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Dynamic Modification of Surface Acid Properties with Hydrogen Molecule for Zirconium Oxide Promoted by Platinum and Sulfate Ions

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The dynamic nature of the protonic acid sites on Pt/SO_4^{2-}–ZrO_2 was studied by IR spectroscopy. The generation and elimination of the protonic acid sites in response to the presence and absence of molecular hydrogen in the gaseous phase were observed by monitoring the IR spectra of adsorbed pyridine. By heating in the presence of molecular hydrogen, the protonic acid sites were generated and the Lewis acid sites were weakened. By evacuation of molecular hydrogen, the surface acidic properties retrieved original states. The generation of the protonic acid sites involves dissociative adsorption of the hydrogen molecule on Pt, spillover of the H atom onto the SO_4^{2-}–ZrO_2 surface, and electron transfer from the H atom to Lewis acid sites leaving H^+ on the surface. The elimination of the protonic acid sites by evacuation of molecular hydrogen involves combination of the H^+ with the electron trapped on Lewis acid sites to form an H atom, reverse spillover of the H atom to Pt, and association of atomic H to form H_2 to be desorbed. Essentially the same dynamic nature was observed on the physical mixture containing Pt black and SO_4^{2-}–ZrO_2, although the extent of the change in acidic properties with heating in the presence of hydrogen or evacuation of hydrogen was small compared to Pt/SO_4^{2-}–ZrO_2.

INTRODUCTION

The acid–base property is one of the important surface chemical properties of the metal oxide catalysts (*1*). The fact that the number of the acidic and basic sites (active sites) initially present on the surface is fixed is the principal assumption of the Langmuir–Hinshelwood kinetics. Although the modification of surface acid–base property by the interaction with gaseous molecules has been scarcely observed, some investigators have reported that the acid–base properties are influenced by the presence of the molecular hydrogen on the basis of the decrease and increase in catalytic activity (*2–5*). In the case of zeolites exchanged with transition metal ions, reduction with hydrogen results in the formation of protons accompanied by the formation of transition metals (*6, 7*).

The hydrogen effects in the acid properties of zirconium oxide promoted by sulfate ions and platinum (Pt/SO_4^{2-}–ZrO_2) were investigated in our laboratory and we found that the surface acid properties of Pt/SO_4^{2-}–ZrO_2 are modified by the interaction with molecular hydrogen (*8, 9*). This arises from the infrared spectroscopic results that the adsorbed pyridine on the Lewis acid sites converts into pyridine adsorbed on Brønsted acid sites (pyridinium ion) by heating the pyridine-covered Pt/SO_4^{2-}–ZrO_2 sample in the presence of molecular hydrogen. We interpreted this result as the formation of the protonic acid sites on the surface of Pt/SO_4^{2-}–ZrO_2 from molecular hydrogen with the concomitant decrease of the Lewis acid sites. We proposed that the molecular hydrogen dissociates on the surface of platinum particles, and the atomic hydrogen undergoes "hydrogen spillover" (*11, 12*) onto the surface of SO_4^{2-}–ZrO_2. At Lewis acid sites, the spiltover hydrogen releases an electron to the Lewis acid sites to form a proton. In

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contrast to the cases of the transition metal ion-exchanged zeolites, where the formation of protons is accompanied by the reduction of transition metal cations, Lewis acid sites on SO_4^{2-}–ZrO_2 appear to act as electron acceptors for the formation of protons in the case of Pt/SO_4^{2-}–ZrO_2. The decrease in the Lewis acid sites by interaction with molecular hydrogen has also been proposed by Matsuda *et al.* (*3*) and Schulz-Ekloff *et al.* (*4*) on Pd-loaded alumina-pillered montmorillonite and H-ZSM-5, respectively.

In this paper, we study the reversibility of the generation of the protonic acid sites from molecular hydrogen over the Pt/SO_4^{2-}–ZrO_2 catalyst. The mechanism and nature of the phenomena are discussed in terms of the hydrogen spillover and its reversal (*13–15*).

