粘土層間化合物を触媒とするデュレンの形状選択的合成

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研究代表者　菊　地　英　一

（早稲田大学理工学部教授）

研究組織

研究代表者：菊地英一　（早稲田大学　理工学部　　教授）
研究分担者：森田義郎　（早稲田大学　理工学部　　教授）

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in the Reaction of 1,2,4-Trimethylbenzene
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Ｐｄの担持によるアルミニウムーモンモリロナイト触媒の酸性質の変化
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Catalytic Properties of Smectite Clays Pillared by Alumina
　　　The 1st Asia Pacific Conference on Catalysis　　１９８７年１２月
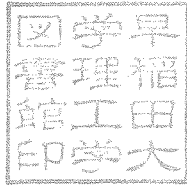
研究成果

DISPROPORTIONATION OF 1,2,4-TRIMETHYLBENZENE OVER MONTMORILLONITE PILLARED BY ALUMINIUM OXIDE

E. KIKUCHI, T. MATSUDA, H. FUJIKI and Y. MORITA

Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo, Japan.

ABSTRACT

   Disproportionation of 1,2,4-trimethylbenzene was investigated in a flow system at 200°C, using montmorillonite intercalated by aluminium chlorohydroxyl complex (Al-mont) as a catalyst. Calcination of the Al-mont at 400°C gave an interlayer spacing of 8.5 A. The Al-mont catalyst was selective for disproportionation to yield 1,2,4, 5-tetramethylbenzene (durene) and xylenes. o-Xylene was produced far more abundantly than expected from thermodynamical equilibrium. A mechanistic consideration suggested that the preferential formation of 1,2,4,5-tetramethylbenzene and o-xylene was a result of restricted transition state selectivity.
   The catalytic activity decreased with time on stream owing to coke deposition. The catalyst deactivation was, however, prevented by supporting a small amount of Pd on the catalyst and using H_2 as a carrier gas, probably as a result of hydrogen spill-over.

INTRODUCTION

   Shape-selectivity has been an important and valid concept in heterogeneous catalysis since the discovery of methanol to gasoline (MTG) conversion by Mobil Oil Co. The most popular shape-selective catalyst is zeolite, of which the pore size is comparable with the dimension of many simple molecules. The reactions of such molecules are often controlled in selectivity by use of zeolite catalysts.

   Clay intercalation compounds have also been given attention as the shape-selective catalyst [1-4]. The interlayer of several kinds of clays can be cross-linked by the "pillar" which controlls the interlayer spacing. The interlayer spacing can be controlled by the condition of preparation or the size of intercalating compounds.

   The purpose of this study is to investigate the application of shape-selective catalysts for disproportionation of trimethylbenzenes to tetramethylbenzenes and xylenes. Among tetramethylbenzenes, the most desirable product is the 1,2,4,5-isomer called durene which will be oxidized to pyromellitic anhydride as the raw material for a

heat-resisting polymer. As the 1,2,3,5-isomer is thermodynamically most stable among tetramethylbenzenes, the production of durene requires the development of a shape-selective catalyst.

Typical shape-selective conversions of aromatic hydrocarbons are disproportion-ation of toluene on mordenite [5,6], and isomerization of xylenes on ZSM-5 [7,8]. Bimolecular disproportionation of trimethylbenzenes seem to require larger pore volume than these zeolites. The present paper will describe the catalytic activity and selectivity for the disproportionation of 1,2,4-trimethylbenzene exhibited by mont-morillonite intercalated by aluminium chlorohydroxyl complex which will be called Al-mont for short.

EXPERIMENTAL
Preparation of catalyst
An Al-mont catalyst was prepared by the ion-exchange method: 20 g of montmoril-lonite powder was added to a 100 ml solution of aluminium chlorohydroxyl complex and stirred for 1 h at about 70°C. The product was filtered and washed several times with hot distilled water to remove excess complex. After dried at 110°C, the cata-lyst was calcined at 400°C for 4 h. The aluminium chlorohydroxyl complex was pre-pared by the reaction of aluminium chloride and aluminium powder in a solution.

Palladium was supported by an ion-exchange technique at ambient temperature using an aqueous solution of ammine complex of palladium. Palladium-containing catalysts were reduced in hydrogen at 400°C for 2 h prior to reaction.

The interlayer spacing of Al-mont catalyst used in the present work was deter-mined to be 8.5 A (0.85 nm) by means of X-ray diffraction measurements.
Procedures
The reaction was carried out in a down-flow continuous reactor with a fixed bed of catalyst. The catalyst (ca. 1 g) was packed in the reactor and the reaction temper-atuer was measured at the center of the catalyst bed. The reactant, 1,2,4-trimethyl-benzene was quantitatively supplied from a microfeeder to the reactor through a va-porizer to mix with a carrier gas in 1:1 molar ratio. Nitrogen or hydrogen was used as the carrier gas.

Reaction products were collected in an ice trap for each 10 min, and were analyzed by means of a gas chromatography using a flame ionization detector and FFAP glass capillary column with temperature-programmed heating from 80 to 170°C. n-Butanol was used as an internal standard.

RESULTS
Principally, 1,2,4-trimethylbenzene (TrMB) was converted by disproportionation, isomerization, and dealkylation. The conversion of TrMB (X), and the selectivities for disproportionation (Sdis), isomerization (Siso), and dealkylation (Sde) were de-fined respectively by the following equations:

$$X\ (\%)\ =\ 1 - \frac{(1,2,4\text{-TrMB})\text{unreacted}}{(1,2,4\text{-TrMB})\text{fed}} \times 100$$

$$S_{dis}\ (\%)\ =\ \frac{2 \times (\text{TeMB})}{X} \times 100$$

$$S_{iso}\ (\%)\ =\ \frac{(1,2,3\text{-TrMB}) + (1,3,5\text{-TrMB})}{X} \times 100$$

$$S_{de}\ (\%)\ =\ \frac{(B) + (T) + (Xy) - (\text{TeMB})}{X} \times 100$$

where (B), (T), (Xy), (TrMB), and (TeMB) referred the amounts of benzene, toluene, xylene, trimethylbenzene, and tetramethylbenzene, respectively.
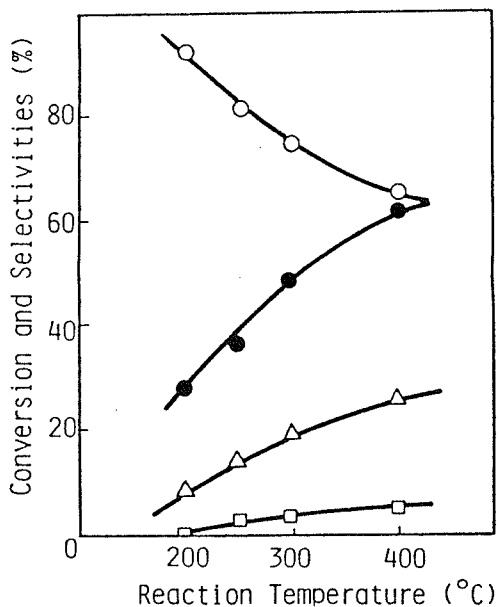

FIGURE 1 Effect of reaction temperature on 1,2,4-TrMB conversion and selectivities for individual reactions: ● , X; ○ , Sdis; △ , Siso; □ , Sde.

Figure 1 shows the effects of reaction temperature on 1,2,4-TrMB conversion and selectivities for individual reactions. These were determined from the reaction products in the initial 10 min on stream. The selectivity for disproportionation decreased with increasing temperature. In the temperature range studied, dealkylation was a minor reaction, especially at low temperature. Further reactions were carried out at 200°C.

Figure 2 shows the variation of catalytic activity and selectivities with time on stream. The conversion of 1,2,4-TrMB decreased markedly with time, while the selec-

tivities scarcely changed. As the calcination of deactivated catalyst at 400°C
mostly regenerated the catalytic activity with CO_2 formation, coke deposition should
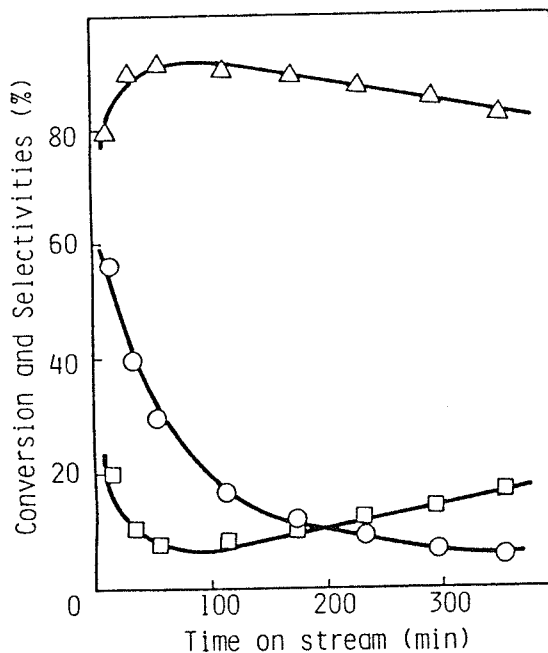be the cause for the decay of activity.

FIGURE 2   Variation with time on stream in 1,2,4-TrMB conversion and selectivities:
O, X; △ , Sdis; □ , Siso.

The catalyst deactivation was suppressed by supporting Pd on the catalyst and
using H_2 as the carrier gas. Typical results are shown in Figure 3. Although the
initial activity of the Pd-loading catalyst was low compared with that of the Al-mont
itself, the deactivation substantially disappeared. As shown in Figure 3, the load-
ing was effective only when the catalyst was used after reduction and in the stream
of H_2. When the Pd-loading catalyst was used in N_2 carrier, the catalyst deactiva-
tion was more pronounced with an evolution of H_2.

Figures 4 and 5 show the distributions of disproportionation products, tetramethyl-
benzenes (TeMB) and xylenes, as a function of 1,2,4-TrMB conversion, respectively.
Although the distribution of xylene isomers was almost unchanged, that of TeMB con-
siderably depended on the level of conversion. Results shown in Figures 4 and 5 in-
clude the data taken with the catalysts with and without Pd. The overlap of data
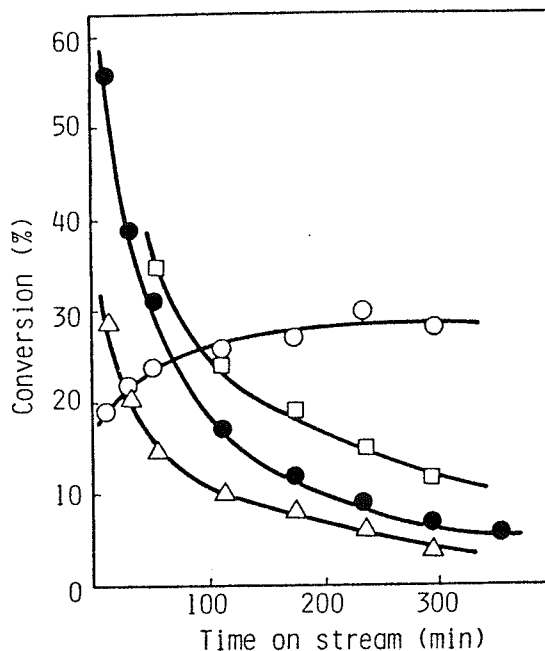showed that the addition of Pd did not alter the catalytic selectivity of Al-mont.

FIGURE 3 Effect of catalyst reduction and carrier gas on the catalytic activity of:
●, Al-mont; ○, Pd/Al-mont reduced at 400°C and used in H_2 carrier; □, Pd/Al-mont
unreduced; △, Pd/Al-mont reduced at 400°C and used in N_2 carrier. Pd-loading was
0.05% by weight.

As the equilibrium composition of TeMB is roughly 52% 1,2,3,5-, 35% 1,2,4,5-, 13%
1,2,3,4-isomers, the results shown in Figure 4 mean the performance of fairly selec-
tive disproportionation to 1,2,4,5-TeMB (durene). Similarly o-xylene was produced
more abundantly than expected from thermodynamical equilibrium (ca. 20%).

Disproportionation and isomerization of 1,2,4-TrMB on the Al-mont catalyst were
found to obey the second and the first order kinetics, respectively. Typical results
are shown in Figure 6, where the fractional conversion of 1,2,4-TrMB by dispro-
portionation and isomerization are expressed by Xdis and Xiso, respectively.

