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Effects of Na addition, pyridine preadsorption, and water preadsorption on the hydrogen adsorption property of Pt/SO_4^{2-}–ZrO_2

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Hydrogen adsorption was studied for Pt/SO_4^{2-}–ZrO_2 samples modified with Na addition, pyridine preadsorption, and water preadsorption to elucidate the relation between the rate and capacity of hydrogen adsorption and the surface state. The surface states were monitored by XRD, IR, ammonia TPD, and measurement of catalytic activity for cyclohexane isomerization. All the modifications suppressed the hydrogen uptake. It was suggested that Lewis acid sites promote the hydrogen uptake by stabilizing spiltover hydrogen atoms.

KEY WORDS: Pt/SO_4^{2-}–ZrO_2; hydrogen adsorption; Lewis acid; spillover.

1. Introduction

We reported that protonic acid sites are formed on Pt/SO_4^{2-}–ZrO_2 when hydrogen is adsorbed above 473 K, and that the catalytic activities of Pt/SO_4^{2-}–ZrO_2 for various acid-catalyzed reactions are enhanced in the presence of hydrogen [1,2]. We named the protonic acid sites formed from hydrogen as "molecular hydrogen-originated protonic acid sites". The idea of "molecular hydrogen-originated protonic acid sites" is applicable to the other catalysts which are composed of a hydrogen-activating phase and a phase possessing Lewis acid sites.

For Pt/SO_4^{2-}–ZrO_2, we have reported a kinetic study of hydrogen adsorption [3]. The number of adsorbed hydrogen atoms far exceeded the number of Pt atoms contained in Pt/SO_4^{2-}–ZrO_2. Thus, hydrogen spillover should occur. The adsorption of hydrogen on Pt/SO_4^{2-}–ZrO_2 involves four steps: dissociative adsorption of hydrogen molecules on Pt sites, spillover of the hydrogen atoms onto SO_4^{2-}–ZrO_2, diffusion of the spiltover hydrogen over the surface of SO_4^{2-}–ZrO_2, and conversion of atomic hydrogen into proton at Lewis acid sites. The protons thus formed act as catalytically active sites for acid-catalyzed reactions. The slow step is the surface diffusion of the spiltover hydrogen, and the activation energy for the surface diffusion is 84 kJ/mol.

The rates of the spillover and the surface diffusion vary with the type of catalyst and the state of the surface where hydrogen atoms undergo surface diffusion [4]. The amount of protons formed from hydrogen molecules and the rate of hydrogen adsorption should affect the catalytic activities for acid-catalyzed reactions in the presence of hydrogen. However, there have been no reports describing the relation of the surface state with the hydrogen adsorption properties for Pt/SO_4^{2-}–ZrO_2. In the present study, the factors affecting the rate and capacity of hydrogen adsorption are examined for Pt/SO_4^{2-}–ZrO_2. We have modified the surface of Pt/SO_4^{2-}–ZrO_2 with Na, pyridine, and water, and measured the hydrogen adsorption to elucidate the factors affecting hydrogen adsorption. We have also examined the effect of the crystal structure of ZrO_2 on hydrogen adsorption.

2. Experimental

2.1. Catalyst preparation

The Pt/SO_4^{2-}–ZrO_2 was prepared as follows. Zirconium hydroxide was prepared from an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (Wako Pure Chemical) by hydrolysis with 2.5 wt% NH_4OH aqueous solution. The final pH value of the supernatant was 9.0. The precipitate was filtered and washed with deionized water. The gel obtained was dried at 383 K to form $Zr(OH)_4$. The sulfate ion-treated $Zr(OH)_4$, which is denoted as SO_4^{2-}–$Zr(OH)_4$, was prepared by impregnation of the $Zr(OH)_4$ with 1 N H_2SO_4 aqueous solution followed by filtration and drying at 383 K. The sulfated zirconia (SO_4^{2-}–ZrO_2) was obtained by calcination of the SO_4^{2-}–$Zr(OH)_4$ at 873 K in air. The Pt/SO_4^{2-}–ZrO_2 was prepared by impregnation of the SO_4^{2-}–ZrO_2 with H_2PtCl_6 aqueous solution followed by drying and calcination at 873 K in air. The content of Pt was adjusted to be 0.5 wt%.

