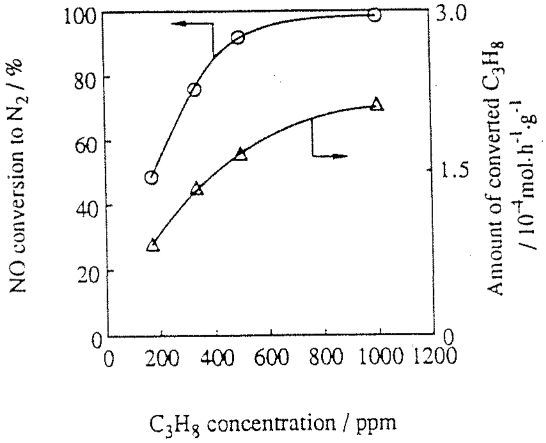

Fig.3. Selective reduction of NO as a function of C_3H_8 concentration over Ga-ferrierite(91).
○, NO conversion to N_2; △, C_3H_8 converted to COx.
NO, 1000ppm; O_2, 10%; GHSV, 12000h^{-1};
Reaction temperature, 500°C.

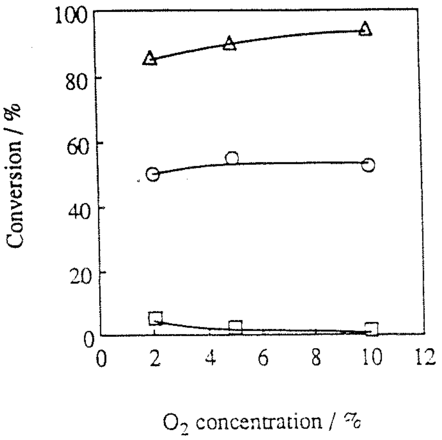

Fig.4. Selective reduction of NO as a function of oxygen concentration over Ga-ferrerite(91).
○, NO conversion to N_2;
△, C_3H_8 conversion to COx;
□, C_3H_8 conversion to hydrocarbons.
NO, 1000ppm; C_3H_8, 167ppm; GHSV, 12000h^{-1}
Reaction temperature, 500°C.

への転化率にはほとんど変化がなかった。

以上のことから、C_3H_8によるNOの還元反応においてGa-ZSM-5, Ga-ferrieriteは広い反応温度域で高活性を示し、NOとC_3H_8の反応がO_2により阻害されず、高選択的に進むことが示された。

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Selective Reduction of Nitric Oxide with Propane on Gallium Ion-exchanged Zeolites

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INTRODUCTION

The removal of nitrogen oxides(NOx) is a serious environmental problem. Cu-ZSM-5 is the most efficient catalyst for this reaction among the catalysts which have been reported.1) However, it is very difficult to accomplish high selectivity for conversion of NO to N_2 on Cu-ZSM-5 if excess oxygen is present, like in the case of diesel or gas turbine exhaust. It is due to the high ability of Cu-ZSM-5 to oxidize hydrocarbons in oxygen-rich atmosphere, resulting in the restriction of selectivity for this conversion. Therefore, it is expected for the practical performance to develop the catalyst having less selectivity for oxidation of hydrocarbons even under oxygen-rich conditions. In our experimental studies, it was found that gallium ion-exchanged zeolites showed high activity and selectivity for the reaction of NO with propane even in high oxygen concentration.

EXPERIMENTAL

Parent zeolites, ZSM-5(molar SiO_2/Al_2O_3 ratio, 23.3), mordenite(19.3), ferrierite(17.8), and Y(14.5) were supplied by Tosoh Corporation. Gallium ion-exchanged zeolites were prepared by ion-exchange of the ammonium form zeolites using aqueous solutions of $Ga(NO_3)_3 \cdot 9H_2O$ at 95°C for 24 h, followed by calcination at 500°C. Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 1000 ppm propane was fed on to 0.5g catalyst at a rate of $100cm^3 \cdot (STP)\ min^{-1}$. After reaching the steady-state, effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO.

RESULTS AND DISCUSSION

Figure 1 compares the catalytic activities of Ga-ZSM-5, H-ZSM-5 and Cu-ZSM-5 for the reduction of NO with propane as a function of reaction temperature. Ga-ZSM-5 showed higher catalytic activity than Cu-ZSM-5 in the temperature range of 300 - 600°C. It is noted that the conversion level of propane was lower on Ga-ZSM-5 than on Cu-ZSM-5, particularly in the low temperature region, although the conversion of NO on Ga-ZSM-5 was higher than on Cu-ZSM-5. Propane was almost completely consumed on Cu-ZSM-5 above 400°C by oxidation. The high oxidation ability limited the reaction of NO to N_2 in the presence of excess oxygen. The ability of Ga-ZSM-5 catalyst for the oxidation of propane was moderate, so that high efficiency was attained for the reaction of propane with NO. Recently, Hamada et al.2) reported that H-form zeolite also showed the catalytic activities for this reaction, and that H-form zeolites attained high selectivity for the reaction of NO with hydrocarbon. Ga-ZSM-5 was more active than H-ZSM-5 at all the temperatures, although the amount of reacted propane was smaller on Ga-ZSM-5 than on H-ZSM-5 in the temperature range 300 - 400°C.

The difference in the catalytic performance of Ga-ZSM-5, H-ZSM-5, and Cu-ZSM-5 became more remarkable, when the concentration of propane in the reactant mixture was smaller. Figure 2 shows the effect of propane concentration on the conversion of NO to N_2 at 500°C. Propane was completely

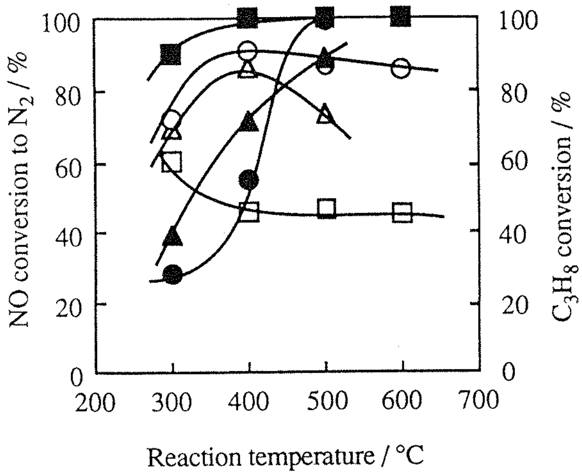

Fig 1. Variation in the catalytic activities of various ion-exchanged ZSM-5 as a function of reaction temperature.
Catalysts: ○ ●, Ga-ZSM-5; △ ▲, H-ZSM-5; □ ■, Cu-ZSM-5; open symbol, NO conversion; solid symbol, C_3H_8 conversion.

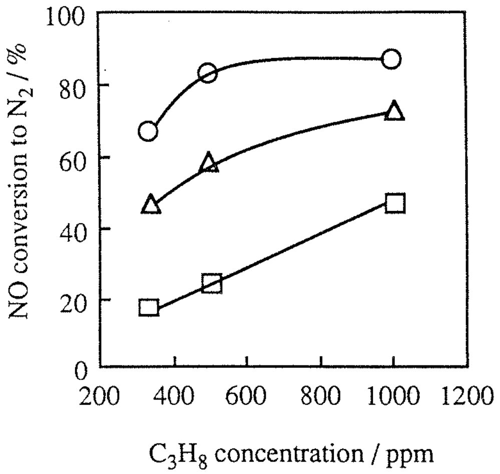

Fig.2 Selective reduction of NO as a function of C_3H_8 concentration over Ga-ZSM-5, H-ZSM-5 and Cu-ZSM-5.
Catalysts: ○, Ga-ZSM-5; △, H-ZSM-5; □, Cu-ZSM-5.
Reaction temperature, 500°C.

consumed on all of these catalysts when the concentration of propane was smaller than 500ppm. The conversion of NO on Cu-ZSM-5 remarkably decreased and less than 20% conversion was shown when the concentration of propane was lowered to 333ppm. On the contrary, 65% conversion of NO was maintained on Ga-ZSM-5 under the same reaction conditions, although almost the same amount of propane was converted on both of these catalysts. The conversion of NO was lower on H-ZSM-5 than on Ga-ZSM-5 under all these conditions.

From these results, it is obvious that the loading of gallium enhances the activity and selectivity of H-ZSM-5 for the reduction of NO with propane, even in the presence of high concentration oxygen. It has been reported that gallium ions in ZSM-5 are effective for the transformation of propane into aromatic hydrocarbons via propene.3) This fact leads us to deduce that gallium ions are effective to activate propane, resulting in the high catalytic activity for the reduction of NO.

CONCLUSION

Although further studies are required to understand the effect of gallium on the catalytic activity, it is concluded in this study that NO can more effectively be reduced into nitrogen on gallium ion-exchanged zeolites with smaller amounts of propane than on Cu-ZSM-5 and on proton type zeolites, and that the gallium ion-exchanged zeolites are the candidate for practical catalysts to remove nitrogen oxides under excess oxygen condition.

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ゼオライト系触媒を用いたＮＯの選択的還元反応

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寺崎郁恵・渡辺弘毅・菊地英一

1. 緒言

ディーゼルエンジン排気ガス等の酸素過剰雰囲気下でのNOxの除去は重要な課題であり、Cu-ZSM-5等のゼオライト系触媒を用いた炭化水素によるNOの還元反応が注目されている1),2)。しかし、高酸素濃度下では炭化水素と酸素との反応が優先し、選択的なNOの還元が困難となることがある。我々はこれまでに炭化水素の酸化能が比較的小さい金属をイオン交換担持したゼオライトについて検討を行い、C_3H_8を還元剤に用いるとGa担持ゼオライトが高いNO転化率を示し、酸素過剰雰囲気下においてもNOと炭化水素の反応が高選択的に進行することを見いだしている3),4)。また、Ga担持ゼオライトは活性を示す温度範囲が極めて広くこのような触媒はこれまでに例がない。

本研究では還元剤として自動車排ガスに多く含まれるC_2H_4について検討を行った。その結果、C_2H_4を還元剤に用いても広い温度範囲で高活性を示し、また高SV条件下$(W/F=0.03 g\cdot s\cdot cm^{-3})$でも高い活性が得られることを見いだしたので報告する。

2. 実験操作

ゼオライトへのGaの担持は、硝酸塩を用いたイオン交換法により行った。また、Cu-ZSM-5は岩本ら5)の方法に従い、酢酸塩水溶液によるイオン交換法により調製した。ゼオライトはZSM-5の他にferrierite, mordenite, USY(以上、東ソー製)について検討した。各々のSiO_2/Al_2O_3比は23.3, 17.8, 19.3, 14.5である。調製した触媒のイオン交換率(%)はICPにより求め、( )内に記した。

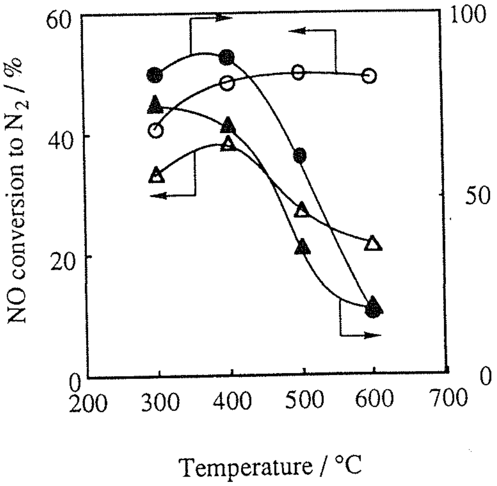

Fig. 1. Variation in NO conversion and CO yield on Ga-ZSM-5 and H-ZSM-5 as a function of reaction temperature.
Catalysts: ○ ●, Ga-ZSM-5(92); △ ▲, H-ZSM-5(100).
Reaction conditions: Catalyst weight, 0.5g
NO, 1000ppm; C_2H_4, 250ppm; O_2, 10%;
Total flow rate, $100cm^3 \cdot min^{-1}$.

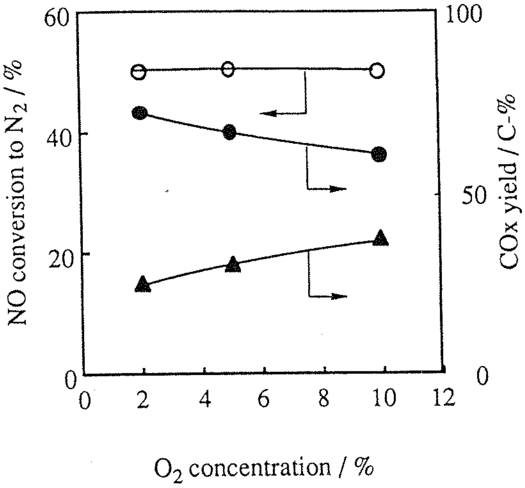

Fig. 2. Effect of oxygen concentration on the selective reduction of NO with C_2H_4 over Ga-ZSM-5(92).
○, NO conversion to N_2; ●, CO yield; ▲, CO_2 yield.
Reaction conditions: Catalyst weight, 0.5g
NO, 1000ppm; C_2H_4, 250ppm; Total flow rate, $100cm^3 \cdot min^{-1}$; reaction temperature, 500°C.

反応は常圧固定床流通式反応装置を用い、反応温度300~600°C，NO濃度1000ppmで行った。また、C_3H_8およびC_2H_4濃度は167~1000ppm，O_2濃度は2~10%，接触時間は全流量$100cm^3 \cdot min^{-1}$で触媒重量を0.05~0.5gの範囲で変化させた。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。なお、活性はすべてN_2への転化率で評価した。

3. 結果と考察

我々はすでにC_3H_8を還元剤に用いた場合、Ga-，H-，Cu-ZSM-5のNO転化率を比較すると、Ga-ZSM-5が広い反応温度域で高活性を示すことを報告している。またこのときのGa-ZSM-5でのC_3H_8の全転化率はH-，Cu-ZSM-5に比べて低く、C_3H_8の酸化に比べてNOとC_3H_8が高選択的に反応していた。

Fig.1に還元剤にC_2H_4を用いたときのGa-ZSM-5とH-ZSM-5の

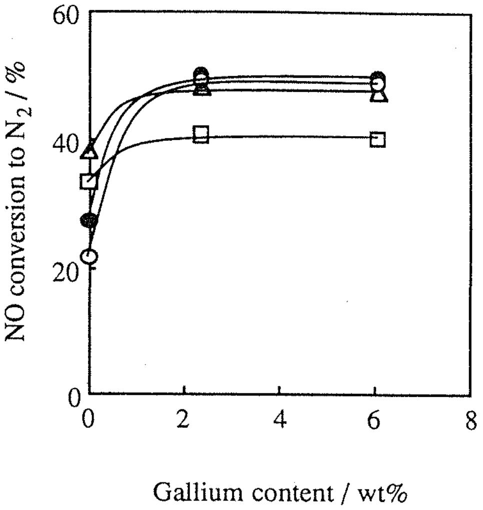

Fig. 3. Dependence of the catalytic activity of Ga-ZSM-5 on gallium content.
Reaction conditions: Catalyst weight, 0.5g; NO, 1000ppm; C_2H_4, 250ppm; O_2, 10%; Total flow rate, 100cm^3·min^{-1}; reaction temperature; 300°C(□), 400°C(△), 500°C(●), 600°C(○) .

