The Effect of Spillover Hydrogen on the Stabilization of Catalytic Activities of Y-Type Zeolite and Pillared Montmorillonite for the Disproportionation of 1,2,4-Trimethylbenzene

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Disproportionation of 1,2,4-trimethylbenzene was carried out at 200°C to investigate the effect of hydrogen spillover on the stabilization of the catalytic activities of ultrastable Y (USY) zeolite and pillared montmorillonite. The catalytic activity of pillared montmorillonite, the acidity of which is mainly due to Lewis acid sites, became stable against deactivation in the presence of spillover hydrogen. There was a less pronounced effect of spillover hydrogen on the deactivation of USY catalyst treated at 400°C. When the surface acidity of USY was converted from Brønsted to Lewis acidity by treatment at temperatures as high as 750°C, however, the deactivation was effectively suppressed by spillover hydrogen. We concluded from these results that the stabilization of activity by spillover hydrogen is linked to Lewis acidity, irrespective of the type of catalyst. © 1995 Academic Press, Inc.

INTRODUCTION

In recent years, molecular sieves have played an increasingly important role in industrial catalysts. The most popular shape-selective catalyst is a zeolite with a pore size comparable to the dimensions of many simple molecules. As a result, shape-selective conversions of organic compounds on zeolite catalysts have been widely investigated. Pillared clays have also aroused much interest in their application as shape-selective catalysts (1–4). Catalysis by shape-selective materials, however, is most often accompanied by deactivation due to the formation of coke. Since catalyst deactivation caused by coke is industrially a very important problem, considerable effort has been undertaken to specify the active site and the mechanism of coke formation or the nature of coke, as well as its effect on activity and selectivity (5–8).

Rollmann and Walsh (9, 10) and Dejaifve *et al.* (11) emphasized the importance of the zeolite pore system for coke formation. In the case of ZSM-5 with a particular small pore structure, coke formation is prevented by its

shape-selective property. On the other hand, it was reported by Itoh and co-workers (12) that deactivation of a zeolite catalyst could be prevented by controlling acidity even if the zeolite had large pores. A different method of preventing the deactivation of zeolite catalysts was proposed by Gnep *et al.* (13, 14): the addition of a hydrogenating component such as Ni, Pt, or Pd to a zeolite is effective when used in a hydrogen atmosphere.

It was shown in our previous work (15) that deactivation of a pillared montmorillonite catalyst in disproportionation of 1,2,4-trimethylbenzene (1,2,4-TMB) was fully suppressed by loading a small amount of Pd on the pillared montmorillonite or by mixing it with a Pd/Al_2O_3 catalyst and using hydrogen as a carrier gas. The same procedures, however, hardly stabilized the activity of pillared montmorillonite for the alkylation of 1,2,4-trimethylbenzene with methanol (16). It is known (17) that disproportionation can proceed on either Brønsted or Lewis sites, while only Brønsted sites are responsible for alkylation. Thus, we deduce that Lewis acidity plays an important role in the stabilization of catalytic activity. The purpose of this paper is to discuss the stabilizing effect of spillover hydrogen on the catalytic activity of USY zeolite in comparison with pillared montmorillonite.

EXPERIMENTAL

An ultrastable NH_4 Y zeolite with a SiO_2/Al_2O_3 molar ratio of 6 was supplied by Tosoh Co. Ltd. The ultrastable NH_4 Y was calcined at 540°C for 4 h to form a proton-type ultrastable Y zeolite (USY). The framework SiO_2/Al_2O_3 molar ratio was 16, as determined by ^{29}Si-MAS NMR measurement. The clay used in this study was a sodium-type montmorillonite obtained by Kunimine Industry Co., designated Kunipia F. Pillared montmorillonite was prepared by intercalation of montmorillonite with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. The detailed method of intercalation has previously been described (15, 18). The interca-

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lated product was dried at 110°C overnight and calcined at 400°C for 4 h. Hydrogen spillover was effected by mixing USY or pillared montmorillonite with 0.5 wt% Pd/Al_2O_3.

The reaction was carried out at atmospheric pressure in a continuous down-flow system with a fixed bed catalyst. The mixture of acid catalyst and 0.5 wt% Pd/Al_2O_3 or the acid catalyst alone was packed in a reactor and was treated in a stream of hydrogen at the desired temperature (400 or 750°C) for 2 h prior to the reaction of 1,2,4-trimethybenzene disproportionation which was performed at 200°C. 1,2,4-trimethylbenzene was quantitatively supplied from a microfeeder to the reactor through a vaporizer using hydrogen as a carrier gas. The partial pressures of 1,2,4-TMB and hydrogen were 33.44 and 67.89 kPa, 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 capillary separation column with temperature-programmed heating from 60 to 170°C.