DISCUSSION
The distributions of disproportionation products obtained in the present work
showed that 1,2,4,5-TeMB and o-xylene were formed in excess of thermodynamical levels
Collins et al. [9] have observed that disproportionation of m-xylene on ZSM-5 cata-
lysts gives larger amounts of 1,2,4-TrMB than equilibrium concentrations due to the
effect of shape-selective diffusion of products from zeolite pores. A similar expla-
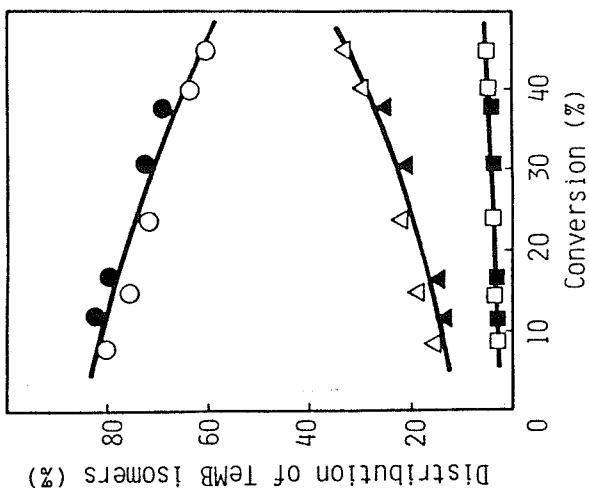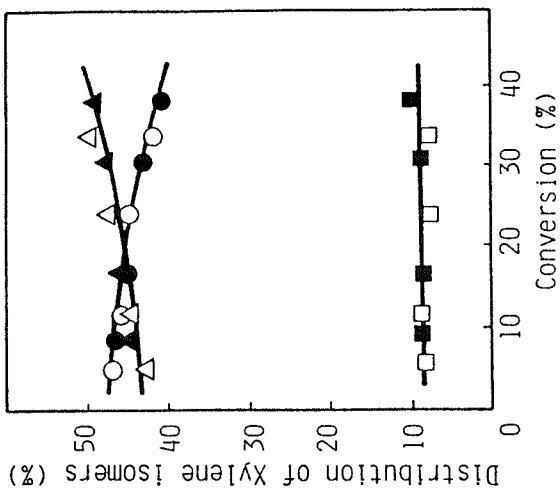
FIGURE 5 Variation in distribution of xylene isomers with the conversion of 1,2,4-TrMB on: open symbols, Pd/Al-mont; solid symbols, Al-mont ($\bigcirc$ $\bullet$, o-; $\triangle$ $\blacktriangle$, m-; $\square$ $\blacksquare$, and p-xylene).

FIGURE 4 Variation in distribution of TeMB isomers with the conversion of 1,2,4-TrMB on: open symbols, Pd/Al-mont; solid symbols, Al-mont ($\bigcirc$ $\bullet$, 1,2,4,5-; $\triangle$ $\blacktriangle$, 1,2,3,5-; $\square$ $\blacksquare$, and 1,2,3,4-TeMB).
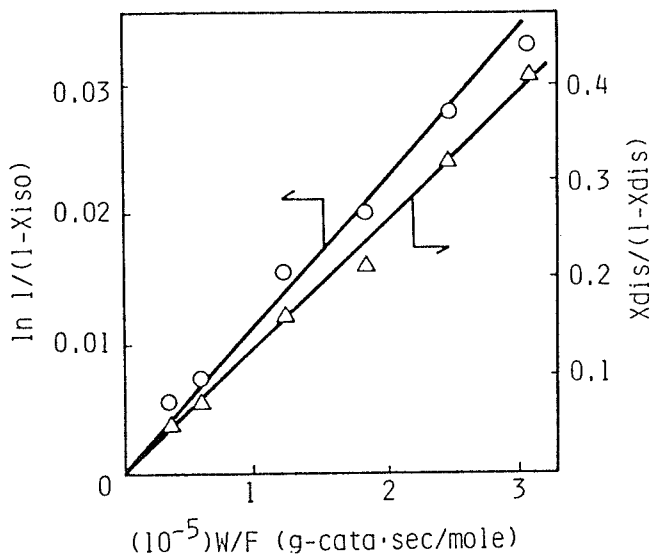
FIGURE 6 Verification of the second order kinetics of disproportionation and the first order kinetics of isomerization of 1,2,4-TrMB on Pd/Al-mont catalyst at 200'C.

nation has been given by Kaeding et al. [10] for alkylation of toluene and Young et al. [11] for isomerization of xylene on ZSM-5 catalysts. The diffusion restriction, however, cannot elucidate the results of the present work, because the smallest xylene isomer is not o-xylene but p-xylene.

Generally accepted mechanisms for acid-catalyzed disproportionation of aromatic hydrocarbons are the consecutive dealkylation-alkylation type at higher temperatures and the bimolecular transition state type at lower temperatures. The mechanism via dealkylation-alkylation was led to unselective disproportionation which is not the case of the present work. Furthermore, as only small amounts of dealkylation products were found in the present work (200°C), more plausible is the mechanism involving relatively large diphenylmethane-like species as the transition state as proposed by Csicsery [12,13] for transalkylation of alkylbenzenes on mordenite catalysts. This is consistent with the second order kinetics observed (Figure 6).

Figure 7 illustrates schematic diagrams including bimolecular transition states to yield 1,2,4,5- and 1,2,3,5-TeMB with xylene isomers. A consideration about the stability of carbonium ions prefers the formation of diphenylmethane-type intermediates to give 1,2,4,5-TeMB, since methyl substituents are electron releasing in nature. A similar conclusion is led from the viewpoint of cross-sectional diameter: transition states leading to 1,2,4,5-TeMB are smallest than those to 1,2,3,5-TeMB.

The mechanism for toluene disproportionation has been proposed by Kaeding et al. [14]. If an analogous mexhanism operates in the disproportionation of 1,2,4-TrMB,
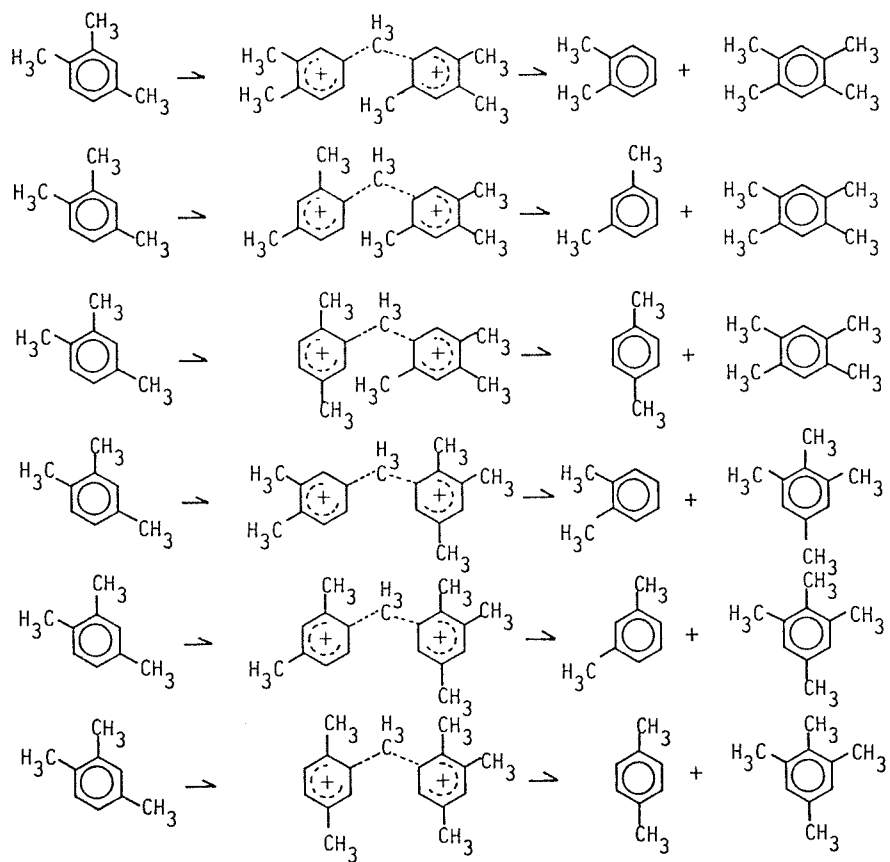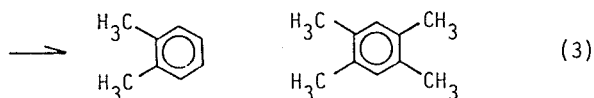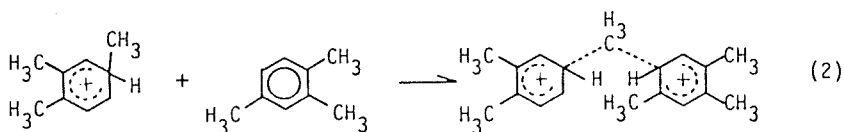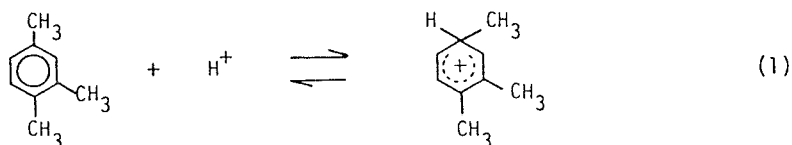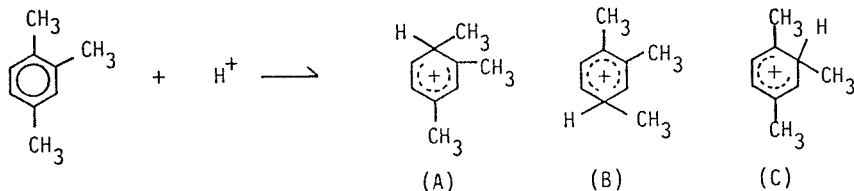
FIGURE 7 Possible bimolecular mechanism for disproportionation of 1,2,4-TrMB.

the formation of the transition state leading to 1,2,4,5-TeMB and o-xylene is written as follows:

$$ (1) $$

$$ (2) $$

$$ (3) $$

Three carbonium ions are possible as the products of protonation to 1,2,4-TrMB:

(A)　　　(B)　　　(C)

The carbonium ions (A), (B), and (C) will lead to 1,2,4,5-TeMB with m-, o-, and p-xylenes, respectively. An investigation on resonating structures of these carbonium ions indicates that the most stable one is form (A) rather than form (B). Thus, it is deduced that the formation of the transition state is not controlled by the stability of carbonium ions. It seems reasonable to account for the preferential formation of 1,2,4,5-TeMB and o-xylene by space restriction caused by pillared interlayers.

The mechanism of catalyst deactivation or coke deposition is not certain at present. Karge et al. [15] have reported relatively fast deactivation of mordenite during disproportionation of ethylbenzene at higher temperatures above 200°C. Their explanation for the deactivation based on the dealkylation-alkylation mechanism operating at high temperatures to give olefine intermediates which caused coke deposition. As dealkylation was a minor reaction in the present case, the catalyst deactivation might be caused differently.

Catalysts containing small amounts of Pd exhibited no deactivation when used in a presence of H_2 carrier, while they showed more accelerated deactivation in N_2 carrier

with an evolution of detectable amounts of H_2. Thus, dehydrogenative condensation of aromatic hydrocarbons is a possible reaction to cause the catalyst deactivation. As the catalytic selectivity was not altered by the addition of Pd, it is improbable that Pd sites participated in the catalytic reaction. They seem to act as the port of hydrogen spillover and reverse-spillover.

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EFFECT OF HIGH-TEMPERATURE TREATMENT ON THE ACTIVITY OF MONTMORILLONITE PILLARED BY
ALUMINA IN THE CONVERSION OF 1,2,4-TRIMETHYLBENZENE

T. MATSUDA, M. ASANUMA AND E. KIKUCHI
Department of Applied Chemistry, School of Science and Engineering, Waseda
University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 160, Japan

ABSTRACT
    Activity of montmorillonite pillared by alumina in the conversion of 1,2,4-tri-
methylbenzene was investigated in relation to its acidic property. Crystallo-
graphically the pillared montmorillonite used in this study possessed thermal
stability up to 650°C, while the catalytic activity remarkably decreased with
increasing pretreatment temperature. NH_3-TPD and IR studies showed that a
high-temperature treatment caused the reduction of strong acid sites and the
conversion of Brönsted acidic sites to Lewis sites, which were responsible for the
decrease in catalytic activity. Disproportionation of 1,2,4-trimethylbenzene on the
pillared montmorillonite catalyst gives a high initial selectivity for 1,2,4,5-
tetramethylbenzene compared with the thermodynamically attainable level, although it
decreases with increasing conversion level, due to isomerization of 1,2,4,5-isomer.
However, the isomerization was remarkably suppressed when the catalyst was treated
above 550°C and consequently a high 1,2,4,5-isomer selectivity was attained even at
high conversion levels. These results were explained by the reduced contribution of
Brönsted acidity.

INTRODUCTION
    Several recent reports have described the preparation of a new class of catalysts
by intercalating clay minerals of smectite type with polycationic complexes. Several
different pillaring materials have been investigated, including Al [1-2], Zr [3-4],
Cr [5] and Ti [6]. Dehydroxylation of the intercalated product by thermal treatment
leads to the formation of a highly porous material, called pillared clay. The
interlayer distance, surface area and thermal stability of the pillared clay are
dependent on the intercalating material and method of preparation. Pillared clays
possess acid sites and are essentially characterized by two dimensional pore systems
having openings in the range 0.5 to 1.5 nm. The advantage of using pillared clays
instead of Y type zeolite for the cracking of bulky molecules has been reported by
Shabtai et al. [7].
    Our previous works [8-9] have shown that a montmorillonite pillared by alumina
having a layer distance of 0.8 nm is active and selective for disproportionation of
1,2,4-trimethylbenzene(TrMB) to yield 1,2,4,5-tetramethylbenzene(TeMB). Tichit et al.
[10] and Occelli et al. [11] have pointed out that a montmorillonite pillared by

alumina is thermally stable up to 500°C and its acidic property changes by a high-temperature treatment. The purpose of this paper is to describe the effect of a high-temperature treatment on the catalytic activity of a montmorillonite pillared by alumina for the conversion of 1,2,4-TrMB.