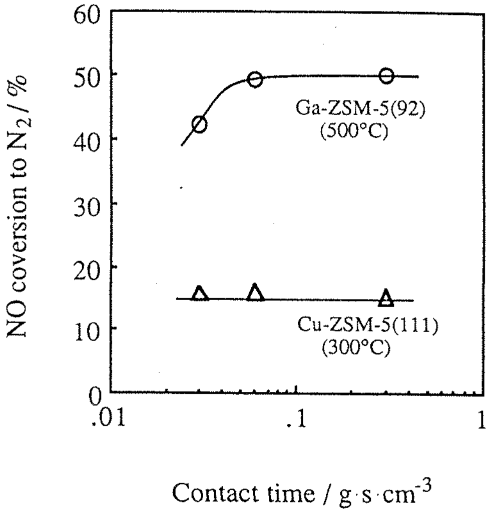

Fig. 4. Correlation between the catalytic activities and contact time.
Catalysts:
○, Ga-ZSM-5(92) reaction temperature, 500°C;
△, Cu-ZSM-5(111) reaction temperature, 300°C.
Reaction conditions: Catalyst weight 0.05 - 0.5g; NO, 1000ppm; C_2H_4, 250ppm; O_2, 10%; Total flow rate, 100cm^3·min^{-1}.

NO転化率の温度依存性の結果を示す。C_3H_8を還元剤とした場合には300～400℃ではH型とGa担持のものとで変化がなく、500℃以上の高温度域で効果がみられたのに対し、還元剤にC_2H_4を用いると300℃でもGaの効果がみられた。またGa-ZSM-5ではH型と比較してCOの生成量が多いことがわかる。

Fig.2に、NO転化率のO_2濃度依存性について示した。O_2濃度が2～10%の間ではN_2への転化率にはほとんど変化がみられなかった。

以上のことから、Ga-ZSM-5はC_2H_4によるNOの還元反応においても広い反応温度域で高活性を示し、NOとC_2H_4の反応がO_2の存在により阻害されず、高選択的に進むことが示された。

ZSM-5についてGa担持量とNO転化率の関係をFig.3に示した。反応温度300～600°Cのいずれの温度でも少量のGaの担持によりNO転化率が向上していることがわかる。担持量を6wt%まで増加させてもNO転化率に変化はみられなかった。

次に接触時間の影響について検討したところ、Ga-ZSM-5は$W/F=0.03 g\cdot s\cdot cm^{-3}$という高SV条件下において、Cu-ZSM-5と比較しても高いNO転化率を示すことがわかった（Fig.4）。

Ga-ZSM-5によるNO還元反応の選択性は極めて高く、生成したN_2と転化した炭化水素の比はほぼN:C=1:1であった。これは以下の(1)あるいは(2)の反応式で示される量論比に近い。

$$2NO + C_2H_4 + O_2 = N_2 + 2CO + 2H_2O \cdots\cdots(1)$$

$$2NO_2 + C_2H_4 = N_2 + 2CO + 2H_2O \cdots\cdots(2)$$

(1)式はHがNOの還元に関与せず酸素と反応しH_2Oを生成する反応である。また本反応に酸素との反応で生成したNO_2が関与しているのであれば(2)式で示されるようにC_2H_4のC,HともにNO_2の還元に関与し選択的にN_2とCOを生成すると考えられる。いずれにせよ、少なくとも炭化水素のCは全て選択的にNOの還元に使われているものと推測される。

以上のことからGa-ZSM-5は酸素過剰雰囲気下においても極めて高選択的にNOと炭化水素が反応し、その結果高いNO転化率を示すことがわかった。

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ＮＯ選択還元反応に対するＦｅ－シリケートの触媒特性

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1. 緒言

ディーゼルエンジン排気ガス等の酸素過剰雰囲気下でのNOxの除去に大きな関心が寄せられている。これまでにCu-ZSM-5等のゼオライト触媒が炭化水素によるNOの還元反応に有効であることがが報告されてる1-3)。我々は酸素過剰雰囲気下でのC_3H_6によるNO還元反応に，Fe-シリケートが300℃という低温で高活性を示すことを見い出し報告した4)。そこで本研究ではSi/Fe比の異なるFe-シリケートを用いてFe-シリケート中のFeの状態とNO還元活性との関連について検討した。

2. 実験操作

本研究に用いたFe-シリケートは，迅速結晶化法により合成した5)。このFe-シリケートを硝酸アンモニウム水溶液でイオン交換した後，空気焼成しプロトン型として反応に供した。XPS測定はJPS-9000(JEOL)を使用し，X線源にはMgKα線を用いた。

反応には常圧固定床流通式反応装置を用い，NOx,1000ppm;C_3H_6,300-1000ppm;O_2,2-10%（Heバランス）のモデルガスを用いて全流量100$cm^3 \cdot min^{-1}$，触媒重量0.5g，反応温度300-600°Cで行った。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。

3. 結果と考察

Table. 1に本研究で用いたFe-シリケートの組成を示した。Si/Fe=80のFe-シリケートではNaとFeの量がほぼ一致したが，Si/Fe比が小さくなるにしたがって、Naの量に対してFeが過剰に存在することがわかる。このことから，Si/Fe比の小さいFe-シリケートほど骨格外のFeが多く存在していると考えられる。NH_3-TPDの結果から（Fig. 1),Si/Fe=25の酸量はSi/Fe比=50とほぼ一致し，骨格中に取り込まれたFeの量はこれらの触媒ではほぼ同程度と考えられる。またXPS測定の結果から，Si/Fe比が小さいものはFe2pのピークの低エネルギー側にショルダーピークが存在し，骨格外のFeの存在が確認された。

Table. 1. Chemical compositions of metallosilicates.

Catalyst	Si/Fe (仕込み)	Si/Fe (ICP)	Si/Fe (XPS)	Na / 10^{-4}mol/g	Fe / 10^{-4}mol/g	Si / 10^{-2}mol/g	Surface area / m^2/g
Fe-silicate	25	23.6	39.8	2.64	6.10	1.44	339
	50	48.9	74.9	2.93	3.11	1.52	303
	80	80.2	124.5	2.00	1.92	1.54	373
HCl-treat./ Fe-silicate	25	47.8	----	----	3.14	1.50	----

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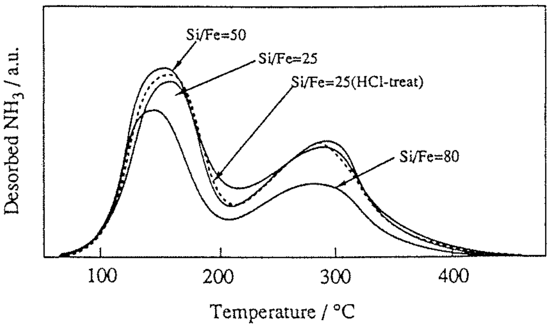

Fig.1. NH_3-TPD spectra of various Fe-silicates.

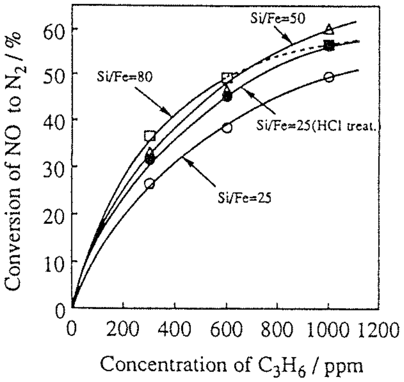

Fig.2. Catalytic activities of H-Fe-silicates as a function of C_3H_6 concentration.
Reaction temperature, 300°C; NO, 1000ppm; O_2 , 10%; total flow rate,100cm^3·min^{-1}; catalyst weight, 0.5g.
□, Si/Fe = 80; △, Si/Fe = 50; ○, Si/Fe= 25;
●, Si/Fe=25(HCl-treat.).

Fig.3にこれらのSi/Fe比の異なるFe-シリケートを用いたときのC_3H_6濃度とNO転化率の関係を示す。C_3H_6濃度が低い場合（≤600ppm）にはSi/Fe比の増加とともにNO転化率が増加した。本反応条件下ではいずれの触媒においてもC_3H_6の転化率は100％であった。したがって，NO転化率の序列はC_3H_6の燃焼活性によるものと考えられる。Si/Fe比が小さいFe-シリケートは骨格外に多量に存在するFeが炭化水素の燃焼反応を促進し，反応の選択性を低下させるものと考えられる。これに対して，Si/Fe=80のFe-シリケートは骨格外にはほとんどFeが存在せず，C_3H_6の燃焼活性が乏しいため，高C_3H_6濃度では経時的にCOx収率が低下し，炭素析出により失活した。そこで骨格外のFeの影響を検討するためにSi/Fe=25のFe-シリケートの骨格外のFeの除去を試みた。0.1Nの塩酸で洗浄することによりFeの量はSi/Fe=50と同程度にまで減少したが，酸量にはほとんど変化がみられなかった。従って、骨格外のFeのみが除去されたものと考えられる。このFe-シリケートを反応に供したところ，Si/Fe=50のFe-シリケートと同程度のNO転化率が得られた。また，Si/Fe=50のFe-シリケートの選択性がSi/Fe=80よりも低いのは骨格中に取り込まれたFe量の増加にともない燃焼活性が増大したためではないかと考えられるが詳細は現在検討中である。

これらのことから，C_3H_6によるNO還元反応においてFe-シリケートは骨格外にFeが存在すると炭化水素と酸素の反応が優先し，反応の選択性を低下させるものと考えられる。その結果，Si/Fe比の小さいFe-シリケートではNO転化率が低下するものと結論した。

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Feーシリケート触媒上でのNO選択還元反応機構の検討

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1.緒言

現在、ディーゼルエンジン排気ガス等の酸素過剰雰囲気下におけるNOxの除去に高い関心が寄せられており、Cu-ZSM-5等のゼオライト触媒が炭化水素によるNO還元に有効であることが報告されている1)。我々は酸素過剰雰囲気下でのC_3H_6によるNO還元反応にFeーシリケートが高活性を示し、触媒表面上に析出した炭素種がNO還元反応に寄与していることを報告した2)。そこで本研究では過渡応答法を用いて反応機構の解明を進め、反応中間体について検討を行った。

2.実験

本研究に用いたFeーシリケートは、迅速結晶化法3)により合成した。このFeーシリケートを硝酸アンモニウム水溶液でイオン交換した後空気焼成し、プロトン型として反応に供した。反応には常圧固定床流通式反応装置を用いた。NO,1000ppm；C_3H_6,500-1000ppm；O_2,1-10%（Heバランス）の混合ガスを用い、全流量100cm^3・min.$^{-1}$，触媒重量0.25-0.5g，反応温度300℃で行った。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。

3.結果と考察

Fig.1にNO,C_3H_6,O_2の混合ガスを用いて反応を行い、NO転化率が定常値を示した後(Reaction-A)、NO,O_2の混合ガスに切り換えたとき(Reaction-B)のN_2生成速度の経時変化を示した。切り換え後COxの生成とともにN_2が生成したが、60分後にはほぼ失活し、COxの生成もほとんど認められなくなった。Reaction-Aにおいて触媒表面上に炭素が析出していること、またNO,O_2の2成分だけではN_2が生成しないことから、触媒表面上に析出した炭素種がNO還元反応に寄与していると考えられる。

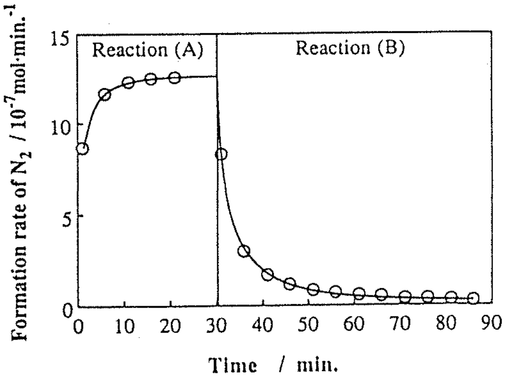

Fig.1. Transient response of the formation of N_2 on H-Fe-silicate when feed composition was changed. Reaction (A): NO, 1000ppm; C_3H_6, 1000ppm; O_2, 10%. Reaction (B): NO, 1000ppm; O_2, 10%. Total flow rate, 100cm^3·min.$^{-1}$; catalyst weight, 0.5g; reaction temperature, 300°C.

そこで、NOの還元に有効な炭素種の生成におよぼす共存ガスの影響について検討を行った。Table.1に示すようにC_3H_6のみを供給した後(Reaction-A)に、NOとO_2を導入したところ(Reaction-B)、析出

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した炭素量に対するN_2の生成量は少なかった。またC_3H_6とO_2を供給した場合にも同様な結果が得られた。これに対して、C_3H_6とNOの2成分を供給した場合にはN_2の生成量が増大した。このことから、NOが共存することによりNOの還元反応に有効な炭素種が生成することが示唆される。

Table. 1. Effect of feed gas composition on the formation of carbonaceous material and nitrogen.

Reaction (A)		Reaction (B)			
Composition	Deposited Carbon / 10^{-6}mol	Composition	N_2 / 10^{-6}mol	N_2 / C / 10^{-2}mol/mol	N_2 / COx / 10^{-2}mol/mol
C_3H_6=1000ppm	42.3	NO=1000ppm O_2=10%	1.51	3.57	8.20
C_3H_6=1000ppm O_2=10%	97.1		3.51	3.61	6.58
C_3H_6=1000ppm NO=1000ppm	56.4		10.6	18.8	28.1
C_3H_6=1000ppm NO=1000ppm O_2=10%	106.4		6.40	6.02	12.5

Total flow rate, 100cm^3·min.$^{-1}$; catalyst weight, 0.5g; reaction temperature, 300°C.

つぎに、C_3H_6とNOの共存により生成した炭素種とNOおよびO_2との反応について検討を行い、その結果をTable.2に示した。Reaction-Bで、NOのみ、もしくはO_2のみを導入してもN_2の生成量は少ない。これに対して、NOとO_2の共存ガスを導入した場合には多量のN_2が生成した。このことから、C_3H_6とNOの共存により生成した炭素種がN_2の生成に寄与するためには、NOとO_2の共存が必要であることがわかった。

Table. 2. Effect of feed gas composition on the reduction of nitric oxide to nitrogen.

Reaction (A)		Reaction (B)			
Composition	Deposited Carbon / 10^{-6}mol	Composition	N_2 / 10^{-6}mol	N_2 / C / 10^{-2}mol/mol	N_2 / COx / 10^{-2}mol/mol
C_3H_6=1000ppm NO=1000ppm	58.1	NO=1000ppm	1.42	2.44	----- a)
	50.1	O_2=10%	1.47	2.93	8.03
	56.4	NO=1000ppm O_2=10%	10.6	18.8	28.1

Total flow rate, 100cm^3·min.$^{-1}$; catalyst weight, 0.5g; reaction temperature, 300°C.
a) : COx was undetectable.

そこでReaction-Bでの酸素分圧の影響について検討を行った。Fig.2に示すように、酸素分圧の低下とともにCOxの生成量が減少し、析出炭素がNO還元に選択的に消費され、生成したN_2とCOxの比が0.5に収束した。このことから還元されたNOと還元反応に消費されたC_3H_6の炭素の原子比は、N:C=1:1であることが示唆される。

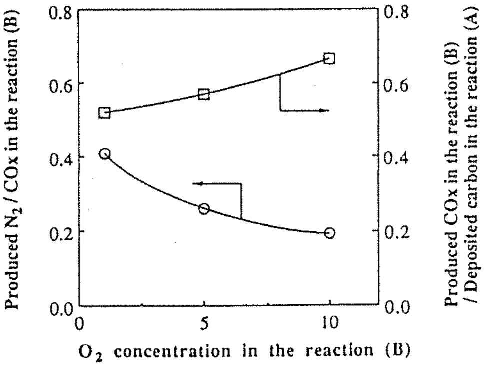

Fig. 2. Effect of oxygen concentration on the selectivity for NO reduction in the reaction (B).
Reaction (A): NO, 1000ppm; C_3H_6, 500ppm.
Reaction (B): NO, 1000ppm.
Total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.25g; reaction temperature, 300°C.

