Hydrogen spillover on Ni(S)/Al_2O_3–ultrastable Y zeolite and its effect on xylene isomerization

Ming-Gang Yang, Ikusei Nakamura and Kaoru Fujimoto [1]

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Received 8 November 1995; accepted 15 February 1996

The catalytic activity of ultrastable Y zeolite (USY) for *m*-xylene isomerization in the presence of hydrogen is markedly promoted by physically mixing with Ni(S)/Al_2O_3 under the conditions of 603 K and 1.0 MPa. The study on H–D exchange of the OH groups on the USY zeolite surface showed that the exchange rate in Ni(S)/Al_2O_3–USY was five times higher than that of USY alone. It was considered that active hydrogen species, formed on Ni(S) sites and spilled over to Al_2O_3 and then to USY, promote the acid catalysis on the USY.

Keywords: hydrogen spillover; xylene isomerization; nickel sulfide; Y-type zeolite; H–D exchange; FT-IR spectrum

1. Introduction

The diffusion of active species on the surface of catalysts is of great importance in the explanation of the kinetics and mechanisms of many heterogeneous catalytic reactions. The migration of a sorbed species, such as hydrogen, from one solid phase, such as a metal where it is easily adsorbed and dissociated, onto another solid phase, such as an oxide, in contact with the first, where it does not directly adsorb, has been defined as spillover [1–3]. One can find experimental evidence of hydrogen spillover in many works, especially in infrared spectroscopy [4–6], often combined with H–D exchange and temperature-programmed desorption [7,8]. The rate of H–D exchange and the temperature at which H–D exchange can occur are dramatically different depending upon the presence or absence of active metals [9] on the oxides or zeolites. Especially supported noble metals such as Pt [10] or Rh [5] promote markedly the H–D exchange of OH groups on Al_2O_3 and on Y type zeolite [11–14].

Xylene isomerization is a commercially important process to maximize the yield of *p*-xylene from C_8 aromatics and has been commercially conducted on metal-supported solid acids under hydrogen atmosphere. Also, most commercial hydrocracking catalysts contain sulfided nickel Ni(S) and solid acid [15], so it is important to clarify the role of the Ni compound in the catalytic reactions. The present authors have found that the hydroisomerization of *n*-paraffins on noble metal–zeolite systems is closely related to hydrogen spillover [16], and that disproportionation of toluene [17,18] and isomerization of xylene on Y-zeolite are effectively catalyzed by mechanical mixtures of transition-metal sulfides supported on Al_2O_3 or SiO_2 and Y-zeolite in the presence of pressurized hydrogen. These facts have been interpreted as that the spilt-over hydrogen through Ni(S) sites from gas phase hydrogen plays important roles in the acid catalysis. Hence, in the present work, we have investigated the phenomenon and kinetics of hydrogen spillover from Ni(S) sites to the surface of ultrastable Y-type zeolite (USY).

2. Experimental

USY zeolite with a SiO_2/Al_2O_3 molar ratio of 8 was obtained from a commercially available one. NiO (2.5 wt% Ni)/Al_2O_3 was prepared by impregnating a commercially available γ-Al_2O_3 with an aqueous $Ni(NO_3)_2$ solution, followed by calcination in air at 723 K. Then NiO/Al_2O_3 was sulfided to Ni(S)/Al_2O_3 with a gas mixture of H_2 and H_2S (4 : 1) at 673 K. The Ni(S)/Al_2O_3–USY sample was prepared by physically mixing Ni(S)/Al_2O_3 and USY zeolite in a certain proportion.

The *m*-xylene isomerization reaction was run in a fixed bed continuous flow type microreactor (made of stainless steel tube, 8 mm inner diameter) apparatus under the standard conditions of total pressure of 1.0 MPa, molar ratio of H_2 (or N_2) : *m*-xylene = 4 : 1, $W/F = 2.7$ g h/mol, and reaction temperature of 603 K. Reaction products were analyzed with an on-line FID gas chromatograph using a packed column (5% Bentone 34 + 5% di-isodecyl phthalate, support: Neopak IA). The amount of deposited coke on the various catalysts was measured with a MT-2 C.H.N. element analyzer (Yanagimoto Mfg. Co., Ltd.).

