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A New Probe Reaction for Studying the Hydrogen Spillover Phenomenon

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It was found by FTIR measurement that pyridine strongly adsorbed on acid sites of 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 phenomena were observed on either H-ZSM-5 or Pt/SiO_2. The phenomenon revealed the occurrence of hydrogen spillover from Pt sites to zeolite acid sites (Brønsted and Lewis). A quantitative description of this reaction was attained by calculating and measuring the amount of zeolite acid on the basis of pyridine chemisorption and hydrogen consumption. In connection with this finding, the dehydrogenation of adsorbed piperidine in correlation with reverse hydrogen spillover was also observed on Pt/H-ZSM-5 catalyst in the temperature range from 623 to 723 K.

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1. INTRODUCTION

Spillover is a phenomenon associated with transport of an active species from one site to another. Many experimental facts prove the occurrence of spillover (1–7), and various experimental methods, including FT-IR spectroscopy, electric conductivity measurement, H_2 adsorption measurement, and H_2-TPD have been applied in the study of spillover (8–13).

As for the spillover of hydrogen towards a zeolite acidic site, the present authors have suggested that it occurs on a $Co/SiO_2 + Pt\text{-}Y$ hybrid catalyst for paraffin hydrocracking (14). The present authors have also pointed out the possibility of the participation of H^+ and H^- which have spilled over from gas phase hydrogen in the hydroisomerization or hydrocracking of aliphatic hydrocarbons over physically mixed Pt/SiO_2 and protonic zeolite systems (15, 16). The present authors demonstrated that acidic protons on Y-type zeolites were exchanged very quickly with hydrogen in the gas phase if the zeolites coexisted with physically mixed nickel sulfide supported on alumina or silica gel and claimed that the dissociated hydrogen on nickel sulfide spills over from the nickel site to the support material and then migrates to the zeolite. This spilled over hydrogen has been pointed out as playing a key role in the disproportionation of toluene and the isomerization of xylene (17). Hattori *et al.* have pointed out that molecular hydrogen dissociates on platinum to hydrogen atoms, which undergo spillover on $SO_4^{2}\text{–}ZrO_2$ and convert to H^+ and e^- or H^-. The H^+ acts as a catalytic site for acid-catalyzed reactions (18–20).

However, the behavior or function of spilled over hydrogen on zeolite is not clear yet. Pyridine, a typical organic base, is chemisorbed on either Brønsted (B) acid sites or Lewis (L) acid sites, forming pyridinium ions or coordinately bonded pyridine complexes with B or L acid sites, respectively, and giving different IR-adsorption bands (21–23). Therefore, the change in the IR band of adsorbed pyridine on B or L acid sites can be attributed to changes in the adsorbed pyridine.

In this paper, pyridine adsorption was utilized to investigate the phenomenon of hydrogen spillover from metal to zeolite acidic centers by observing hydrogenation of chemisorbed pyridine on B or L acid sites of ZSM-5 zeolite. A quantitative analysis of this phenomenon was also tried.

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

Pt/H-ZSM-5 (0.5 wt% loading) was prepared using the ion-exchange method. Pt was introduced by ion exchanging a commercially available H-ZSM-5 (Toso, HSZ-840NHA, silica/alumina ratio of 44) with a 0.1 wt% aqueous solution of tetraamineplatinum chloride. The ion exchange was carried out at 353 K for 6 h under stirring. The catalyst was activated in air at 723 K for 2 h prior to reaction. Supported Pt/SiO_2 was prepared by impregnating a commercially available SiO_2 (Aerosil 380, BET specific surface area 380 m^2/g) with an aqueous solution of H_2PtCl_6. After removal of most of the water by evaporation, the samples were calcined in air at 723 K for 2 h to convert the sample to PtO/SiO_2. H-ZSM-5 were activated in air at 823 K for 2 h before use. A hybrid catalyst was prepared by grinding a mixture of 4 parts by weight of H-ZSM-5 with one part Pt/SiO_2 and pressure molding the mixture to granules to 20/40 mesh. All of the catalysts were reduced

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in situ in flowing hydrogen at 673 K for 1 h prior to the experiments.