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ゼオライト触媒上でのNO選択還元反応に対するGaの効果の検討

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１．緒言

ディーゼルエンジン等の酸素を過剰に含む排気ガスからのNOxの除去技術として、炭化水素によるNOの還元が注目されている。この反応にはCu-ZSM-5等のゼオライト系触媒が有効であることが報告されている1),2)。我々はこれまでの研究で、還元剤として$C_3H_8$3)および$C_2H_4$4)を用いた場合、Ga担持H型ゼオライトが今までに報告されたゼオライト系触媒よりも広い反応温度域で高いNO転化率を示すことを報告した。そこで、本研究では、Gaの担持状態および担体の影響について調べ、GaのNO還元反応におよぼす役割について検討した。

２．実験

ZSM-5（東ソー製，$SiO_2/Al_2O_3=23.3$）へのGaの担持は、硝酸塩を用いたイオン交換法により行った。また、Cu-ZSM-5は岩本らの方法に従い、酢酸塩水溶液を用いて調製した。調製した触媒の金属担持量はICPにより求め、イオン交換率(%)として()内にGa, Naの順序で記した。反応には常圧固定床流通式反応装置を用い、NO濃度1000ppm，O_2濃度10%，C_3H_8濃度167-1000ppm（Heバランス）のモデルガスを用いて、全流量100cm^3/min，触媒重量0.5g，反応温度300-600°Cの条件で行った。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。

３．結果と考察

Fig.1にGa/H-ZSM-5およびH-ZSM-5のC_3H_8のNO還元反応に対する選択性を示す。Ga/H-ZSM-5，H-ZSM-5ともにC_3H_8濃度が高い領域では、C_3H_8の燃焼反応が進行し、NO還元反応への選択性は低い。しかし、C_3H_8濃度が低下するとともに選択性は向上し、還元されたNOと生成したCOxのNとCの原子比がN：C＝１：１に収束した5)。また、H型にGaを担持することにより、どの反応温度においても、選択性が向上することがわかった。

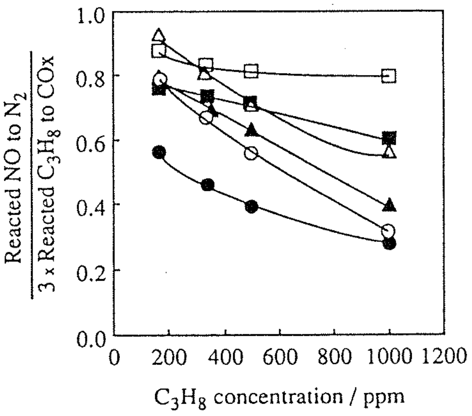

Fig.1 Ratio in conversion of NO to C in propane on Ga/H-ZSM-5(79)(open symbol) and H-ZSM-5 (solid symbol). NO, 1000ppm; O_2.10%; total flow rate, 100cm^3 min^{-1}; catalyst weight, 0.5g; reaction temperature, 300°C(□), 400°C(△), 500°C(○).

次に、Gaの役割を明らかにするために、固体酸性の影響について検討した。その結果をFig.2に示す。Na-ZSM-5から調製したGa/Na-ZSM-5はNH_4-ZSM-5から調製したGa/H-ZSM-5に比べNO転化率が低かった。これらの触媒の Ga担持率は Gaが、

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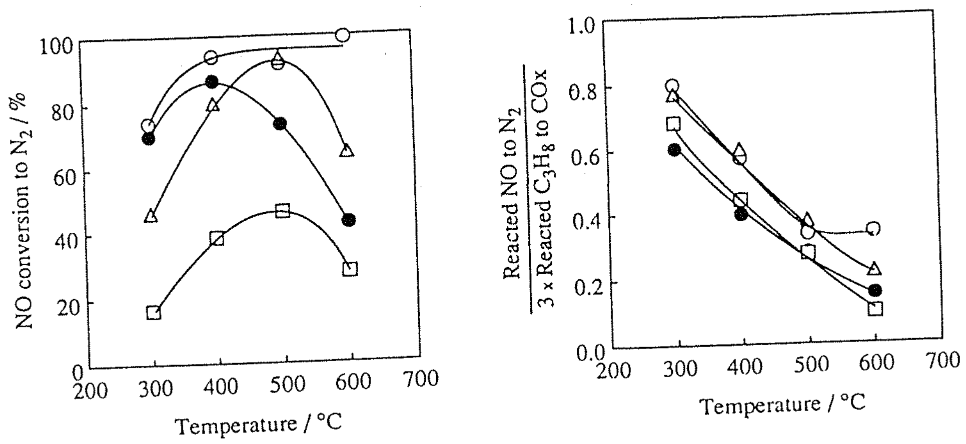

Fig.2 Selective reduction of NO on various ion-exchanged zeolites as a function of C_3H_8 concentration.
Catalysts: ○, Ga/H-ZSM-5(94); ●, H-ZSM-5; △, Ga/Na-ZSM-5(105, 37);
□, Na-Ga/Na-ZSM-5(95, 69).
NO, 1000ppm; C_3H_8, 1000ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight; 0.5g.

Ga^{3+}としてイオン交換したと仮定すると約100%と相違はみられなかったが、Na型から調製した触媒ではイオン交換サイトの約40%のNaが残存していることが化学分析により示された。このGa/Na-ZSM-5をさらにNaでイオン交換したところ、Na量は40%から70%へと増加し、NO転化率は著しく低下した。また、C_3H_8のNO還元反応に対する選択性はGa/Na-ZSM-5はGa/H-ZSM-5と、Na-Ga/Na-ZSM-5はH-ZSM-5とほぼ同じであった。Fig.3に示すように、各ZSM-5における高温側の酸量はH＞Ga/H＞Ga/Na＞Na-Ga/Naの順で減少した。したがって、Ga/H-ZSM-5の高いNO転化率と選択性は、Gaと酸点の相乗効果であると考察した。

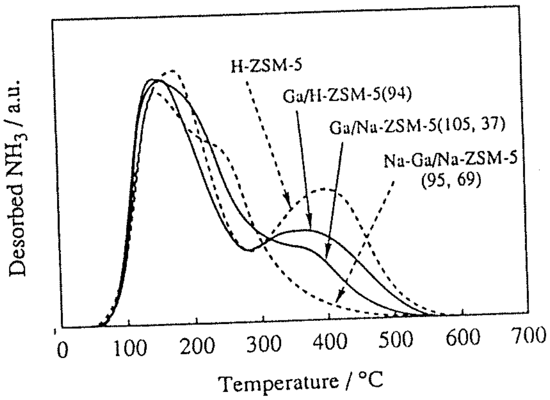

Fig.3 NH_3-TPD spectra on various cation exchanged ZSM-5.

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NOの炭化水素還元におけるゼオライト触媒の選択性

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1. はじめに

燃焼装置から発生する窒素酸化物(NOx)の低減には触媒を用いる排気ガスの処理が実施されてきた。ガソリンエンジンの排ガスには三元触媒法が，大型ボイラーの排ガスにはアンモニア選択還元法が実用化されている。しかし高い燃焼効率を得る希薄燃焼排ガス，例えばガスタービンやディーゼルエンジン，希薄燃焼ガソリンエンジンの排ガス中には酸素が過剰に存在するため，これらの排ガス浄化は従来の触媒方式では現実的に困難である。また有毒なアンモニアを使用することも技術的に問題がある。従って，新たな触媒プロセスの開発が望まれている。

Cu-ZSM-5触媒を用いた炭化水素によるNOの還元反応が岩本ら1)により報告されて以来，ゼオライト系触媒を中心として検討がなされ種々の触媒で本反応が進行することが明かとなった2-5)。我々はこれまでにFe-シリケートがC_3H_6を還元剤として用いた場合，300℃という低温で本反応に対して高活性を示すことを見いだしている2)。しかし，これらの触媒ではまだ高酸素濃度下で炭化水素と酸素との反応が優先し，NOの還元の選択性は十分に高くなく選択性の向上が望まれている。これまでに，H型ゼオライト3)，$Al_2O_3$4)等の固体酸触媒が本反応に対して比較的高い選択性を有することが報告されているが，高GHSV条件下では活性が低い。

我々は種々の金属イオンで交換したゼオライトについてNOの炭化水素による還元を検討したところ，C_3H_8を還元剤に用いるとGaイオン交換ゼオライトが高いNO転化率を示し，酸素過剰雰囲気下においてもNOと炭化水素の反応が高選択的に進行することを見いだした5),6)。また，Gaイオン交換ゼオライトはこれまでに報告された中では極めて広い温度範囲で高い活性を示すことを明らかにした。本講演ではGaイオン交換ゼオライトを中心にNO還元反応の選択性について述べる。

2. 実験

本研究で用いたFe-シリケートは乾らの方法7)により合成した。またゼオライトへの金属の担持は，硝酸塩（Ga,Al,Zn）あるいは塩化物（Ti,In,Sn）を用い，イオン交換法により行った。Cu-ZSM-5は岩本ら8)の方法に従い，酢酸塩水溶液によるイオン交換法により調製した。ゼオライトはZSM-5の他にferrierite，mordenite，USY(以上、東ソー製)につい

て検討した。各々のSiO_2/Al_2O_3比は23.3，17.8，19.3，14.5である。調製した触媒のイオン交換率(%)はICPにより求め，( )内に記した。Al_2O_3（触媒化成 ACP-1）は500℃焼成したものを用いた。

反応は常圧固定床流通式反応装置を用い，反応温度300－600°C，NO濃度1000ppmで行った。また，炭化水素濃度は167－1000ppm，O_2濃度は2－10%，空間速度は7200－144000h^{-1}（全流量100－200$cm^3 \cdot min^{-1}$，触媒重量0.05－0.5g）の範囲で変化させた。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。なお，活性はすべてN_2への転化率で評価した。

3. 結果と考察

3-1. Fe-シリケート上でのNO選択還元反応機構

最初にFe-シリケートによる還元反応の結果を示す。Fe-シリケートは還元剤にC_3H_6を用いると，300℃という比較的低温において高い活性を示す。反応ガス組成を変えた実験から触媒表面上の炭素種が本反応に関与すると考えられる(Fig.1)。Fe-シリケート上でのC_3H_6によるNO還元の反応機構を過渡応答法により検討した結果，NO→C_3H_6の順に触媒層にガスを導入した場合にはNO還元がほとんど起こらないことから，反応の第一ステップはC_3H_6の触媒表面への吸着であると考えられる（Scheme 1）9)。岩本ら10)によりCu-ZSM-5の場合でも IRによる同様の報告がなされてい

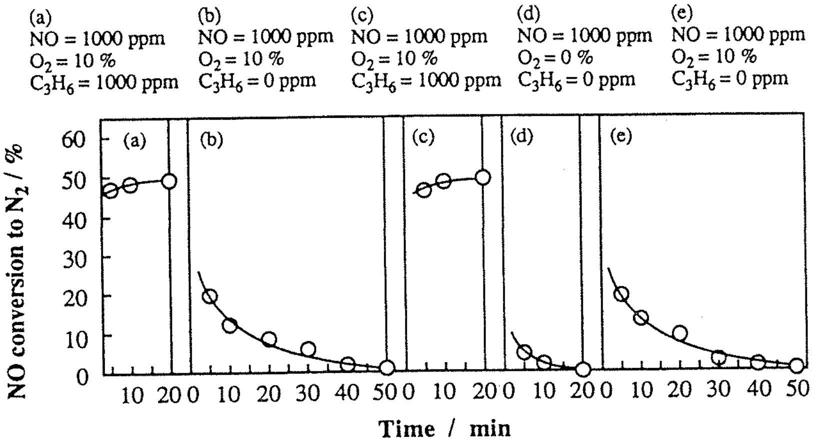
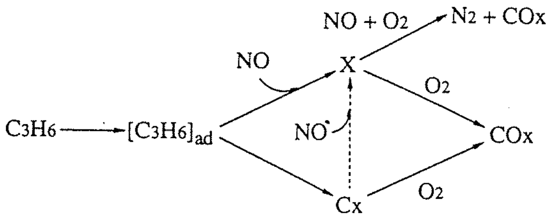


Fig. 1. Effect of reactant components on NO conversion to N_2.
(Fe-silicate catalyst, 300°C)



Scheme 1.　Reaction mechanism of NO reduction with C_3H_6 on Fe-silicate catalyst.

る。また，Scheme 1に示すように本反応はC, N, O, (H)からなる中間体をへて進行すると考えられる。これに関連して御園生ら11)は悪臭分子であるアミン類のN_2への分解に対してCuイオン交換ゼオライト等のNO還元反応に有効な触媒がよい選択性を示すことを報告しており，含窒素化合物の分解によりNO還元が進行することが示唆される。反応機構に関してはこの他にも種々の説12-15)が提唱されているが，還元剤，触媒，反応条件等が異なるため現在のところ定説はない。

しかし上述したように，Fe-シリケートでは酸素過剰雰囲気下においては触媒表面上の炭素種に対するNOと酸素の競争反応となると考えられる。従って，実用条件のようにNO濃度が低い場合，炭化水素の燃焼反応が優先し，NO還元反応の選択性が悪くなるという欠点がある。酸素過剰雰囲気下でNOを効率良く除去するためには還元剤とNOの反応の選択性を高める必要がある。選択性を高める方法として

(1)酸素による燃焼活性を押える。
(2)NOを触媒表面上に濃縮する。

等の方法が考えられる。ただし(1)では炭素析出による劣化が問題となることが考えられる。

3-2.Gaイオン交換ゼオライトによる選択還元挙動

NO還元反応の選択性を高めることを目的として，種々のカチオンをイオン交換担持したゼオライトの選択性についての検討を行った。ZSM-5についてC_3H_8のCOxへの転化率に対するNOxのN_2への転化率を示す(Fig.2)。Cu-ZSM-5は本反応条件下ではC_3H_8は100％近く転化し，NO転化率は50％前後であった。これに対して，Ga-ZSM-5は300－600℃という広い反応温度域で極めて高いNO転化率を示した。またこの時のC_3H_8転化率はCu-ZSM-5等に比べて低く，NOの還元が高選択的に進むことがわかる。Ga以外にもInが300－400℃で高い活性を示し，選択性も高い。InはC_3H_6による還元反応でも比較的高い活性を示すことが御園生ら16)により報告されている。またZnも500℃ではNO転化率，選択性ともに高い値

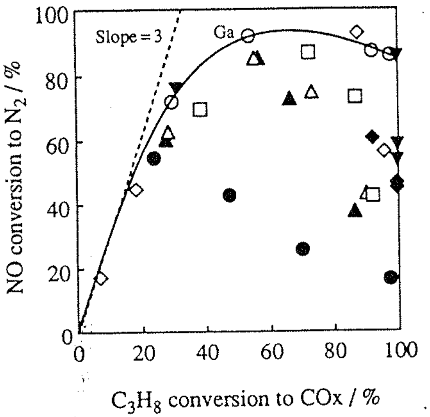


Fig.2. Relationships between NO conversion and C_3H_8 conversion on:
○, Ga-ZSM-5(79); △, Al-ZSM-5(53);
▼, In-ZSM-5(65); ●, Sn-ZSM-5(104);
▲, Ti-ZSM-5(11); ◇, Zn-ZSM-5(97);
□, H-ZSM-5; ◆, Cu-ZSM-5(111).
Catalyst weight, 0.5g; NO,1000ppm; O_2, 10%; C_3H_8, 1000ppm, total flow rate, $100cm^3 \cdot min^{-1}$; reaction temperature, 300 - 600°C;
Values in parentheses are ion-exchanged level.