EXPERIMENTAL

Preparation of catalyst

The clay used in this study was a sodium-type montmorillonite obtained from Kunimine Industry Co., designated as Kunipia F, of which the cation exchange capacity was 119 meq/100 g. The method of intercalation of montmorillonite with Al_{13}-complex (aluminium chlorohydroxyl complex) was previously described in detail [12]. The intercalated montmorillonite was treated at a temperature in the range of 300 to 650°C for 4 hr in a stream of air. The treated product is abbreviated to Al-mont.

Measurements of layer distance and surface area

Al-mont was characterized by the layer distance and surface area. The layer distance was measured by X-ray diffraction from (001) planes, and the surface area was determined from a nitrogen adsorption isotherm using a Langmuir equation.

Apparatus and procedures

Reactions were carried out at atmospheric pressure in a continuous flow system with a fixed bed of catalyst. The catalyst was packed in the reactor and was treated again for 1 hr prior to reaction which was carried out at 200°C. 1,2,4-TrMB was quantitatively supplied from a microfeeder to the reactor through a vaporizer using N_2 as a carrier gas. The partial pressures of 1,2,4-TrMB and N_2 were 0.1 and 0.9 atm, respectively.

Liquid products were collected in an ice trap every 10 min and were analyzed by means of gas chromatography using a flame ionization detector and a FFAP glass capilary separation column with temperature-programmed heating from 60 to 170°C. n-Octane was used as the internal standard.

Temperature-programmed desorption (TPD) measurements

In each TPD experiment, a sample weighing 0.5 g was placed in the cell, which was pretreated in vacuo at a desired temperature (300-550°C) for 1 hr and then cooled to 100°C. NH_3 of 100 Torr was adsorbed at 100°C for 30 min and evacuated for 30 min. This sample was kept in a stream of He (60 cc/min, 100 Torr) for 60 min to attain the steady flow, followed by heating at a rate of 10°C/min. A thermal conductivity detector was used to monitor desorbed NH_3. Since H_2O was desorbed simultaneously with NH_3 in the temperature range higher than the pretreatment temperature, the NH_3-TPD spectrum was obtained by point-by-point subtraction of the H_2O desorption spectrum obtained with the sample which had not adsorbed NH_3.

Infrared spectroscopy

IR spectrum was recorded with IRA-2 diffraction-grating infrared spectrometer (Japan Spectroscopic Co., Ltd.). The sample was pressed at 500 kg/cm^2 into a self-supporting wafer (20-mm diameter, ca. 30 mg), which was mounted in a cell
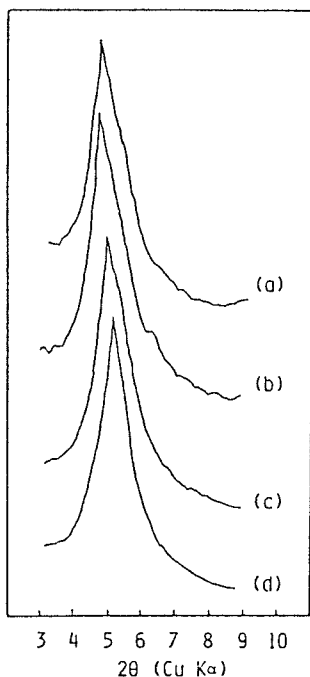
FIGURE 1 XRD patterns of Al-mont treated at 300°C(a), 400°C(b), 550°C(c) and 650°C(d)

connected to a vacuum system and then was pretreated at an elevated temperature (300-650°C) for 1 hr. Pyridine of 5 Torr was adsorbed on the sample at 200°C for 1 hr and then evacuated at a desired temperature for 1 hr. The measurement was carried out at room temperature.

RESULTS

1. Thermal stability

The observation of the effect of treatment temperature on the d(001) peak and the surface area is a convenient way to investigate the thermal stability of pillared clays. As shown in Fig. 1, treatment of Al-mont in the temperature range from 300 to 650°C hardly affected the intensity of the d(001) peak. This result means that the regularity of the two dimensional lattice generated upon intercalation is fairly well retained after treatment in this temperature range. However, the d(001) reflection shifted to a higher angle by a high-temperature treatment: the layer distance shrank by 0.1 or 0.15 nm by increasing treatment temperature from 300 to 650°C. This shrinkage may arise from dehydration of Al-mont and from further dehydroxylation of partially remained aluminium hydroxide pillars into alumina.

As shown in Table 1, the increase in treatment temperature caused a gradual decline in the surface area. It should be noted, however, that Al-mont has a large

TABLE 1

Catalytic activities of Al-mont treated at various temperatures for the conversion of 1,2,4-TrMB

Treatment temperature ($^{\circ}$C)	300	400	550	650
Surface area (m^2/g)	368	383	341	309
Layer distance (nm)	0.88	0.89	0.81	0.75
Conversion (%)	41.8	19.4	7.0	5.9
Selectivity for				
Disproportionation	79.5	90.8	96.4	96.8
Isomerization	20.5	9.2	3.6	3.2
Composition of Xylene isomers				
o-	31.9	46.2	47.5	46.9
m-	55.8	44.9	43.9	44.3
p-	12.3	8.9	8.6	8.8
Composition of TeMB isomers				
1,2,4,5-	54.7	70.7	81.5	81.0
1,2,3,5-	39.7	25.6	16.2	16.5
1,2,3,4-	5.6	3.7	2.3	2.5

Reaction condition: W/F = 4000 (g-cat.min/mol)

surface area compared with montmorillonite (30 m^2/g) even after treatment at 650°C.

2. Activity and selectivity

Principally, 1,2,4-TrMB is converted by disproportionation and isomerization. The conversion of 1,2,4-TrMB and the selectivities for disproportionation and isomerization were respectively defined by the following equations:

$$\text{Conversion (\%)} = \frac{(1,2,4\text{-TrMB})_{fed} - (1,2,4\text{-TrMB})_{unreacted}}{(1,2,4\text{-TrMB})_{fed}} \times 100$$

$$\text{Selectivity for disproportionation (\%)} = \frac{(\text{Xylene}) + (\text{TeMB})}{(1,2,4\text{-TrMB})_{reacted}} \times 100$$

$$\text{Selectivity for isomerization (\%)} = \frac{(1,3,5\text{-TrMB}) + (1,2,3\text{-TrMB})}{(1,2,4\text{-TrMB})_{reacted}} \times 100$$

where (Xylene),(TrMB) and (TeMB) referred the amounts of these compounds.

Table 1 shows the effect of a high-temperature treatment on the catalytic activity of Al-mont. Since catalyst deactivation was unavoidable, the activity and selectivity were compared using the data taken in the initial 10-20 min of run. Although H-type montmorillonite was inactive in this reaction because of a small interlayer distance (about 0.3 nm), Al-mont catalyst showed a high activity in the reaction of 1,2,4-TrMB. This can be explained by a increase in the interlayer distance. The activity of Al-mont decreased remarkably with increasing treatment temperature.
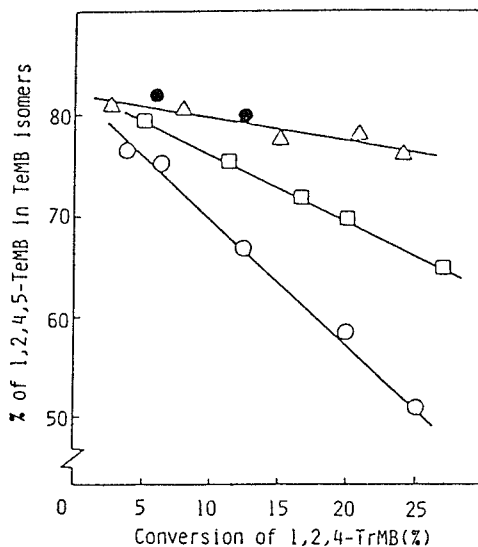
FIGURE 2   Variation in percentage of 1,2,4,5-TeMB in TeMB isomers as a function of conversion of 1,2,4-TrMB on Al-mont treated at 300°C(○), 400°C(□), 550°C(△) and 650°C(●).

However, the high-temperature treatment enhanced the selectivity for disproportionation against isomerization and finally disproportionation predominated after a treatment at 650°C.

Concurrently, the highest selectivity for 1,2,4,5-TeMB formation was attained upon the treatment above 550°C, though the activity was conspicuously low. It was pointed out in our previous work [8] that the 1,2,4,5-TeMB selectivity depended on the level of conversion. So, the 1,2,4,5-TeMB selectivity was compared at various levels of conversion. Figure 2 shows the 1,2,4,5-TeMB selectivity expressed by the fraction of 1,2,4,5-TeMB in TeMB isomers produced as a function of 1,2,4-TrMB conversion. These data were obtained by changing the contact time. When treated at 300°C, 1,2,4,5-TeMB was formed far more abundantly at low conversion levels than expected from thermodynamic equilibrium composition (35%). The increase of conversion, however, reduced the formation of 1,2,4,5-isomer and enhanced that of 1,2,3,5-isomer. The latter isomer is thermodynamically the more favorable product. Al-mont exhibited a high activity for isomerization of TeMB. When treated at temperatures higher than 550°C, however, the composition of TeMB isomers, in other words the fraction of 1,2,4,5-isomer, hardly changed regardless of the level of conversion, showing a reduction in isomerization activity. Consequently, a high 1,2,4,5-TeMB selectivity was maintained even at high levels of 1,2,4-TrMB conversion.

As shown in Table 1, disproportionation of 1,2,4-TrMB on Al-mont yielded o-xylene
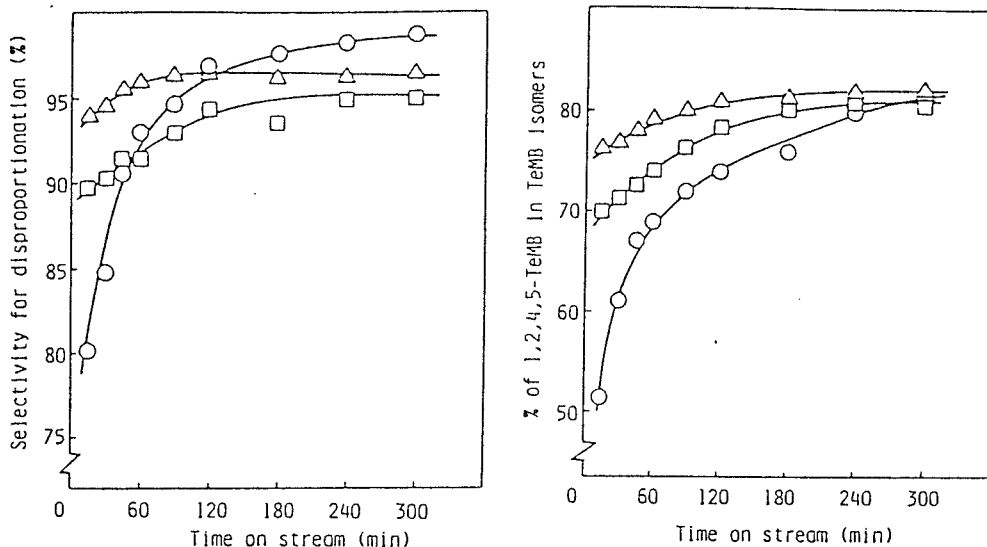
FIGURE 3 Variation in selectivity for disproportionation over Al-mont treated at
300°C(○), 400°C(□), and 550°C(△) with time on stream.
FIGURE 4 Variation in percentage of 1,2,4,5-TeMB in TeMB isomers over Al-mont
treated at 300°C(○), 400°C(□), and 550°C(△) with time on stream.

in excess of thermodynamical composition (ca. 20%). The fraction of o-xylene in
xylene isomers was also dependent on the levels of 1,2,4-TrMB conversion and on the
treatment temperature of Al-mont. At a low conversion level, however, Al-mont showed
the same fraction of o-xylene (ca. 48%), irrespectively of the treatment temperature.

3. Time on stream changes in activity and selectivity

The catalytic activity markedly decreased with time on stream. The decay of the
activity was independent of the treatment temperature. Since calcination of the
deactivated catalyst to regenerate the activity led the evolution of CO_2, coke
formation should be the main cause of catalyst deactivation.

The deactivation was accompanied by the change in selectivity for disproportiona-
tion against isomerization. Figure 3 shows the selectivity for disproportionation as
a function of time on stream. The selectivity for disproportionation increased
significantly with time on stream over the catalyst treated at 300°C, while there was
little change in the disproportionation selectivity if treated at 550°C. A similar
trend was observed on the fraction of 1,2,4,5-TeMB in TeMB isomers, as shown in
Fig. 4.