2.2. *IR Measurement of Hydrogenation of Chemisorbed Pyridine*

Infrared measurements were carried out with a glass cell equipped with CaF_2 windows and connected to a glass vacuum system. In situ treatment, such as in situ reduction, was possible with this setup. A Perkin–Elmer 1600 series FT-IR spectrometer was used to monitor the spectrum change during the reaction. All the test samples were pressed into wafers; the weight of one wafer was approximately 10 mg. Pyridine, placed in a flask, was introduced via an autovaporization-to-vacuum system. The test procedure can be described as follows: reduction at 673 K for 1 h (i) → evacuation at 773 K for 1 h (ii) → pyridine adsorption at 423 K, 8.0 Torr (iii) (1 Torr = 133.3 Pa) → evacuation at 673 K for 30 min (iv) → hydrogen introduction at 473 K or 423 K, 600 Torr (v). At every step, IR spectra were recorded.

2.3. *Hydrogenation of Chemisorbed Pyridine*

Hydrogenation of adsorbed pyridine was conducted similarly to IR measurement with another vacuum system. Samples (1.0 g) were placed in a U-type sample cell connected to the vacuum system for each test. The procedure for the static experiment was basically the same as that for the IR measurement, except that at the last step the initial hydrogen pressure was 300 Torr for the hydrogenation experiment. The weights (sample + cell) after step ii and after step iv were measured and the weight increment before and after pyridine adsorption was calculated. The quantity of hydrogen consumed during the reaction was determined by measuring the decrease in hydrogen pressure.

3. RESULTS

3.1. *Infrared Measurement of Hydrogenation of Adsorbed Pyridine*

Figure 1 shows the IR spectra which appeared after the adsorption of pyridine on H-ZSM-5 at 423 K. As shown in the figure, four vibration adsorption peaks were observed at 1621, 1544, 1490, and 1454 cm^{-1}, which were attributed to B + L, B, B + L, and L acidic sites, respectively. After hydrogen was introduced to this pyridine-adsorbed H-ZSM-5 at 423 K, no notable change in the IR spectrum was observed in 1 h, as shown in Fig. 2. The observation was continued for another hour at 473 K, with little change in the spectra. These results indicate that the adsorbed pyridine on H-ZSM-5 is quite stable against gaseous hydrogen. On the other hand, when pyridine was introduced to Pt/SiO_2, two bands appeared (Fig. 3) which are the same as the IR-adsorption bands of the gas phase pyridine. After the system was evacuated at 473 K, the two peaks disappeared rapidly, indicating that pyridine molecules are adsorbed only weakly on Pt/SiO_2 and little adsorbed pyridine exists on the SiO_2 surface at 473 K under vacuum.

In Figs. 4 and 5, the IR spectra of adsorbed pyridine on Pt/H-ZSM-5 and on the Pt-H-ZSM-5 hybrid catalyst were quite similar to those obtained from H-ZSM-5. However, after hydrogen was introduced to Pt/H-ZSM-5, the

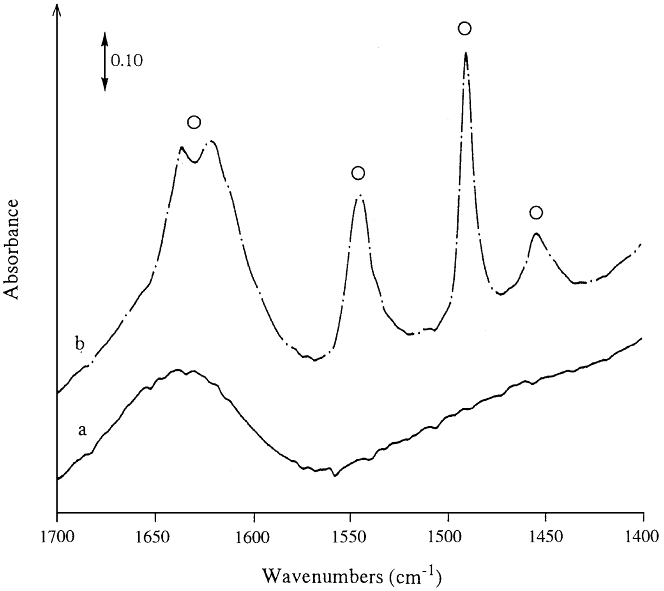

FIG. 1. Infrared spectra of fresh H-ZSM-5 (a) and pyridine adsorbed on H-ZSM-5 at 423 K (b). (○) Bands due to pyridine adsorption.