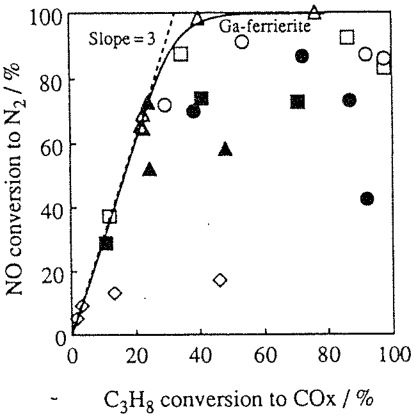


Fig.3. Relationships between NO conversion and C_3H_8 conversion on Ga- and H-zeolites.
○, Ga-ZSM-5(79); ●, H-ZSM-5;
△, Ga-ferrierite(91);▲, H-ferrierite;
□, Ga-mordenite(103); ■, H-mordenite;
◇, Ga-USY(106). Catalyst weight, 0.5g; NO,1000ppm; O_2, 10%; C_3H_8, 1000ppm; total flow rate, $100cm^3 \cdot min^{-1}$; reaction temperature, 300 - 600°C.

を示したが他の温度域での活性は低かった。Znについても岩本ら17)によりC_2H_4について既に同様の報告がされている。これらのNO還元反応に対して高選択性を示すものはいずれもNOxセンサーとなることが知られている18)。またこれ以外に本反応に対して高選択性を示す例として，御園生ら19)のC_3H_6を還元剤としたCeイオン交換ゼオライトの報告がある。Ce-zeoliteの高選択性はCeがNOxを吸着し，表面上にNOxが濃縮されるためとしている。従って，NOx還元反応の選択性を高める一因として触媒表面上へのNOxの吸着サイトの増大が考えられる。

次に，Gaイオン交換ゼオライトの選択的挙動についてさらに調べた。種々のGa交換ゼオライトについて検討を行った結果をFig.3に示す。フェリエライトが高活性を示し，その選択性も極めて高いことがわかる。これらの図中に点線で示したように，本反応の選択性はC_3H_8が1分子に対してNOが約3分子反応していることがわかる。従って本反応の化学量論は次式で示される。

$$3NO + C_3H_8 + kO_2 = 3/2N_2 + mCO + nCO_2 + 4H_2O \ldots\ldots (1)$$
$$\{k=1/2(m+2n+1),\ m+n=3\}$$

COおよびH$_2$ではこれらの触媒上でNOの還元反応は起こらないことから炭化水素分子のCがNO還元に選択的に使われていると考えることもできる。

3-3. NO選択還元に対する炭化水素の種類の効果

次に還元剤の影響について検討を行った。Fig.4に還元剤にC$_2$H$_4$を用いたときのGa-ZSM-5とH-ZSM-5のNO転化率の温度依存性の結果を示す。Ga-ZSM-5はC$_2$H$_4$によるNOの還元反応においても広い反応温度域で高活性を示し，NO還元反応の選択性は極めて高く，生成したN$_2$と転化した炭化水素のモル比はほぼ1:1であった(Fig.5)。C$_2$H$_4$によるNOの還元反応は以下の(2)の反応式の量論で示される。

$$2NO + C_2H_4 + kO_2 = N_2 + mCO + nCO_2 + 2H_2O \ldots\ldots (2)$$
$$\{k=1/2(m+2n),\ m+n=2\}$$

次に還元剤としてCH$_4$およびC$_2$H$_6$についても検討を行った。岩本と浜田20)はCu-ZSM-5及びAl$_2$O$_3$上でのNO還元反応を調べ，炭化水素を選択的(C$_2$H$_4$, C$_3$H$_6$, C$_3$H$_8$, C$_4$H$_8$)及び非選択的(H$_2$, CO, CH$_4$, C$_2$H$_6$)な還元剤とに分類している。これまでCH$_4$, C$_2$H$_6$ではNO選択還元はほとんど起こらないと考えられてきた。Al$_2$O$_3$はC$_3$H$_8$によるNO還元反応に対して高選択性を示すことが知られているが4)，CH$_4$では燃焼反応が優先し，NO還元反応の選択性は極めて低い。しかし，Gaイオン交換ゼオライトを用いるとCH$_4$およびC$_2$H$_6$でもNO選択還元が可能となる(Figs.6,7)。これらの反応のNO還元の選択性についてみると，

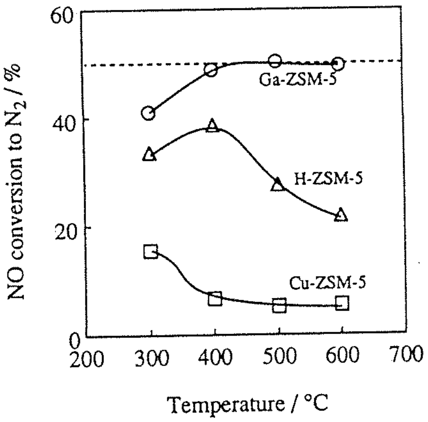


Fig.4. Variation in NO conversion on Ga-ZSM-5, H-ZSM-5, and Cu-ZSM-5 as a function of reaction temperature. ○, Ga-ZSM-5(92); △, H-ZSM-5(100); □, Cu-ZSM-5(111). Catalyst weight, 0.5g; NO, 1000ppm; C$_2$H$_4$, 250ppm; O$_2$, 10%; total flow rate, 100cm^3·min^{-1}.

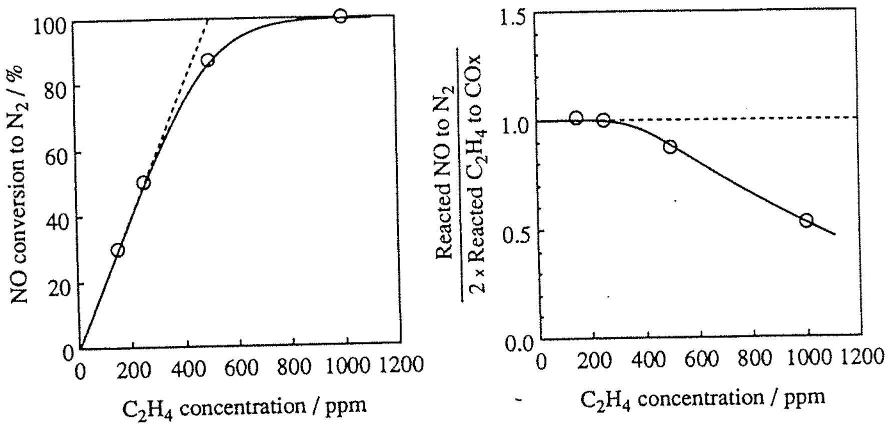


Fig.5. NO reduction on Ga-ZSM-5(92) as a function of C_2H_4 concentration. NO, 1000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight; 0.5g; reaction temperature, 500°C.

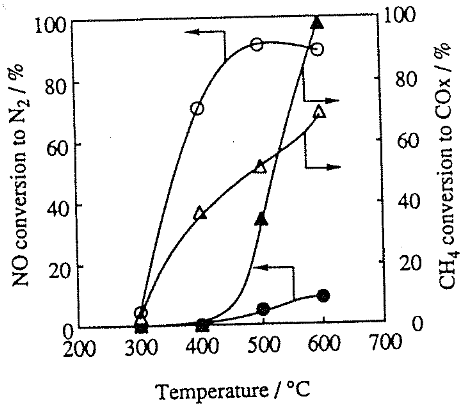


Fig.6. Variation in NO conversion and CH_4 conversion on Ga-ZSM-5(open symbol) and Al_2O_3(solid symbol) as a function of reaction temperature.

○ ●, NO conversion to N_2;

Δ ▲, CH_4 conversion to COx.

NO, 1000ppm; CH_4, 1000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.5g.

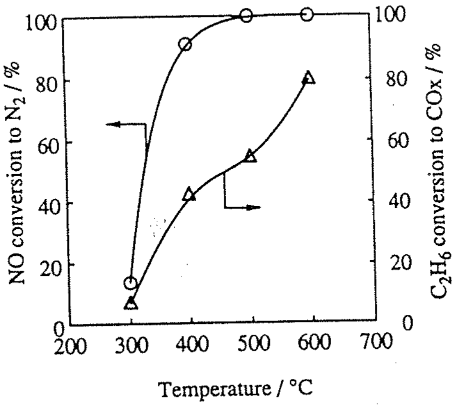


Fig.7. Variation in NO conversion and C_2H_6 conversion on Ga-ZSM-5 as a function of reaction temperature.

○, NO conversion to N_2;

Δ, C_2H_6 conversion to COx.

NO, 1000ppm; C_2H_6, 1000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.5g.

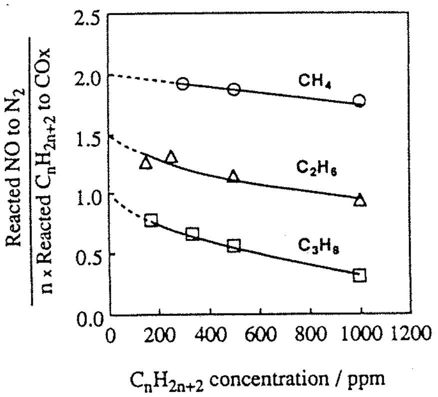


Fig.8. Ratio in conversion of NO on Ga/H-ZSM-5 to C in hydorogarbon.
○, CH_4; △, C_2H_6; □, C_3H_8.
NO, 1000ppm; O_2, 10%;
total flow rate, $100cm^3 \cdot min^{-1}$;
catalyst weight, 0.5g;
reaction temperature, 500°C.

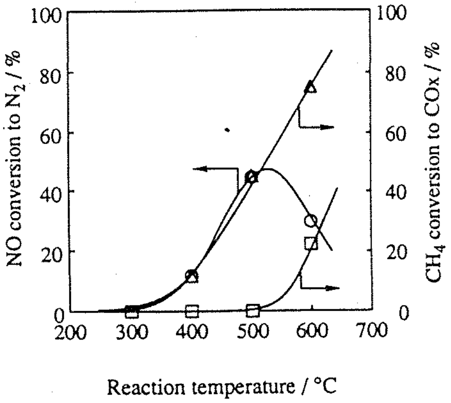


Fig.9. Variation in NO conversion and CH_4 conversion on H-ZSM-5 as a function of reaction temperature.
○, NO conversion (NO, 1000ppm; CH_4, 1000ppm; O_2, 10%);
△, CH_4 conversion (NO, 1000ppm; CH_4, 1000ppm; O_2, 10%);
□, CH_4 conversion (NO, 0 ppm; CH_4, 1000ppm; O_2, 10%);
total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.5g.

$$2NO + CH_4 + kO_2 = N_2 + CO_x + 2H_2O \quad \text{.......}(3)$$

$$3NO + C_2H_6 + kO_2 = 3/2N_2 + 2CO_x + 3H_2O \quad \text{.......}(4)$$

のようになる。すなわち，反応の選択性は炭化水素の炭素数が小さくなるほど効率的にNOの還元が起こっていることがわかる(Fig.8)。また，プロトン型ゼオライト上でもCH_4によるNO還元反応が比較的高い選択性で進行する(Fig.9)。本反応条件下ではプロトン型ゼオライトの化学量論は(5)式で示される。

$$NO + CH_4 + kO_2 = 1/2N_2 + CO_x + 2H_2O \quad \text{.......}(5)$$

Ga-ZSM-5ではNO:CH_4=2:1であるのに対し，H-ZSM-5上ではほぼNO:CH_4=1:1となる。すなわちGaの存在によりNO還元の選択性が向上していることがわかる。本反応には酸素の存在が不可欠であること，及びH-ZSM-5上では500℃以下ではCH_4の燃焼反応が全く起こらないことから，CH_4はNO_2との反応により活性化されると考えられる。またGa-ZSM-5でもH-ZSM-5と同様に500℃以下ではCH_4の燃焼活性はほとんど発現しない。

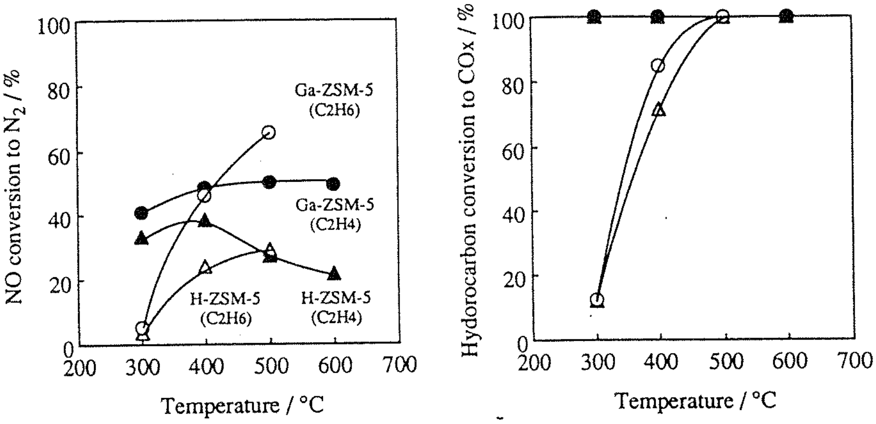


Fig.10. NO conversion and Hydorocarbon conversion on H-ZSM-5(Δ) and Ga/H-ZSM-5(O) as a function of reaction temperature.
NO, 1000ppm; C_2H_4(solid symbol) or C_2H_6(open symbol), 250ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.5g.

従って本反応にはNO_2が関与すると現在のところ考えている。

またGa-ZSM-5においてC_2H_4とC_2H_6の結果を比較すると500℃ではC_2H_6の方がC_2H_4よりも高いNO転化率を示すことは非常に興味深い(Fig.10)。Ga-ZSM-5でもH_2およびCOではNOの還元が全く起こらないことから，Gaにより引き抜かれた水素がNO還元に有効に働くと考えているが現在のところ詳細は不明であり，炭素数による選択性の変化は今後の研究課題の一つである。

4.結論

以上述べてきたように，ゼオライト系触媒によるNO還元反応に対して，Gaイオン交換ゼオライトは高い選択性を示し，NO還元反応の選択性は炭化水素の炭素数が少ないほど向上する。また，プロトン型ゼオライトと比較してNO還元の選択性が向上することから，Gaイオン交換ゼオライトの高選択性はGaがNOxを触媒表面に吸着するためと現在のところ考えている。

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11. NO還元反応におけるGaイオン交換ゼオライトの選択的挙動

（早大理工）○余語克則・井原道人・寺崎郁恵・菊地英一

1．緒言

ディーゼルエンジン等の酸素を過剰に含む排気ガスからのNO_xの除去技術として炭化水素によるNOの選択還元が注目されている。この反応にはCu-ZSM-5等のゼオライト系触媒が有効であることが報告されている[1-4]。しかし，高酸素濃度下では炭化水素と酸素の反応が優先し，選択的なNOの還元が困難となることがある。そこで我々はNO還元反応の選択性を高めることを目的として，種々のカチオン交換ゼオライトの選択性についての検討を行った。還元剤としてC_3H_8を用いた場合，Gaイオン交換ゼオライトが高いNO転化率を示し，NO還元反応の選択性が極めて高いことを見いだした[5,6]。本研究ではGaイオン交換ゼオライトのNO還元反応に対する触媒特性を調べ，Gaの効果について検討を行った。

2．実験

ゼオライトへの金属の担持は，硝酸塩（Ga,Al,Zn）あるいは塩化物（Ti,In,Sn）を用い，イオン交換法により行った。本研究ではゼオライトはZSM-5の他にferrierite, mordenite, USY（以上，東ソー製）について検討した。各々のSiO_2/Al_2O_3比は 23.3, 17.8, 19.3, 14.5 である。また

Table 1. Catalytic activities of various ion-exchanged ZSM-5.