4. Acidity

Figure 5 shows the NH_3-TPD spectra observed for Al-mont treated at various
temperatures. The NH_3-TPD spectrum of Al-mont treated at 300°C consisted of two peak
maxima; the low and high temperature maxima appeared at about 210 and 350°C,
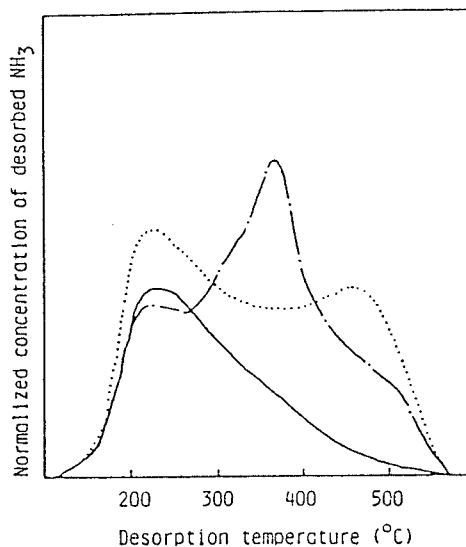
FIGURE 5 NH_3-TPD spectra of Al-mont treated at 300°C(—·—), 400°C(······), 550°C(——).

respectively. When treated at 400°C, the peak maxima appeared at about 210 and 460°C with a small decrease in the amount of NH_3 desorbed in the high temperature region. However, treatment at 550°C led to a remarkable decrease in NH_3 desorption above 400°C. These results indicate that the amount of strong acid sites is sensitive to the treatment temperature.

Figure 6 shows the infrared spectra of pyridine adsorbed on Al-mont treated at various temperatures. Al-mont treated at 300°C gave an absorption band appearing at 1450 cm^{-1} due to pyridine chemisorbed on Lewis acid sites and a band at 1540 cm^{-1} due to pyridine on Brönsted sites. The intensity of absorption at 1540 cm^{-1} decreased more than that at 1450 cm^{-1} on high-temperature treatment, although the intensities of both of these two bands decreased. Finally, Al-mont exhibited Lewis acidity alone when treated at 550°C and above.

In order to evaluate the strength of acid sites, infrared spectra were measured after adsorbed pyridine was evacuated at four different temperatures. Figure 7 shows the spectra for Al-mont treated at 400°C. Upon heating in vacuo, pyridine chemisorbed on Brönsted acid sites was rapidly removed by evacuation above 300°C and only pyridine chemisorbed on Lewis acid sites was detected. Similar spectra were obtained with Al-mont treated at other temperatures: however, Brönsted acidity disappeared by evacuating at 200°C when Al-mont was treated above 550°C, as shown in Fig. 6. It is concluded from these results that the nature of strong acid sites on Al-mont is mostly Lewis acidic.
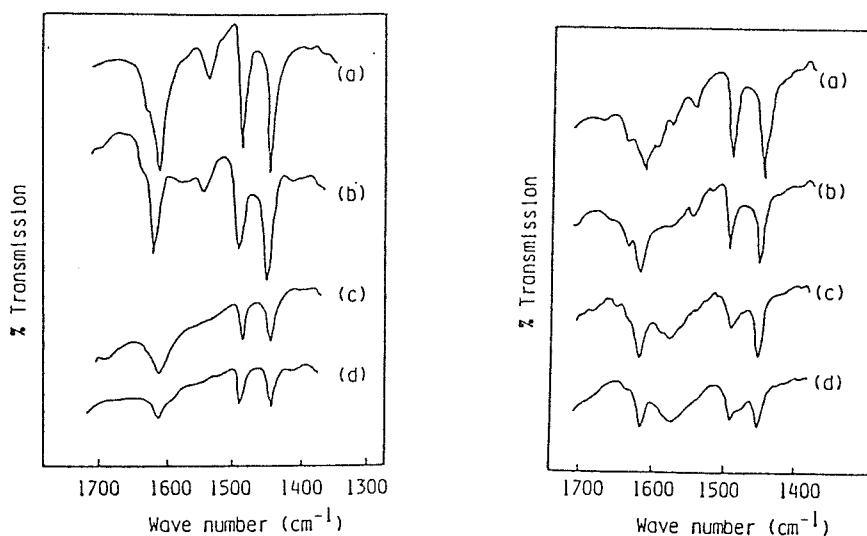
FIGURE 6   Infrared spectra of pyridine-loaded Al-mont treated at 300°C(a), 400°C(b), 550°C(c), and 650°C(d). Pyridine-loaded sample was evacuated at 200°C in vacuo prior to the measurment.

FIGURE 7   Infrared spectra of pyridine loaded Al-mont evacuated at 100°C(a), 200°C(b), 300°C(c) and 400°C(d). Al-mont treated at 400°C was used.

DISCUSSION

The two dimensional pore system of Al-mont generated by intercalation was fairly well retained after a treatment in the temperature range from 300 to 650°C. However, the catalytic activity remarkably decreased with increasing treatment temperature. The results shown in Fig. 6 indicate, in agreement with the results of Tichit et al. [10] and Occelli et al. [11], that the high temperature treatment changes the acidic nature of Al-mont from Brönsted to Lewis type. The variation in the activity caused by the high-temperature treatment is, therefore, attributed to the decrease in Brönsted acidity.

Upon treatment above 550°C, the high-temperature desorption of NH_3 almost completely disappeared, as shown in Fig. 5, and infrared studies showed that the surface acidity of Al-mont evacuated above 300°C was mostly of the Lewis type. Consequently, it is implied that the high-temperature treatment brings about a decrease in strong Lewis acidity as well as the change in acidic nature from Brönsted to Lewis type. Infrared results shown in Fig. 6 support this consideration: the intensity of the absorption band due to Lewis acidity is also lowered when Al-mont is treated at higher temperatures. Plee et al. [13] have suggested that water molecules hydrating the pillars are the potential source of Brönsted acidity on pillared clays. Moreover, Take et al. [14] have proposed that Lewis acidity is mainly due to exposed Al cations on pillars. This idea is based on the experimental observation that the absorption band due to pyridine chemisorbed on Lewis acid sites of Al-mont appears at

a similar position to that on Lewis acid sites of silica-alumina. Thus, although the reason for the decrease in Lewis acidity is not obvious at present, the change in chemical structure of pillars from ionic hydroxide to oxide form seems to rationalize the decrease in Lewis acidity.

1,2,4-TrMB is converted via disproportionation and isomerization. Different kinds of sites have been proposed for disproportionation and isomerization [15.16]. Only Brönsted acid sites are responsible for isomerization, whereas both Brønsted and Lewis acid sites can catalyze disproportionation: Brönsted acid sites, however, are far more active than Lewis acid sites. As shown in Table 1, 1,2,4-TrMB was converted mostly by disproportionation on every Al-mont catalysts. These results allow us to conclude that the reduction of activity due to high-temperature treatment is attributed not only to the conversion of Brönsted sites to Lewis acid sites but also to the decrease in strong Lewis acidity.

Concurrently with the decrease in the activity, the selectivity of Al-mont for disproportionation against isomerization was enhanced by the high-temperature treatment. As Lewis acid sites are considered to catalyze only disproportionation as mentioned above, the increased disproportionation selectivity caused by the high-temperature treatment seems to be attributed to the reduced contribution of Brönsted acidity.

Disproportionation of 1,2,4-TrMB on Al-mont catalysts yielded 1,2,4,5-TeMB and o-xylene in excess of thermodynamical equilibrium at low conversion due to the restricted transition state selectivity as proposed in the previous works [8-9]. Increase of conversion, however, reduced the 1,2,4,5-TeMB selectivity as a result of isomerization of 1,2,4,5-TeMB to other TeMB isomers. This kind of isomerization reaction was not observed over Al-mont treated above 550°C and consequently 1,2,4,5-TeMB was selectively formed even at high conversion levels. These results can also be understood by taking the acidic property into consideration as observed for the change in the disproportionation selectivity.

The disproportionation and 1,2,4,5-TeMB selectivities changed markedly with time on stream (Fig. 3 and 4). Since disproportionation requires a larger reaction space than isomerization, these results cannot be explained by the concept proposed by Kaeding et al. [17-18]: the deposition of carbonaceous matters enhances the shape selective property. It is possible to consider that the acidic property changes by the deposition of carbonaceous matters. As mentioned above, the Lewis acidic Al-mont catalyst exhibits high disproportionation and 1,2,4,5-TeMB selectivities. Therefore, although the change in acidity with time on stream is not measured at this moment, the disproportionation and 1,2,4,5-TeMB selectivities will increase with time on stream if Brönsted acid sites deactivate faster than Lewis acid sites by carbonaceous deposits. It can also elucidate by the concept that these selectivities change more markedly with time on stream on the catalyst treated at lower temperatures, namely on the catalyst having more Brönsted acidic sites.

CONCLUSION

The treatment of Al-mont at high-temperatures is accompanied by the reduction of strong Lewis acidity and the conversion of Brönsted acid sites to Lewis acid sites. These variations in acidic properties affect the activity and the selectivity, while catalyst deactivation hardly depends on them. Isomerization of 1,2,4,5-TeMB which is an unfavorable reaction for the selective formation of 1,2,4,5-TeMB from 1,2,4-TrMB disproportionation is suppressed when the catalyst is treated above $550^{\circ}C$. In consequence, a high 1,2,4,5-isomer selectivity is attained even at high conversion levels, while the catalytic activity decreases. These results are interpreted by taking a reduced contribution of Brönsted acidity into consideration.

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PHYSICAL AND CATALYTIC PROPERTIES OF SMECTITE CLAYS PILLARED BY ALUMINA IN THE REACTION OF 1,2,4-TRIMETHYLBENZENE

T. MATSUDA, H. NAGASHIMA and E. KIKUCHI

Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 160, JAPAN

ABSTRACT

The physical and catalytic properties of montmorillonite, saponite, and laponite pillared by alumina were compared. It was shown by XRD and nitrogen adsorption studies that pillared montmorillonite possessed microporosity due to a well-ordered face to face lamellar structure, while face to edge or edge to edge aggregation leading to the formation of macroporosity was observed with saponite and laponite. Pillared saponite had strong Bronsted acidity compared with other pillared clays. This can be explained by the presence of Si-O-Al linkages in the tetrahedral layer. However, pillared montmorillonite having less Bronsted acidity was far more active in the reaction of 1,2,4-trimethylbenzene(TrMB) than other pillared clays. It is proposed that microporosity enhances the concentration of reactant(1,2,4-TrMB) around the acid sites, resulting in a high catalytic activity. Pillared saponite showed a lower selectivity for the formation of 1,2,4,5-tetramethylbenzene than pillared montmorillonite. This can easily be understood by taking their porous structure into consideration. However, the activity of pillared saponite was stable against deactivation probably due to its macroporosity.

INTRODUCTION

Zeolite-like materials having high surface areas have been prepared by intercalation of smectite clays with inorganic hydroxyl compounds such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. Vaughan and Lussier[1] have first pointed out the selective sorption property of pillared montmorillonite using various probe hydrocarbons with molecular dimensions from 0.46 to 1.04 nm. Shape-selective catalysis by pillared clays has been reported by Shabtai et al.[2]: the rate of esterification on montmorillonite pillared by 1,4-diazabicyclo[2,2,2]octane significantly decreases when bulky alcohols or carboxylic acids are used as reactants. It was shown in our previous papers[3-5] that montmorillonite pillared by alumina (Al-mont) with an interlayer distance of 0.90 nm showed shape selective property for the formation of 1,2,4,5-tetramethylbenzene(1,2,4,5-TeMB) through disproportionation of 1,2,4-trimethylbenzene(1,2,4-TrMB).

The interlayer distance, surface area, and thermal stability of pillared clays are influenced by the method of preparation or the kind of intercalating species[6-8]. Recently, it has been pointed out[9-11] that physical properties of pillared clays vary prominently with the nature of smectite clays. The purpose of this paper is to investigate the interrelationship between the structural and physical properties of

alumina-intercalated smectite clays and the their catalytic properties for the reaction of 1,2,4-TrMB.

EXPERIMENTAL
Preparation of pillared clays

    The clays used in this study were sodium-type natural montmorillonite, synthetic saponite and laponite obtained from Kunimine Industry Co. Their cation exchange capacities were 119, 80, and 80 meq./100g, respectively. A $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ cation was prepared from a hydrolyzed $AlCl_3$ solution by the addition of a NaOH solution to yield the OH/Al molar ratio of 2.5. Since the addition of a NaOH solution to a $AlCl_3$ solution yielded a precipitate, the hydrolyzed $AlCl_3$ solution was aged at $50^\circ C$ for about 12 hr until the precipitate vanished. 24 g of clay was slowly added to this solution. The aluminum was present in large excess, typically 7 mmole Al/meq. clay, to ensure the complete saturation of exchangeable sites. The reaction mixture was allowed to age for 12 hr at $50^\circ C$, and then was filtered and washed several times to remove excess complexes and chlorine ions. The intercalated product was dried at $110^\circ C$ overnight and calcined at $400^\circ C$ for 4 hr. Alumina pillared montmorillonite, saponite, and laponite will be abbreviate Al-mont, Al-sapo, and Al-lapo, respectively. Al^{3+}-exchanged clays were prepared by an ion exchange at $50^\circ C$ for 12 hr using a 0.1 N $AlCl_3$ solution. The subsequent procedures were the same as those described above.

Characterization of pillared clays

    A conventional high vacuum static system was used to measure the adsorption of N_2 at $-196^\circ C$. Once loaded into the system the pillared clay sample was pretreated in vacuo for 1 hr at $200^\circ C$. Surface area was determined from Langmuir equation. The content of intercalated or exchanged Al was measured with fluorescence X-ray spectrometer. The X-ray diffraction analysis was carried out using a Rigaku computer controlled diffractmeter with Cu radiation.