The number of catalytically active acid sites was evaluated by the temperature-programmed desorption (TPD) of ammonia. In each TPD experiment, a sample was heated *in vacuo* to 400 or 750°C and was kept at this temperature for 1 h. After ammonia was adsorbed at 250°C for 30 min and evacuated for 30 min, the sample was heated at a rate of 10°C/min from 200 to 700°C. It has been reported (19–21) that the NH_3-TPD profile of zeolites is affected by the evacuation temperature, and a rather long time is needed for desorbing the physically or weakly adsorbed NH_3. Under our measurement conditions, the TPD profile did not change at all when the evacuation time was longer than 30 min.

The nature of the acid sites was determined by infrared spectroscopy using pyridine as a probe molecule. IR spectra were obtained with an IR-810 infrared spectrometer (Japan Spectroscopic Co.). The sample was pressed into a self-supporting wafer (20 mm diameter, ca. 30 mg), which was mounted in a cell and evacuated at the elevated temperature of 400 or 750°C for 1 h. Pyridine was adsorbed on the wafer at 200°C for 1 h and was evacuated at 400°C for 3 h. The measurement was carried out at room temperature.

H–D exchange at OH groups on the acid catalysts was measured by means of infrared spectroscopy. The mixture of acid catalyst and 0.5 wt% Pd/Al_2O_3 (a mixing ratio of 9 to 1 by weight) was pressed into a self-supporting wafer and was mounted in the cell. Afterward the sample was reduced at 400°C for 2 h and was evacuated at the same temperature for 1 h. A pressure of 13.33 kPa deuterium was introduced into the cell at 200°C and the measurement was performed at the same temperature.

Chemisorptive uptakes of carbon monoxide on Pd in 0.5 wt% Pd/Al_2O_3 were measured at ambient temperature

by use of a pulse technique, after reduction at 400 or 750°C.

RESULTS AND DISCUSSION

Table 1 shows the activities of pillared montmorillonite and USY catalysts for the conversion of 1,2,4-TMB. These catalysts were treated at 400°C. The catalytic activity was compared using the data taken in the initial 10–20 min of the run. Under these reaction conditions, disproportionation was the main reaction on both pillared montmorillonite and USY, especially on pillared montmorillonite, with a minor contribution of isomerization. Pillared montmorillonite was selective for disproportionation of 1,2,4-TMB to 1,2,4,5-tetramethylbenzene (1,2,4,5-TeMB), although the catalytic activity of pillared montmorillonite was low compared with that of USY. As shown in Fig. 1, the catalytic activity of pillared montmorillonite decreased rapidly with time on stream. As the deactivated catalyst was mostly regenerated by calcination at 400°C with an evolution of CO_2, coke formation is the main cause of catalyst deactivation.

The catalytic activity of pillared montmorillonite, however, was completely stabilized against deactivation by mixing it with Pd/Al_2O_3 and using hydrogen as a carrier gas, although the initial activity was lowered. In contrast, deactivation was accelerated with the evolution of a detectable amount of hydrogen, when the mixture of pillared montmorillonite and Pd/Al_2O_3 was used in a nitrogen atmosphere after hydrogen reduction. Morevoer, no stabilization of catalytic activity was observed when the mixture was used without reduction. The stabilizing effect appears

TABLE 1

Catalytic Activities of Pillared Montmorillonite and USY[a]

Catalyst:	Pillared montmorillonite	USY	Equilibrium
W/F (g-catalyst min/mol)	2300	200	
% Conversion	25.4	24.9	
Selectivity for			
Disproportionation	90.8	82.4	
Isomerization	9.2	17.6	
Composition of Xylene isomers			
o-	46.2	34.7	(20.3)
m-	44.9	51.2	(55.6)
p-	8.9	14.1	(24.1)
TeMB isomers[b]			
1,2,4,5-	70.0	50.8	(35.4)
1,2,3,5-	26.3	43.3	(51.4)
1,2,3,4-	3.7	5.9	(13.2)