Catalyst (Ion-exchange level %)	Conv. of NO to N_2 / % [C_3H_8 to CO_x / %] 300℃	400℃	500℃	600℃
H-ZSM-5	69.6 [38.5]	86.6 [72.2]	73.2 [86.5]	42.7 [92.1]
Cu(111)/Na(7)-ZSM-5	60.5 [92.1]	46.1 [100]	46.9 [100]	45.2 [100]
Ga(79)/H-ZSM-5	71.9 [29.5]	91.1 [53.8]	87.2 [91.9]	85.9 [97.6]
Al(53)/H-ZSM-5	62.8 [28.1]	85.0 [55.4]	74.8 [73.1]	43.4 [90.0]
Ti(11)/H-ZSM-5	60.2 [27.5]	85.3 [56.5]	72.7 [66.2]	37.8 [86.3]
Zn(97)/H-ZSM-5	18.1 [7.1]	45.3 [18.6]	93.0 [88.0]	56.5 [96.0]
In(65)/H-ZSM-5	76.0 [30.9]	85.8 [99.9]	53.8 [100]	57.7 [100]
Sn(104)/H-ZSM-5	54.8 [23.8]	43.0 [47.0]	25.9 [69.7]	16.4 [97.1]

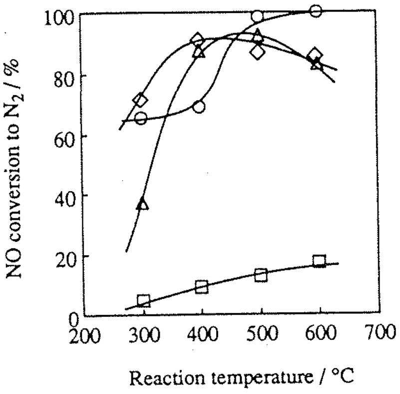

Fig.1. Variation in NO conversion on various gallium ion-exchanged zeolites as a function of reaction temperature.
Catalysts:
◇, Ga(79)/H-ZSM-5; △, Ga(106)/H-mordenite;
○, Ga(91)/H-ferrierite; □, Ga(103)/H-USY.

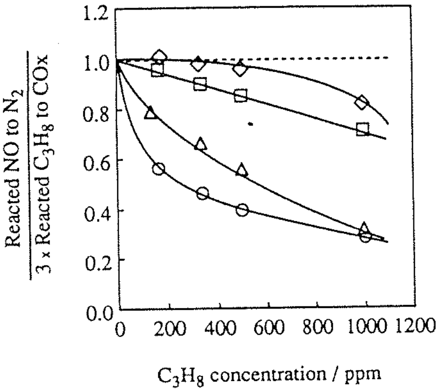

Fig.2. Ratio in conversion of NO to C in propane.
Catalysts: △, Ga(79)/H-ZSM-5; ○, H-ZSM-5;
◇, Ga(91)/H-ferrierite; □, H-ferrierite.
reaction temperature, 500°C.

調製した触媒の金属担持量はICPにより求め，イオン交換率(%)として()内に記した。反応には常圧固定床流通式反応装置を用い，NO濃度1000ppm，O_2濃度10%，炭化水素濃度150－1000ppm（Heバランス）のモデルガスを用いて，全流量100cm^3/min，触媒重量0.5g，反応温度300－600°Cの条件で行った。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。なお，活性は全てN_2への転化率で評価した。

3．結果と考察

表1に種々の金属担持ZSM-5を用いたNO還元反応の結果を示した。Al, Ti-ZSM-5は反応温度300－500℃でH-ZSM-5とほぼ同程度の転化率を示した。また，Zn-ZSM-5は500℃，In-ZSM-5は300－400℃の範囲で高い転化率を示したが，その他の反応温度域での転化率は低かった。これに対して，Ga-ZSM-5は300－600℃でH-ZSM-5より高いNO転化率を示し，広い温度範囲でNOの還元反応に有効な触媒であることがわかった。

Fig.1に種々のGaイオン交換ゼオライトの活性の比較を行った結果を示した。500－600℃の範囲でferrieriteは特に高い転化率を示した。mordeniteも高温域では高い転化率を示したが，300℃では低活性であった。また，USYの活性は他のゼオライトに比べて著しく低かった。以上

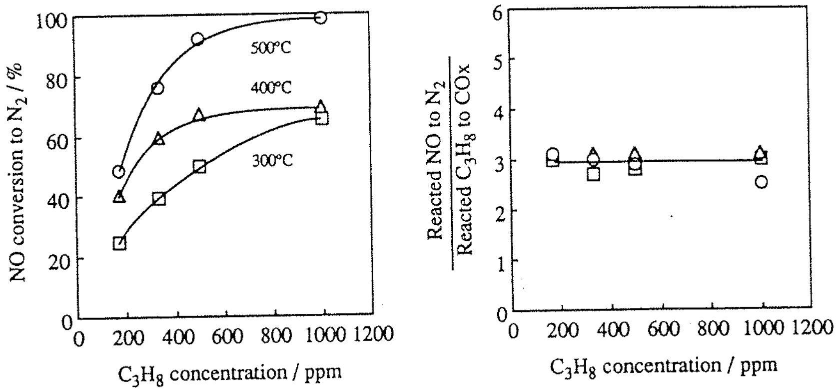

Fig.3. NO reduction on the most selective catalyst(Ga(91)/H-ferrierite) as a function of C_3H_8 concentration.
Reaction temperature, 300°C(□), 400°C(△), 500°C(○).

から，Ga-ZSM-5の他にGa-ferrieriteが広い反応温度域でNO還元反応に対して有効であることが示された。また，Gaイオン交換型とプロトン型を比較すると反応温度300－400℃ではほぼ同程度の活性を示したが，500－600℃ではGaイオン交換型の方が高いNO転化率を示した。

これらの触媒のNO転化率とCOx収率の検討の結果，C_3H_8が1分子に対してN_2へ還元されたNO分子数はほぼ3となる。これらの触媒上ではCOおよびH_2によるNOの還元反応は起こらないことから，炭化水素分子のCがNO還元に選択的に使われていると考えることもできる（Fig.2）。

そこでこれらの触媒の中で最も選択性の高いGa-ferrieriteについてNO転化率のC_3H_8濃度依存性について検討した。Fig.3に示すようにC_3H_8濃度を減少させるとNO転化率も減少したが，500℃ではC_3H_8濃度が167ppmと少量の場合でも50％程度のNO転化率が得られ，C_3H_8がNOと選択的に反応していることがわかる。このときのNO還元反応の選択性は，いずれの場合でもCOxへと転化したC_3H_8が1分子に対してN_2へ還元されたNO分子数は3であった。以上のように，Ga-ferrieriteはC_3H_8によるNO還元反応に対して極めて高い選択性を有することが示された。

そこで次に，Gaの役割を明らかにするために固体酸性の影響について検討した。Fig.4に示すように，Na-ZSM-5から調製したGa/Na-ZSM-5はNH_4-ZSM-5から調製したGa/H-ZSM-5に比べNO転化率が低い。これらの触媒のGa担持率は，Gaが3価としてイオン交換したと仮定すると約100％で差がなかったが，Na型から調製した触媒では，イオン交換サイトの約

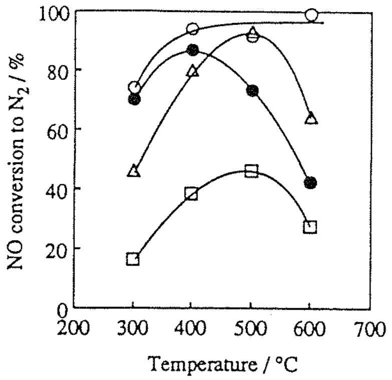

Fig.4. Selective reduction of NO on various ion-exchanged zeolites as a function of C_3H_8 concentration.
Catalysts: ○, Ga/H-ZSM-5(94); ●, H-ZSM-5; △, Ga/Na-ZSM-5(105, 37); □, Na-Ga/Na-ZSM-5(95, 69).

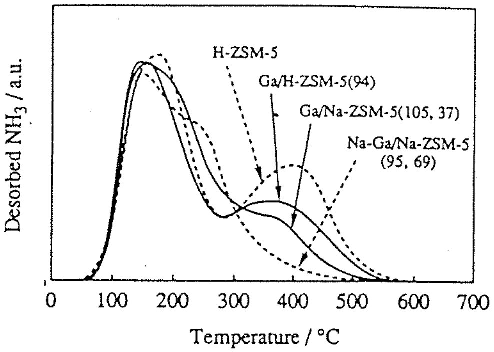

Fig.5. NH_3-TPD spectra on various cation exchanged ZSM-5.

40%にNaが残存していることが化学分析により示された。このGa/Na-ZSM-5をさらにNaでイオン交換したところ，Na量は40%から70%へと増加し，NO転化率は著しく低下した。またFig.5に示すように，各ZSM-5の高温側の酸量はH＞Ga/H＞Ga/Na＞Na-Ga/Naの順で減少している。したがって，Ga/H-ZSM-5の高いNO転化率と選択性はGaと酸点の相乗効果であると考察した。

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ガリウムイオン交換ゼオライト上での NO還元反応における炭化水素の種類の効果

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1．緒言

酸素過剰雰囲気での炭化水素によるNO還元反応に対してCu-ZSM-5等のゼオライト系触媒が有効であることが報告されている1)。我々はこれまでの研究で，Gaイオン交換ゼオライトが種々の炭化水素によるNO還元反応に対して高活性を示し，NO還元の選択性が極めて高いことを報告した2)。そこで本研究ではGaイオン交換ゼオライト上でのNO還元反応の選択性に及ぼす炭化水素の種類の効果について検討を行った。

2．実験

ZSM-5（東ソー製，SiO_2/Al_2O_3=23.3）へのGaのイオン交換は，硝酸塩を用いて行った。反応は常圧固定床流通式反応装置を用い，NO濃度1000ppm，O_2濃度10％，炭化水素濃度150-1000ppm（Heバランス）のモデルガスを用いて，全流量100cm^3/min，触媒重量0.5g，反応温度300-600℃の条件で行った。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。

3．結果と考察

Fig.1にGa/H-ZSM-5によるNO還元反応に対する炭化水素の種類の効果を示す。炭素数が小さくなるにつれて炭化水素の反応性が低下し，低温域でのNO転化率は低下したが，400℃以上の温度域では本反応条件下ではいずれも高転化率を示した。これらの反応のNO還元の選択性の変化をFig.2に示す。反応した炭化水素1分子当たりのN_2へ還元されたNOの分子数の比は$NO:C_3H_8=3:1$，$NO:C_2H_6=3:1$，$NO:CH_4=2:1$となり，炭素数が減少しても高選択的にNO還元が進行することがわかる。炭化水素の濃度の増大に伴い，C_3H_8，及びC_2H_6の場合にはNO還元の選択性は低下するが，CH_4ではほぼ一定値を示した。CH_4は反応性が非常に乏しく，燃焼反応は本反応条件下では起こらないために選択性の変化がほとんどないものと考えられる。

また，C_2H_4とC_2H_6の結果を比較した図をFig.3に示す。300℃程度の低温域ではオレフィンの方が反応性が高く，高いNO転化率を示したが，

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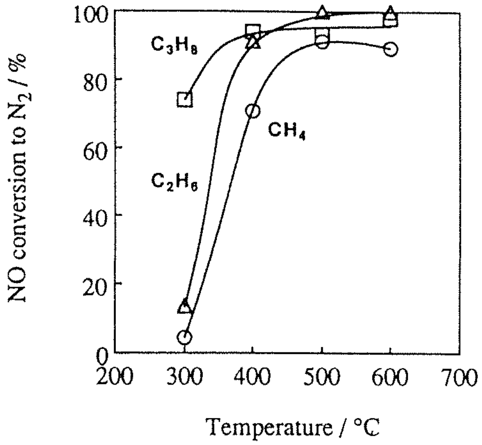

Fig.1. NO conversion on Ga/H-ZSM-5 as a function of reaction temperature. Hydorocarbons(1000ppm): ○, CH_4; △, C_2H_6; □, C_3H_8.

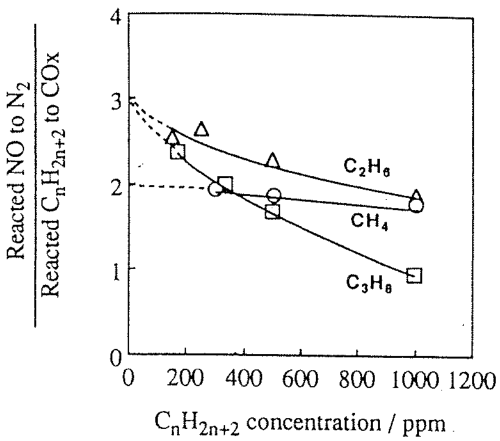

Fig.2. NO reduction on Ga/H-ZSM-5 as a function of hydorocarbon concentration. Hydorocarbons: CH_4(○), C_2H_6(△), C_3H_8(□). Reaction temperature, 500°C.

500℃では逆にC_2H_6を還元剤に用いた方が高転化率を示し，NO還元反応の選択性もC_2H_4より高い。これはGaにより引き抜かれた水素が有効にNO還元に働くためと考えられるが，現在のところ詳細は不明である。

Gaイオン交換ゼオライトは種々の炭化水素を還元剤とするNO還元反応に対して高選択性を示す。これまでのところではGaを添加したNOxセンサーが報告されていること$^{3)}$，及び種々のアルキル配位子をもつGa錯体が知られていることからNOxと炭化水素の両方がGa上に吸着し，反応が容易に起こるためと考えている。

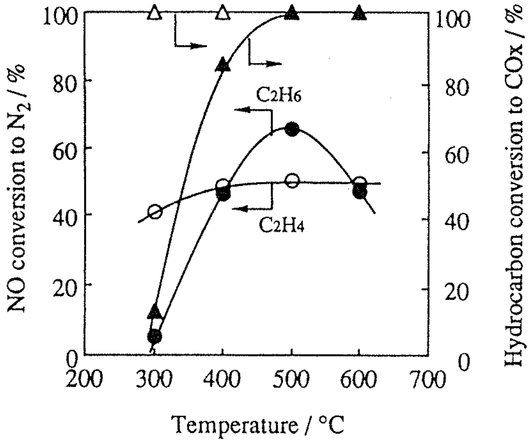

Fig.3. NO conversion and Hydorocarbon conversion on Ga/H-ZSM-5(○) as a function of reaction temperature. Hydrocarbons(250ppm): C_2H_4(solid symbol), C_2H_6(open symbol).

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Selective Catalytic Reduction of NO by Methane in Oxidizing Atmosphere

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INTRODUCTION

The reduction of nitrogen oxides(NOx) to molecular nitrogen is an important task for environmental chemistry. Iwamoto et al. [1] and Hamada et al. [2] have studied the reduction of NO by various types of hydrocarbons in the presence of oxygen on Cu-ZSM-5 and Al_2O_3 catalysts, respectively. It has been reported by these authors [3] that CH_4 is not effective for this reaction. As hydrocarbon species found in exhaust from the gas-cogeneration system should mainly be CH_4, however, it has been expected to develop a catalyst being active for the reduction by CH_4.

Meanwhile, we studied the selectivity of zeolites which were ion-exchanged with various types of cations, and found that gallium ion-exchanged ZSM-5 and ferrierite were highly active and selective for NO reduction when C_3H_8 or C_2H_4 was used as a reducing agent [4]. In the recent study, we have found that Ga-ZSM-5 shows high catalytic activity and extremely high selectivity for NO reduction by CH_4 [5], and also found that this reaction is moderately promoted even by H-form zeolites [6].