EXPERIMENTAL METHOD

Catalyst preparation. The precursor of the support, sulfate ion-treated $Zr(OH)_4$ (SO_4^{2-}–$Zr(OH)_4$), was prepared by the impregnation of $Zr(OH)_4$ with 1 *N* H_2SO_4 aqueous solution followed by drying at 383 K. The $Zr(OH)_4$ was obtained by the hydrolysis of $ZrOCl_2 \cdot 8H_2O$. The Pt/SO_4^{2-}–ZrO_2 samples (0.5 and 5 wt% Pt) were prepared by impregnation of SO_4^{2-}–$Zr(OH)_4$ with 1% H_2PtCl_6 aqueous solution. The Pt/SO_4^{2-}–ZrO_2 samples containing different wt% of platinum (0.5, 5 wt%) were prepared by adjusting the amount of H_2PtCl_6 solution. The samples were dried at 383 K and calcined at 873 K. The TEM study showed that the mean particle sizes of platinum in the samples containing 0.5 and 5 wt% were 40 and 50 Å, respectively. Detailed preparation methods of Pt/SO_4^{2-}–ZrO_2 are described elsewhere (*9*). The physical mixture of Pt and SO_4^{2-}–ZrO_2 was prepared by grinding a mixture containing the Pt black and the SO_4^{2-}–ZrO_2 obtained by calcination of SO_4^{2-}–$Zr(OH)_4$ at 873 K. The Pt content was adjusted to be 0.5 wt%. The surface areas were measured by BET method after calcination at 873 K followed by treatment with hydrogen at 623 K.

Infrared spectroscopy. A self-supported wafer placed in an *in situ* IR cell with CaF_2 windows was pretreated at 623 K for 2 h in a hydrogen flow. After cooling the sample to room temperature in the presence of hydrogen, the hydrogen was evacuated for 15 min. The pretreated sample wafer was exposed to 1 Torr of pyridine (purified by repeated freeze–thaw degassing cycles) at 423 K for 15 min followed by evacuation at 673 K for 15 min. In the H_2-exposure process, the pyridine-covered Pt/SO_4^{2-}–ZrO_2 was exposed to 500 Torr of hydrogen at room temperature. The sample was heated stepwisely from 373 to 523 K or 573 K by 50 K increments. During heating in the presence of hydrogen, the amounts of hydrogen adsorbed on the sample were measured volumetrically. In the evacuation process, the sample was successively evacuated stepwisely from 373 to 623 K by 50 K increments. At each temperature, evacuation was continued for 15 min. All IR spectra were recorded on an IR-700 infrared spectrometer (Japan Spectroscopic Co., Ltd.) at room temperature.

For determination of the number of protonic acid sites and Lewis acid sites on the surface, the integrated absorbances of the bands at 1450 cm^{-1} (due to pyridine chemisorbed on Lewis acid sites, L-Py) and 1490 cm^{-1} (due to both the L-Py and pyridine chemisorbed on protonic acid sites, B-Py) (*16*) were used with the tangent background for all samples, employing the apparent integrated absorption proposed by Hughes and White (*17*). The values obtained were normalized to the weight of the sample wafer. To obtain the apparent absorption coefficients of the bands, a known amount of pyridine was adsorbed on the sample, and the absorption of each band was measured. As the apparent absorption coefficient for a certain band is different for a different wafer, the calibration of the apparent absorption coefficient was performed for each wafer.

TABLE 1

BET Surface Areas, Amounts of S, Pt, and Zr Atoms of the Samples

Catalyst	SO_4^{2-}-ZrO_2	Pt/SO_4^{2-}-ZrO_2 (0.5 wt% Pt)	Pt/SO_4^{2-}-ZrO_2 (5 wt% Pt)
BET surface area (m^2 g^{-1})	35	114	110
Amount of SO_4^{2-} (mmol g^{-1})	0.469	0.466	0.445
Conc. of S (atoms m^{-2})	8.07×10^{18}	2.46×10^{18}	2.44×10^{18}
Amount of Pt (mmol g^{-1})	0	0.026	0.256
Conc. of Pt (atoms m^{-2})	0	0.14×10^{18}	1.40×10^{18}
Conc. of surface Zr atoms[a] (atoms m^{-2})	1×10^{19}	1×10^{19}	1×10^{19}

[a] Calculated on the assumption of one Zr^{4+} for every 10 Å^2 surface.

RESULTS

Surface areas and amounts of S and Pt of the samples are summarized in Table 1. The concentrations of S and Pt per unit surface area were calculated on the assumption that all S and Pt are located on the surface. Surface concentration of Zr^{4+} ion is also indicated in Table 1 for a comparison.