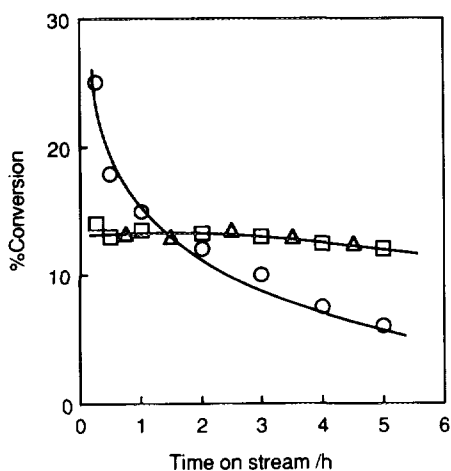[a] Data were taken after 10–20 min of run.
[b] TeMB, tetramethylbenzene.

FIG. 1. The effect of the amount of Pd/Al₂O₃ added to pillared montmorillonite on deactivation: (O) pillared montmorillonite; (□) pillared montmorillonite with Pd/Al₂O₃ (10 wt%); (△) pillared montmorillonite with Pd/Al₂O₃ (50 wt%). Reaction conditions: temperature, 200°C, W/F, 2300 g-catalyst min/mol.

only when the mixture is used in a hydrogen atmosphere after reduction.

Deuterium exchange with protons at the OH groups on pillared montmorillonite was carried out at 200°C. Typical infrared spectra obtained before and after exposure to deuterium for varying periods of time are shown in Fig. 2. Before exposure to deuterium, the absorption band due to OH groups on pillared montmorillonite was observed at 3650 cm⁻¹. When the sample consisting of pillared
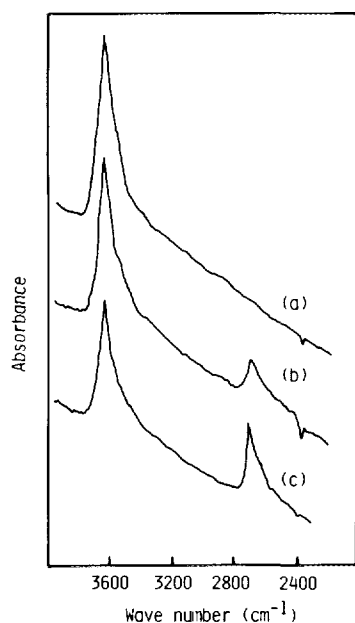

FIG. 2. Deuterium exchange with protons on pillared montmorillonite at 200°C: (a) before exposure to D₂; (b) after exposure to D₂ for 30 min; (c) after exposure for 2 h.

montmorillonite and Pd/Al₂O₃ was exposed to deuterium, the intensity of the OH band decreased gradually and the absorption band due to OD groups appeared at 2700 cm⁻¹. In contrast, the absorption band corresponding to the OH groups was unchanged by exposure to deuterium without Pd/Al₂O₃. Thus, it is deduced that the H–D exchange observed is caused by the migration of deuterium from Pd/Al₂O₃ to pillared montmorillonite. It is therefore considered from these results that the above-mentioned stabilization of catalytic activity is the result of hydrogen spillover.

Figure 3 shows the time-dependent variation of the catalytic activity of USY zeolite which had been pre-treated at 400°C. Deactivation of USY was moderated slightly by mixing it with Pd/Al₂O₃ and using hydrogen as a carrier. The catalytic activity of USY zeolite was lowered by high temperature treatment, but it did not affect the degree of deactivation. As shown in Fig. 4, however, deactivation of the USY catalyst was effectively prevented by spillover hydrogen when the USY was mixed with Pd/Al₂O₃ and reduced at 750°C.

As shown in Fig. 5, interparticle migration of deuterium from Pd/Al₂O₃ to USY was confirmed. When USY was in contact with deuterium in the presence of Pd/Al₂O₃, OH absorption bands at 3740 and 3580 cm⁻¹ disappeared and OD bands appeared at 2750 and 2640 cm⁻¹. H–D exchange at OH groups on USY took place only when Pd/Al₂O₃ was present. OH groups on USY were completely converted to OD groups by exposure to deuterium for 30 min, while the band due to the OH groups was observed on pillared montmorillonite even after exposure to deuterium for 2 h. Pillared montmorillonite showed an OH absorption band even after adsorption of pyridine at 200°C. In contrast, the OH bands of USY disappeared by pyridine
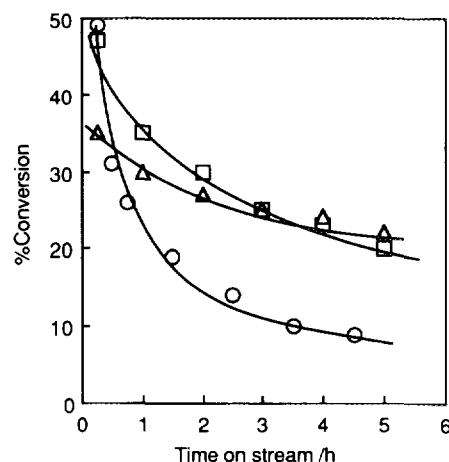