    The acidic properties of pillared clays were determined by means of the NH_3-TPD and the infrared spectroscopy using pyridine as a probe molecule. In each TPD experiment, a sample weighing 0.5 g was placed in the cell, which was pretreated in vacuo at $400^\circ C$ for 1 hr and then cooled to $100^\circ C$. NH_3 of 100 Torr was adsorbed at $100^\circ C$ for 30 min and evacuated for 30 min. This sample was kept in a stream of He (60 cc/min, 100 Torr) for 60 min to attain the steady flow, followed by heating at a rate of $10^\circ C$/min. A thermal conductivity detector was used to monitor desorbed NH_3. Since H_2O was desorbed simultaneously with NH_3 above $400^\circ C$, the NH_3-TPD spectrum was obtained by point-by-point subtraction of the H_2O desorption spectrum obtained with the sample which had not adsorbed NH_3 molecule. Infrared spectra were obtained with a IR-810 infrared spectrometer(Japan Spectroscopic Co. Ltd.). A self-supporting wafer of 20 mm diameter was prepared by pressing ca.30 mg of a pillared clay. Prior to pyridine adsorption, the wafer was mounted in a cell and was activated in vacuo at $400^\circ C$ for 1 hr. The pyridine adsorbed sample was then heated in vacuo to a desired
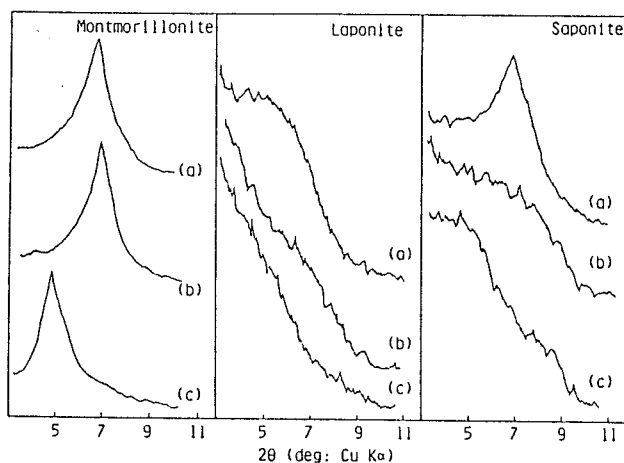
FIGURE 1 XRD patterns of clay compounds. (a), Na$^+$; (b), Al^{3+}; (c), pillared.

temperature range of 200-400°C for a period of 1 hr and the spectrum was obtained at room temperature.

Apparatus and procedures

Reactions were carried out at atmospheric pressure in a continuous flow system with a fixed bed of catalyst. The catalyst was packed in the reactor and was treated at 400°C for 1 hr in a stream of N$_2$ to remove water prior to reaction which was carried out at 200°C. 1,2,4-TrMB was quantitatively supplied from a microfeeder to the reactor through a vaporizer using N$_2$ as a carrier gas. The partial pressures of 1,2,4-TrMB and N$_2$ were 0.1 and 0.9 atm, respectively.

Liquid products were collected in an ice trap every 10 min and were analyzed by means of a gas chromatography using a flame ionization detector and a FFAP glass capilary separation column with temperature-programmed heating from 60 to 170°C.

RESULTS AND DISCUSSION

XRD and adsorption studies

The construction of pillared structure depended on the kind of smectite clays. This can be judged from the intensity of d(001) reflection. As shown in Fig. 1, the d(001) reflection line of montmorillonite was shifted to a lower angle by the intercalation, showing an increase in the interlayer distance. The d(001) reflection of Na$^+$-exchanged saponite was observed, while it disappeared when intercalated by Al$_{13}$-complex cations or exchanged by Al^{3+} ions. The XRD pattern of laponite showed no discrete d(001) reflection, regardless of exchanged cations.

Table 1 summarizes the surface area and the intercalated amount of Al. There was little difference in the content of intercalated Al between these three pillared clays, although their XRD patterns were markedly different. These results seem to imply that the intercalation of saponite and laponite by Al$_{13}$-complex cations

Table 1 Surface areas and Al contents of the various clay compounds

Clay	Na+ exchanged Surface area (m²/g)	Al³⁺ exchanged		Pillared	
		Surface area (m²/g)	Al content (mmol/g)	Surface area (m²/g)	Al content (mmol/g)
Montmorillonite	30	28	0.74	452	3.30
Saponite	178	201	0.67	252	2.20
Laponite	392	390	0.78	398	2.45

proceeds similarly to that of montmorillonite. Pinnavaia and co-workers[9] have recently demonstrated that the flocculation of smectite clays by Al_{13}-complex cations can lead to delaminated aggregates when the layer lateral dimensions are smaller than 0.5 μm or the layer morphology is lath-like. Under these conditions, edge to face or edge to edge layer aggregation competes favorably with face to face aggregation. The well ordered face to face aggregation preferentially occurs when the layer size is large and pancake-like in morphology. It has also been pointed out by these authors[9] that the manner of aggregation is dependent on the nature of clay: laponite and saponite have a high tendency to give edge to edge or edge to face aggregation, while montmorillonite and beidellite tend to aggregate in the face to face manner. Thus, it is suggested on the basis of the XRD results that Al-mont has a well-ordered face to face lamellar structure, whereas Al-sapo and Al-lapo have delaminated structures.

Montmorillonites exchanged by Na^+ and Al^{3+} showed remarkably low surface areas because the adsorption of nitrogen in the interlayer space was suppressed due to the narrow interlayer distance(ca.0.3 nm). However, the surface area markedly increased by the intercalation of Al_{13}-complex cations. This is accountable by its large interlayer distance(ca.0.9 nm). These results indicate that Na^+ and Al^{3+} type montmorillonites also aggregate in the face to face manner. Saponites intercalated by Al_{13}-complex and Al^{3+} cations showed slightly larger surface areas than the Na^+ type. It is possibly considered from the XRD patterns shown in Fig. 1(C) that Na^+-type saponite has some face to face layer ordering while Al^{3+}-type saponite and Al-sapo mostly aggregate in the edge to edge or edge to face manner. This seems to be a reason for a small surface area of Na^+ type compared with those of other types. Due to the delaminated structure, there was no appropriate difference in the surface area among three types of laponite.

As shown in Fig. 2, the BET isotherm provided better fits of the nitrogen adsorption data for Al-sapo and Al-lapo than the Langmuir isotherm. It is obvious from these results that Al-sapo and Al-lapo exhibit a multilayer adsorption behavior. A similar tendency was observed on Na^+ and Al^{3+} types of these clays. For Al-mont, however, the Langmuir equation provided a satisfactory linear fit of the nitrogen adsorption data while the BET equation did not, showing a monolayer adsorption behavior on Al-mont. Thus, it is suggested that Al-sapo and Al-lapo consist
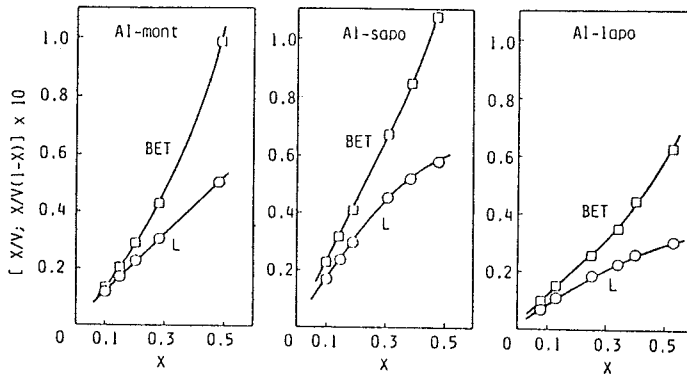
FIGURE 2 Nitrogen adsorption data plotted according to Langmuir equation [X/V vs X] and BET equation [X/V(1-X) vs X], where X = P/Po.
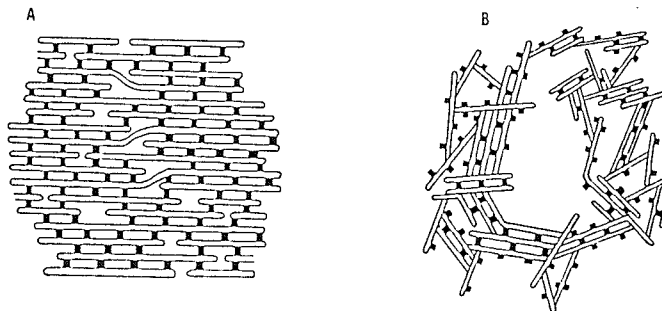

FIGURE 3 The long-range layer stacking in a well-ordered clay(A) and card-house structure for a delaminated clay(B).

significantly of macropores(Fig. 3-B) while Al-mont has a zeolite-like regular micropores due to a well-ordered face to face aggregation(Fig. 3-A).

Acidic properties

The acidic properties of the clay compounds used in this study were measured by means of NH_3-TPD and infrared spectroscopy using pyridine as a probe molecule. Figure 4 shows the NH_3-TPD spectra obtained with the pillared clays. In a NH_3-TPD spectrum of Al-mont, two desorption peak maxima were observed at 210 and 460°C. A similar spectrum was obtained with Al-sapo; however, the desorbed amount of NH_3 from Al-sapo was larger than that from Al-mont. On the contrary, Al-lapo gave a large amount of desorbed NH_3 compared with other pillared clays, although NH_3 was mostly desorbed in the low temperature region. It is obvious from these results that the amount and the strength of surface acidity remarkably vary from clay to clay.

Figure 5 illustrates the NH_3-TPD spectra of Al^{3+}-exchanged smectite clays. A remarkable difference in the amount of desorbed NH_3 was observed among these clays: the desorbed amounts of NH_3 from the saponite and laponite were prominently large
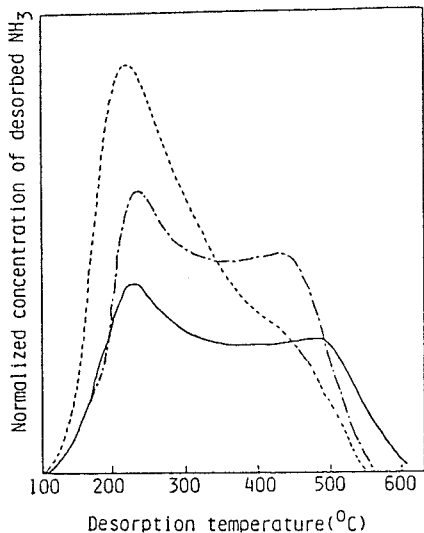
FIGURE 4 NH$_3$-TPD spectra of pillard montmorillonite(——), saponite(—·—), and laponite(-----).
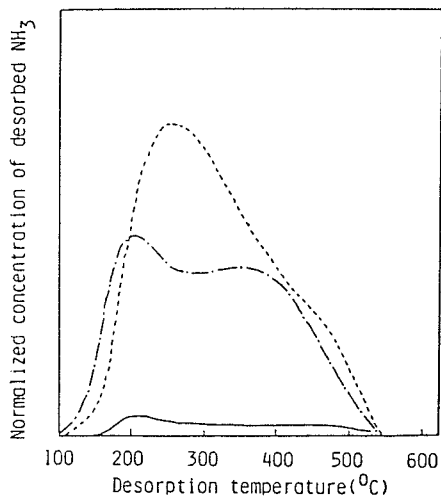
FIGURE 5 NH$_3$-TPD spectra of Al^{3+} type montmorillonite(——), saponite(—·—) and laponite(-----).

compared with that from the montmorillonite. This result is possibly interpreted in terms of the difference in the structures. Since Al^{3+}-exchanged montmorillonite has a well ordered face to face lamellar structure, almost all of the acid sites were located in the interlayer region. Thus, the interaction of NH$_3$ with the acid sites on Al^{3+}-exchanged montmorillonite should be restricted by its small interlayer distance. In the cases of Al^{3+}-exchanged saponite and laponite, however, most of the acid sites are considered to exist on the outer surface due to their delaminated structure and consequently NH$_3$ is accessible to the acid sites.

Figure 6 shows the infrared spectra of adsorbed pyridine on Al-mont, Al-sapo, and Al-lapo. These pillared clays contained both Bronsted and Lewis acid sites as characterized by the absorption bands of pyridine appearing at 1540 cm^{-1} and 1450 cm^{-1}, respectively, after evacuating in vacuo at 200°C. With regard to Al-mont and Al-lapo, however, pyridine chemisorbed on Bronsted acid sites was rapidly removed by evacuation at 300°C with some pyridine chemisorbed on Lewis acid sites being detected. In contrast, Al-sapo retained pyridine chemisorbed on Bronsted acid sites even after evacuation at 400°C in vacuo. A similar difference in the acidic property between pillared montmorillonite and pillared beidellite has been reported by Plee et al.[12] and Poncelet et al.[13]. Saponite is tetrahedrally charged smectite with Al^{3+} substituting for Si^{4+} like in beidellite. On the contrary, montmorillonite and laponite are octahedrally charged smectites. In Al-sapo, protons liberated during dehydroxylation of pillars will be captured by tetrahedral Si-O-Al linkages and
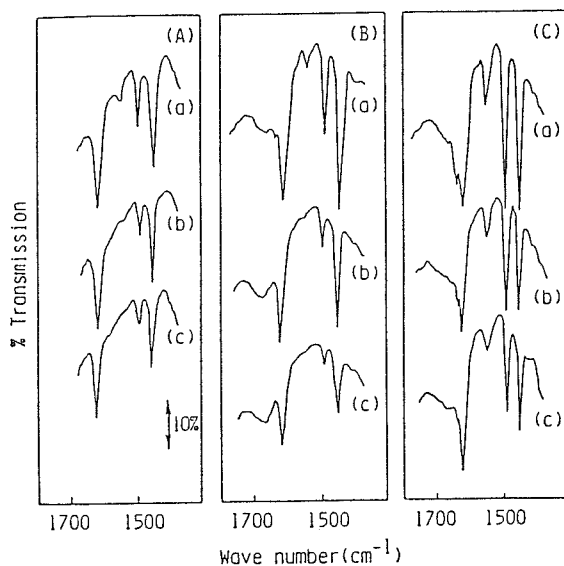
FIGURE 6 Infrared spectra of pyridine adsorbed on Al-mont(A), Al-lapo(B), and Al-sapo(C). Pyridine adsorbed sample was evacuated at (a) 200°C, (b) 300°C, and (c) 400°C.

consequently Si-OH-Al linkages similar to those formed on zeolites will be generated. The strong Bronsted acidity of Al-sapo may be mainly associated to those Si-OH-Al linkages. The less Bronsted acidic properties of Al-mont and Al-lapo seem to be explained by the absence of tetrahedral Si-O-Al linkages.