IR spectra of pyridine adsorbed on the Pt/SO_4^{2-}-ZrO_2 (0.5 wt% Pt) followed by heating in the presence of hydrogen (500 Torr) at different temperatures are shown in Fig. 1. The peaks at 1450, 1490, and 1540 cm^{-1} were observed after the evacuation of the pyridine-covered sample at 673 K (Fig. 1a). The total concentration of pyridine adsorbed on the surface was 0.067 μmol/m^2. Among them, the concentration of pyridine coordinated to Lewis acid sites (L-Py) was 0.046 μmol/m^2, and that of pyridinium ion (B-Py) was 0.021 μmol/m^2. The former was two times higher than the latter, indicating that Lewis acid sites dominated over protonic acid sites before introduction of hydrogen.

Heating in the presence of hydrogen molecule caused the peak intensity at 1450 cm^{-1} to decrease, and the peak intensities at 1490 and 1540 cm^{-1} to increase. The interaction

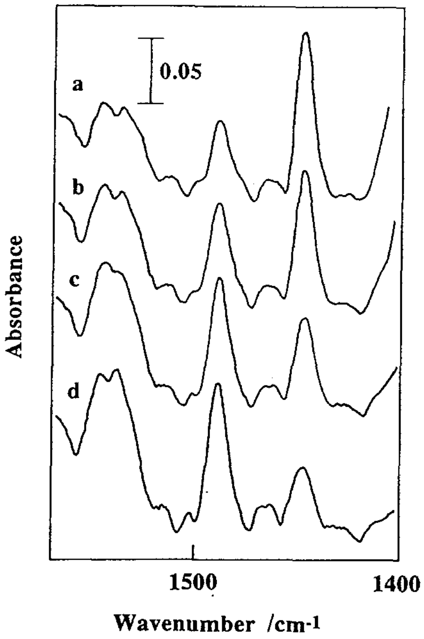


FIG. 1. The changes in IR spectra of pyridine adsorbed on Pt/SO_4^{2-}-ZrO_2 (0.5 wt% Pt) caused by heating in the presence of hydrogen (500 Torr) at different temperatures. (a) before heating, (b) 373 K, (c) 473 K, (d) 573 K. The hydrogen-pretreated sample was exposed to pyridine (1 Torr) at 423 K and evacuated at 673 K before introduction of hydrogen.

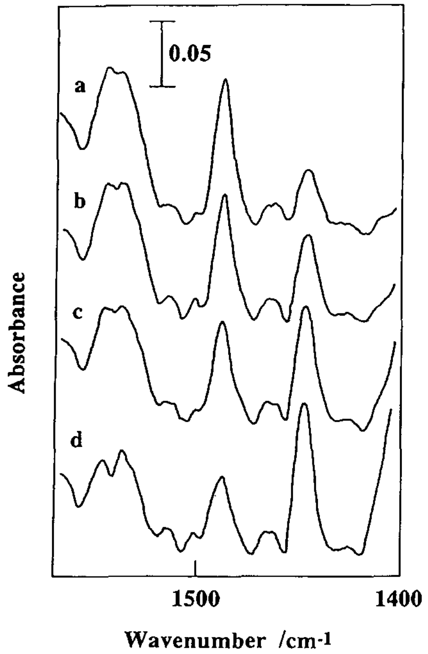


FIG. 2. The changes in IR spectra of pyridine adsorbed on Pt/SO_4^{2-}–ZrO_2 (0.5 wt% Pt) caused by evacuation at different temperatures. (a) 373 K, (b) 473 K, (c) 573 K, (d) 673 K. The hydrogen-pretreated sample was exposed to pyridine (1 Torr) at 423 K and evacuated at 673 K, then exposed to hydrogen (500 Torr) stepwisely at from 423 to 573 K with 50 K increment.

between the hydrogen molecule and the Pt/SO_4^{2-}–ZrO_2 (0.5 wt% Pt) caused the increase in the number of the protonic acid sites on the surface.

Following heating in the presence of hydrogen at 573 K (Fig. 1d), the IR spectral changes caused by evacuation at different temperatures are shown in Fig. 2. The evacuation caused the peak intensities at 1540 and 1490 cm^{-1} to decrease and the peak intensity at 1450 cm^{-1} to increase. The final IR spectrum of adsorbed pyridine over Pt/SO_4^{2-}–ZrO_2 (Fig. 2d) is similar to that observed before heating in the presence of hydrogen (Fig. 1a). The recovery of the spectrum by evacuation indicates that the change in the surface acid properties of Pt/SO_4^{2-}–ZrO_2 induced by hydrogen molecule is a reversible process.

