Promoting effect of hydrogen spillover on pyridine migration adsorbed on Lewis acid sites in USY zeolite

Ryo Ueda, Keiichi Tomishige and Kaoru Fujimoto *

Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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The effect of hydrogen spillover over Pd/SiO_2 + USY on pyridine chemisorbed on acid sites of USY zeolite was investigated. According to FTIR measurement, pyridine adsorbed on Lewis acid sites migrated to Brønsted acid sites under hydrogen-flowing atmosphere. The rate of migration was drastically promoted by physically mixed Pd/SiO_2 catalysts. This suggests that spilt-over hydrogen enhance the migration of pyridine adsorbed on Lewis acid sites.

Keywords: hydrogen spillover, zeolite, hybrid catalyst, Brønsted and Lewis acid sites, pyridine migration

1. Introduction

Spilt-over hydrogen is known to have a strong effect on catalytic reaction systems on solid acid catalysts. Nakamura et al. found that a hybrid catalyst, i.e., the physical mixture of Pt/SiO_2 and HZSM-5, was very effective for the isomerization of n-pentane, n-hexane and other paraffinic hydrocarbons under hydrogen atmosphere [1–5]. They concluded that both high conversion and high selectivity were due to the effect of hydrogen spillover, and suggested that spilt-over hydrogen has two forms, H^+ and H^-, and that the former regenerates Brønsted acid sites while the latter stabilizes the carbenium ion intermediate by its hydrogenation. Hattori et al. pointed out that hydrogen promoted the activity of cumene cracking over Pt/SO_4^{2-}–ZrO_2 and inhibited its deactivation. It is expected that Brønsted acid sites generated from spilt-over hydrogen act as the active sites for the catalytic reaction [6]. Hosoi et al. found that, when Pt/SO_4^{2-}–ZrO_2 was used as a catalyst for skeletal isomerization of n-pentane in the presence of hydrogen, it showed not only high activity but also persistence of the activity for a long period, more than 1000 h. They explained that the hydrogen had the effect on the removal of coke formed during the reaction by hydrogenating it [7]. It has been reported that spillover of hydrogen occurs even when a physical mixture of a supported metal catalyst and zeolite, namely hybrid catalyst, is exposed to hydrogen atmosphere [8]. Hydrogen molecules in gas phase are dissociated on the metal surface to atomic hydrogen at first and then migrate onto the support surface, and further, onto the surface of adjacent zeolite particles. Zhang et al. reported that pyridine chemisorbed on acid sites of zeolite could be hydrogenated into piperidine by spilt-over hydrogen [9].

There is a lot of discussion about the nature of spilt-over hydrogen species, such as H atoms, radicals, H^+ and H^- ions, ion pairs, H_3^+ species or protons and electrons [10,11]. Protons formed from spilt-over hydrogen are suggested to act as catalytic active sites for acid-catalyzed reactions [12–14]. The present authors have pointed out the possibility of the participation of H^+ and H^- which are produced from spilt-over hydrogen in the hydro-isomerization or hydrocracking of aliphatic hydrocarbons over Pt- or Pd-supported zeolite or the physically mixed Pt/SiO_2-protonic zeolite system [1,5,15]. Roland et al. have given a clear proof for the electrical charge of the spilt-over species, which was obtained through H–D exchange studies on the influence of a homogeneous magnetic field. The migration of spilt-over hydrogen (deuterium) in Pt/NaY–HNaY catalyst was hindered, which was attributed to the influence of the Lorentz force on the electrically charged moving particles [16,17].