All samples for the H–D exchange reaction were pressed to wafers (∅ 8 mm, 15–20 mg/cm^2) under a

---

[1] To whom correspondence should be addressed.

pressure of 60 MPa. The exchange reactions were followed using a Perkin-Elmer model 1800 series infrared spectrometer with a measuring quartz cell having CaF_2 windows. After evacuation (10^{-6} kPa) at 723 K for 5 h, the sample was cooled to the measuring temperature, then deuterium gas (62.5 kPa) was introduced into the sample cell and the spectra of H–D exchange were recorded.

Table 1
Amount of coke deposited on catalyst after *m*-xylene transformation. Reaction conditions: $T = 603$ K, $P = 1.0$ MPa, $W/F = 2.71$ g-cat h mol^{-1}, $H_2(N_2)$/*m*-xylene (mol) = 4 : 1, time on stream = 5 h

Catalyst	Carrier gas	Amount of coke (%)
Ni(S)/Al_2O_3	H_2	0.14
Ni(S)/Al_2O_3–USY	H_2	7.9
Ni(S)/Al_2O_3–USY	N_2	14.2
Al_2O_3–USY	H_2	10.3
Al_2O_3–USY	N_2	11.2

3. Results and discussion

Fig. 1 shows the catalytic activity of hybrid catalysts containing USY zeolite for *m*-xylene isomerization. As it is clear from the figure, although Ni(S)/Al_2O_3 showed negligible catalytic activity, Ni(S)/Al_2O_3–USY showed much higher catalytic activity and better stability than the Al_2O_3–USY catalyst. The better catalytic performances appeared only in the presence of gaseous hydrogen. In the absence of hydrogen, in contrast, it showed even worse activity than the Ni(S)-free catalyst did. On the other hand, the Ni(S)-free catalyst was scarcely affected by gaseous hydrogen in its catalytic performances.

The higher catalytic activity of the Ni(S)/Al_2O_3–USY in hydrogen atmosphere cannot be only attributed to the effect of Ni(S) on suppression of coke deposition on the USY surface. It was observed that Ni(S) rarely suppressed coke formation on the USY zeolite in toluene disproportionation on the Ni(S)/SiO_2–USY hybrid catalyst [17], but it could effectively decrease coke deposited on the Al_2O_3 support. So the difference between Ni(S)/Al_2O_3–USY and Al_2O_3–USY in the amount of coke (in H_2 atmosphere), as shown in table 1, should be considered to be due to the decrease of coke deposited on Ni(S)/Al_2O_3 (only 0.14%). Therefore, since the amount of coke deposited on the USY zeolite during the reaction was almost similar, the difference in catalytic activity should not be attributed to the difference in the number of acid sites on the USY zeolite but to the effectiveness of each acid site. The present authors have shown that the hybrid catalyst composed of Pt/SiO_2 or Pd/SiO_2 and H-ZSM-5 shows excellent catalytic activity for the hydroisomerization of paraffins in spite of the rather poor activity of each component and have claimed that the spilt-over hydrogens (H^+) on acid sites promote the activation of paraffin molecules to carbenium ions and stabilize the isomerized carbenium ions to isomerized molecules [19]. In the present system, the possibility of hydrogen spillover from Ni(S)/Al_2O_3 to USY and its participation in the acid catalyzed isomerization of xylene is also proposed.

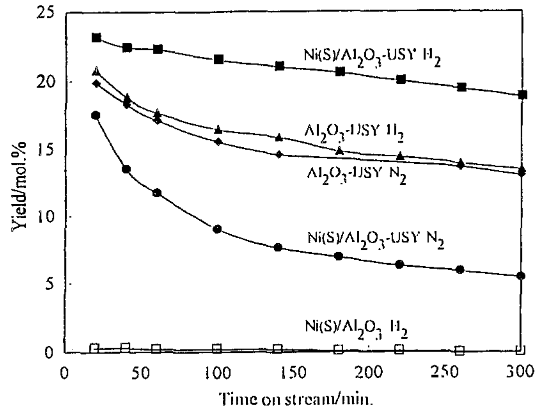

Fig. 1. Effect of Ni(S) on *m*-xylene isomerization yield in H_2 or N_2 at 603 K, 1.0 MPa.