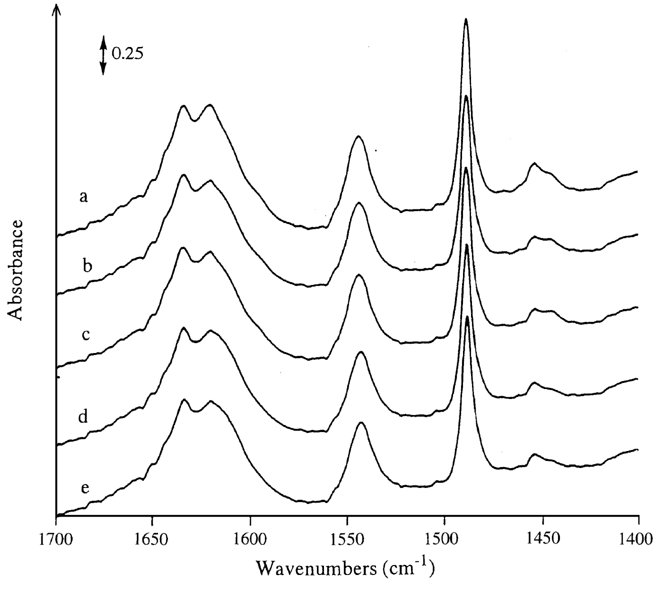

FIG. 2. Infrared spectra of pyridine adsorbed on H-ZSM-5 after pretreatment (a), after H_2 introduction at 423 K for 5 min (b) and 60 min (c), and at 473 K for 10 min (d) and 60 min (e).

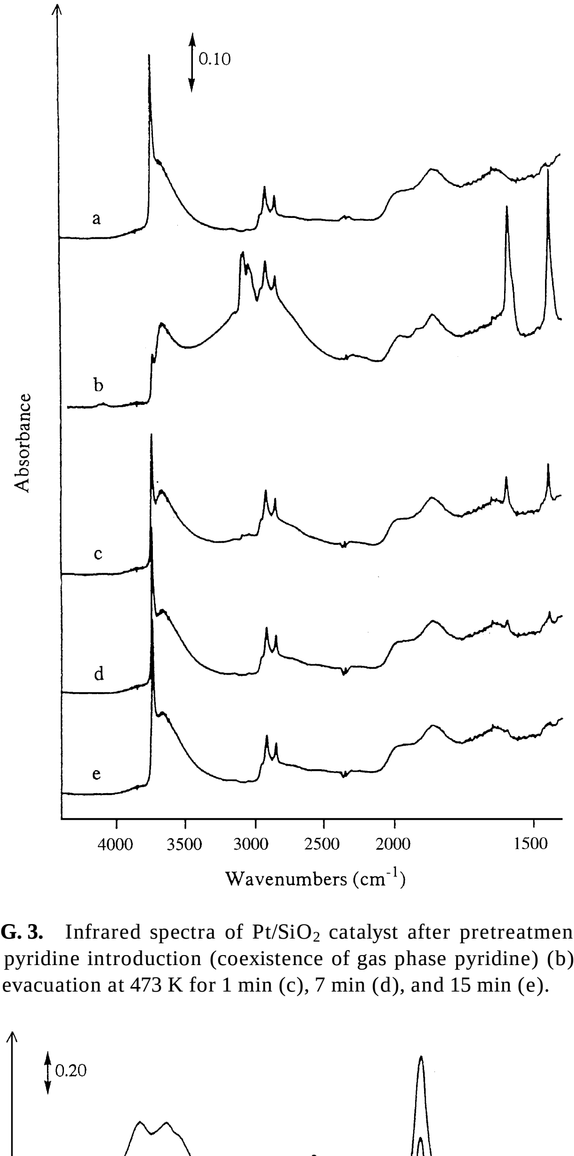

FIG. 3. Infrared spectra of Pt/SiO_2 catalyst after pretreatment (a), after pyridine introduction (coexistence of gas phase pyridine) (b), and after evacuation at 473 K for 1 min (c), 7 min (d), and 15 min (e).