Pyridine is a typical organic base and can be chemisorbed on both Brønsted (B) acid sites and Lewis (L) acid sites in zeolite catalysts, while pyridinium ions and coordinately bonded pyridine complexes are formed on B and L sites, respectively, giving different IR-adsorption bands on each occasion [18–20]. Zhang et al. reported that they found by FTIR that pyridine strongly adsorbed on acid sites of H-ZSM-5 was hydrogenated over Pt/H-ZSM-5 (0.5 wt%) and a Pt-hybrid catalyst (a physically mixed catalyst with a weight ratio of Pt/SiO_2 (2.5 wt%) : H-ZSM-5 = 1 : 4) to adsorbed piperidine in the presence of gaseous hydrogen at around 473 K, whereas no such phenomenon was observed on either H-ZSM-5 or Pt/SiO_2, and claimed that this phenomenon revealed the occurrence of hydrogen spillover from Pt sites to zeolite acid sites (Brønsted and Lewis). They also gave a quantitative description of the reaction which was attained by calculating and measuring the amount of zeolite acid on the basis of pyridine chemisorption and hydrogen consumption [9]. Fan et al. reported that this hydrogenation rate was dependent not only on the nature of supported metals in the hybrid catalyst system but also on the acidic strength of zeolite catalysts [21].

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* To whom correspondence should be addressed.

In this letter, we report the behavior of pyridine adsorbed on Brønsted and Lewis acid sites of USY zeolite by means of FTIR observation under varying pyridine coverage and atmosphere, which led us to a new concept on the behavior of spilt-over hydrogen and the mechanism of hydrogenation of adsorbed pyridine.

2. Experimental

Supported Pd/SiO_2 (2.5 wt% loading) was prepared by impregnating a commercially available SiO_2 (Aerosil 380, BET specific surface area 380 m^2/g) with aqueous solution of $PdCl_2$. Dilute HCl aqueous solution was added to make $PdCl_2$ soluble to water. After impregnation, the sample was dried at 393 K for 12 h and was calcined at 723 K in air for 3 h. The hybrid catalyst was prepared by co-grinding the mixture of above Pd/SiO_2 and H-USY (Tosoh Co., HSZ-330HUA, $SiO_2/Al_2O_3 = 6.3$). In this study, the weight ratio of the hybrid catalyst is $Pd/SiO_2 : \text{H-USY} = 1:19$.

Pyridine chemisorption and the introduction of H_2 gas on the hybrid catalysts were carried out in a quartz-made *in situ* IR cell with KBr windows connected to the vacuum closed circulating system and atmospheric gas-flow system. All samples were pressed into self-supporting wafers (pressure 400 kg /cm^2) with diameter of 10 mm and weight of about 10 mg. The samples were reduced in flowing H_2 at 673 K for 1 h and outgassed *in vacuo* at 773 K for 1 h as pretreatment procedure. The samples were exposed to 1.0 kPa vapor of pyridine at 423 K for 30 min, followed by evacuation at 423 K for 30 min in order to remove gaseous and weakly adsorbed pyridine. In this paper, the coverage of pyridine after this evacuation at 423 K is defined as saturated coverage. In order to control the coverage of pyridine adsorption on acid sites, additional evacuation at higher temperature was carried out. The introduction of hydrogen gas to pyridine-covered samples was performed at 423 K. Flow rate of the gas was 15 ml/min.

FTIR spectra were taken on a Nicolet Protégé 460 FT-IR spectrometer with MCT detector. Coverage on Brønsted or Lewis acid sites by pyridine was estimated by the ratio of the peak area to its saturation. Since the peak of piperidine overlapped the peak of pyridine adsorbed on Lewis acid site, subtraction between the spectra was used for estimation of coverage of Lewis acid site. All the spectra were measured at 423 K.

3. Results and discussion

Figure 1 shows the change of FTIR spectra when hydrogen gas was introduced to the sample on which pyridine adsorbed at saturation level. The peak at 1450 cm^{-1} denoted as L peak is attributed to pyridine on L acid sites of the zeolite, while the 1540 cm^{-1} peak denoted as B peak is attributed to pyridine on B sites [22]. With the introduction of H_2, the change began, and the two peaks gradually decreased and finally disappeared, while, in contrast, new peaks around 1460 and 1475 cm^{-1} appeared. Spectrum (e) in figure 1 is similar to that of chemisorbed piperidine [9,21]. In this condition, it seems that pyridine on both B and L sites was hydrogenated into piperidine, as was claimed by Zhang et al. [9,21]. Figure 2 shows the conversion of pyridine on each type of acid site estimated from the peak. The result indicates that, on the sample with saturated coverage of pyridine, the hydrogenation of pyridine on both acid sites proceeded at almost the same rate, though there seems to be a slight difference between initial rates. In fact, the hydrogenation turned out to have multi-steps, as described below.