Na-loaded Pt/SO_4^{2-}–ZrO_2 was prepared by impregnation of Pt/SO_4^{2-}–ZrO_2 with aqueous NaOH, followed by

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drying and calcining at 723 K in air. The content of Na was adjusted to be 0.1 and 0.5 wt%. Na-loaded Pt/SO_4^{2-}–ZrO_2 samples are designated as xNa–Pt/SO_4^{2-}–ZrO_2, where x denotes the wt% of Na loaded.

Pyridine-preadsorbed Pt/SO_4^{2-}–ZrO_2 was prepared as follows. The Pt/SO_4^{2-}–ZrO_2 was pretreated in a hydrogen flow at 573 K for 3 h followed by outgassing at 573 K. The pretreated Pt/SO_4^{2-}–ZrO_2 was then exposed to 3.5 torr pyridine at 543 K for 0.5 h followed by outgassing at 543 or 558 K.

Samples of Pt supported on zirconias of different crystal structures were prepared as follows. Zirconium hydroxide was calcined at 500, 600, and 800 K for 3 h in air. The resulting zirconias contained tetragonal phase and monoclinic phase in different percentages. Concerning the crystal phase, the samples calcined at 500, 600, and 800 K contained tetragonal phase at 63, 22, and 7%, respectively, and they are denoted as Pt/ZrO_2(T63), Pt/ZrO_2(T22), and Pt/ZrO_2(T7), respectively. Platinum was supported on these zirconias by impregnating with H_2PtCl_6 aqueous solution followed by drying and calcining at 623 K in air. The content of Pt was 0.5 wt% for all Pt/ZrO_2 samples. The ratio of monoclinic to tetragonal phase of zirconia was calculated from XRD peaks using the formula proposed by Toraya *et al.* [5].

2.2. Characterization

X-ray powder diffraction patterns of the sample were recorded using a JEOL JDX-3500 with a CuKα radiation source.

The specific surface area was determined for the samples outgassed at 573 K by the BET method using a Coulter SA 3100 instrument.

The sulfur content of sample catalysts was determined by XRF using a JEOL JSX-3220Z instrument.

Temperature-programmed desorption (TPD) of ammonia was carried out with Bell Multitask TPD as follows. The sample was pretreated with hydrogen flow at 673 K for 3 h followed by purging with He flow for 30 min. Then, the pretreated sample was exposed to dehydrated ammonia (10 torr) at 373 K followed by purging with He flow at 373 K. The TPD was run at a heating rate of 10 K/min from room temperature to 950 K, and the desorbed ammonia was detected by mass spectrometry.

IR measurement was carried out using a Perkin-Elmer Spectrum One FTIR spectrometer equipped with a MCT detector. The sample of self-supported wafer was pretreated in a hydrogen flow at 623 K followed by outgassing at 673 K. For the measurement of pyridine adsorbed on the sample, the sample was exposed to 2 torr of pyridine at 423 K followed by outgassing at 673 K for 15 min. The spectrum was recorded at room temperature with a spectral resolution of 4 cm^{-1} and with 128 scans.

2.3. Hydrogen adsorption

The hydrogen uptake was measured by Belsorp 28SA automatic gas adsorption apparatus. The sample was pretreated in hydrogen flow at 573 K for 3 h, followed by outgassing at 573 K for 2 h, and cooled to an adsorption temperature of 523 K. Hydrogen (100 torr) was then introduced to the system, and hydrogen pressure change with time was monitored. The hydrogen uptake was calculated from a pressure change.

2.4. Reaction procedures

Isomerization of cyclohexane was carried out in a closed recirculation reactor. The catalyst (0.4 g) was pretreated with circulating hydrogen (100 torr) at 573 K followed by outgassing at 573 K. A mixture containing cyclohexane (25 torr) and hydrogen (150 torr) was allowed to react at 473 K. The products were analyzed by on-line gas chromatography, a VZ-7 column being used.

3. Results

3.1. Characterization

3.1.1. Surface area, contents of Na and S, and crystal phase

The surface areas, the contents of Na and S, and crystal phase for the prepared samples are summarized in table 1. The surface area and content of S did not change much by addition of Na to Pt/SO_4^{2-}–ZrO_2. The surface area of Pt/ZrO_2 decreased much with increasing calcination temperature of ZrO_2, and, therefore, the surface area of Pt/ZrO_2 samples decreased with increasing fraction of monoclinic phase.