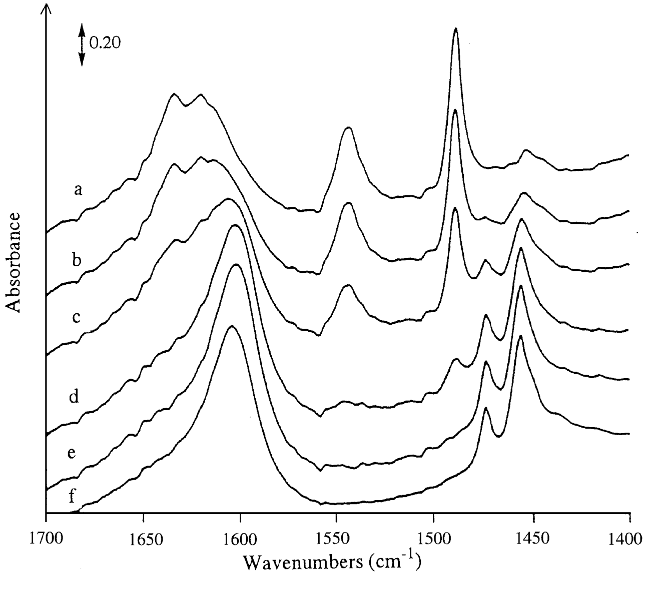

FIG. 4. Changes of IR spectra arising from hydrogenation of adsorbed pyridine on Pt/H-ZSM-5 catalysts after H_2 introduction at 473 K for 0 min (a), 7 min (b), 20 min (c), 40 min (d), and 60 min (e), and IR spectrum of adsorbed piperidine on H-ZSM-5 at 473 K (f).

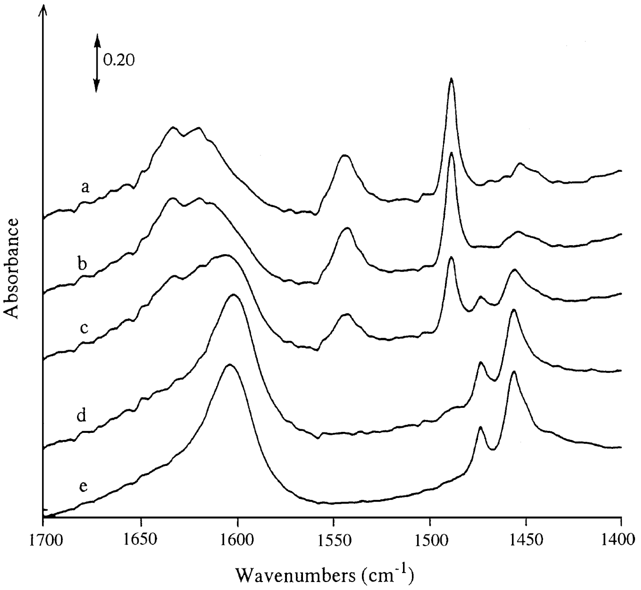

FIG. 5. Changes of IR spectra arising from hydrogenation of adsorbed pyridine on Pt-hybrid catalysts after H_2 introduction at 473 K for 0 min (a), 2 min (b), 12 min (c), and 40 min (d), and IR spectrum of adsorbed piperidine on H-ZSM-5 at 473 K (e).

intensities of the bands at 1544 cm^{-1} and at 1490 cm^{-1} decreased gradually and finally disappeared completely, while a new peak at 1472 cm^{-1} appeared and increased with exposure time. After 1 h of exposure of the catalysts to hydrogen, only the new band at 1472 cm^{-1} remained. The spectrum at this stage was identified as being the same as that of chemisorbed piperidine ($C_5H_{11}N$) on ZSM-5, as shown in Fig. 4. The phenomenon observed above indicates that the adsorbed pyridine molecules on zeolite acidic sites (both on Brønsted and Lewis acidic sites) were hydrogenated. Clearly, hydrogen cannot be supplied directly from gas-phase hydrogen because no such changes in the IR band were observed on H-ZSM-5; therefore the only possible way for the hydrogen to be supplied is from the Pt site. This subject will be discussed later.