A series of infrared spectra of the USY zeolite surface is shown in fig. 2a. In spectrum A, corresponding to the freshly prepared sample, three strong features are observed in the OH stretching vibration region from 3740 to 3450 cm^{-1}. The feature near 3730 cm^{-1} is attributed to a silanol OH stretching vibration on the zeolite surface. The feature in the region of 3622 cm^{-1} is attributed to the OH group located in the supercages, and the third sharp peak (3557 cm^{-1}) to the OH group located in the sodalite cages or hexagonal prisms of USY zeolite [20,21]. Both the latter two OH groups are acidic OH groups. They play an important role in the acid catalysis as Brønsted acid sites. The spectra B and C correspond to continued $D_2(g)$ exchange with OH species at

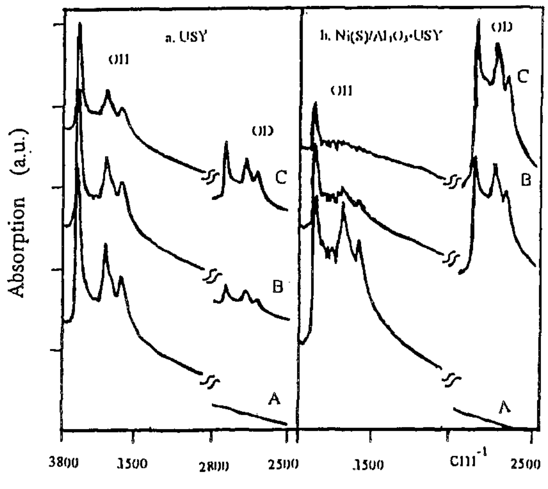

Fig. 2. Spectra of H–D exchange on USY in (a) USY zeolite alone and (b) Ni(S)/Al_2O_3–USY at 523 K and 62.5 kPa. Time exposed to D_2: (A) 0; (B) 2; (C) 30 min.

P_{D_2} = 62.5 kPa and at 523 K. It can be seen that a slight decrease in the intensity of the OH peaks is accompanied by the development of lower-wavenumber features in the region of 2750–2500 cm^{-1}. The three OD species arise directly from the three observed OH species because they exhibit very similar ν_{OH}/ν_{OD} ratios ($\sim$ 1.357).

The infrared spectra for Ni(S)/Al_2O_3–USY shown in fig. 2b are similar to the infrared spectra of the USY sample. It is noteworthy that the H–D exchange rate of the mixture of Ni(S)/Al_2O_3 and USY zeolite is very high at 523 K. As shown in fig. 3, when the Ni(S)/Al_2O_3–USY sample was exposed to D_2(g) for 2 min, the H–D exchange of OH groups on the USY zeolite for Ni(S)/Al_2O_3–USY was 72%, five times more than that for USY alone. These results indicate that Ni(S) has a promoting effect on the H–D exchange on USY. As one of the components in mechanically mixed Ni(S)/Al_2O_3–USY, under the same reaction conditions, Ni(S)/Al_2O_3 also showed 3.5 times higher H–D exchange rate than Al_2O_3 at the initial period of the exchange, showing that Ni(S) on the Al_2O_3 promotes the H–D exchange of the OH group on the Al_2O_3 surface, as shown in fig. 4. This effect may be considered as a spillover process, in which the deuterium gas would dissociate at Ni(S) sites to produce reactive deuterium species. These species would migrate from the Ni(S) sites to the Al_2O_3 surface and exchange with OH groups on the Al_2O_3 surface.

The presence of Ni(S) in the Ni(S)/Al_2O_3–USY hybrid sample also accelerated largely the H–D exchange rate occurring on the USY zeolite surface. This could be explained as the Ni(S) becoming an active site for dissociating deuterium (or hydrogen) molecules as in the case of an active carbon carrier [22]. Thus, the large amount of deuterium may enter the Al_2O_3 surface through the Ni(S) sites, first, the reactive deuterium species would exchange with the OH group on the Al_2O_3 surface, and then it would further migrate into the USY surface and exchange with the OH groups on the USY zeolite.