Figure 3 shows the changes in the amount of pyridine adsorbed on the protonic acid sites and the Lewis acid sites of Pt/SO_4^{2-}–ZrO_2 on heating in the presence of hydrogen (500 Torr) in the temperature range 423–573 K and the successive changes on evacuation in the temperature range 373–623 K. The concentration of the pyridinium ion increased by increasing the heating temperature in the presence hydrogen. On raising the evacuation temperature, the concentration of B-Py gradually decreased and the concentration of L-Py increased. The curves for heating give images almost reverse those for evacuation.

The changes in the amount of pyridine adsorbed on the protonic acid sites (B-Py) and Lewis acid sites (L-Py) of Pt/SO_4^{2-}–ZrO_2 (5 wt% Pt) on heating in the presence of hydrogen (500 Torr) and the successive changes on evacuation are shown in Fig. 4. The increase of the B-Py and decrease of the L-Py are also observed on the surface of Pt/SO_4^{2-}–ZrO_2 (5 wt% Pt) by increasing the hydrogen exposure temperature as observed on Pt/SO_4^{2-}–ZrO_2 (0.5 wt% Pt). Hydrogen exposure at 523 K, however, caused the decrease of the amount of B-Py as compared to that observed when the

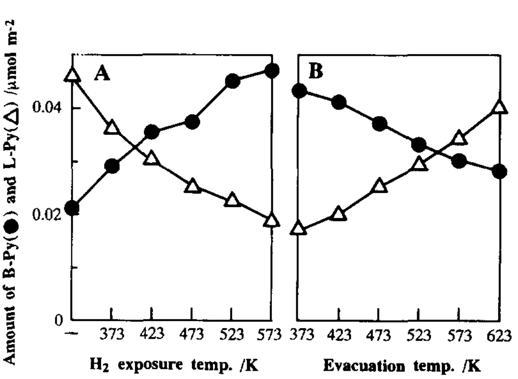


FIG. 3. The change in the amount of pyridine adsorbed on protonic acid sites and Lewis acid sites of Pt/SO_4^{2-}–ZrO_2 (0.5 wt% Pt) on (A) heating in the presence of hydrogen (500 Torr) in the temperature region 423–573 K and (B) evacuation in the temperature region 373–623 K. Pyridine (1 Torr) was adsorbed on the hydrogen-treated sample at 423 K and then evacuated at 673 K for 10 min before introduction of hydrogen.

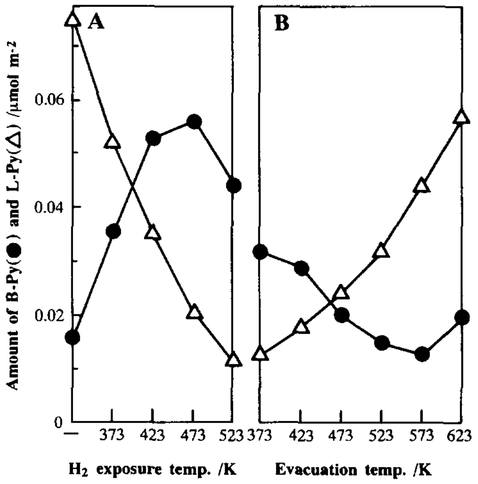


FIG. 4. The change in the amount of pyridine adsorbed on protonic acid sites and Lewis acid sites of Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt) on (A) heating in the presence of hydrogen (500 Torr) in the temperature region 423–523 K and (B) evacuation in the temperature region 373–623 K. Pyridine (1 Torr) was adsorbed on the hydrogen-treated sample at 423 K and then evacuated at 673 K for 10 min before introduction of hydrogen.

sample was exposed to hydrogen at 473 K, which is considered to be due to decomposition of adsorbed pyridine in part. The changes in the amount of B-Py and L-Py against hydrogen exposure temperature up to 423 K observed on Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt) were larger than those observed on Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt% Pt), suggesting that the modification of the acid properties by hydrogen exposure is faster for 5 wt% Pt/SO$_4^{2-}$-ZrO$_2$ than for Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt% Pt) in the temperature range 373–423 K.