Catalytic properties

These smectite clays pillared by alumina and exchanged by Al^{3+} were used as catalysts for the reaction of 1,2,4-TrMB. The catalytic properties were compared using the data taken after the initial 10-20 min of run. As shown in Table 2, the catalytic activity of alumina pillared clays varied with the kind of smectite clays: Al-mont showed the highest activity among the catalysts tested and Al-lapo was the least active. The activity difference cannot be explained by the acidity as determined by the NH_3-TPD and the infrared spectra of adsorbed pyridine: the least acidic Al-mont showed the highest catalytic activity.

HY zeolite is commonly believed to be remarkably active for the reactions of various organic compounds compared with amorphous silica-alumina. This has been interpreted in terms of the difference in the acidic property. However, it has been pointed out by Fraissard[14] that the difference in the activity between HY and silica-alumina cannot be explained only by the acidic property. And he has proposed that the high activity of HY can be explained by a structural effect which imposes upon the reactant molecule a much greater number of active center collisions than in the case of an amorphous solid. This proposal is based on the experimental

Table 2 Catalytic activities of various clay compounds for the reaction
of 1,2,4-TrMB

Clay	Montmorillonite		Saponite		Laponite
Type	Pillared	Al^{3+}	Pillared	Al^{3+}	Pillared
Conversion(%)	43.21	0	15.38	8.32	3.20
Selectivity for					
Disproportionation	84.93	-	81.57	81.71	90.71
Isomerization	15.07	-	18.43	18.29	9.29
Dealkylation	0	-	0	0	0

Reaction condition: W/F = 8000 (g-cat.min/mol)

observation: a NMR study of adsorbed xenon reveals that for a given gas pressure the
molecule adsorbed in a zeolite cavity is subjected to pressure about 100 times
greater than the pressure upon a molecule in contact with a planar surface. As
mentioned above, Al-mont possesses zeolite-like micropores whereas Al-sapo and
Al-lapo have macropores. So, it is a possible explanation for Al-mont to exhibit a
high activity that its regular microporous structure will permit a high concentration
of 1,2,4-TrMB around the acid sites.

   Al-sapo showed a higher activity than Al-lapo, although they had similar
delaminated structures. Two explanations will be put forward to account for it. One
is the difference in Bronsted acidity: Al-sapo has a stronger Bronsted acidity than
Al-lapo due to the existence of Si-O-Al linkages. The other is the difference in the
position of acid sites. Since Li^+ was octahedrally substituted for Mg^{2+} in laponite,
cation exchange sites which seem to act as acid sites on laponite may exist in the
octahedral layer. Moreover, the octahedral layer is sandwiched by the two
tetrahedral layers. So, the interaction of 1,2,4-TrMB with the acid sites will be
suppressed by the steric effect. On the contrary, cation exchange sites on saponite
mainly exist in the tetrahedral layer due to the substitution of tetrahedral Si^{4+} by
Al^{3+}, resulting in the easy accessibility of 1,2,4-TrMB to the acid sites. These
considerations seem to be reasonable to account for the activity difference between
Al-sapo and Al-lapo.

   Al^{3+}-exchanged saponite showed a catalytic activity of a similar order to Al-sapo.
However, Al^{3+}-exchanged montmorillonite with a well order face to face lamellar
structure was inactive. These results are consistent with the results obtained from
the NH_3-TPD experiments. Thus, these results will similarly be interpreted in terms
of the difference in the structure.

   Figure 7 illustrates the difference in selectivity between Al-mont and Al-sapo:
the fraction of 1,2,4,5-TeMB in TeMB isomers produced from 1,2,4-TrMB disproportiona-
tion are shown as a function of the conversion level of 1,2,4-TrMB. Al-mont was more
selective for disproportionation of 1,2,4-TrMB to yield 1,2,4,5-TeMB than Al-sapo.
As shown in our previous works[3-5], the 1,2,4,5-TeMB selectivity is dependent on the
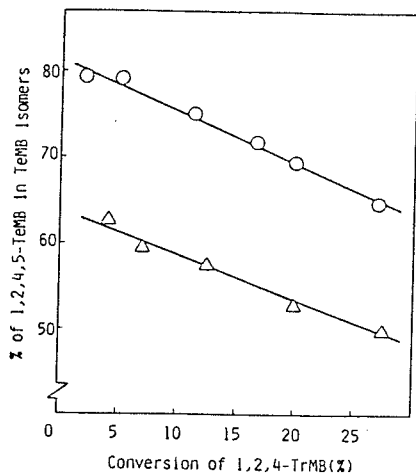shape-selective property of a catalyst. The higher shape selectivity of Al-mont is

FIGURE 7 Variation in percentage of 1,2,4,5-TeMB in TeMB isomers as a function of 1,2,4-TrMB conversion over Al-mont(○) and Al-sapo(△).
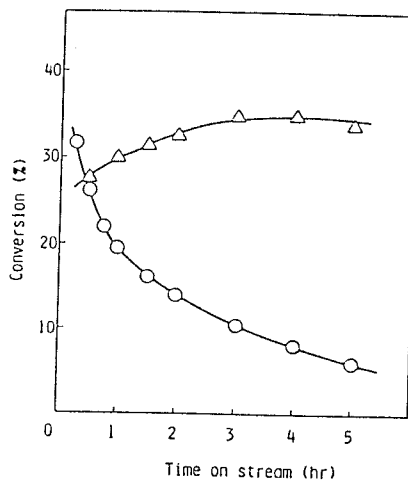
FIGURE 8 Variation in 1,2,4-TrMB conversion with time on stream over Al-mont(○) and Al-sapo(△).

attributed to the well-ordered face to face lamellar structure, while the lower selectivity of Al-sapo is due to the delaminated or card house structure.

On the other hand, the catalytic activity of Al-sapo was more stable against deactivation than that of Al-mont as shown in Fig. 8. A similar result has been reported by Pinnavaia et al.[9] for dealkylation of isopropylnaphthalene on pillared and delaminated clays. It has generally been admitted that the strong acid site accelerates coke formation which is the main cause for deactivation of solid acid catalysts. As Al-sapo possesses the stronger Bronsted acidity than Al-mont, however, the high stability of Al-sapo against deactivation seems to be attributed to its macroporosity. The macroporosity may favor the desorption of high molecular weight hydrocarbons which otherwise would be retained as coke.

CONCLUSION

Al-mont exhibited a well-ordered face to face lamellar structure and consequently showed microporosity. On the contrary, Al-sapo and Al-lapo aggregated in the face to edge or edge to edge manner, which generated macropores. It was shown in NH_3-TPD and infrared spectra of adsorbed pyridine that the acidic property of pillared clays was influenced by the nature of clays. The strong acid sites on Al-mont and Al-lapo were mainly Lewis type, whereas that on Al-sapo consisted of both Bronsted and Lewis types. This strong Bronsted acidity on Al-sapo is probably attributed to Si-O-Al linkages in the tetrahedral layer.

The catalytic activity was not satisfactorily related to the acidic property but it was markedly affected by the structure of pillared clays. Al-mont having a smaller acidity was far more active in the reaction of 1,2,4-TrMB than Al-sapo and Al-lapo. It is proposed that the concentration of 1,2,4-TrMB around the acid sites may be enhanced by the microporosity of Al-mont, resulting in the high activity. Due to the delaminated structure, Al^{3+}-exchanged saponite showed a similar activity to Al-sapo, whereas Al^{3+}-exchanged montmorillonite was inactive. Since the shape-selective property is essential to the selective formation of 1,2,4,5-TeMB, the presence of macropores is unfavorable for this purpose, although the macroporosity stabilizes the catalytic activity against deactivation.

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The Effect of Spilled-Over Hydrogen on the Activity of Montmorillonite Pillared by Aluminum Oxide for Conversion of Trimethylbenzenes

T. Matsuda, T. Fuse, and E. Kikuchi

Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo, Japan

The effect of Pd loading on the catalytic activity of montmorillonite pillared with alumina (Al-mont) was investigated. The catalyst deactivation was prevented by loading a small amount of Pd on Al-mont and using H_2 as a carrier gas, although the initial activity was reduced. Since the mixing of 0.5 wt% Pd/Al_2O_3 with Al-mont gave similar effects to those from the Pd loading, the stabilization of activity in the presence of both Pd and H_2 may be caused by spilled-over hydrogen. By comparison, the activity of H–Y was not stabilized under the same condition. The strong acid sites of Al-mont, which were mostly Lewis acidic, decreased by Pd loading in the atmosphere of H_2 stream, whereas those of H–Y changed little, due to Brönsted acidity. These results suggest that Lewis acid sites can play a very important role in the stabilization of the catalytic activity by spilled-over hydrogen. © 1987 Academic Press, Inc.

INTRODUCTION

Pillared clay is a new family of molecular sieve materials obtained by exchanging charge compensating cations between the silicate layers of clays, such as montmorillonite or hectorite, with large polyoxycations. On heating, inorganic oxide clusters are formed; they prop open the clay layers permanently to generate a microporous structure. The pore size of pillared clays, which is determined by both the interlayer distance and the lateral distance, can be controlled by the choice of conditions and method of preparation or by the kind of intercalating materials. So the application of pillared clays as shape-selective catalysts has become important. Pillared clays have been practically applied as catalysts for cracking (1–4), oligomerization (5), alkylation (6), disproportionation (7), and methanol conversion (8–9).

Catalysis by solid acid, particularly when it exhibits shape selectivity, is most often accompanied by catalyst deactivation due to coke, which is an inevitable by-product in many heterogeneously catalyzed organic conversions. As catalyst deactivation due to coke formation is industrially a very important problem, it has often been discussed in relation to zeolites (10). This coke formation is in some cases prevented by using a proper zeolite having a particular pore structure like ZSM-5 or by controlling acidic properties. An alternative way to prevent catalyst deactivation is the addition of a hydrogenating component such as Ni, Pt, or Pd. This is effective for stabilization of the catalytic activity when used in a H_2 atmosphere, but the detailed mechanism has not been well explained.

Our previous work (11) showed that a montmorillonite pillared by alumina having a layer distance of 8.5 Å is active and selective for disproportionation of 1,2,4-trimethylbenzene (TrMB) to yield 1,2,4,5-tetramethylbenzene (TeMB), while the catalyst deactivation is rather fast. The purpose of this paper is to describe the stabilization of the catalytic activity of Al-mont

by the addition of palladium on to Al-mont and to discuss the effect by comparison with the results for H–Y.

EXPERIMENTAL

Preparation of Catalyst

The clay used in this study is a sodium-type montmorillonite obtained from Kunimine Industry Co., designated as Kunipia F, its cation exchange capacity is 119 meq/100 g. An intercalation of mont-morillonite by Al_{13}-complex was performed at the Al/clay ratio of 4 mmole/meq clay which was a little in excess of the stoichiometric Al/clay ratio of 2.21 mmole/meq clay: 100 ml of aluminum chlorohydroxyl complex solution, whose Al concentration was 0.5 mole/liter, was adjusted at pH 3.8 and then 10 g montmorillonite was added to this solution. After the mixture was stirred for 1 hr at about 70°C, the product was filtered and washed several times with hot distilled water to remove excess complexes and chlorine ions. The intercalated product was dried at 110°C overnight and calcined at 400°C for 4 hr. The layer distance and the surface area of Al-mont calcined at 400°C were 8.5 Å and 380 m^2/g, respectively, and they were little changed by Pd loading or H_2 reduction.

The aluminum chlorohydroxyl complex (Al_{13} complex) was prepared according to the method reported by Vaughan et al. (12). 100 g aluminum powder was added to 500 ml of 1 M solution of aluminum chloride and heated at 70°C in water bath. After H_2 evolution was terminated, unreacted aluminum powder was removed by filtration.

Na–Y zeolite having a SiO_2/Al_2O_3 ratio of 5.0 was supplied by Toyo Soda Manufacturing Co. Na–Y zeolite was converted to NH_4–Y by exhaustive exchange with 0.1 M solution of NH_4Cl at 80°C and then NH_4–Y was calcined at 540°C for 4 hr to form a proton-type zeolite.