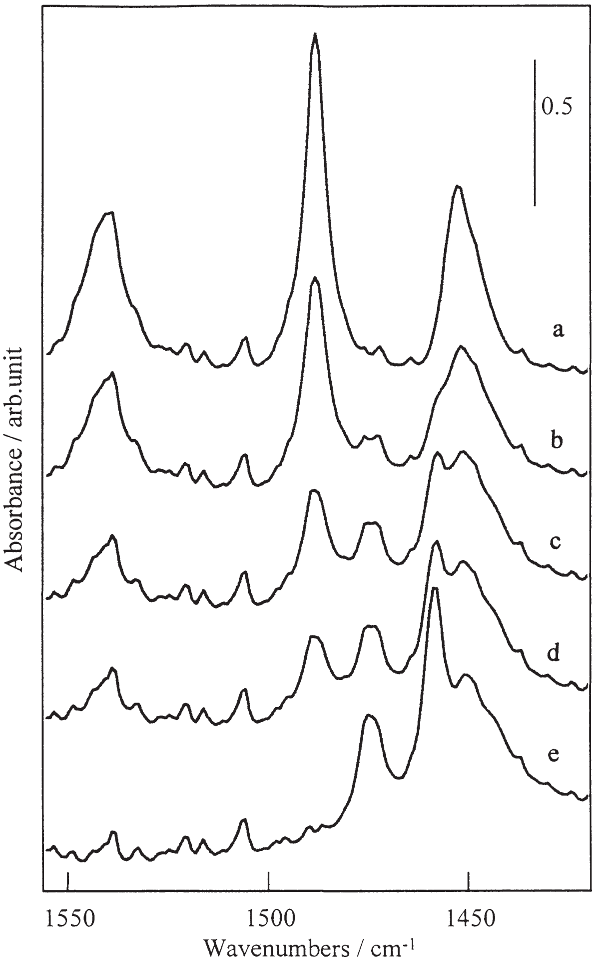

Figure 1. FTIR spectra of pyridine adsorbed on Pd/SiO_2 + USY hybrid catalyst at saturated coverage. (a) Evacuation at 423 K; time on stream of H_2: (b) 20 min, (c) 40 min, (d) 50 min, and (e) 90 min. Conditions of H_2 flow: 423 K, 15 ml/min, pure H_2. Initial coverage of pyridine: B 100%, L 100%. Pyridine adsorption temperature: 423 K.

Figure 3 shows the change of IR spectra when hydrogen gas was introduced to the sample on which pyridine adsorbed at medium coverage. In this case, the sample was evacuated at 598 K for 30 min after pyridine adsorption. The amounts of pyridine left on B and L sites were 85 and 50% to saturated amount, respectively (figure 3(b)). At initial stage, the L peak decreased and the B peak increased with time on stream without the peak growth of piperidine.

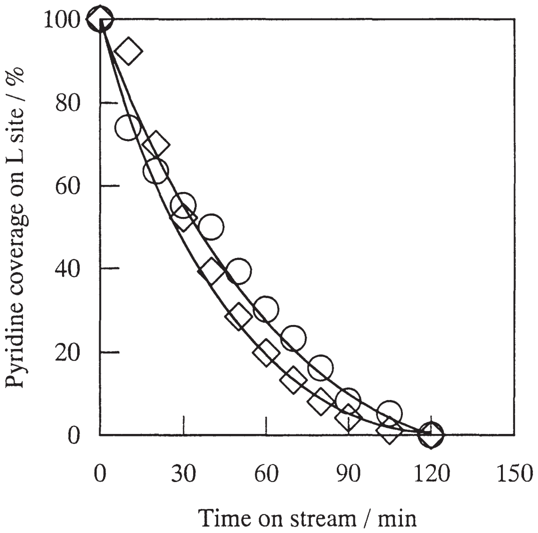

Figure 2. Pyridine coverage on Brønsted (◇) and Lewis (○) acid sites of Pd/SiO_2 + USY zeolite as a function of time on stream. Reaction and measurement conditions are same as figure 1.