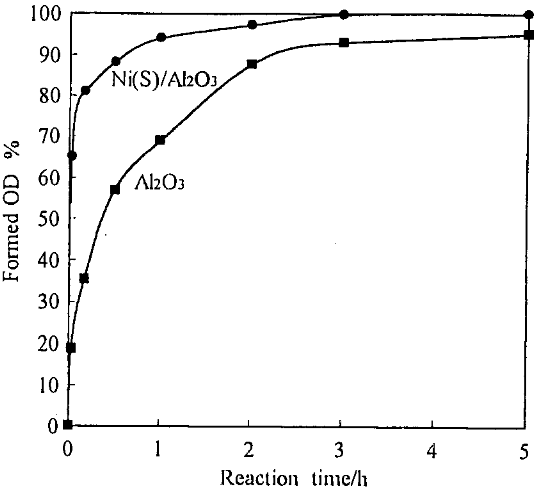

Fig. 4. Effect of Ni(S) on H–D exchange rate over Al_2O_3 surface at 523 K and 62.5 kPa.

Under a certain range of reaction temperature the Ni(S) as an active site plays an important role in H–D exchange on the USY surface. When the reaction temperature decreased to 423 K, the H–D exchange rate on the USY surface for the samples Ni(S)/Al_2O_3–USY, Al_2O_3–USY and USY alone was nearly equal, as shown in fig. 5. This fact should be attributed to the fact that, at such a low temperature, the deuterium gas could not be dissociated on the Ni(S) site and, therefore, the H–D exchange could occur directly between gaseous deuterium and the USY surface OH groups. Hence, in this case, the H–D exchange on the USY surface occurred through the same mechanism in which the deuterium in the gas phase would directly exchange with the OH groups on the surface, not through the Ni(S) sites as in the case of the Ni(S)/Al_2O_3–USY sample at higher temperatures.

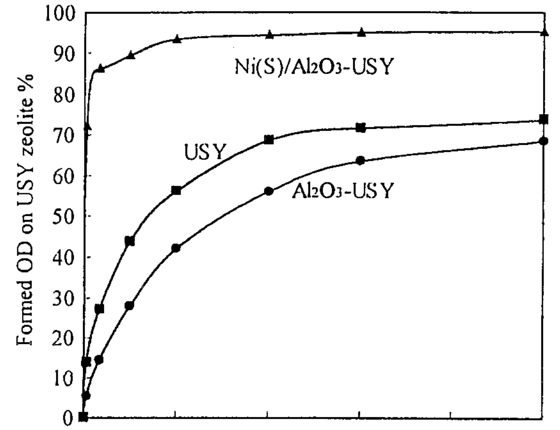

Fig. 3. H–D exchange rate on USY surface in various catalysts at 523 K and 62.5 kPa.

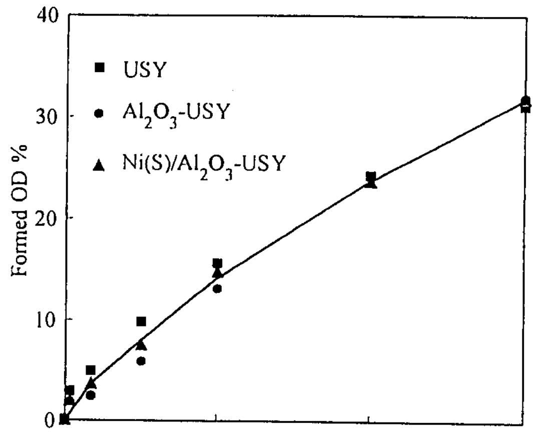

Fig. 5. H–D exchange rate on USY surface in Ni(S)/Al_2O_3–USY and Al_2O_3–USY and USY alone at 423 K and 62.5 kPa.

With increasing reaction temperature the activity of the Ni(S) for dissociating deuterium gas increased as shown in fig. 6. The rate of H–D exchange on the Ni(S)/Al_2O_3–USY sample is larger than that on Al_2O_3–USY at the temperature in the range of 465–523 K. This suggests that at this reaction temperature range the Ni(S) can effectively dissociate the deuterium (or hydrogen) molecule and most reactive deuterium species for H–D exchange in the Ni(S)/Al_2O_3–USY sample could enter the USY surface through the Ni(S) sites. This means that the H–D exchange on the USY surface in the Ni(S)/Al_2O_3–USY sample would involve two processes. The first is the spillover of deuterium from the Ni(S) site to the Al_2O_3 surface and its migration to the USY surface as shown in fig. 7 and the second, which is a minor route, is the direct exchange of gaseous deuterium with the OH groups on the surface.