3.1.2. XRD

Figure 1 shows the XRD patterns for Pt/SO_4^{2-}–ZrO_2 samples, unmodified and modified with Na. The peak at about $2\theta = 30^\circ$ is assigned to tetragonal ZrO_2, and the peaks at about 28° and 32° to monoclinic ZrO_2. For all samples, the peak ascribed to tetragonal ZrO_2 was predominant. In particular, the unmodified Pt/SO_4^{2-}–ZrO_2 scarcely showed the peaks ascribed to monoclinic ZrO_2. By modification with Na, the peaks ascribed to monoclinic ZrO_2 developed, although the fraction of monoclinic ZrO_2 was small as compared to that of tetragonal ZrO_2. The fraction of monoclinic ZrO_2 increased with Na loading.

3.1.3. Ammonia TPD

Figure 2 shows ammonia TPD plots for Pt/SO_4^{2-}–ZrO_2 samples, unmodified and modified with Na. The

Table 1
Surface areas, contents of Na and S, and crystal phase for prepared samples

Sample	Surface area (m^2/g)	Content of Na (wt%)	Content of S (wt%)	Ratio of M[a]/T[b] phase of ZrO_2
Pt/SO_4^{2-}–ZrO_2	119	–	1.69	9/91
0.1Na–Pt/SO_4^{2-}–ZrO_2	117	0.1	1.64	19/81
0.5Na–Pt/SO_4^{2-}–ZrO_2	116	0.5	1.61	36/64
Pt/ZrO_2(T63)	90	–	–	37/63
Pt/ZrO_2(T22)	40	–	–	78/22
Pt/ZrO_2(T7)	13	–	–	93/7

[a] Monoclinic phase.

[b] Tetragonal phase.

TPD plots consisted of two peaks: one peak appearing at about 443 K and the other about 623 K. The TPD plot did not change much by addition of 0.1 wt% Na, but changed considerably by addition of 0.5 wt% Na. On addition of 0.5 wt% Na, the intensity of the peak at about 623 K decreased and the intensity of the peak at about 443 K increased. Strong acid sites were converted into weak acid sites by addition of Na, although the conversion was too small to be detected by the ammonia TPD when 0.1 wt% Na was added.

3.1.4. *IR spectroscopy*

Figure 3 shows IR spectra in the S=O stretching region for sulfate ions of Pt/SO_4^{2-}–ZrO_2 samples, unmodified and modified with Na. IR spectra observed after adsorption of pyridine are also shown as dotted lines. All the samples were treated in hydrogen flow at 623 K followed by outgassing at 673 K. Without Na addition, the sample showed a peak at 1396 cm^{-1} which is assigned to the asymmetric S=O stretching mode of the sulfate groups bound by bridging oxygen atoms to the surface [6,7,8]. The addition of Na to Pt/SO_4^{2-}–ZrO_2 caused a slight decrease in the intensity of the band and a shift of the peak position to a lower frequency of 1385 cm^{-1}, and the appearance of a band at about 1300 cm^{-1} as well. This spectral change indicates that a part of the sulfate groups changed the state on addition of Na. The formation of sodium sulfate by addition of Na to Pt/SO_4^{2-}–ZrO_2 is not plausible, because a band at 1100 cm^{-1} would have appeared if sodium sulfate were formed [9].

It was reported that the position of the peak ascribed to the S=O stretching mode reflects the strength of Lewis acid sites which are associated with the sulfate groups. The shift of the S=O stretching band to a lower wavenumber corresponds to a decrease in the strength of the Lewis acid sites [7]. The results caused by the Na addition indicate that a part of the Lewis acid sites was weakened by the addition of Na. The same phenomenon of the band at about 1390 cm^{-1} decreasing and the band at about 1300 cm^{-1} increasing was observed when hydrogen was adsorbed on Pt/SO_4^{2-}–ZrO_2, and it was concluded that the adsorption of hydrogen weakened the Lewis acid sites [2,10].

Adsorption of pyridine resulted in the shift of the band 1396 cm^{-1} to about 1369 cm^{-1}. The shift was larger for the pyridine-preadsorbed Pt/SO_4^{2-}–ZrO_2 than

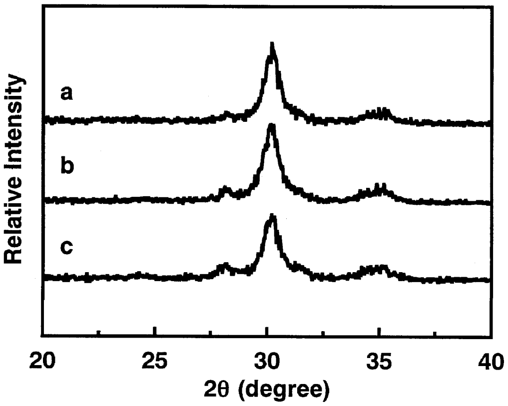

Figure 1. XRD patterns for Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na: (a) Pt/SO_4^{2-}–ZrO_2, (b) 0.1Na–Pt/SO_4^{2-}–ZrO_2, (c) 0.5Na–Pt/SO_4^{2-}–ZrO_2.

