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

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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.

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

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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 montmorillonite 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

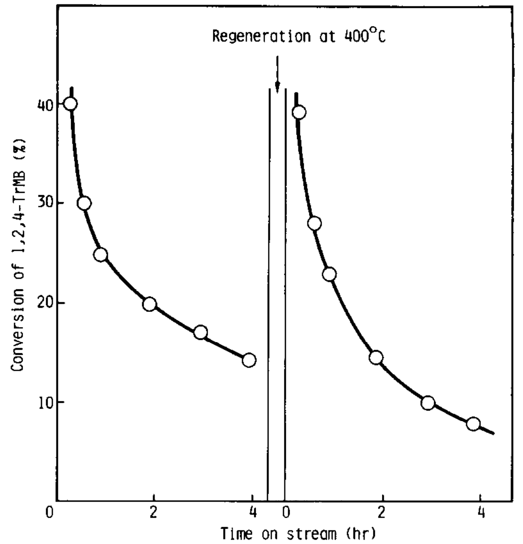


FIG. 1. Variation in conversion of 1,2,4-TrMB over Al-mont catalyst at 200°C. Reaction conditions: W/F, 2.3×10^5 (g-cat s/mol); H_2/1,2,4-TrMB, 1 (molar ratio).

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 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-

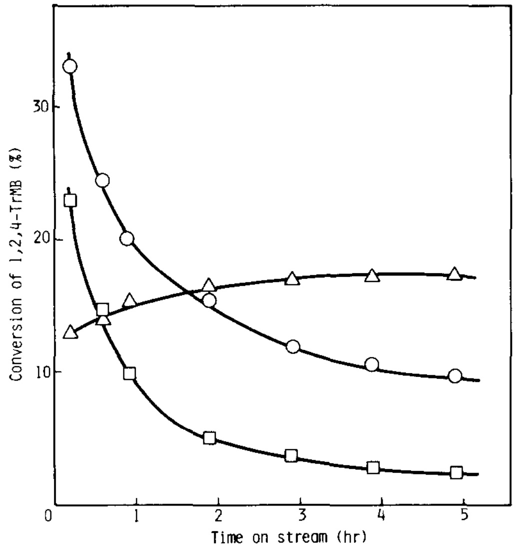


FIG. 2. Effect of catalyst reduction and carrier gas on the catalytic activity in the reaction of 1,2,4-TrMB: ○, Al-mont; △, 0.05 wt% Pd/Al-mont reduced at 400°C and used in H_2 carrier; □, 0.05 wt% Pd/Al-mont reduced at 400°C and used in N_2 carrier. Reaction conditions: W/F, 1.6×10^5 (g-cat s/mol);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

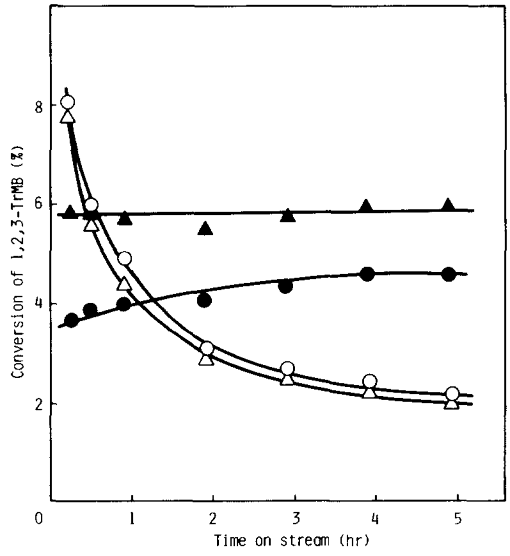


FIG. 3. Variation in the activities for disproportionation (○, ●) and isomerization (△, ▲) in the reaction of 1,2,3-TrMB: open symbol, Al-mont; solid symbol, 0.05 wt% Pd/Al-mont. Reaction conditions: W/F, 1.6 $\times$ 10^5 (g-cat s/mol); H_2/1,2,3-TrMB, 2 (molar ratio).