Because of the large difference between these two processes in the rate of hydrogen transfer under the reaction conditions, the main route on the Ni(S)/Al_2O_3–USY catalyst is the spillover route. Therefore, the promotive effect of hydrogen on xylene isomerization, which essentially needs no hydrogen in its stoichiometry, on the Ni(S)/Al_2O_3–USY hybrid catalyst should be closely related to the spillover of hydrogen from gas phase to acid sites on the USY though the Ni(S)/Al_2O_3 component.

4. Conclusion

The activity of *m*-xylene isomerization on solid acidic catalyst (ultrastable Y zeolite) in the presence of hydrogen is markedly promoted by a nickel sulfide supported on alumina (Ni(S)/Al_2O_3). The catalyst Ni(S)/Al_2O_3–USY is a physical mixture of Ni(S)/Al_2O_3 and USY zeolite. Such a promotive effect of Ni(S) on the acid catalysis is closely related to the process of hydrogen spillover, in which gaseous hydrogen is dissociated on the Ni(S) site to form active hydrogen species, and then the hydrogen species spill over to the Al_2O_3 surface and to the USY surface. This spilt-over hydrogen could affect xylene conversion on acid sites in the USY surface. This assumption is demonstrated by the FT-IR spectrum of H–D exchange on the same catalyst system. At the initial period of H–D reaction, the rate of H–D exchange of Ni(S)/Al_2O_3–USY is five times higher than that of the USY zeolite alone. These results have shown that most deuterium (or hydrogen) species for H–D exchange of OH groups on the USY zeolite surface come from Ni(S) active sites by the spillover process and the spilt-over hydrogens promote acidic catalytic reactions.

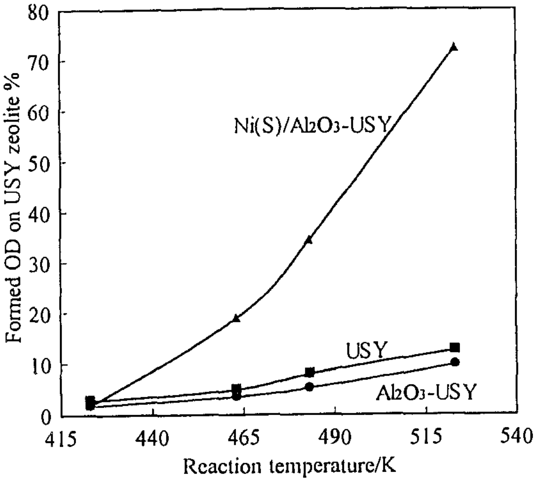

Fig. 6. Effect of temperature on H–D exchange rate on USY surface in various catalysts at 62.5 kPa exposed to D_2 for 2 min.

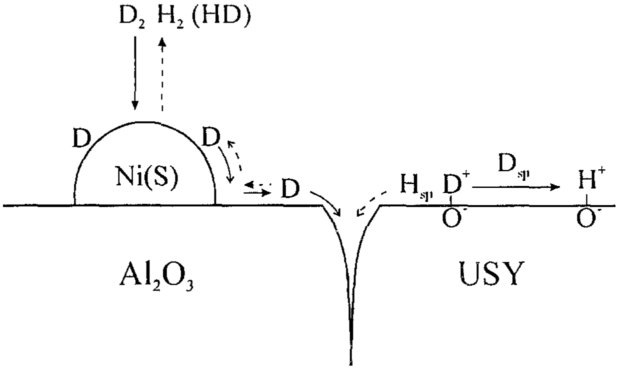

Fig. 7. Model of hydrogen spillover on the Ni(S)/Al_2O_3–USY system.

References

[1] W.C. Conner, G.M. Pajonk and S.J. Teichner, in: *Advances in Catalysis*, Vol. 34, eds. D.D. Eley, P.W. Selwood and P.B. Weisz (Academic Press, New York, 1986) p. 1.