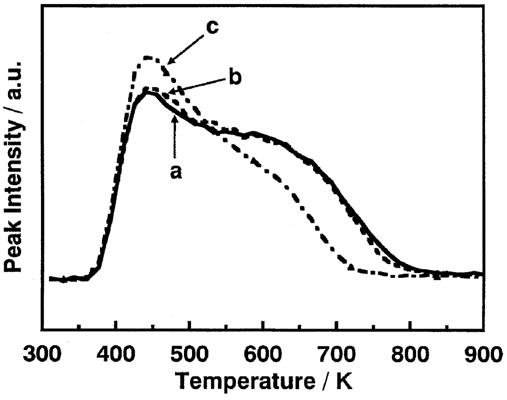

Figure 2. Ammonia TPD plots for Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na: (a) Pt/SO_4^{2-}–ZrO_2, (b) 0.1Na–Pt/SO_4^{2-}–ZrO_2, (c) 0.5Na–Pt/SO_4^{2-}–ZrO_2.

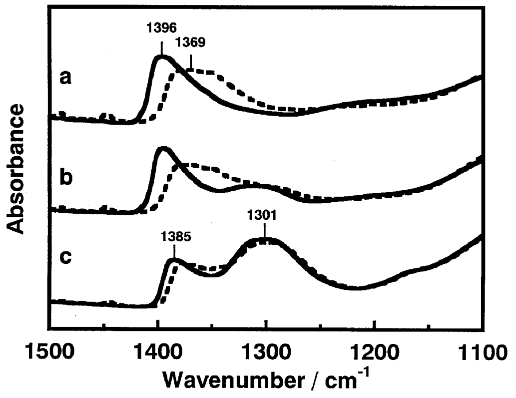

Figure 3. IR spectra in the S=O stretching region before (solid line) and after (dotted line) preadsorption of pyridine for Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na: (a) Pt/SO_4^{2-}–ZrO_2, (b) 0.1Na–Pt/SO_4^{2-}–ZrO_2, (c) 0.5Na–Pt/SO_4^{2-}–ZrO_2. Preadsorbed pyridine was outgassed at 673 K.

for Na-added samples. The band at about 1300 cm^{-1} which was observed for the Na-added samples did not change much on adsorption of pyridine.

Figure 4 shows IR spectra of pyridine adsorbed on Pt/SO_4^{2-}–ZrO_2 samples unmodified and modified with Na. Since the samples were outgassed at 673 K after exposure to pyridine vapor, the peaks in the spectra should be due to the pyridine adsorbed only on the strong acid sites. The band at 1450 cm^{-1} is due to pyridine adsorbed on Lewis acid sites, the band at 1490 cm^{-1} to pyridine adsorbed on Lewis acid sites and on protonic acid sites, and the band at 1540 cm^{-1} to pyridine adsorbed on protonic acid sites [11]. The unmodified Pt/SO_4^{2-}–ZrO_2 sample showed all three bands, indicating both Lewis acid sites and protonic acid sites were present. On addition of Na, the intensities of all the bands decreased. In particular, the band at 1540 cm^{-1} decreased to a great extent. The addition of Na caused a more extensive decrease in the number of strong protonic acid sites than in the number of strong Lewis acid sites.

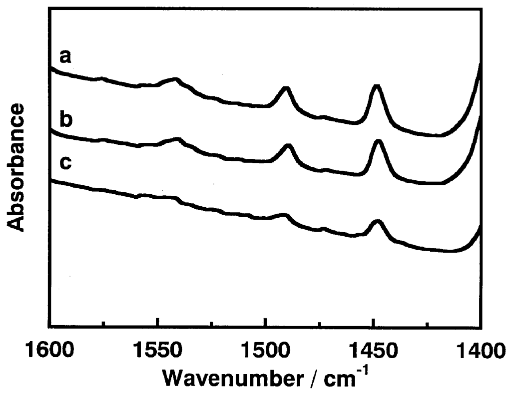

Figure 4. IR spectra of pyridine adsorbed on Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na: (a) Pt/SO_4^{2-}–ZrO_2, (b) 0.1Na–Pt/SO_4^{2-}–ZrO_2, (c) 0.5Na–Pt/SO_4^{2-}–ZrO_2. Preadsorbed pyridine was outgassed at 673 K.