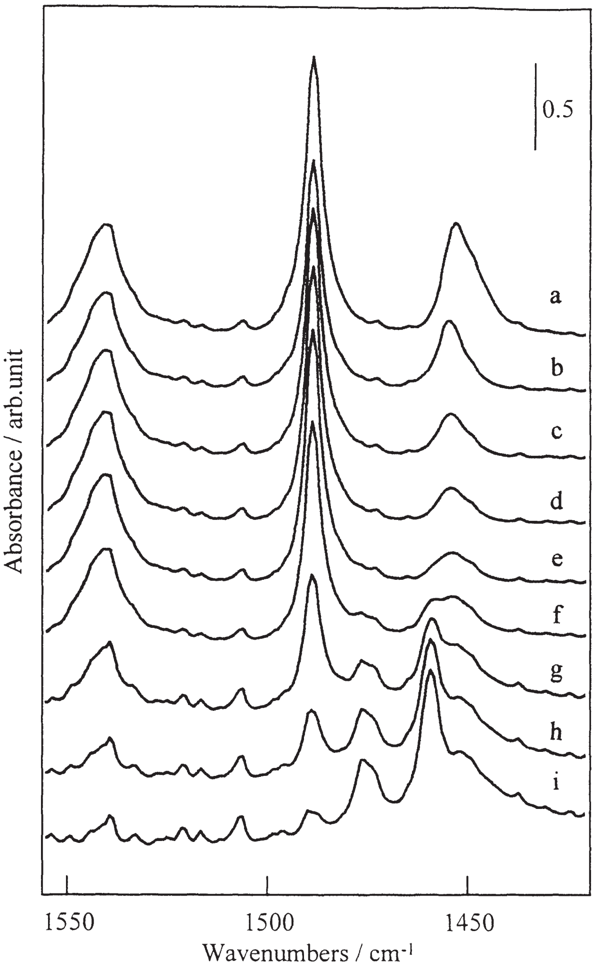

Figure 3. FTIR spectra of pyridine adsorbed on Pd/SiO_2 + USY hybrid catalyst at medium coverage. Evacuation at (a) 423 K and (b) 598 K; time on stream of H_2: (c) 5 min, (d) 10 min, (e) 30 min, (f) 90 min, (g) 180 min, (h) 270 min, and (i) 360 min. Conditions of H_2 flow: 423 K, 15 ml/min, pure H_2. Initial coverage of pyridine: B 85%, L 50%. Pyridine adsorption temperature: 423 K.