As Al-mont calcined at 400°C still kept 10 meq/100 g of cation exchange capacity, palladium was loaded by an ion-exchange technique at ambient temperature. 10 g Al-mont calcined at 400°C was dispersed into 100 ml distilled water and then 0.01 M solution of $Pd(NH_3)_4Cl_2$ was titrated to attain the content of Pd in the range 0.05–0.5% by weight. The ion exchange was performed at about pH 4. After filtration and washing, $Pd(NH_3)_4^{2+}$-exchanged Al-mont was calcined at 400°C for 4 hr. Similar procedures were carried out to prepare Pd-loaded H–Y. A commercial 0.5 wt% Pd/Al_2O_3 catalyst was obtained from Nippon Engelhard Ltd.

Apparatus and Procedures

Reactions were carried out at atmospheric pressure in a continuous flow system with a fixed bed of catalyst. The catalyst was packed in the reactor (Pyrex, 15-mm diameter) and treated at 400°C for 30 min in a stream of N_2. The Pd-loaded Al-mont and Pd/Al_2O_3 catalysts were reduced in H_2 at 400°C for 3 hr prior to the reaction, which was carried out at 200°C. The reactant, 1,2,4-TrMB or 1,2,3-TrMB, was supplied quantitatively from a microfeeder to the reactor through a vaporizer. N_2 or H_2 was used as a carrier gas.

Liquid products were collected in an ice trap every 10 min and were analyzed by means of gas chromatography using a flame ionization detector and a FFAP glass capillary column with temperature-programmed heating from 80 to 170°C.

Temperature-Programmed Desorption (TPD) Measurements

TPD experiments were performed to characterize the acidic properties of catalysts. The instrument used in TPD experiments was essentially similar to that described by Dawson et al. (13). A thermal conductivity detector was used to detect desorbed NH_3. The data were collected with points taken at 6-s intervals, which were signals of both the concentration of desorbed NH_3 and the temperature changes. These signals were amplified and

then fed into a Shimadzu C-R2AX chromatopac for data storage, processing, and plotting.

In each TPD experiment, a sample weighing about 0.5 g was placed in the cell, which was evacuated at 400°C for 1 hr and then cooled to 100°C. A sample of Pd-loaded catalyst was reduced in H_2 at 400°C for 3 hr and evacuated at this temperature for 1 hr. Ammonia gas of 100 Torr (1 Torr = 133.3 Nm^{-2}) was adsorbed at 100°C for 15 min and evacuated for 15 min. The sample was kept in the stream of He or H_2 (100 Torr) for 90 min to attain the steady state flow, prior to heating at a rate of 10°C/min. As H_2O, which was produced from dehydroxylation, was desorbed simultaneously with NH_3, the NH_3 TPD spectrum was obtained by point-by-point subtraction of the H_2O desorption spectrum obtained with the same catalyst which had not adsorbed NH_3.

Infrared Spectroscopy

The adsorption of pyridine monitored by infrared spectroscopy was used to distinguish the Brönsted and Lewis acid sites on the catalysts. Each spectrum was recorded on IRA-2 diffraction-grating infrared spectrometer (Japan Spectroscopic Co., Ltd.). A sample was pressed at 500 kg/cm^2 into a self-supporting wafer (20-mm diameter, ca. 30 mg). The wafer was then mounted in a quartz sample holder, which was introduced in the infrared cell. After the wafer was activated at 400°C for 1 hr *in vacuo*, pyridine of 5 Torr was adsorbed on the sample at 100°C for 1 hr. Then this sample was evacuated at the desired temperature (100–400°C) for 1 hr. The measurement was carried out at room temperature.

RESULTS

The catalytic activity of Al-mont in the conversion of 1,2,4-TrMB decreased remarkably with time on stream, as shown in Fig. 1, while the surface area and the layer distance hardly changed at all. As the calcination of the deactivated catalyst at 400°C mostly regenerated the catalytic activity
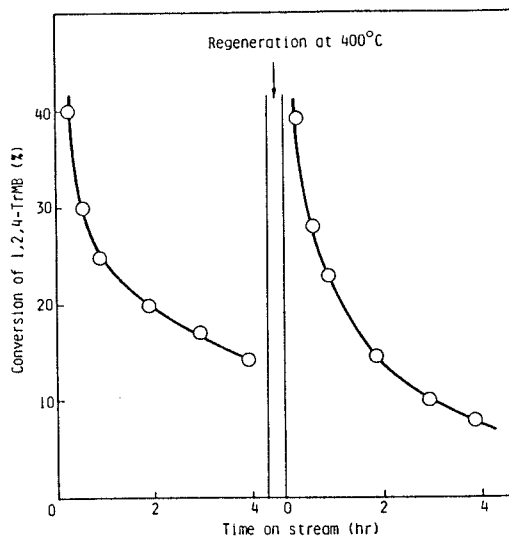

FIG. 1. Variation in conversion of 1,2,4-TrMB over Al-mont catalyst at 200°C. Reaction conditions: W/F, 2.3×10^5 (g-cat s/mol); H_2/1,2,4-TrMB, 1 (molar ratio).

with the formation of CO_2, coke deposition should be one cause of the catalyst deactivation.

The decay of the catalytic activity was thoroughly suppressed by loading Pd on Al-mont and using H_2 as a carrier gas. Typical results are shown in Fig. 2. Although the initial activity of 0.05 wt% Pd/Al-mont reduced at 400°C was low compared with Al-mont itself in the stream of H_2, deactivation substantially disappeared. When this catalyst was used in the stream of N_2, however, deactivation was accelerated with the evolution of detectable amount of H_2, while the initial activity was depressed. Moreover, no stabilization of the catalytic activity was observed with 0.05 wt% Pd/Al-mont which had either not been reduced or had been reduced at a temperature as low as 300°C. Thus, the loading of Pd seems effective to stabilize the activity only when the catalyst is used in H_2 atmosphere after H_2 reduction at a high temperature such as 400°C. In further experiments, reactions were carried out in H_2 atmosphere after H_2 reduction at 400°C.

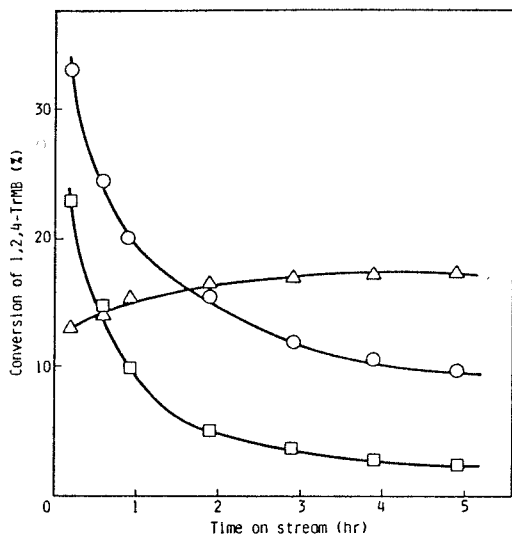TrMB was converted by disproportion-

FIG. 2. Effect of catalyst reduction and carrier gas on the catalytic activity in the reaction of 1,2,4-TrMB: O, Al-mont; △, 0.05 wt% Pd/Al-mont reduced at 400°C and used in H_2 carrier; □, 0.05 wt% Pd/Al-mont reduced at 400°C and used in N_2 carrier. Reaction conditions: W/F, 1.6×10^5 (g-cat s/mol); H_2/1,2,4-TrMB, 2 (molar ratio).

ation and isomerization. The effects of Pd loading on stabilization of catalytic activity for these reactions are shown in Fig. 3. Here, 1,2,3-TrMB was used as reactant instead of 1,2,4-TrMB, since the conversion of 1,2,4-TrMB by isomerization is too small to allow the change in the activity for isomerization to appear. The isomerization activity in the conversion of 1,2,3-TrMB was determined from the yields of 1,2,4- and 1,3,5-TrMB's and the disproportionation activity was determined from the yields of xylenes and TeMBs.

The activities of Al-mont catalyst for disproportionation and isomerization decreased similarly with time on stream, while the decay of catalytic activities for both of these reactions was not observed in the case of 0.05 wt% Pd/Al-mont. Although the existence of Pd and H_2 lowered the activities of Al-mont for both reactions, the effect was more remarkable for disproportionation than for isomerization. The amount of Pd loaded on Al-mont did not give any difference over the range 0.05–

0.5% by weight. As shown in Fig. 4, similar results were brought about when 0.5 wt% Pd/Al_2O_3 was mixed with Al-mont. Thus, it is suggested that the above-mentioned stabilization of catalytic activity and the decrease in the initial activity of Al-mont are caused by spilled-over hydrogen.

Figure 5 shows the effect on the catalytic activity of mixing 0.5 wt% Pd/Al_2O_3 with H–Y zeolite. The initial activities of H–Y catalyst for both of these reactions were lowered by spilled-over hydrogen; disproportionation was more pronouncedly reduced than isomerization. However, the mixing of the Pd/Al_2O_3 did not stabilize the activity of H–Y catalyst even in the presence of a high partial pressure of H_2 (H_2/1,2,3-TrMB = 9/1 molar ratio). These results suggest that the effect of hydrogen spillover on catalyst deactivation depends on the nature of active sites for coke formation.

The effect of spilled-over hydrogen on the acidity of catalyst was investigated by means of NH_3 TPD. Typical NH_3-TPD spectra are shown in Fig. 6. These spectra
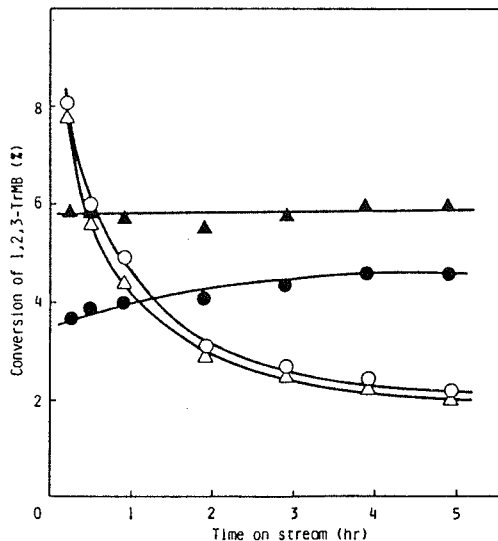

FIG. 3. Variation in the activities for disproportionation (O, ●) and isomerization (△, ▲) in the reaction of 1,2,3-TrMB: open symbol, Al-mont; solid symbol, 0.05 wt% Pd/Al-mont. Reaction conditions: W/F, 1.6×10^5 (g-cat s/mol); H_2/1,2,3-TrMB, 2 (molar ratio).
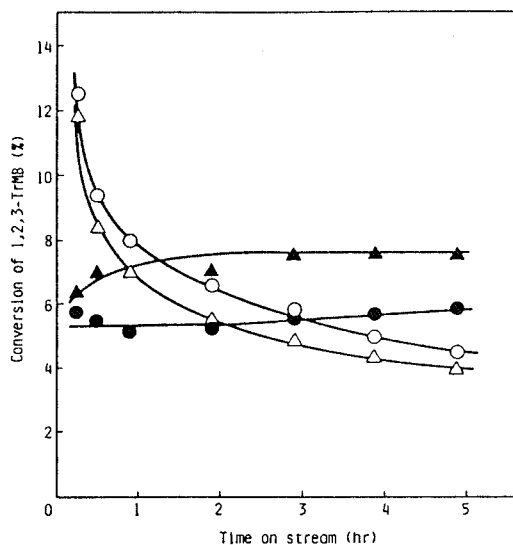
-34-

FIG. 4. Effect of Pd mixture on the activities of Al-mont for disproportionation (○, ●) and isomerization (△, ▲) of 1,2,3-TrMB: open symbol, Al-mont (50 wt%) and Al$_2$O$_3$ (50 wt%); solid symbol, Al-mont (50 wt%) and 0.5 wt% Pd/Al$_2$O$_3$ (50 wt%). Reaction conditions: W/F, 2.8 × 10^5 (g-cat s/mol); H$_2$/1,2,3-TrMB, 2 (molar ratio).