The reversible changes in hydrogen-induced acid properties caused by evacuation were also observed for Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt). The changes in the amount of B-Py and L-Py against evacuation temperature were very close to those obtained on Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt% Pt). This suggests that the interconversion of B-Py to L-Py by evacuation is not dependent on the Pt loading amount.

The changes in the amount of B-Py and L-Py of the physical mixture (0.5 wt% Pt) on heating in the presence of hydrogen (500 Torr) are shown in Fig. 5 together with successive changes on evacuation in the temperature region 373–623 K. Even for the physical mixture, the hydrogen exposure caused the increase in the amount of B-Py and decrease in the amount of L-Py. The feature that differs from Pt/SO$_4^{2-}$-ZrO$_2$ samples (Figs. 3 and 4) is the small extent of the changes in B-Py and L-Py against hydrogen exposure temperatures. The amounts of B-Py and L-Py were not affected by the evacuation between 373 and 473 K. Evacuation above 473 K caused the decrease in the amount of B-Py and increase in the amount of L-Py. The changes in the amount of B-Py and L-Py against evacuation temperatures above 473 K resembled qualitatively those obtained on Pt/SO$_4^{2-}$-ZrO$_2$ samples (Figs. 3 and 4).

For SO$_4^{2-}$-ZrO$_2$ containing no Pt, spectral change of adsorbed pyridine could not be observed when heated at 573 K in the presence of hydrogen.

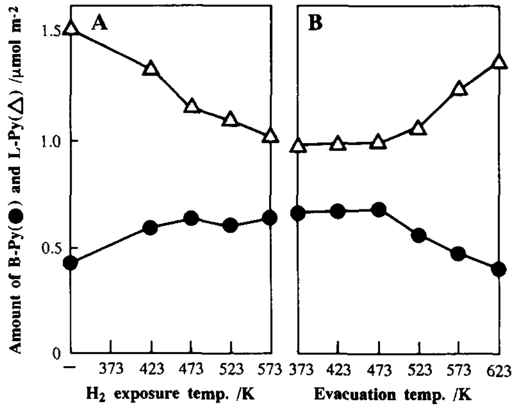


FIG. 5. The change in the amount of pyridine adsorbed on protonic acid sites and Lewis acid sites of physical mixture (Pt + SO$_4^{2-}$-ZrO$_2$, 0.5 wt% Pt) on (A) heating in the presence of hydrogen (500 Torr) in the temperature region 423–573 K and (B) evacuation in the temperature region 373–623 K. Pyridine (1 Torr) was adsorbed on the hydrogen-treated sample at 423 K and then evacuated at 673 K for 10 min before introduction of hydrogen.

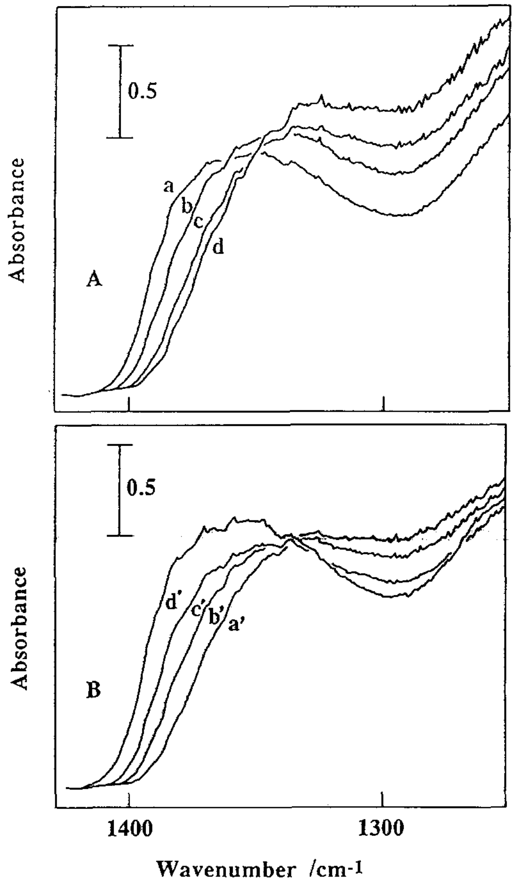


FIG. 6. The changes in the IR spectra due to the S═O band of sulfate ion of Pt/SO$_4^{2-}$–ZrO$_2$ (0.5 wt% Pt) caused by (A) heating in the presence of hydrogen (a) before hydrogen exposure, (b) at 373 K, (c) at 473 K, (d) at 573 K, and (B) evacuation at (a') 373 K, (b') 473 K, (c') 573 K, and (d') 673 K. The sample was pretreated with hydrogen at 623 K and exposed to pyridine (1 Torr) and 423 K, then evacuated at 673 K before introduction of hydrogen.