FIG. 3. The effect of the amount of Pd/Al₂O₃ added to USY on deactivation: (O) USY; (□) USY with Pd/Al₂O₃ (50 wt%); (△) USY with Pd/Al₂O₃ (90 wt%). Reaction conditions: temperature, 200°C, W/F, 500 g-catalyst min/mol. The catalyst was reduced at 400° C.
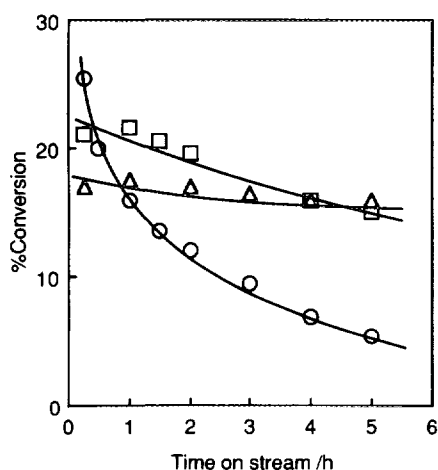
FIG. 4. The effect of the amount of Pd/Al₂O₃ added to USY on deactivation: (O) USY; (□) USY with Pd/Al₂O₃ (50 wt%); (△) USY with Pd/Al₂O₃ (75 wt%). Reaction conditions: temperature, 200°C, W/F, 500 g-catalyst min/mol. Catalyst was reduced at 750°C.

adsorption. The difference in the rate of H–D exchange between USY and pillared montmorillonite may be related to the strength of the Brønsted acidity, namely the OH bond strength. Since the extent of H–D exchange reaction is connected with the accessibility of OH groups, it is also possible that the OH groups on pillared montmorillonite are less accessible than those on USY.

The role of spiltover hydrogen in the stabilization of catalytic activity is considered as follows: Coke precursors are eliminated from acid sites by spiltover hydrogen before they have a change to undergo further coking reactions on acid sites. As a result, the overall deactivation rate declines. According to this concept, there is a possibility that the degree of stabilization of the catalytic activ-

ity by spiltover hydrogen is influenced by the ratio of metal sites to acid sites as well as by the nature of the acid sites, because the rates of hydrogen spillover and coke formation are related to the number of metal sites and acid sites, respectively.

In the case of USY zeolite, the degree of stabilization increased with increasing amount of Pd/Al₂O₃ added (Figs. 3 and 4). As shown in Fig. 1, however, the stabilization of catalytic activity of pillared montmorillonite was brought about by the addition of a small amount of Pd/Al₂O₃, and the degree of stabilization was independent of the amount of Pd/Al₂O₃ added. USY had a large number of acid sites compared with pillared montmorillonite. Treatment of USY at 750°C reduced the number of acid sites as a result of the conversion of Brønsted sites to Lewis sites. Thus, the less effective stabilization observed for USY may be due to a small ratio of metal to acid sites.

In order to express the degree of deactivation quantitatively, the deactivation of USY and pillared montmorillonite was expressed using the equation reported by Vorrhies (22).

$$A_t = A_0 t^{-n},$$

where t stands for time on stream and n is a deactivation factor which increases with increasing deactivation rate. A_0 is the initial activity and A_t is the activity at t. This equation fitted the experimental results satisfactorily. The degree of catalyst deactivation will be discussed in terms of the n value.