[2] S. Asaoka, K. Masamizu, K. Fujimoto and T. Kunugi, Nihon Kagaku Kaishi (1975) 1293.

[3] K. Fujimoto and S. Toyoshi, in: *Proc. 7th Int. Congr. on Catalysis*, Tokyo 1980, eds. T.S. Seiyama and K. Tanabe, p. 235.

[4] D. Bianchi, M. Lacroix, G.M. Pajonk and S.J. Teichner, J. Catal. 59 (1979) 467.

[5] R.R. Cavanagh and J.T. Yates Jr., J. Catal. 68 (1981) 22.

[6] J.A. Rabo, C.L. Angell, P.H. Kasai and V. Schomaker, Discussions Faraday Soc. 71 (1966) 328.

[7] R. Kramer and M. Andre, J. Catal. 58 (1979) 287.

[8] J.M. Parera, E.M. Traffano, J.C. Musso and C.L. Pieck, in: *Stud. Surf. Sci. Catal.*, Vol. 17, eds. G.M. Pajonk, S.J. Teichner and J.E. Germain (Elsevier, Amsterdam, 1983) p. 101.

[9] W.C. Conner, J.F. Cevallos-Candau, N. Shah and V. Haensel, in: *Stud. Surf. Sci. Catal.*, Vol. 17, eds. G.M. Pajonk, S.J. Teichner and J.E. Germain (Elsevier, Amsterdam, 1983) p. 31.

[10] J.L. Carter, P. Corneil, D.J.C. Yates, P.J. Lucchesi and J.H. Sinfelt, J. Phys. Chem. 69 (1965) 3070.

[11] R.V. Dmitrieve, K.H. Steinberg, A.N. Detjuk and C.M. Minacheve, in: *Stud. Surf. Sci. Catal.*, Vol. 17, eds. G.M. Pajonk, S.J. Teichner and J.E. Germain (Elsevier, Amsterdam, 1983) p. 17.

[12] U. Rolard, H. Winkler and K.H. Steinberg, in: *Second Conf. on Spillover*, eds. K.H. Steinberg, Karl-Marx-Universität (Leipzig, 1989) p. 63.

[13] R. Salzer, J. Dressler, K.H. Steinberg, U. Roland, H. Winkler and P. Klaeboe, Vibr. Spectrosc. 1 (1991) 363.

[14] U. Roland, R. Salzer and S. Stolle, in: *Stud. Surf. Sci. Catal.*, Vol. 84, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) p. 1231.

[15] J.W. Ward, in: *Preparation of Catalyst 3*, eds. G. Poncelet, P. Grange and P. Jacobs (Wiley, New York, 1983) p. 587.

[16] K. Fujimoto, K. Maeda and K. Aimoto, Appl. Catal. A 91 (1992) 81.

[17] M.-G. Yang, I. Nakamura and K. Fujimoto, Appl. Catal. A 127 (1995) 115.

[18] I. Nakamura, R. Iwamoto and A. I-ino, in: *Stud. Surf. Sci. Catal.*, Vol. 77, eds. T. Inui, K. Fujimoto, T. Uchijima and M. Masai (Elsevier, Amsterdam, 1993) p. 77.

[19] I. Nakamura, A. Zhang and K. Fujimoto, in: *Stud. Surf. Sci. Catal.*, Vol. 94, eds. H.K. Beyer, H.G. Karge, I. Kiricsi and J.B. Nagy (Elsevier, Amsterdam, 1995) p. 464.

[20] M.A. Makarova and J. Dwyer, J. Phys. Chem. 97 (1993) 6337.

[21] D. Barthomeuf, in: *Stud. Surf. Sci. Catal.*, Vol. 5, eds. B. Imelik, C. Naccache, Y. Ben Taarit, J.C. Vedrine, G. Coudurier and H. Praliaud (Elsevier, Amsterdam, 1980) p. 55.

[22] K. Fujimoto, in: *Stud. Surf. Sci. Catal.*, Vol. 77, eds. T. Inui, K. Fujimoto, T. Uchijima and M. Masai (Elsevier, Amsterdam, 1993) p. 9.