The hydrogenation character of the Pt-hybrid catalyst was roughly the same as that of the Pt/H-ZSM-5 catalyst.

3.2. *Hydrogen Uptake by Adsorbed Pyridine on H-ZSM-5*

In order to measure the hydrogenation of adsorbed pyridine quantitatively, the rate and the amount of hydrogen consumption were determined by a volumetric method. Theoretically, the mole ratio of hydrogen uptake to the adsorbed pyridine is 3 ($C_5NH_5 + 3H_2 \rightarrow C_5NH_{11}$). If pyridine is adsorbed on all of the aluminum sites of the present H-ZSM-5 (SiO_2/Al_2O_3 ratio is 44), the amounts of adsorbed pyridine and consumed hydrogen gas should be 168 μmol/g and 504 μmol/g, respectively (23).

Table 1 shows the amount of adsorbed pyridine on Pt/H-ZSM-5 and Pt-hybrid as well as the amount of hydrogen

TABLE 1

Measured and Evaluated Hydrogen Consumption for Pyridine Hydrogenation

	Catalyst (1.0 g)	
	Pt/H-ZSM-5	Pt-hybrid
Amount of ZSM-5/g	1.0	0.8
Acid amount/μmol[a]	168	134
Weight increase/mg[b]	11.0	8.8
Molar amount of pyridine/μmol	139.2	111.4
H_2 consumption/μmol[c]	417.6	334.2
H_2 uptake/μmol, after 260 min	367.0	303.0

[a] Evaluated by assuming that all Al sites are acid.

[b] After pyridine adsorption.

[c] Evaluated from pyridine adsorption.

consumed at 473 K for 2 h of hydrogen exposure. It is clear that the amount of adsorbed pyridine is close to that for the acid site on H-ZSM-5.

The hydrogenation behavior of adsorbed pyridine is shown in Fig. 6. Similar to the IR measurement results, little hydrogen consumption was detected on H-ZSM-5. On the other hand, a rapid drop in pressure was observed in the experiment with Pt/H-ZSM-5, especially in the initial period, indicating, along with the facts shown in Fig. 4, that the adsorbed pyridine was hydrogenated to piperidine. The pressure change was recorded continuously for 260 min. Before the measurement ended, 370 μmol/g zeolite of hydrogen was consumed, which corresponds to 88% of the amount calculated from the weight increase by pyridine adsorption, and was tending to increase continuously until it approached the calculated value.

In the case of the Pt-hybrid catalyst, the initial hydrogenation rate was about half that on Pt/H-ZSM-5, but the final amount of hydrogen per unit weight of H-ZSM-5 was nearly the same.

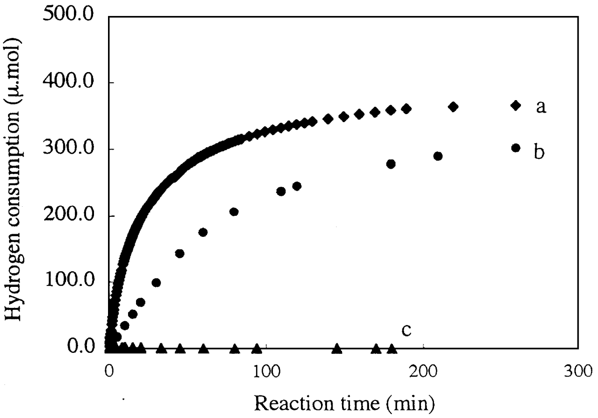

FIG. 6. Time dependence of hydrogen consumption due to hydrogenation of adsorbed pyridine over Pt/H-ZSM-5 (a), Pt-hybrid (b), and H-ZSM-5 (c) catalysts (1.0 g) at 473 K.