Metallic dispersions of Pd/Al₂O₃ after reduction at 400 and 750°C were determined to be 0.42 and 0.03, respectively, from chemisorptive uptakes of carbon monoxide. The number of active sites was evaluated by TPD of
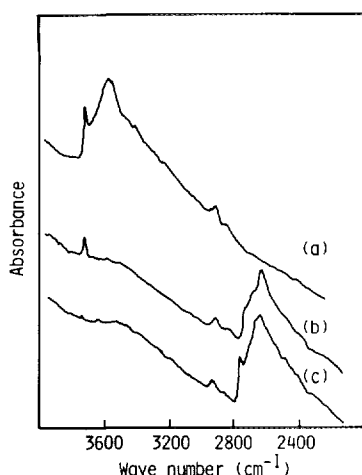

FIG. 5. Deuterium exchange with protons on USY at 200°C. (a) before exposure to D₂; (b) after exposure to D₂ for 30 min; (c), after exposure for 2 h.
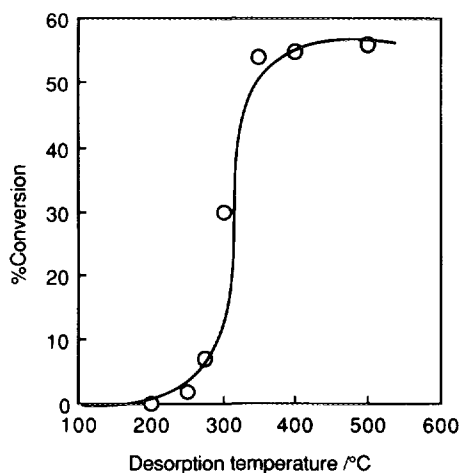

FIG. 6. The effect of the desorption temperature of ammonia on the catalytic activity of USY. Reaction conditions: temperature, 200°C, W/F, 500 g-catalyst min/mol.

ammonia. Figure 6 shows the catalytic activity of USY zeolite after preadsorbing ammonia as a function of evacuation temperature. As the catalytic activity appeared only when preadsorbed ammonia was removed above 250°C, the number of catalytically active acid sites was determined from the amount of ammonia desorbed above 250°C.

Figure 7 shows the relation between the n value and the amount of Pd/Al$_2$O$_3$ added to pillared montmorillonite or USY. The catalytic activity of USY became more stable against deactivation with an increase in the amount of Pd/Al$_2$O$_3$ added. Figure 8 illustrates the n value as a function of the ratio of metal sites to acid sites. At any ratio of metal to acid sites, USY gave a larger n value than pillared montmorillonite, and high temperature treatment of USY reduced the n value. Thus, it is difficult to assign the less effective stabilization observed for USY as an influence of metal sites per acid site.

The acidic nature of the active sites was determined by infrared spectroscopy using pyridine as a probe molecule. The catalytic activity of USY zeolite after preadsorbing pyridine was strongly dependent on the evacuation temperature. Since the catalytic activity appeared only when preadsorbed pyridine was evacuated and removed above 400°C, the infrared spectra of adsorbed pyridine were measured after evacuation at 400°C. The catalytically active sites on pillared montmorillonite were mostly Lewis type, while those on USY zeolite consisted to Brønsted and Lewis sites. Treatment of USY at 750°C reduced the number of Brønsted acid sites as a result of conversion of Brønsted sites to Lewis sites, although some Brønsted sites still remained.

Figure 9 shows the n-value detemined at constant ratios of metal to acid sites as a function of the percentage of
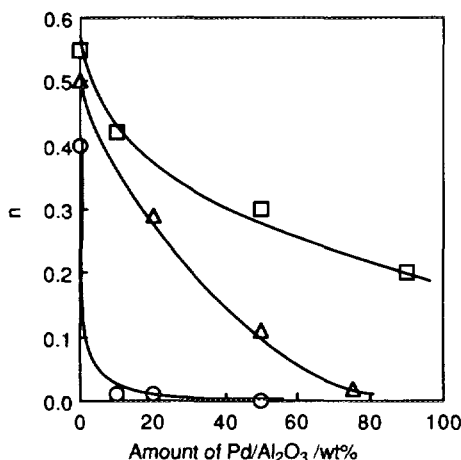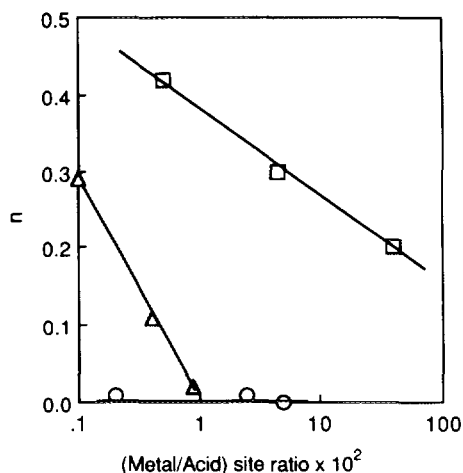

FIG. 8. Relation between the n value and the ratio of metal sites to acid sites; (O) pillared montmorillonite; (□) USY treated at 400°C; (△) USY treated at 750°C.