Figure 6 shows the IR spectra in the S═O bond stretching region for sulfate ion on Pt/SO$_4^{2-}$–ZrO$_2$ (0.5 wt% Pt) after heating in the presence of hydrogen (A), and successive evacuation at different temperatures (B). On raising the hydrogen exposure temperature, the absorption around 1380 cm^{-1} decreased and absorption around 1300 cm^{-1} increased (Fig. 6A). On the other hand, the absorption around 1370 cm^{-1} increased and adsorption at around 1300 cm^{-1} decreased on raising the evacuation temperature. The existence of isosbestic point at about 1345 cm^{-1} was noted. Thus, it is concluded that the change in the S═O bond on raising the hydrogen exposure temperature is not due to the loss of sulfate ion but due to the conversion of one type of sulfate ion to the other type. Correlation between the S═O stretching band position and the strength of Lewis acid sites was reported by Jin *et al.* (*18*) for sulfate ion-added ZrO$_2$, Fe$_2$O$_3$, and TiO$_2$ (*18*). They concluded that the shift of the S═O stretching band to a lower frequency corresponds to a decrease in the strength of the Lewis acid sites (*18*).

The changes in the IR spectra due to the S═O bond of sulfate ion of Pt/SO$_4^{2-}$–ZrO$_2$ (5 wt% Pt) caused by heating in the presence of hydrogen and evacuation at different temperatures are shown in Fig. 7. Essentially the same spectral change was observed for both Pt/SO$_4^{2-}$–ZrO$_2$ (5 wt% Pt) and Pt/SO$_4^{2-}$–ZrO$_2$ (0.5 wt% Pt) on heating in the presence of hydrogen and the following evacuation. The evacuation at 673 K restored to its initial peak intensity and position. The extent of peak intensity changes by hydrogen exposure and evacuation was larger for Pt/SO$_4^{2-}$–ZrO$_2$ (5 wt% Pt) than for Pt/SO$_4^{2-}$–ZrO$_2$ (0.5 wt% Pt).

The S═O bond changes for physical mixture by hydrogen exposure were unmeasurable because of the strong noises at around 1300–1400 cm^{-1}. This may be due to the presence of hydrocarbons that were formed by the hydrogenolysis of the adsorbed pyridine molecule.

The amounts of adsorbed hydrogen on the pyridine-covered Pt/SO$_4^{2-}$–ZrO$_2$ (0.5 and 5 wt% Pt) samples during heating in the presence of hydrogen (500 Torr) at different temperatures are shown in Fig. 8. The amounts of adsorbed hydrogen were increased by increasing the hydrogen exposure temperatures for both samples. It should be noted that the hydrogen to platinum (H/Pt) ratio is far more than unity. This strongly indicates that the hydrogen spillover from the supported platinum onto the SO$_4^{2-}$–ZrO$_2$ occurs