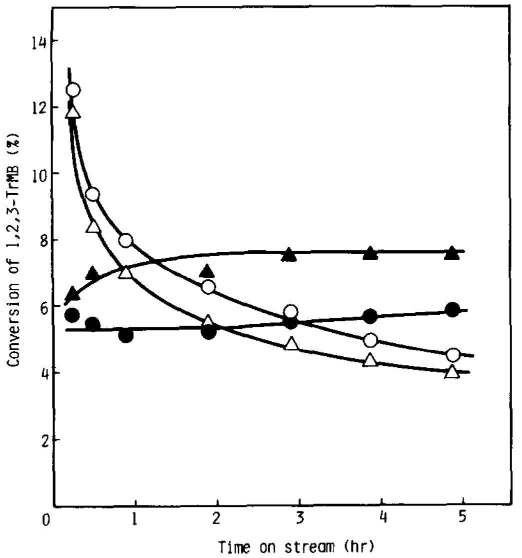


FIG. 4. Effect of Pd mixture on the activities of Al-mont for disproportionation (○, ●) and isomerization (△, ▲) of 1,2,3-TrMB: open symbol, Al-mont (50 wt%) and Al_2O_3 (50 wt%); solid symbol, Al-mont (50 wt%) and 0.5 wt% Pd/Al_2O_3 (50 wt%). Reaction conditions: W/F, 2.8×10^5 (g-cat s/mol); H_2/1,2,3-TrMB, 2 (molar ratio).

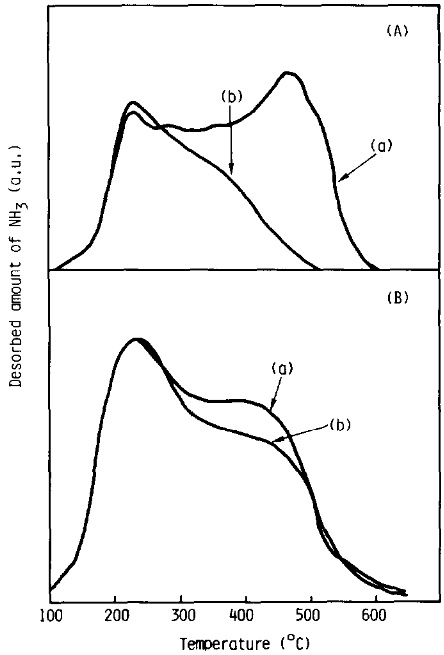


FIG. 6. NH_3–TPD spectra of Al-mont (A) and H–Y (B): (a) without Pd; (b) 0.05 wt% Pd loaded.

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

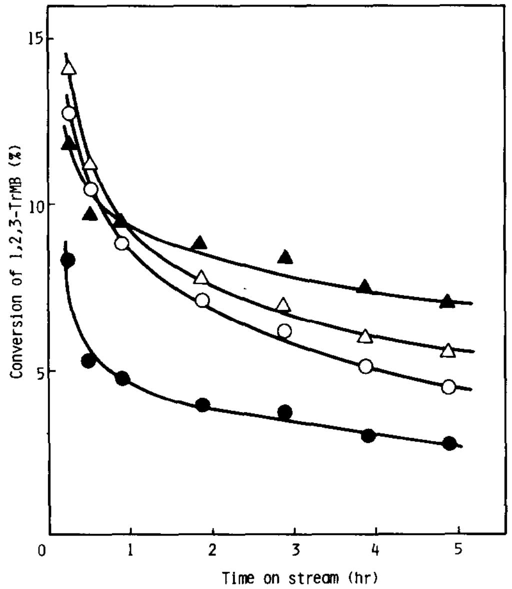


FIG. 5. Effect of Pd mixture on the activities of H–Y for disproportionation (○, ●) and isomerization (△, ▲) of 1,2,3-TrMB: open symbol, H–Y (50 wt%) and Al_2O_3 (50 wt%); solid symbol, H–Y (50 wt%) and 0.5 wt% Pd/Al_2O_3 (50 wt%). Reaction conditions: W/F, 2.3×10^4 (g-cat s/mol); H_2/1,2,3-TrMB, 9 (molar ratio).

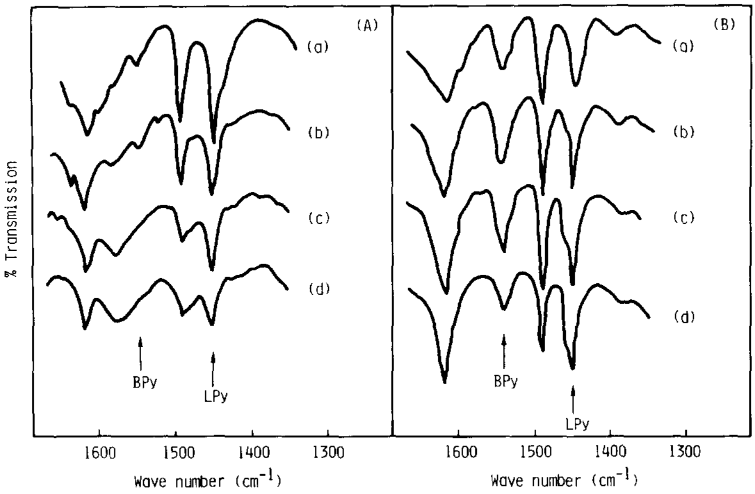


FIG. 7. Infrared spectra of pyridine loaded Al-mont (A) and H–Y (B) evacuated at (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C.