Brønsted acid sites to total acid sites. Here, the molar extinction coefficients reported by Hughes and White (23) were used for the calculations. The percentages of Brønsted acid sites on pillared montmorillonite and USY treated at 400°C or at 750°C were determined to be 0, 60, and 24%, respectively, by the absorption bands of pyridine adsorbed on Brønsted (1540 cm^{-1}) and Lewis (1450 cm^{-1}) sites. It is obvious from Fig. 9 that the activity of the Lewis acidic catalyst was stabilized more effectively by spiltover hydrogen than that of the Brønsted acidic catalyst. In the case of the catalyst where the surface acidity was mainly Lewis acidic, the stabilizing effect of spiltover hydrogen appeared even at a small metal/acid sites ratio. On the other hand, a large metal/acid sites ratio or a large amount of spiltover hydrogen was required to prevent deactivation of the Brønsted acidic catalyst. The difference in the stabilizing effect of spiltover hydro-

FIG. 7. Relation between the n value and the amount of Pd/Al$_2$O$_3$ added to acid catalysts; (O) pillared montmorillonite; (□) USY treated at 400° C; (△) USY treated at 750°C.
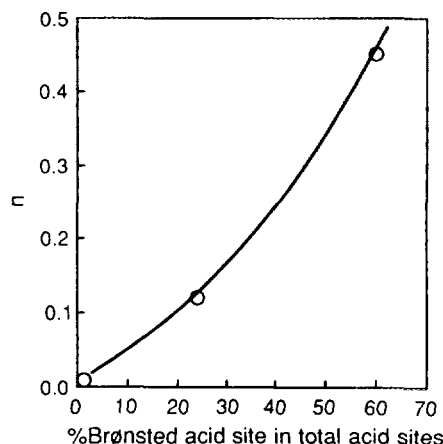

FIG. 9. Effect of the acidic property of a catalyst on the n value at metal/acid sites ratio of 0.005.

gen seems to result from different mechanisms operative in coke formation on Lewis and Brønsted acid sites, although these are not obvious at present.

As shown in Figs. 1 and 4, the stabilization of catalytic activity by spiltover hydrogen was accompanied by a decrease in disproportionation activity. These results suggest that spiltover hydrogen acts on disproportionation as well as coke formation. It has been proposed that disproportionation proceeds via a benzylic intermediate on Lewis acid sites and via a benzenium intermediate on Brønsted sites (17). Coke formation on Lewis acid sites is also considered to proceed through the benzylic intermediate, while the benzenium carbocation will be an intermediate for coke formation on Brønsted acid sites. The stabilization of catalytic activity by spiltover hydrogen is considered to be caused by the interaction between spiltover hydrogen and the intermediate for coke formation, resulting in a decrease in the amount of coke precursor. As the decay in the activity of a Lewis acidic catalyst is effectively prevented by spiltover hydrogen compared with that of a catalyst having Brønsted acid sites, we deduce that spiltover hydrogen interacts far more strongly with the benzylic carbocation formed on Lewis sites than with the benzenium carbocation on Brønsted sites.

CONCLUSION

The catalytic activity of pillared montmorillonite exhibiting Lewis acidity was stabilized against deactivation by spiltover hydrogen. Spiltover hydrogen stabilized the catalytic activity of USY less effectively than that of pillared montmorillonite, although deuterium exchange with protons at the OH groups on USY was remarkably faster than on pillared montmorillonite. Deactivation of USY, however, was effectively suppressed by spiltover hydrogen when the acid sites were converted from Brønsted to Lewis type by high temperature treatment. In the case of pillared montmorillonite, the degree of stabilization was independent of the metal/acid sites ratio, while the deactivation of USY having Brønsted sites varied with the metal/acid sites ratio. These results suggest that a large amount of spiltover hydrogen is required to prevent the deactivation of Brønsted acidic catalyst. We deduce, on the basis of the mechanism of coke formation, that

spiltover hydrogen interacts far more strongly with the intermediate formed on Lewis acid sites than that on Brønsted acid sites.

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