EXPERIMENTAL

Na form ZSM-5 having a molar SiO_2/Al_2O_3 ratio of 23.3 was supplied by Tosoh Corp., and it was converted NH_4-form by a conventional method. Gallium ion-exchanged ZSM-5 was prepared by ion-exchange of the NH_4-ZSM-5 at 95 °C for 24 h using an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$, being followed by calcination at 500 °C. The solution was compounded to give a concentration of gallium cations equal to one

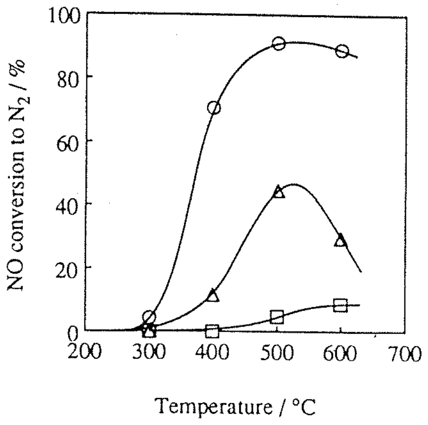

Fig.1. Reduction of NO by CH_4 on various catalysts: ○, Ga/H-ZSM-5(92); △, H-ZSM-5; □,Al_2O_3.

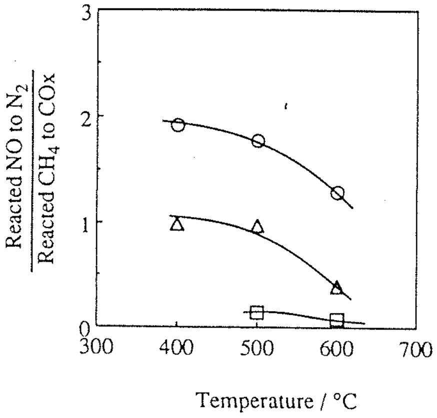

Fig.2. Selectivity expressed by the ratio of reacted NO to consumed CH_4 as a function of temperature. ○, Ga/H-ZSM-5(92); △, H-ZSM-5; □, Al_2O_3.

third of Al in ZSM-5, meaning a 100% ion-exchange level as Ga^{3+}. The value in parenthesis for the expression of catalysts represents the exchange level of gallium determined by ICP. Alumina, used as a reference catalyst, was obtained from Catalysts & Chemical Ind. Co.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. Unless otherwise mentioned, a mixture of 1000 ppm NO(or NO_2), 10% O_2, 1000 ppm CH_4 and He was fed to 0.5 g catalyst at a rate of 100 cm^3(STP)·min^{-1}, corresponding to SV equal to 7200 h^{-1}. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence NOx analyzer. The catalytic activity was evaluated by the level of NO conversion to N_2.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of catalytic activity of Ga-ZSM-5 for NO reduction by CH_4 in a comparison with H-ZSM-5 and Al_2O_3. Ga-ZSM-5 showed high catalytic activity at temperatures higher than 400 °C. H-ZSM-5 was also active for this reaction. On the other hand, the catalytic activity of Al_2O_3 was extremely low compared with those of Ga- and H-ZSM-5. Although it has been shown that Al_2O_3

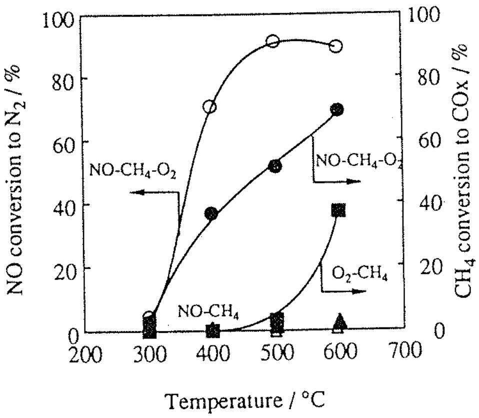

Fig.3. Catalytic activities of Ga/H-ZSM-5(92) in NO-CH_4-O_2(○, ●), NO-CH_4(△, ▲), and CH_4-O_2(■) reaction.

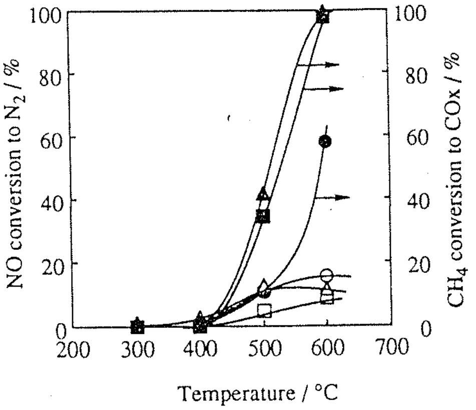

Fig.4. Catalytic activities of Ga_2O_3(○, ●), Ga/Al_2O_3(△, ▲), and Al_2O_3(□, ■), for NO conversion (open symbol) and CH_4 conversion (solid symbol).

exhibits high selectivity for NO reduction by C_3H_8 [2], combustion of CH_4 preferentially took place and the selectivity was extremely low as shown in Fig.2. H-ZSM-5 was less selective than Ga-ZSM-5.

As shown in Fig.3, NO(1000 ppm)-CH_4(1000 ppm) reaction hardly proceeded in the absence of O_2, showing that O_2 is a necessary component for NO reduction. Furthermore, CH_4(1000 ppm)-O_2(10%) reaction also did not take place below 500°C in the absence of NO. In comparison with the results on NO_2-CH_4-O_2 reaction, it is deduced that NO_2 should be concerned in the selective reduction. It has similarly been reported by Hamada and co-workers [7] that selective reduction by C_3H_8 on Al_2O_3 and H-form zeolites proceeds via NO_2 intermediate.

Figure 4 shows the catalytic activities and selectivities of Ga_2O_3 unsupported and supported on Al_2O_3, and those of Al_2O_3. The selectivity was low when Al_2O_3 was used as a support of gallium, and the selectivity of unsupported Ga_2O_3 was likewise low. From these results, it is considered that ion-exchange onto zeolite is needed to attain high selectivity of gallium. Gallium cations in zeolite should have higher degree of coordinative unsaturation than Ga_2O_3, even supported on Al_2O_3.

The high selectivity of gallium cations in ZSM-5 can be attributed to their high affinity to NOx and alkyl species. Gallium oxide is used for NOx sensor materials with high sensitivity [8], meaning the selective adsorption of these molecules. Furthermore, Ga^{3+} cation is also known to form alkyl complexes [9]. We thus deduce that extremely high selectivity of gallium ion-exchanged ZSM-5 is achieved by efficient coordination of NO_2 and hydrocarbon species at unsaturated gallium cations in zeolite.

CONCLUSION

Summarizing the present work, it is concluded as follows:

1) Gallium ion-exchanged ZSM-5 exhibits high selectivity for NO reduction by CH_4, and that CH_4 can be a selective reducing agent for NO reduction.
2) NO_2 seems to be concerned with the selective reduction.
3) The high selectivity of gallium ion-exchanged ZSM-5 is brought about by the reaction between NO_2 and CH_4 proceeding efficiently on coordinatively unsaturated gallium sites.

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2 F1 32

Fe-シリケート上でのNO選択還元反応機構の過渡応答法による検討

（早大理工）　余語克則○小野　隆・小倉　賢・菊地英一

1.我々はこれまでにFe-シリケート上でのNO選択還元反応機構について過渡応答法による検討を行い,NO-C_3H_6-O_2系で生成する中間体からN_2が生成する過程にNOとO_2の共存が不可欠であることを報告した。Fe-シリケート上ではO_2の共存下でNOがNO_2に酸化されやすいことから,本研究ではNO_2の寄与について検討を行った。

2.本研究では迅速結晶化法1)により合成したFe-シリケートを用いた。反応には組成の異なるガスを瞬時に切りかえ,導入できる装置を用いた。全流量100cm^3·min^{-1},触媒重量0.5g,反応温度300℃,反応ガスの分析にはガスクロマトグラフを用いた。

3.NO-C_3H_6-O_2系の反応(ReactionA)後,反応ガス組成を切りかえて反応(ReactionB)を行った。Fig.1に示すように,ReactionA後にNO-O_2ガスを導入したときのN_2生成速度の対数と反応時間に直線関係があることから,反応は中間体について1次であることが示される。次にReactionA後にNO_2ガスを導入したところ同様に直線関係が得られ,反応速度が増大した。NOとO_2のみを供給した場合65%がNO_2に酸化されることを考慮すると,中間体とNO_2により還元反応が進行するものと考察した。

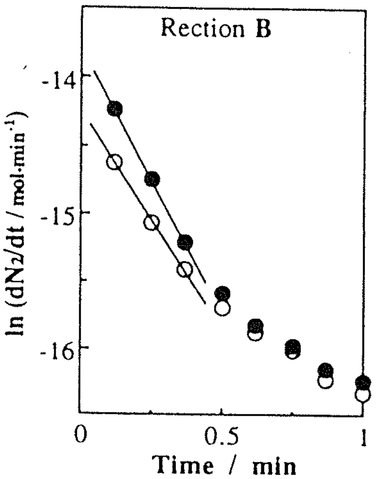

Fig. 1. Effect of NO_2 on the rate of N_2 formation in reaction **B**.
Reaction A:
NO, 2000 ppm; C_3H_6, 500 ppm; O_2, 10 %; 0.5 min
Reaction B:
○; NO, 1000 ppm; O_2, 10 %
●; NO_2, 1000 ppm

1)T.Inui et al., Proc. 8th Intern.Conger. Catal., Ⅲ-568 (1984)

2 F1 41

GaおよびInイオン交換ゼオライトを用いたメタンによるNOの選択還元反応

（早大理工）余語克則・井原道人○寺崎郁恵・菊地英一

1．<u>緒言</u>　我々はこれまでに、Ga/H-ZSM-5がメタンによるNO還元反応に対して高活性を示し、また、極めて高選択的にNO還元反応が進行することを報告した1)。本研究ではGaと同族元素であるInをイオン交換したZSM-5について、Ga/H-ZSM-5と比較，検討を行った。

2．<u>実験</u>　GaおよびIn/H-ZSM-5はNH_4-ZSM-5(SiO_2/Al_2O_3=23.3, 東ソー製)をGa(NO_3)$_3$および$InCl_3$水溶液中でイオン交換し調製した。触媒のイオン交換率[%]は（）内に記した。反応には常圧固定床流通式反応装置を用いた。NO, 1000ppm; CH_4, 1000ppm; O_2, 10%(Heバランス)の反応ガスを用い，全流量100cm^3·min^{-1}，触媒重量0.5g，反応温度300～600°Cで反応し、生成ガスの分析にはガスクロマトグラフ，化学発光式NOx分析計を用いた。

3．<u>結果</u>　Fig. 1にGa/H-ZSM-5およびIn/H-ZSM-5上でのCH_4によるNO還元反応の結果を示した。Ga/H-ZSM-5と比較して、In/H-ZSM-5は、より低温で高活性を示し、高選択的にNO還元反応が起こることが明らかとなった。また、Ga/H-ZSM-5ではCOの生成が多くみられたのに対して、In/H-ZSM-5では反応したメタンのほとんどがCO_2まで酸化された。

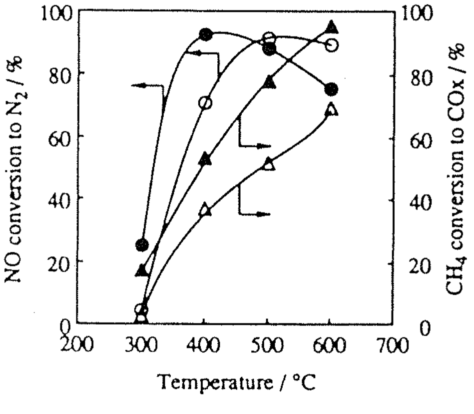

Fig. 1. NO and CH_4 conversion on Ga/H-ZSM-5 (92)(open symbol) and In/H-ZSM-5(65)(solid symbol) as a function of reaction temperature. ○, NO to N_2; Δ, CH_4 to COx.

1) K. Yogo et al., Chem. Lett., 1993, 229.

Selective Reduction of Nitric Oxide by Methane on Ga- and In-ZSM-5 Catalysts in Oxygen-rich Atmosphere

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INTRODUCTION

The reduction of nitrogen oxides(NOx) to molecular nitrogen is an important task for environmental chemistry. Iwamoto1) and Hamada2) have studied the reduction of NO with hydrocarbons in the presence of oxygen on Cu-ZSM-5 and Al_2O_3 catalysts, respectively. It has been mentioned by these authors3) that CH_4 is not effective for this reaction. As hydrocarbon species found in the exhaust from gas-cogeneration system is mainly CH_4, however, it has been expected to develop a catalyst being active for selective reduction of NO by CH_4 in oxygen-rich atmosphere.

In the recent study, we have found that Ga- and In-ZSM-5 show high catalytic activity and extremely high selectivity for this reduction, and also that various H-form zeolite catalysts are active and considerably selective. As both NO-CH_4 and O_2-CH_4 reactions hardly proceed on H- and Ga-ZSM-5, it seems that NO_2 plays an important role for this catalytic reaction.

EXPERIMENTAL

Na form ZSM-5 having a molar SiO_2/Al_2O_3 ratio of 23.3 was supplied by Tosoh Corp. Gallium ion- and indium ion-exchanged ZSM-5 catalysts were prepared by ion-exchange of NH_4-ZSM-5 at 95 °C for 24 h using aqueous solutions of $Ga(NO_3)_3 \cdot 9H_2O$ and $InCl_3$, respectively, being followed by calcination at 500 °C. The solution was compounded to give a concentration of gallium or indium cations equal to one third of Al in ZSM-5, meaning an 100% ion-exchange level as Ga^{3+} or In^{3+}. The value in parenthesis for the expression of catalysts represents the level of gallium or indium exchange determined by ICP. Alumina, as a reference catalyst, was obtained from Catalysts & Chemical Ind. Co.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO(or NO_2), 10% O_2, and 1000 ppm CH_4 was fed to 0.5 g catalyst at a rate of 100 cm^3(STP)$\cdot$min^{-1}, corresponding to SV equal to 7200 h^{-1}. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence detection of NO. The catalytic activity was evaluated by the level of NO conversion to N_2.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the catalytic activity of Ga- and In-ZSM-5 for NO reduction by CH_4 in a comparison with Al_2O_3. NO was selectively reduced to N_2 on Ga-ZSM-5 and In-ZSM-5. Hamada and co-workers2) reported that reduction of NO with CH_4 slightly proceeded on Al_2O_3 catalyst only when reaction temperature was higher than 500°C. As shown in Fig.1, the catalytic activity of Al_2O_3 was extremely low compared with those of Ga- and In-ZSM-5, and CH_4 was mainly consumed by reaction with O_2 on Al_2O_3 catalyst, resulting in low levels of NO conversion.

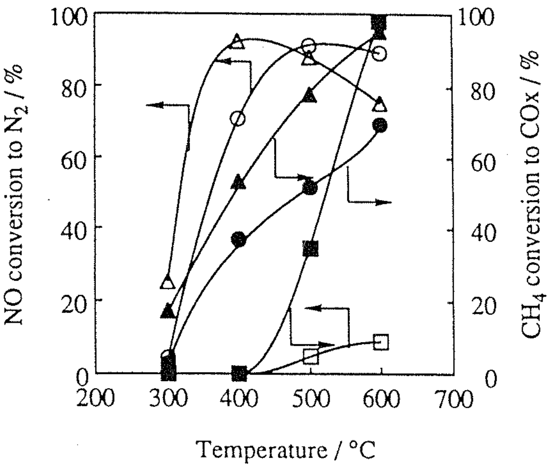

Fig.1. Variation in NO conversion(open symbol) and CH_4 conversion(solid symbol) on Ga/H-ZSM-5(○, ●), In/H-ZSM-5(△, ▲), and Al_2O_3(□, ■) as a function of reaction temperature.