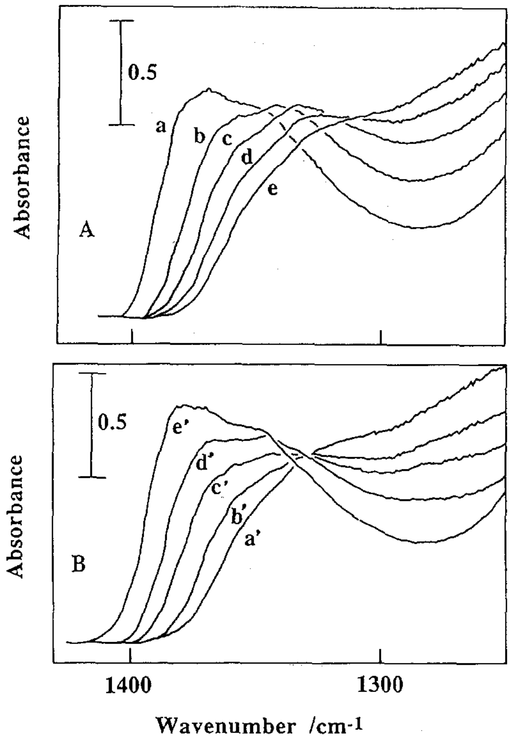


FIG. 7. The changes in the IR spectra due to S=O band of sulfate ion of Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt) caused by (A) heating in the presence of hydrogen (a) before hydrogen exposure, (b) at 373 K, (c) at 423 K, (d) at 473 K, (e) at 523 K, and (B) evacuation at (b') 373 K, (c') 473 K, (d') 573 K, (e') 673 K, and (a') is similar to (e). The sample was pretreated with hydrogen at 623 K and exposed to pyridine (1 Torr) and 423 K, then evacuated at 673 K before introduction of hydrogen.

during the heating in the presence of hydrogen. Compared with the amounts of S, the amounts of hydrogen adsorbed at 523 K were larger by about 3 times for Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt%) and about 4 times for Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt%). Compared with the amounts of adsorbed pyridine, the amounts of hydrogen adsorbed at 523 K were two orders of magnitude larger for both samples. The increase in the amount of adsorbed hydrogen per unit surface area of catalyst was larger for Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt) than for Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt% Pt). However, the H_2/Pt ratio is smaller for Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt) than for Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt% Pt).

DISCUSSION

Generation and elimination of the protonic acid sites in response to heating in the presence of hydrogen and evacuation of hydrogen, respectively, are clearly demonstrated for the Pt/SO$_4^{2-}$-ZrO$_2$ catalyst. In addition to the dynamic behavior of the protonic acid sites, the strength of the Lewis acid sites decreases and restores in response to the generation and elimination of the protonic acid sites. Such dynamic behaviors of the protonic acid sites allow us to control the surface acidic properties by adjusting the hydrogen pressure and temperature. Consequently, the catalytic activities for acid-catalyzed reactions can be controlled by the hydrogen pressure and temperature. Actually, the catalytic activities of Pt/SO$_4^{2-}$-ZrO$_2$ for skeletal isomerization of alkanes are reported to increase markedly with the increases in the hydrogen pressure and temperature (9).

While Pt/SO$_4^{2-}$-ZrO$_2$ was heated in the presence of hydrogen, a large amount of

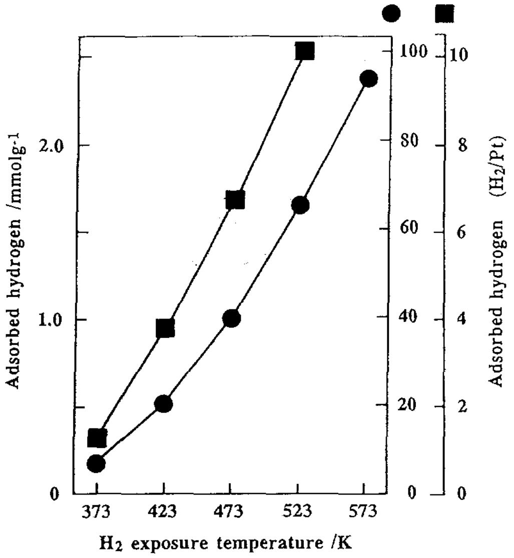


FIG. 8. The amount of hydrogen adsorbed on Pt/SO$_4^{2-}$-ZrO$_2$ (0.5 wt% Pt, ●) and Pt/SO$_4^{2-}$-ZrO$_2$ (5 wt% Pt, ■) samples during heating in the presence of hydrogen (500 Torr).

hydrogen was adsorbed. The H_2/Pt ratios were far more than unity. It is suggested that the generation of the protonic acid sites from molecular hydrogen involves the phenomenon referred to as hydrogen spillover. Without hydrogen spillover, the H/Pt ratio would not exceed 1–2. The maximum H/Pt ratio on Pt particles reported so far was 1–2 (*19*).

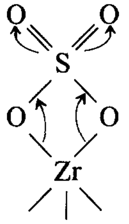
Since the hydrogen spillover is known to occur on the physical mixture of the hydrogen activator and the acceptor, observation of the dynamic behavior of acid sites for the physical mixture of platinum black and SO_4^{2-}–ZrO_2 supports the participation of hydrogen spillover in the generation and elimination of protonic acid sites.