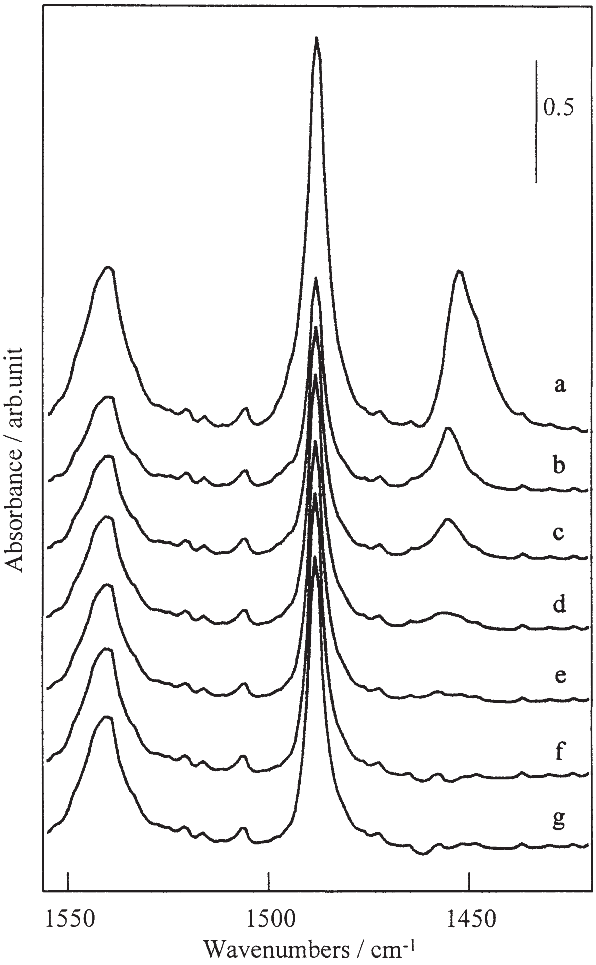

Figure 4. FTIR spectra of pyridine adsorbed on Pd/SiO_2 + USY hybrid catalyst at low coverage. Evacuation at (a) 423 K and (b) 698 K; time on stream of H_2: (c) 1 min, (d) 2 min, (e) 3 min, (f) 15 min, and (g) 150 min. Conditions of H_2 flow: 423 K, 15 ml/min, pure H_2. Initial coverage of pyridine: B 55%, L 25%. Pyridine adsorption temperature: 423 K.

When the B peak reached the saturation level, piperidine began to be formed. The result indicates that, when vacant B acid sites exist, pyridine adsorbed on L acid sites migrates to the B sites, and, after the coverage on B sites becomes saturated with pyridine, hydrogenation of pyridine starts.

Figure 4 shows the change of IR spectra of the sample with low coverage of pyridine, 55% B site and 25% L site. From the IR spectra it was found that pyridine migrated from L to B sites. Under these conditions, all of the residual pyridine adsorbed on L sites migrated to B sites. After that, there were still vacant B sites since total pyridine coverage at initial stage did not reach the saturation of B sites. The peak of the hydrogenated product has not been observed for 150 min or more. This means that the hydrogenation does not occur on acid sites of zeolite and that pyridine is likely to be converted into piperidine on the metal surface with gaseous hydrogen.

In order to clarify the effect of spilt-over hydrogen on the migration of pyridine from Lewis to Brønsted sites, we investigated the difference in the rate of pyridine migration between the hybrid catalyst system and the USY catalyst system. In figure 5, pyridine coverage on L sites as a function of reaction time is shown under each condition. It is estimated that, on the hybrid catalyst system, the rate of pyridine migration was about three times as high as that on the USY catalyst. It is clear that spilt-over hydrogen from supported metal catalyst to zeolite enhances the desorption of pyridine on L sites, promotes the migration of pyridine, and thus plays an important role in pyridine hydrogenation.

Based on the results shown above, it is suggested that spillover hydrogen has a stronger interaction with Lewis acid sites than with Brønsted acid sites, and that one of the species of spilt-over hydrogen is of H^- type, the species which has higher basicity. Considering the charge balance, coexistence of H^+ on the zeolite surface is surely expected, but it cannot be identified by this experimental method. As to H^+, we are now carrying out a successful FTIR observation of interaction between spilt-over hydrogen and Brønsted acid sites using D_2 [23]. Here, we propose a reaction mechanism for hydrogenation of pyridine chemisorbed on acidic sites of zeolite in the hybrid catalyst system. The scheme is shown in figure 6. First, pyridine on a L acid site of zeolite is desorbed and moves to the vacant B acid site until all the B sites become saturated. Then, after the saturation of B sites, excess pyridine from L sites moves to the metal and is hydrogenated into piperidine. As piperidine has more basicity than pyridine, the exchange of piperidine with pyridine on both acid sites occurs easily, and thus the reaction continues until all of the pyridine on the acid sites is converted into piperidine. The transportation of pyridine in this reaction is supposed to be surface diffusion, as total amount of pyridine (and piperidine) was sustained during the whole reaction.