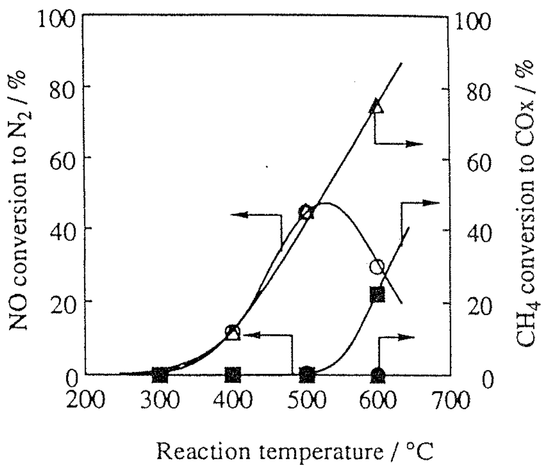

Fig.2. Variation in NO conversion and CH_4 conversion on H-ZSM-5 as a function of reaction temperature.
○, NO conversion in NO-CH_4-O_2 reaction;
△, CH_4 conversion in NO-CH_4-O_2 reaction;
●, NO conversion in NO-CH_4 reaction;
▲, CH_4 conversion in NO-CH_4 reaction;
■, CH_4 conversion in CH_4-O_2 reaction.

Figure 2 shows the catalytic activities of H-ZSM-5 for conversions of NO to N_2 and CH_4 to COx at various reaction temperatures. H-form zeolites were also active and fairly selective for this reaction. NO-CH_4 reaction hardly proceeded at these temperatures in the absence of O_2, showing that NO reduction was promoted by O_2. Furthermore, oxidation of CH_4 reaction did not proceed below 500°C in the absence of NO. Since NO reduction occurred under the conditions where CH_4-O_2 reaction did not proceeded, NO_2 should be concerned in selective reduction. This is in accordance with an observation by Hamada and co-workers$^{4)}$ that selective reduction of NO by C_3H_8 on Al_2O_3 and H-form zeolites proceeds via NO_2-C_3H_8 reaction. All the H-form zeolites and Ga-ZSM-5 used in this study were inactive for reduction of NO with CH_4 in the absence of O_2 and also for oxidation of CH_4 in the absence of NO. Thus, we deduce that the selective reduction of NO by CH_4 proceeds on these catalysts with NO_2 as an intermediate.

CONCLUSION

We found that reduction of NO proceeded on Ga-ZSM-5, In-ZSM-5, and H-ZSM-5 even when CH_4 was used as a reductant, and that CH_4 was an effective reductant for selective reduction of NO. It seems that NO_2 is an intermediate for this reaction.

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3H325

ゼオライトおよびアルミナ上でのCH_4による NO選択還元反応に対する水蒸気の影響

（早大理工）余語克則○小倉　賢・新谷紀行・杉浦行寛・菊地英一

ゼオライトおよびアルミナ上でのCH_4によるNO選択還元反応に対する水蒸気の影響について検討を行った。水蒸気存在下でNO-CH_4-O_2反応およびNO_2-CH_4-O_2反応を行った結果，In-ZSM-5は水蒸気存在下においても活性を示すこと，NO_2系ではNO系に比べて活性が向上することがわかった。したがって，In-ZSM-5ではNO酸化によるNO_2生成過程に対して水蒸気の阻害効果がより大きいものと考察した。

NO・選択還元・NO酸化・水蒸気

1.緒言

我々は，これまでにプロトン型およびGaイオン交換ゼオライトがCH_4によるNO選択還元反応に高活性を示し，高選択的に反応が進行することを報告した1)。しかし，これらの触媒は水蒸気の存在により活性が低下する。そこで本研究では，CH_4によるNO選択還元反応が次の２段階で起こると考え，それぞれの反応に対する共存水蒸気の影響について検討した。

$NO+O_2 \rightarrow NO_2$　　······ (1)［NO酸化過程］

$NO_2+CH_4 \rightarrow N_2+CO_x$　　······ (2)［NO_2-CH_4反応過程］

2.実験

実験に使用した各種金属イオン交換ZSM-5は，Na-ZSM-5（東ソー製，$SiO_2/Al_2O_3=23.8$）を硝酸アンモニウム水溶液にてアンモニウム型にした後，硝酸塩，または酢酸塩水溶液を用いてイオン交換法により調製した。また，触媒の金属担持量はICPにより求めた。反応には常圧固定床流通式反応装置を用い，反応温度300-600℃，NOx濃度1000ppm，O_2濃度10％ CH_4濃度2000ppm，H_2O濃度10％，全流量$100cm^3 \cdot min^{-1}$（Heバランス），触媒重量0.25 gの条件で行った。生成ガスの分析にはガスクロマトグラフ及び化学発光式NOx分析計を用い，NOx転化率は生成したN_2により評価した。

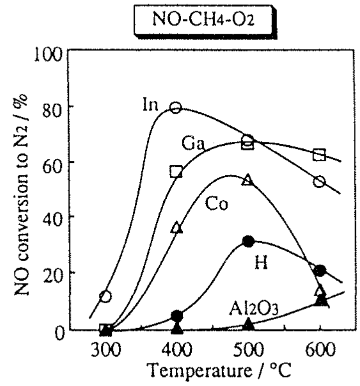

Fig.1. Selective reduction of NO by CH_4 on various ion-exchanged ZSM-5 and Al_2O_3.
NO, 1000ppm; CH_4, 2000ppm; O_2, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.25g.
○, In/H-ZSM-5; □, Ga/H-ZSM-5; △, Co/H-ZSM-5; ●, H-ZSM-5; ▲, Al_2O_3.

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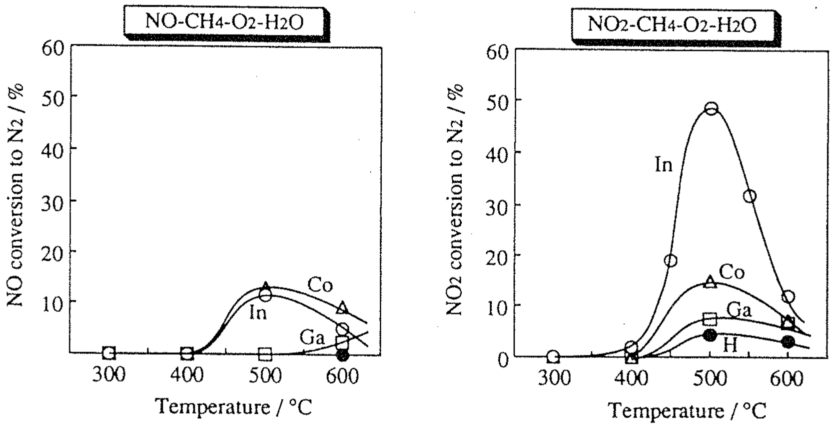

Fig.2. Reduction of NOx by CH_4 in the presence of water vaporon various ion-exchanged ZSM-5. NOx, 1000ppm; CH_4, 2000ppm; O_2, 10%; H_2O, 10%; total flow rate, $100cm^3 \cdot min^{-1}$; catalyst weight, 0.25g.

○, In/H-ZSM-5; △, Co/H-ZSM-5; □, Ga/H-ZSM-5; ●, H-ZSM-5.

3.結果と考察

Fig. 1に水蒸気非存在下でのNO-CH_4-O_2反応の結果を示す。本反応条件では，Ga-，およびIn-ZSM-5が高活性を示し，NO還元反応が高選択的に進行した。これに対しアルミナでは、同一条件下では活性が著しく低かった。

そこで，各種金属イオン交換ゼオライト上でのNOおよびNO_2還元反応に対する水蒸気の影響について検討を行った（Fig.2）。H-およびGa-ZSM-5は，NO-CH_4-O_2反応，NO_2-CH_4-O_2反応ともに水蒸気の共存により大きく阻害を受けることがわかる。また，NO酸化反応に対する水蒸気の影響を検討したところ，これらの触媒はNO酸化反応が水蒸気の共存により阻害されていることが明らかとなった。したがって，これらの触媒上では，第1段階のNO酸化過程が阻害されるばかりではなく，第2段階のNO_2-CH_4反応過程も大きく阻害されるものと考えられる。これに対し，In-およびCo-ZSM-5は，水蒸気が存在すると活性は低下するものの，水蒸気存在下でも比較的高い活性を示した。また，In-ZSM-5の活性はNO_2系ではNO系に比べ著しく大であることから，水蒸気の影響は主としてNO酸化過程に現れると考えられる。一方，水蒸気存在下でも本反応に有効であると報告されているCo-ZSM-5$^{2)}$は本反応条件下ではNO系，NO_2系ともに水蒸気の共存により活性が低下し，両系に大きな差はみられなかった。

以上のことから，In-ZSM-5は，水蒸気共存下でもNO還元反応に活性を示し，NO_2系ではかなり高い活性を示すことが明らかになった。

1）余語，井原，梅野，寺崎，渡辺，菊地，触媒，35，126 (1993).

2）Y.Li and J.N.Armor, Applied Catal. B, 2, 239 (1993).

3H326　　Gaイオン交換ゼオライト上でのNO選択還元反応機構

（早大理工）　余語克則○小野　隆・岡崎尚彦・菊地英一

Gaイオン交換ゼオライト上でのCH_4によるNO選択還元反応機構を過渡応答法により検討した。本反応は$NOx:CH_4=2:1$の化学量論で進行すること，NOの酸化によるNO_2生成が必須でありNO_2とCH_4の反応により本反応が進行すること，さらにN_2は中間体とNOの反応により生成することから，NO_2とCH_4の反応により形成された反応中間体がNOと反応してN_2を生成することを示した。

NO・選択還元・反応機構・ガリウム・ZSM-5

1．緒言

我々はこれまでに，酸素過剰雰囲気下でのCH_4によるNO還元反応に対してGaイオン交換ゼオライトが高活性，高選択性を示し，反応するNOxとCH_4の比は$NOx:CH_4=2:1$であることを見いだした[1]。またNO還元活性を示す温度域では酸素によるCH_4の燃焼反応はほとんど進行しないこと，本反応の第一ステップはNOの酸化によるNO_2の生成であることから，反応性に富むNO_2とCH_4の反応により本反応が進行することを報告している[2]。そこで本研究では，過渡応答法を用いGaイオン交換ゼオライト上でのCH_4によるNO選択還元反応機構について検討を行った。

2．実験

本研究で用いた触媒は，ZSM-5型ゼオライト（東ソー製，$SiO_2/Al_2O_3=23.3$）を既報[1]の方法に従って硝酸ガリウム水溶液中でイオン交換することにより調製し，Ga担持量(2.76wt%)はICPにより求めた。反応には組成の異なるガスを瞬時に切り換え導入できる常圧固定床流通式反応装置を用い，NO濃度1000-2000ppm，O_2濃度5-10%，CH_4濃度1000ppm（Heバランス）の反応ガスを用い，反応温度500℃で行った。また，空間速度は7200-72000h^{-1}（全流量100cm^3·min^{-1}，触媒重量0.05-0.5g）の範囲で変化させた。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。

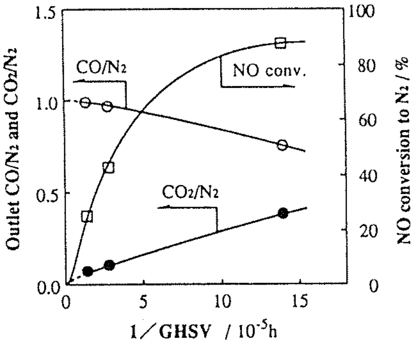

Fig. 1. NO conversion to N_2(□) and ratio of produced CO to N_2(○) and CO_2 to N_2(●) on Ga/H-ZSM-5.
NO, 1000ppm; CH_4, 1000ppm; O_2, 10%; total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.05-0.5g; reaction temperature; 500°C.

3．結果および考察

NO-CH_4-O_2反応において生成するN_2およびCO_xについて検討したところ(Fig. 1)，高GHSV

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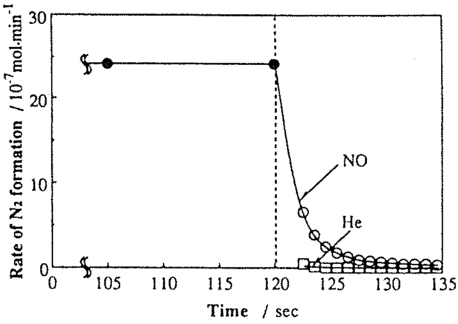

Fig. 2. Effect of reactant components on N_2 formation on Ga/H-ZSM-5.
Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5% (●);
Reaction (B): NO, 2000ppm (○);
none [balance gas (He) only] (□);
total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.2g;
reaction temperature, 500°C.

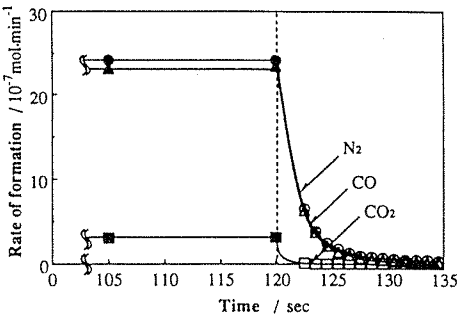

Fig. 3. Transient response of N_2, CO and CO_2 formation on Ga/H-ZSM-5 when reactant component was changed.
Reaction (A): NO, 2000ppm; CH_4, 1000ppm; O_2, 5%;
Reaction (B): NO, 2000ppm;
○,●: N_2; △,▲: CO; □,■: CO_2;
total flow rate, 100cm^3·min^{-1}; catalyst weight, 0.2g;
reaction temperature, 500°C.

条件下においてN_2とCOがほぼ1:1で生成し，CO_2は生成しないことがわかった。また，Ga/H-ZSM-5上では反応するNOxとCH_4の比がNOx:CH_4=2:1であること，NO_2とCH_4の反応により本反応が進行することから，本反応は

$$CH_4 + NO_2 + NO = N_2 + CO + 2H_2O \quad \cdots\cdots (1)$$

の化学量論で示されるものと考えられる。

そこで過渡応答法により反応機構を検討した。NO-CH_4-O_2反応が定常に達した後(2min)に反応ガスをHeのみに切り換えたところ，N_2の生成はみられなかった(Fig.2)。しかしこれに対してNOを導入したところN_2が生成し，切り換えた瞬間に外挿すると定常時のN_2生成速度にほぼ一致した。このことからN_2は反応中間体とNOの反応により生成するものと考えられる。

さらにこのときに生成するCO, CO_2について検討したところ(Fig.3)，NOを導入するとN_2の生成とともにほぼ同量のCOが生成し，CO_2はほとんど生成しなかった。

以上の結果より，現段階では次の反応機構を提唱する。NOが酸化されてNO_2を生成し，NO_2とCH_4の反応により形成された反応中間体がNOと反応してN_2を生成する。

$$NO \xrightarrow{1/2O_2} NO_2 \xrightarrow{CH_4} \underset{(中間体)}{X^*} \xrightarrow{NO} N_2 + CO$$

Scheme. 1. Reaction mechanism of NO reduction by CH_4 on Ga/H-ZSM-5.

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1) K. Yogo, M. Ihara, I. Terasaki, and E. Kikuchi, Chem. Lett., 1993, 229.
2) 余語，井原，梅野，寺崎，渡辺，菊地，触媒，35，126 (1993).

A17.