As shown in Fig. 8, the amount of adsorbed hydrogen increased as the temperature increases, which is opposite to a usual adsorption isobar. Since hydrogen spillover preferably occurs at higher temperature as reported for Pt/TiO_2 (*20, 21*) and Pt/Al_2O_3 (*22*), it is also suggested that hydrogen spillover is involved in the adsorption of hydrogen.

In hydrogen spillover, importance of the interface between the hydrogen activator and acceptor phase has been demonstrated by Fujimoto and Toyoshi (*23*). In the present work too, a higher rate for the proton formation was observed with the sample of larger Pt loading. The physical mixture showed the lowest rate for the proton formation.

In the S=O stretching region, two peaks exist with an isosbestic point. The existence of the isosbestic point indicates the existence of two types of surface species; they are interconvertible with each other upon heating in the presence of hydrogen and evacuation.

It has been reported that the S=O stretching absorption band for sulfate ion on ZrO_2 shifted to lower frequencies as pyridine was adsorbed on the Lewis acid sites (*18*). The shift was interpreted by the decrease in the S=O bond order due to coordination of pyridine molecule to the Lewis acid sites. The Lewis acid site is located adjacent to the SO_4^{2-} ion as illustrated (*18*)



in which Zr^{4+} is supposed to be the Lewis acid site, and the arrows indicate the electron shift occurring when pyridine is adsorbed. The S=O bond stretching peak position is sensitive to the electron transfer to the Lewis acid sites. It seems plausible that the shift of the S=O stretching band to a lower frequency by heating in the presence of hydrogen is caused by the electron transfer from the spiltover hydrogen atom to the Lewis acid sites as

$$H + \sqcup \rightarrow \boxed{e^-} + H^+,$$

where $\sqcup$ represents a Lewis acid site. As a result of electron transfer from the H atom to the Lewis acid site, the proton is formed and the Lewis acid site is weakened. The proton is most likely located on the O^{2-} ion near the Lewis acid site.

The Lewis acid sites are considered to be the Zr^{4+} cations bound to SO_4^{2-}. Therefore, the maximum amount of Lewis acid sites is equal to the amount of S on the surface. Although the amounts of hydrogen adsorbed at 373 K were smaller than those of S for both Pt/SO_4^{2-}–ZrO_2 (0.5 wt% Pt) and Pt/SO_4^{2-}–ZrO_2 (5 wt% Pt), the amounts of hydrogen adsorbed at 573 K exceeded those of S. It seems that all of the spiltover hydrogen atoms did not form protons at 573 K; some of the spiltover hydrogen atoms remained as such on the surface.

By evacuation of molecular hydrogen, the reverse process will take place.

$$H^+ + \boxed{e^-} \rightarrow H + \sqcup$$

The hydrogen atom undergoes spillover reverse to that of the Pt particle, where two H atoms combine to form molecular hydrogen and are desorbed from the surface.

It should be noted that the amounts of

pyridine are two orders of magnitude smaller than those of SO_4^{2-}; therefore, the observed spectral changes in the S=O stretching region represent the change in the properties of the Lewis acid sites on which pyridine is not adsorbed.

The extent of the increases in the S=O stretching band at 1380 cm^{-1} by evacuation was larger for Pt/SO_4^{2-}-ZrO_2 (5 wt% Pt) (Fig. 7) than for Pt/SO_4^{2-}-ZrO_2 (0.5 wt% Pt) (Fig. 6). This means that the rate for the overall reverse process is higher for Pt/SO_4^{2-}-ZrO_2 (5 wt% Pt) than for Pt/SO_4^{2-}-ZrO_2 (0.5 wt% Pt). This coincides with the suggestion by Altham and Webb (*24*) that the reverse spillover became faster as the percentage of metal loading was increased.

Unlike the decrease in the S=O stretching band at 1380 cm^{-1}, the decrease in the B-Py band intensity with increasing evacuation temperature was almost the same for 0.5 wt% Pt/SO_4^{2-}-ZrO_2 (0.5 wt% Pt) and Pt/SO_4^{2-}-ZrO_2 (5 wt% Pt). This is probably due to the fact that the abstraction of proton from pyridinium ion to form H^+ and a pyridine molecule is slower than the reverse hydrogen spillover. The slowest process for interconversion of B-Py and L-Py is the abstraction of H^+ from B-Py; the following reverse hydrogen spillover should be faster than the abstraction of H^+ from B-Py. Therefore, the extent of the spectral change, B-Py to L-Py, was independent of the Pt loading.

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