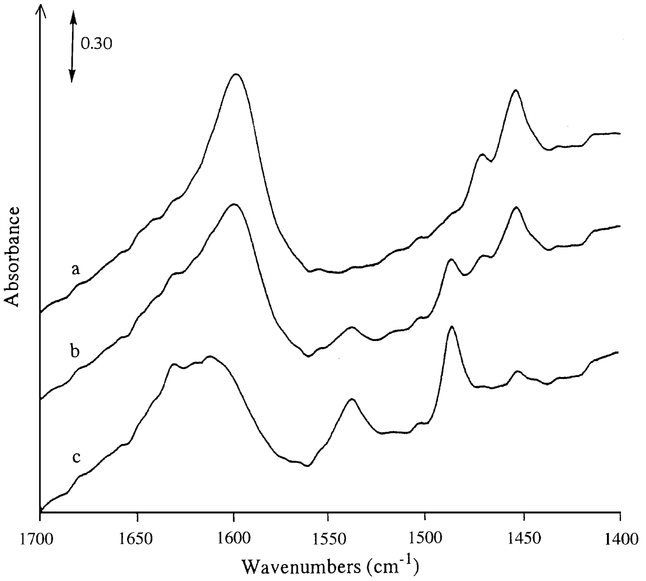

FIG. 7. Changes of IR spectra arising from dehydrogenation of adsorbed piperidine on Pt/H-ZSM-5 catalyst after evacuation at 573 K (a), 623 K (b), and 673 K (c).

3.3 Dehydrogenation of Chemisorbed Piperidine

Dehydrogenation of chemisorbed piperidine was studied using IR measurement. The experimental procedures were reduction at 673 K for 1 h → evacuation at 773 K for 1 h → piperidine adsorption at 473 K at 8.0 Torr → evacuation at 473 K for 30 min → temperature increase to 773 K.

In contrast to our finding of hydrogenation of the chemisorbed pyridine by spilled over hydrogen at low temperature (423–473 K), another important experimental fact which correlates to reverse hydrogen spillover was noted (24, 25). As shown in Fig. 7, the IR spectrum of adsorbed piperidine on Pt/H-ZSM-5 changed back to that of adsorbed pyridine with increasing temperature, while this phenomenon was not observed on H-ZSM-5 (Fig. 8). The results indicate that the piperidine adsorbed on the zeolite acid site was dehydrogenated only when it contained platinum. The most plausible explanation for this phenomenon is that the adsorbed piperidine is dehydrogenated on zeolite, and the hydrogen atoms generated then migrate on the zeolite surface to reach platinum sites, recombine into hydrogen molecules, and desorb into the gas phase. Thus the platinum does not act as the dehydrogenation site but rather acts as a “porthole” for hydrogen release to the gas phase. This is a basic fact associated with the reverse spillover concept, which has been associated with paraffin dehydrogenation on metal-supported active carbon (24, 25) and paraffin dehydroaromatization on Ga-ZSM-5 (26–28).

4. DISCUSSION

The phenomenon in which spilled over hydrogen hydrogenates pyridine adsorbed on acidic sites of ZSM-5 can be

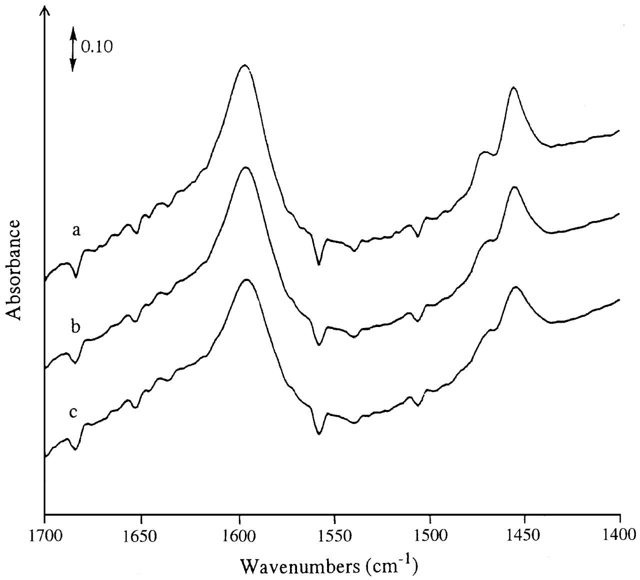

FIG. 8. Changes of IR spectra of piperidine adsorbed on H-ZSM-5 caused by evacuation at 573 K (a), 623 K (b), and 673 K (c).

schematically expressed as the model shown in Fig. 9. The gas phase hydrogen is first dissociated on metal sites and then spills over to ZSM-5 as in the case of Pt/H-ZSM-5, or moves to a SiO_2 support first, then crosses the interface between Pt/SiO_2 and H-ZSM-5, and finally moves to zeolite acidic sites through surface migration, as in the case of the Pt-hybrid catalyst. Here, pyridine molecules bonded on ZSM-5 acid sites acted as an acceptor for the spilled over hydrogen.