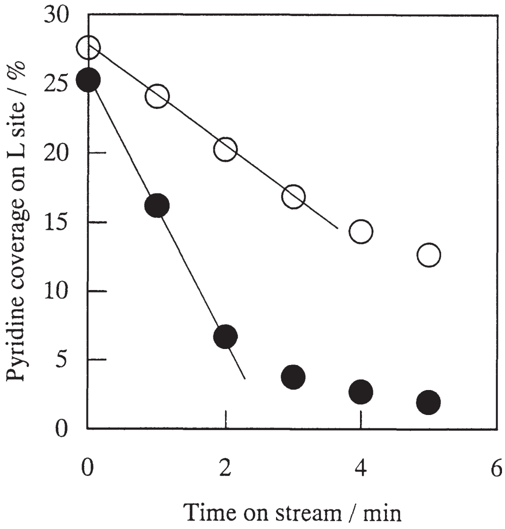

Figure 5. Pyridine coverage on Lewis acid site as a function of time on stream. (●) Pd/SiO_2 + USY (hybrid), (○) USY. Conditions of H_2 flow: 423 K, 15 ml/min, pure H_2. Initial coverage of pyridine: B 55% and L 25% (Pd/SiO_2 + USY), B 60% and L 28% (USY). Pyridine adsorption and evacuation temperature: 423 and 698 K (Pd/SiO_2 + USY), 423 and 698 K (USY).

The phenomenon in our study means that the desorption of basic molecules on Lewis acid sites is promoted by spilt-over hydrogen, probably hydride ion. This seems to correlate that hydrogen spillover has effect on the inhibition of poisoning acid sites in various catalytic reactions. Further studies are necessary to elucidate the genesis of hydrogen spillover effect.

4. Conclusion

FTIR measurement of the behavior of pyridine chemisorbed on Brønsted and Lewis acid sites of zeolite in the Pd/SiO_2-USY hybrid catalyst system under hydrogen atmosphere was carried out. It was observed that pyridine migrated from Lewis acid sites to Brønsted acid sites and migration was drastically promoted by hydrogen spillover effect. Spilt-over hydrogen is suggested to be supplied to Lewis acid sites in the form of H^-.

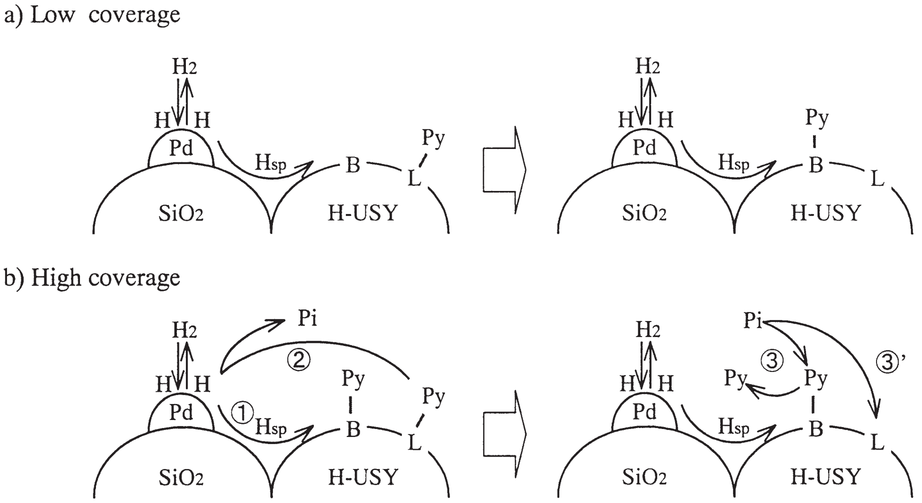

Figure 6. Proposed schematic of migration of pyridine chemisorbed on Brønsted and Lewis acid sites of zeolite promoted by hydrogen spillover effect and hydrogenation of pyridine in Pd/SiO_2 + USY hybrid catalyst system. Py = pyridine, Pi = piperidine, H_{sp} = spilt-over hydrogen species.

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