FIG. 6. NH$_3$–TPD spectra of Al-mont (A) and H–Y (B): (a) without Pd; (b) 0.05 wt% Pd loaded.
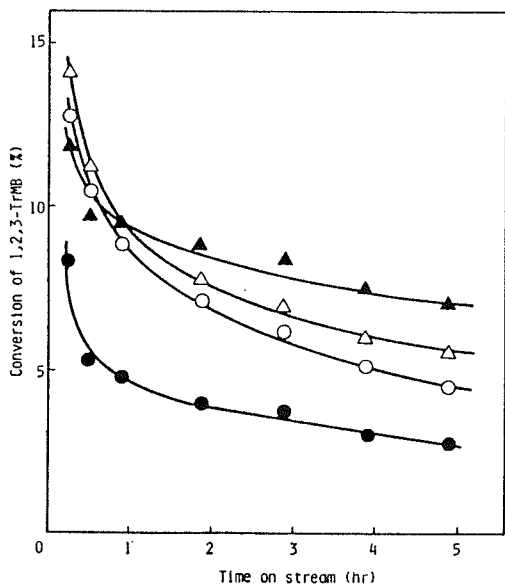

FIG. 5. Effect of Pd mixture on the activities of H–Y for disproportionation (○, ●) and isomerization (△, ▲) of 1,2,3-TrMB: open symbol, H–Y (50 wt%) and Al$_2$O$_3$ (50 wt%); solid symbol, H–Y (50 wt%) and 0.5 wt% Pd/Al$_2$O$_3$ (50 wt%). Reaction conditions: W/F, 2.3 × 10^4 (g-cat s/mol); H$_2$/1,2,3-TrMB, 9 (molar ratio).
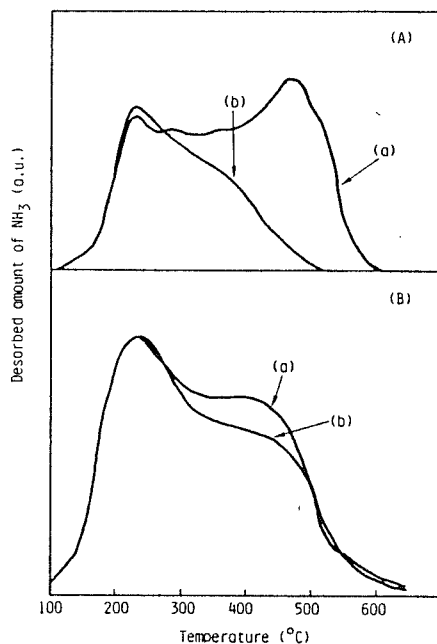
were obtained using H$_2$ as a carrier gas. The spectrum for Al-mont consisted of two desorption maxima: low- and high-temperature maxima appeared at 210 and 460°C, respectively. On loading Pd, most of the high-temperature desorption of NH$_3$ disappeared (Fig. 6A, curve b). When He was used as the TPD carrier instead of H$_2$, almost the same TPD spectrum as that of Al-mont was obtained from 0.05 wt% Pd/Al-mont. These results show that the adsorbed NH$_3$ which gives the high-temperature desorption peak is removed from the acidic sites by spilled-over hydrogen prior to the programmed heating. On the contrary, no such phenomena were discerned with H–Y. As shown in Fig. 6B, 0.05 wt% Pd/H–Y gave a similar TPD spectrum to that of H–Y, although the amount of NH$_3$ desorbed in the high-temperature region slightly decreased.

Figure 7 shows the infrared spectra of pyridine adsorbed on Al-mont and H–Y. The spectra for Al-mont given in Fig. 7A show that the intensity of absorption band
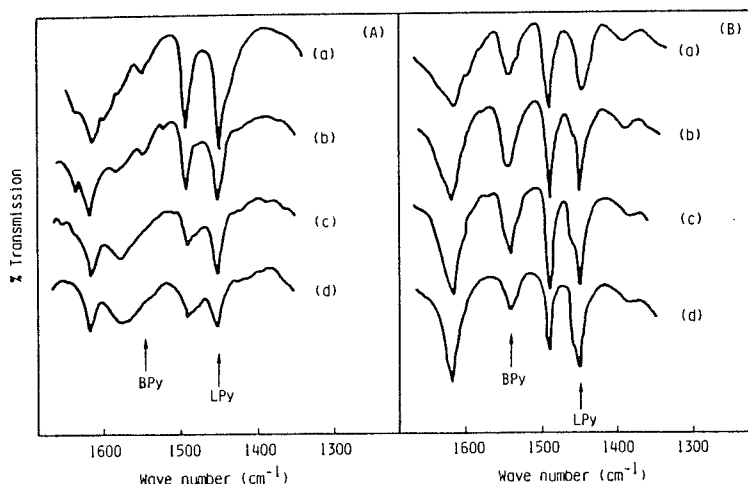
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FIG. 7. Infrared spectra of pyridine loaded Al-mont (A) and H–Y (B) evacuated at (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C.

at 1450 cm⁻¹ due to pyridine chemisorbed on Lewis acid sites is far stronger than that of the band at 1550 cm⁻¹ due to pyridine chemisorbed on Brönsted acid sites. Upon heating *in vacuo*, pyridine adsorbed on Brönsted acid sites decreased and only pyridine coordinated to Lewis acid sites was detected after evacuation above 300°C. On the contrary, the infrared spectra obtained from H–Y revealed that pyridine adsorbed on both Brönsted and Lewis acid sites remained after evacuation at 400°C. As NH₃ is far more strongly adsorbed on acid sites than is pyridine, due to its larger basicity, the sites to adsorb pyridine detected by spectroscopy after evacuation at 200°C seem to correspond to the sites which release NH₃ in the high-temperature region. These results suggest that the strong acid sites on Al-mont giving the high-temperature desorption peak of NH₃ are mainly Lewis acidic, whereas those of H–Y consist of both Brönsted and Lewis acid sites.

DISCUSSION

In the stream of H₂, 0.05 wt% Pd/Al-mont was found to be more stable against deactivation than Al-mont, while its initial activity was low compared with that of Al-

mont itself. Such an effect of Pd loading was not observed when the reaction was carried out in N₂ atmosphere. Furthermore, the mixing of 0.5 wt% Pd/Al₂O₃ with Al-mont brought forth the same effect. These results show that the stabilization of catalytic activity and the decrease in the initial activity can be attributed to spilled-over hydrogen.

NH₃-TPD experiments showed that the number of strong acid sites of 0.05 wt% Pd/Al-mont markedly decreased in the presence of H₂, while the number of Al-mont sites was unchanged, regardless of H₂ or He being used as a carrier gas. As there was no difference in the acid amount determined by NH₃ TPD between Al-mont and 0.05 wt% Pd/Al-mont under He, the decrease in high-temperature desorption of NH₃ from Pd-loaded Al-mont under H₂ atmosphere seems to be caused by replacement of adsorbed NH₃ with spilled-over hydrogen.

H₂ seems to be dissociatively adsorbed on metallic sites on metal-loaded acid catalysts, and the dissociated species seem to migrate to the acceptor sites on the acid (*14*). It has been advocated that the hydrogen which migrated over acidic supports exists as a proton (*15*). Heterolytic scission

of H_2 and migration of protons and hydride ions have also been proposed (16). Protons will migrate to O^{2-} anions, possibly to provoke the formation of new acid centers, and hydride ions will be captured by Lewis acid sites with the donation of paired electrons.

In the present case of Al-mont, the migration of a proton should give a very weak acid center which cannot act as active sites for the conversion of TrMB. As shown in Fig. 7A, the surface acidity of Al-mont evacuated above 300°C is mostly Lewis acidic. Consequently we propose that the decrease in the amount of strong acid sites is to be attributed to the reaction between Lewis acid sites and hydride ions. This reaction, leading to the decrease in strong Lewis acid sites, may influence the catalytic activity of Al-mont.

Guisnet et al. (17) have proposed that disproportionation of o-xylene proceeds via a benzylic carbocation intermediate and isomerization via a benzenium ion intermediate. This idea was based on experimental observations that the addition of alkanes, which can react only with the benzylic carbocation intermediates, to the reaction system causes a decrease in disproportionation activity, but leaves the isomerization activity unchanged. Furthermore, Poustma (18) explained that a benzylic carbocation is

formed on Lewis acid sites and is responsible for disproportionation. As the surface acidity of Al-mont is mostly Lewis acidic, disproportionation mainly proceeds via a benzylic carbocation mechanism, as shown in Scheme 1.

Occelli et al. (2) reported that coke formation from gas oil conversion on Al-mont is greater at least by a factor of 2 than that on H–Y catalyst. They have presented an explanation that high coke formation on Al-mont should be attributed to its strong Lewis acidity. As coke formation is considered to take place more easily on stronger acid sites, coke formation on Al-mont catalyst in the conversion of TrMB's mainly proceeds on Lewis acid sites involving the same intermediate as that in disproportionation. Hydride ions are considered to act similarly on a benzylic carbocation as on Lewis acid sites, resulting in the decrease in its concentration. Consequently, it is possible to explain the effect of spilled-over hydrogen on the stabilization and on the decrease in initial activity for disproportionation by this mechanistic consideration as well as by the decrease in the strong Lewis acid sites.

However, the present work has shown that the activity of Al-mont catalyst for isomerization is also affected by spilled-
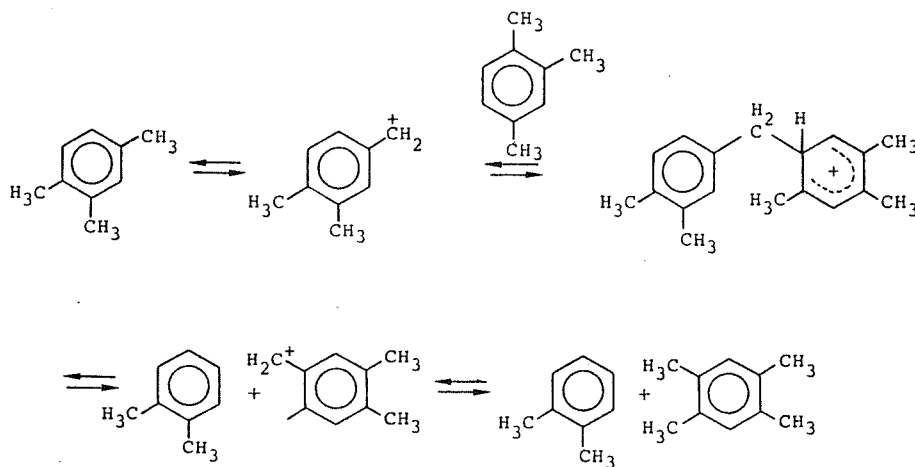
SCHEME 1. Disproportionation mechanism of 1,2,4-TrMB via a benzylic carbocation intermediate.
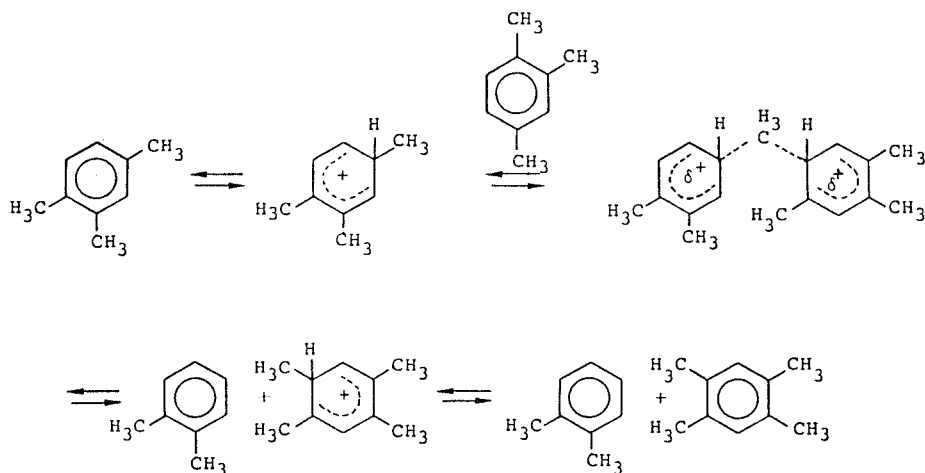
SCHEME 2. Disproportionation mechanism of 1,2,4-TrMB via a benzenium ion intermediate.

over hydrogen as well, like that for disproportionation. The active site for isomerization seems to be a Brönsted acid site rather than a Lewis acid site. Hence, the decrease in isomerization activity cannot be explained directly by the effect of hydride ions migrating over Al-mont, as in the case of disproportionation. Lusford (19) has proposed that positively charged SiO_3^+ group acts inductively through the lattice on Brönsted OH groups to produce a partial negative charge across the lattice. This electrostatic interaction between Lewis acid sites and Brönsted OH groups reduces the electron density of hydroxyl groups, resulting in a stronger Brönsted acidity. As previously mentioned, the number of Lewis acid sites on Al-mont is considered to diminish in the presence of Pd and H_2. Thus, there is a possibility that the strength of the Brönsted acid sites on Al-mont is weakened by spilled-over hydrogen as a result of this indicated effect caused by the decrease in Lewis acid sites.

This consideration can explain the decrease in initial activities not only for isomerization but also for disproportionation, since disproportionation also proceeds on Brönsted acid sites via a benzenium ion mechanism, as shown in Scheme 2. As the isomerization activity of Al-mont decayed

with time on stream, coke formation is considered to take place also on the Brönsted acid sites. Thus, coke formation seems to be suppressed by weakening the strength in Brönsted acidity as well as by decreasing the number of strong Lewis acid sites.

Although the initial activities of H–Y catalyst for disproportionation and isomerization were similarly lowered by spilled-over hydrogen, the activities for both of these reactions were not stabilized. Langer (20), Fajula et al. (21), and Blackmound et al. (22) have given evidence to show that strong Brönsted acid sites are more active for coke formation than strong Lewis acid sites. As H–Y catalyst possesses strong Brönsted acid sites, as shown in Fig. 7, coke formation on H–Y may take place mainly on Brönsted acid sites. The number of acid sites on H–Y is less sensitive to spilled-over hydrogen compared with the number of sites on Al-mont, due to its Brönsted acidity. Therefore, the strength in Brönsted acidity of H–Y catalyst may not have been weakened by spilled-over hydrogen enough to suppress coke formation. These results allow us to conclude that spilled-over hydrogen acts mainly on Lewis acid sites and retards isomerization, disproportionation, and coke formation taking

place on both Lewis and Brönsted acid sites.

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