Of course, there is the alternate possibility that the adsorbed pyridine moves to a metal site and comes back to an acidic site after being hydrogenated. However, the following phenomena disprove this possibility:

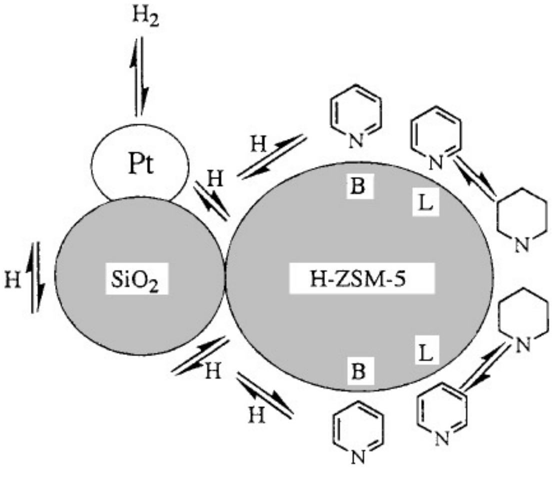

FIG. 9. Schematic of hydrogenation of adsorbed pyridine and dehydrogenation of adsorbed piperidine on Pt-hybrid catalyst.

(1) Weakly adsorbed pyridine molecules should have been removed during the evacuation at 673 K; therefore, the pyridine remaining after this treatment would be tightly bound to the zeolite acid sites and should not migrate quickly at 473 K.

(2) If pyridine had moved to another site, the IR adsorption wavenumbers of the adsorbed pyridine would shift correspondingly to lower or higher regions, but this was not observed.

Of course, hydrogenation of adsorbed pyridine or dehydrogenation of adsorbed piperidine currently has no practical application. Here pyridine or piperidine acts merely as an acceptor for spillover species or as a source for reverse spillover. The important point of this study is that it offers more direct and convincing evidence of the participation of spilled over hydrogen in hydrogenation and other acid-catalyzed reactions. Developing this into a new probe reaction for characterizing hydrogen spillover processes involved in zeolite or other acidic supports is the focus of our future work. Specifically, the nature of spilled over hydrogen is the subject of considerable controversy. The mechanism and the nature of the species should depend on the surface of the support or the acceptor. Parallel mechanistic paths may exist that give rise to the same net effects. Neikam and Vannice reported that spilled over hydrogen supplied from Pt black reacts with perilene ion radicals adsorbed on Ce–Y mixed with the Pt black, and proposed, based on the ESR measurement results, that the active species are hydrogen radicals (29). On the other hand, Khoobiar utilized electron conductivity measurements to suggest that protonic hydrogen is formed on Pt and diffuses across Al_2O_3 onto the separate WO_3 particles (3). The present authors have pointed out the possibility of the participation of H^+ and H^- which have spilled over from gas phase hydrogen in hydroisomerization or hydrocracking of aliphatic hydrocarbons over physically mixed Pt/SiO_2 and protonic zeolite systems (15, 16). Either hydrogen radicals or the H^+ supplied by spillover can react with one of the double bonds of pyridine by electrophilic addition. Following the addition of a hydrogen radical or H^-, the hydrogenation of the double bond is complete.

CONCLUSIONS

(1) Infrared measurements of the hydrogenation of chemisorbed pyridine to adsorbed piperidine on either Pt/H-ZSM-5 or a Pt/SiO_2-H-ZSM-5 hybrid revealed the occurrence of spillover of gaseous hydrogen to zeolite acid sites via the Pt sites and its reaction with adsorbed species.

(2) The amount of hydrogen consumed agreed well with the stoichiometry of the hydrogenation of pyridine nuclei.

(3) Dehydrogenation of chemisorbed piperidine was also observed, which correlates with the reverse hydrogen spillover process.

(4) This method suggests the possibility of characterizing the hydrogen spillover involved in zeolite or other acidic supports as a probe reaction.

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