水蒸気存在下におけるGaおよびInイオン交換ゼオライト上でのCH_4によるNO選択還元反応

（早大理工）○余語克則・小野　隆・小倉　賢・寺崎郁恵・菊地英一

1. 緒言

我々はこれまでにGaおよびInイオン交換ゼオライトが酸素過剰雰囲気下でのCH_4によるNO還元反応に高活性，高選択性を示すことを見いだした$^{1)}$。また本反応はゼオライト酸点上でのNOのNO_2への酸化が第一段階であり，NO_2とCH_4がGaおよびIn上で反応しN_2を生成する機構を提唱している$^{2)}$。そこで本研究ではこれらの触媒上でのNO還元反応に及ぼす共存水蒸気の影響について検討を行った。

2. 実験

本研究で用いた触媒は，ZSM-5型ゼオライト（東ソー製）を硝酸塩水溶液中でイオン交換することにより調製し，イオン交換率はICPにより求めた。反応には常圧固定床流通式反応装置を用い，NOx濃度1000ppm，O_2濃度10%，CH_4濃度1000-2000ppm，H_2O濃度0-10%（Heバランス）の反応ガスを用い，全流量$100cm^3 \cdot min^{-1}$，触媒重量0.1-0.25gで行った。生成ガスの分析にはガスクロマトグラフおよび化学発光式NOx分析計を用いた。

3. 結果と考察

Ga-ZSM-5上でのNOおよびNO_2還元反応への共存水蒸気濃度の影響をFig. 1-aに示す。NO系，NO_2系ともに少量の水蒸気の共存により転化率が著しく低下し，水蒸気が10%存在するとほとんど還元反応が進行しないことわかった。またNOのNO_2への酸化も水蒸気の共存により大きく阻害されることから，Ga-ZSM-5上ではNOのNO_2への酸化およびNO_2とCH_4による還元反応の両反応ともに大きく阻害されていることがわかる。

同様にIn-ZSM-5についても共存水蒸気濃度の影響について検討を行ったところ(Fig. 1-b)，NO系ではGa-ZSM-5と同様に少量の水蒸気の共存でも反応が著しく阻害された。しかし，これらに比べてNO_2系では阻害の程度が比較的小さいことがわかる。このことからNO_2への酸化反応は両触媒ともに大きく阻害されるが，NO_2とCH_4の反応に対する阻害効果はIn-ZSM-5はGa-ZSM-5に比べて小さいと考えられる。

つぎに，In-ZSM-5についてイオン交換率の影響を検討した(Fig. 2)。NO_2系では水蒸気が共存しない場合，イオン交換率の増加とともに転化率が増大し，本条件下ではイオ

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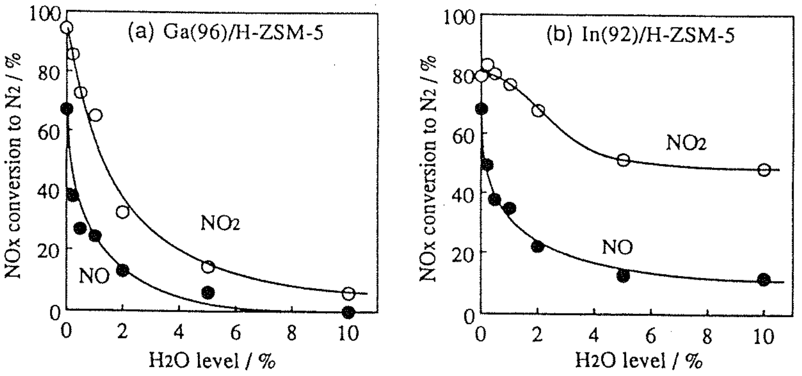

Fig. 1 Effect of water addition on NOx reduction by CH_4 on Ga/ and In/H-ZSM-5 as a function of water level.
NOx, 1000 ppm; CH_4, 2000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; reaction temperature, 500 °C; catalyst weight, 0.25 g.
● : NO-CH_4-O_2; ○ : NO_2-CH_4-O_2.

ン交換率51%で転化率がほぼ100%に達した。一方，NO系では水蒸気が共存しない場合，イオン交換率とともに転化率が増大するが過剰のイオン交換によりむしろ若干低下した。また，水蒸気の共存により，NO系，NO_2系ともに反応は大きく阻害を受けるが，NO_2系のほうがNO系よりも高い転化率を示し，イオン交換率の増加とともに転化率は増大した。

これらの結果は，NO_2への酸化反応がIn上ではなくゼオライト上で進行し，InはNO_2とCH_4の反応を促進することを示している。

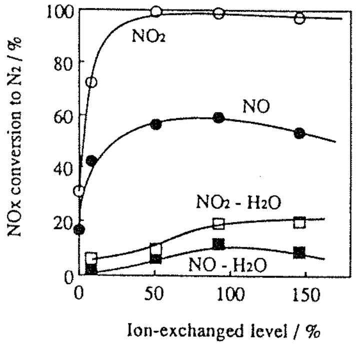

Fig. 2 Effect of water vapor on NOx reduction by CH_4 on In/H-ZSM-5 as a function of In ion-exchanged level.
● : NO, 1000 ppm;
○ : NO_2, 1000 ppm;
■ : NO, 1000 ppm, H_2O 10%;
Δ : NO_2, 1000 ppm, H_2O 10%;
CH_4, 1000 ppm; O_2, 10%;
total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.1 g;
reaction temperature, 500 °C.

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1) 余語，井原，寺崎，菊地，日本化学会第65春季年会予稿集，2F141.

2) 余語，井原，梅野，寺崎，渡辺，菊地，触媒，35，126 (1993).

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Selective Reduction of NO with Propylene on Fe-silicate Catalysts

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H-form Fe-silicate catalysts showed high activity and stability for the reduction of NO with propylene in the presence of a high concentration of oxygen. The catalytic activity of Fe-silicate was hardly affected by the presence of SO_2.

The removal of nitrogen oxides (NO_x) is a serious environmental problem. Iwamoto et al.1) reported that copper ion-exchanged ZSM-5 zeolites (Cu-ZSM-5) showed high catalytic activities for the direct decomposition of NO. And it was shown that these catalysts were also highly active for the reduction of NO with hydrocarbons in the presence of oxygen,2) although the role of copper in this reaction was not wholly explained. In practical use, the catalyst must be active in the exhaust stream including some hydrocarbons and SO_2. Recently, it was reported that H-form zeolites were also active for the reduction of NO with hydrocarbons.3) In our experimental studies, it was found that H-form metallosilicates showed catalytic activities for the reduction of NO with propylene, and Fe-silicate was the most active and stable for this reaction even in the presence of SO_2.

Metallosilicates (Fe-, B-, and Ga-silicates) were synthesized according to the rapid crystallization method reported by Inui et al.4) Thus synthesized metallosilicates were converted into the H-form by ion-exchange method using a 1 M NH_4NO_3 solution, followed by calcination at 540 °C. The X-ray diffraction patterns for the metallosilicates were similar to that of H-ZSM-5, indicating that these metallosilicates had a pentasil pore-opening structure. A Na-ZSM-5 having an atomic Si/Al ratio of 25 was supplied by Tosoh Corp.

The measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 1000 ppm propylene and balance nitrogen was fed on to 0.5 g catalyst at a rate of 92 $cm^3(STP) \cdot min^{-1}$. Effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO.

Figure 1 shows the time-on-stream variation in catalytic activities of various metallosilicates for the reduction of NO at 300 °C. As shown here, H-Fe-silicates were active

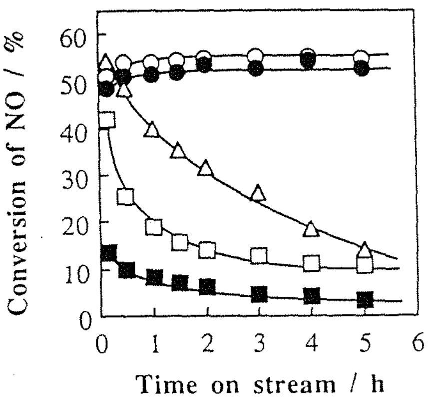

Fig. 1. Time-on-stream variation in the activities of various metallosilicates at 300 °C. Catalysts: ● , H-Fe-silicate (Si/Fe = 25); △ , H-ZSM-5 (Si/Al = 25); ○ , H-Fe-silicate (Si/Fe = 50); ■ , H-B-silicate (Si/B = 50); □ , H-Ga-silicate (Si/Ga = 50).

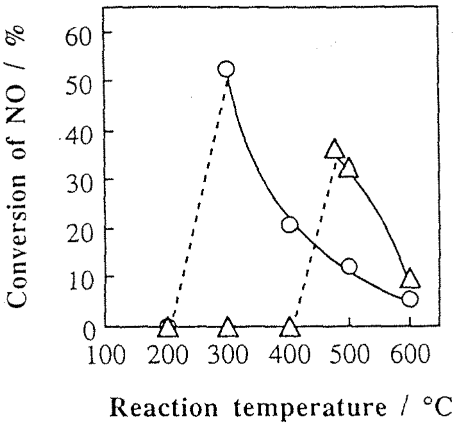

Fig. 2. Catalytic activities of H-Fe-silicate and H-ZSM-5 as a function of reaction temperature. Catalysts: ○ , H-Fe-silicate (Si/Fe = 25); △ , H-ZSM-5 (Si/Al = 25).

and stable catalysts for this reaction. The activity of either Fe-silicate initially increased slightly and reached a maximum after 1 h. The initial activities of H-ZSM-5 and Ga-silicate were comparably high, although they gradually decreased with time on stream and finally diminished under these reaction conditions.

Figure 2 compares the catalytic activities of H-Fe-silicate and H-ZSM-5 for the reduction of NO with propylene as a function of reaction temperature. The minimum temperature for the steady states activity of H-Fe-silicate was 300 °C and that for H-ZSM-5 was 475 °C. Below these temperatures, the activities of these catalysts gradually decreased and diminished finally. The steady state activities of both catalysts decreased with increasing reaction temperature. The decrease of catalytic activity at high temperatures is not attributable to catalyst deactivation, since high activities of the same level with the fresh catalysts were reproduced when the reaction temperature was decreased after the measurements of catalytic activity at these high temperatures. Probably it is due to the increased contribution of catalytic combustion of propylene at high temperatures leading to the decrease in the conversion of NO.

Figure 3 shows the effect of SO_2 on the activities of H-Fe-silicate and Cu-ZSM-5. The steady state catalytic activity of Cu-ZSM-5 was reduced to lower levels at the low temperature

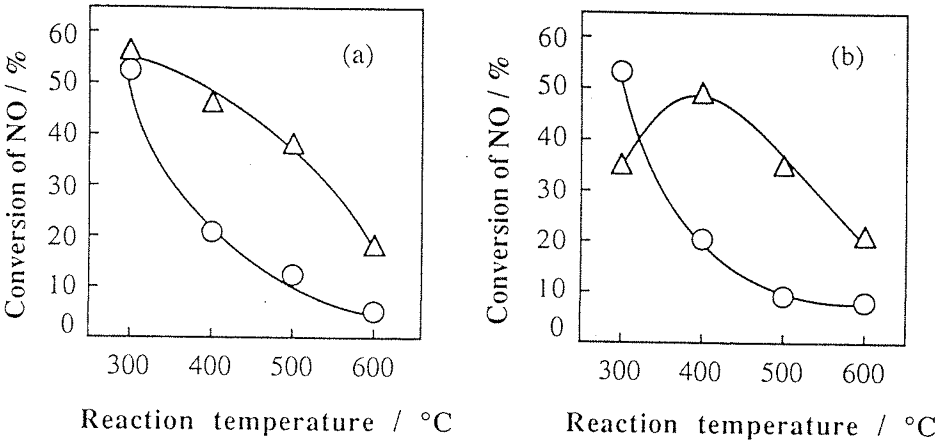

Fig. 3. The effect of SO_2 on the catalytic activities of H-Fe-silicate and Cu-ZSM-5. Reaction conditions: S.V., 12000 h^{-1}; feed concentrations, NO = 1000 ppm, O_2 = 10 %, C_3H_6 = 1000 ppm, SO_2 = 0 ppm (a), and 240 ppm (b).
Catalysts: ○ , H-Fe-silicate (Si/Fe = 25); △ , Cu-ZSM-5 (Si/Al = 25).

region by the presence of SO_2. On the contrary, SO_2 hardly gave an influence on the catalytic activity of H-Fe-silicate. Thus, it is that H-Fe-silicate is less sensitive than Cu-ZSM-5.

At reaction temperatures lower than 300 °C, the activity of H-Fe-silicate decreased with time on stream. The catalyst changed color from light brown to brown by use in reaction, and the activity of deactivated catalyst was restored by calcination in air at 500 °C for 1 h with an evolution of CO_2. At the same time, the color of the catalyst became light brown. It is, therefore, plausible that the catalyst deactivation was caused by the deposition of carbonaceous materials on the active sites.

A series of experiments were conducted at 300 °C to observe the effect of carbonaceous deposits on the activity of H-Fe-silicate. The results are shown in Fig. 4. In these runs, the catalyst bed was purged for 30 min at the same temperature after each set of reaction. After an ordinary reaction (a), the feed of propylene in the reactant stream was stopped (b), and it was found that the conversion of NO decreased gradually and completely terminated after 50 min with no more formation of CO_2. When the feed of propylene was restarted (c), the activity increased rapidly and reached the same level as that of the experiment (a). This suggests that carbonaceous deposits play an important role in this reaction. When the supply of both O_2 and propylene was stopped and only 1000 ppm NO was streamed (d), almost no reaction was observed with H-Fe-silicate. If O_2 was admitted to the reactant gas flow,

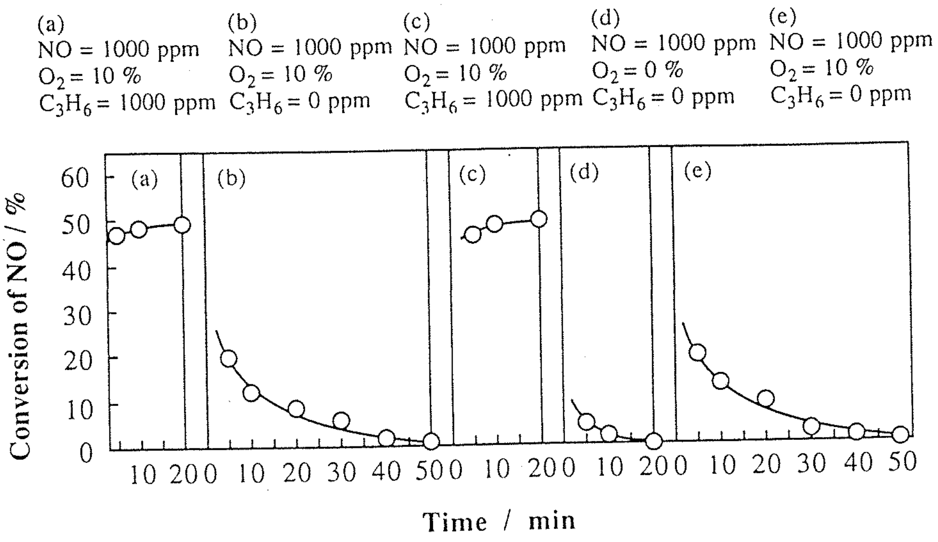

Fig. 4. Response of the conversion of NO on H-Fe-silicate when the feed composition was changed.

however, the activity manifested and it decreased with time on stream similarly to the experiment (b). Thus, oxygen is a necessary component for this reaction.

Consequently, we conclude that H-Fe-silicate is a highly active and stable catalyst for the reduction of NO with propylene, and that carbonaceous deposits on the catalyst activated by oxygen are probably concerned with this reaction.

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