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 NH_3 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 NH_3 in the high-temperature region. These results suggest that the strong acid sites on Al-mont giving the high-temperature desorption peak of NH_3 are mainly Lewis acidic, whereas those of H–Y consist of both Brönsted and Lewis acid sites.

DISCUSSION

In the stream of H_2, 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 N_2 atmosphere. Furthermore, the mixing of 0.5 wt% Pd/Al_2O_3 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.

NH_3-TPD experiments showed that the number of strong acid sites of 0.05 wt% Pd/Al-mont markedly decreased in the presence of H_2, while the number of Al-mont sites was unchanged, regardless of H_2 or He being used as a carrier gas. As there was no difference in the acid amount determined by NH_3 TPD between Al-mont and 0.05 wt% Pd/Al-mont under He, the decrease in high-temperature desorption of NH_3 from Pd-loaded Al-mont under H_2 atmosphere seems to be caused by replacement of adsorbed NH_3 with spilled-over hydrogen.

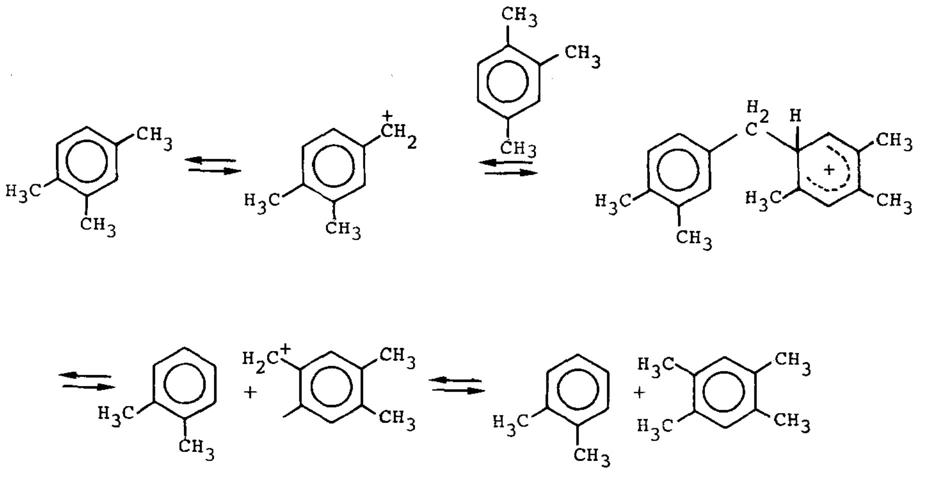
H_2 seems to be dissociatively adsorbed on metallic sites on metal-loaded acid catalysts, and the dissociated species seem to migrate to the acceptor sites on the acid (*14*). It has been advocated that the hydrogen which migrated over acidic supports exists as a proton (*15*). Heterolytic scission of 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.

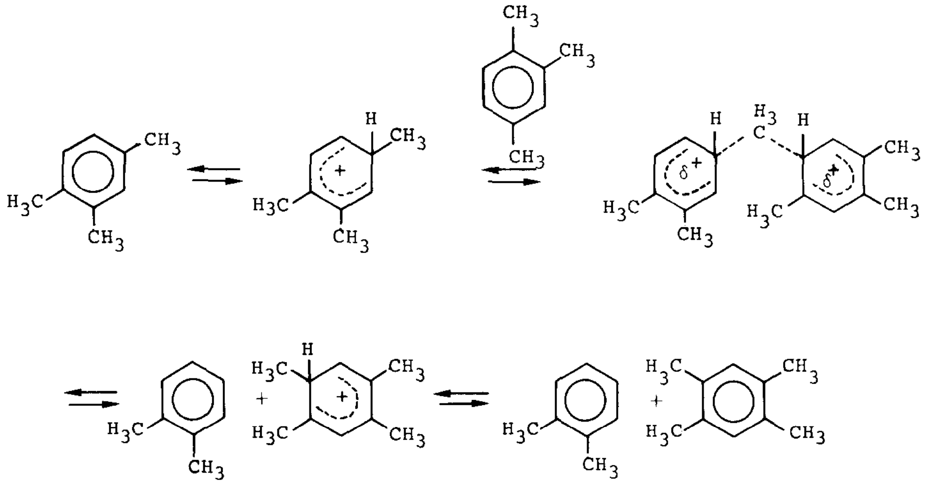
Guisnet *et al.* (*17*) have proposed that disproportionation of *o*-xylene proceeds via a benzylic carbocation intermediate and isomerization via a benzenium ion intermediate. This idea was based on experimental observations that the addition of alkanes, which can react only with the benzylic carbocation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