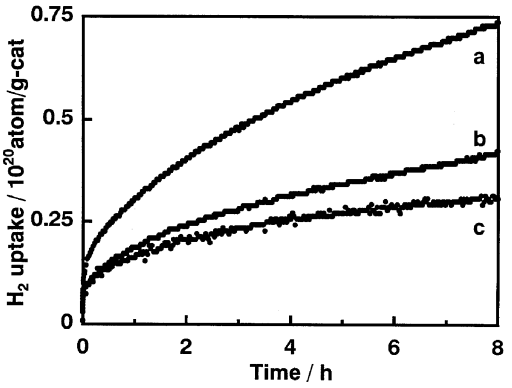

Figure 5. Variations of hydrogen uptake as a function of time for Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na: (a) Pt/SO_4^{2-}–ZrO_2, (b) 0.1Na–Pt/SO_4^{2-}–ZrO_2, (c) 0.5Na–Pt/SO_4^{2-}–ZrO_2. Adsortion temperature was 523 K and hydrogen pressure was ~100 torr (1.33×10^4 Pa).

3.2. Hydrogen uptake

3.2.1. Effect of Na addition

Figure 5 shows the variations of hydrogen uptake as a function of time at an adsorption temperature of 523 K for Pt/SO_4^{2-}–ZrO_2 samples unmodified and modified with Na. As reported in a previous paper for unmodified Pt/SO_4^{2-}–ZrO_2, the hydrogen uptake continued for more than 8 h [3]. The hydrogen uptake reached 7.37×10^{19} atom/g-cat in 8 h for unmodified Pt/SO_4^{2-}–ZrO_2, which corresponds to a H/Pt ratio of 4.79. The addition of Na to Pt/SO_4^{2-}–ZrO_2 decreased the hydrogen uptake. The hydrogen uptakes in 8 h for the samples modified with 0.1 wt% Na and 0.5 wt% Na were 4.24×10^{19} and 3.09×10^{19} atom/g-cat, respectively. These numbers correspond to H/Pt ratios of 2.75 and 2.01, respectively.

3.2.2. Effect of pyridine preadsorption

Pyridine was adsorbed on both Lewis acid sites and protonic acid sites on the surfaces as shown in figure 4. Hydrogen uptake was measured for Pt/SO_4^{2-}–ZrO_2 samples which preadsorbed pyridine in different amounts. The variations of hydrogen uptake for the samples adsorbing pyridine in different amounts as a function of time are shown in figure 6. The sample that adsorbed pyridine followed by outgassing at 543 K should retain a larger amount of pyridine than the sample outgassed at 558 K, although the absolute amounts were not measured. The results shown in figure 6 indicate that the hydrogen uptake decreased with the amount of pyridine adsorbed.

3.2.3. Effect of water preadsorption

The variations of hydrogen uptake as a function of time for Pt/SO_4^{2-}–ZrO_2 samples which adsorbed water at different amounts are shown in figure 7. As opposed

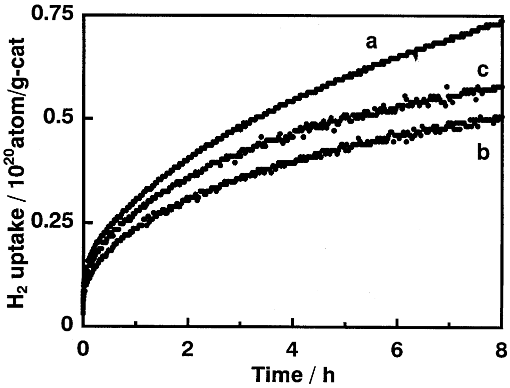

Figure 6. Variations of hydrogen uptake as a function of time for pyridine preadsorbed Pt/SO_4^{2-}–ZrO_2: (a) Pt/SO_4^{2-}–ZrO_2 without preadsorption of pyridine, (b) Pt/SO_4^{2-}–ZrO_2 exposed to pyridine followed by outgassing at 543 K, (c) Pt/SO_4^{2-}–ZrO_2 exposed to pyridine followed by outgassing at 558 K.

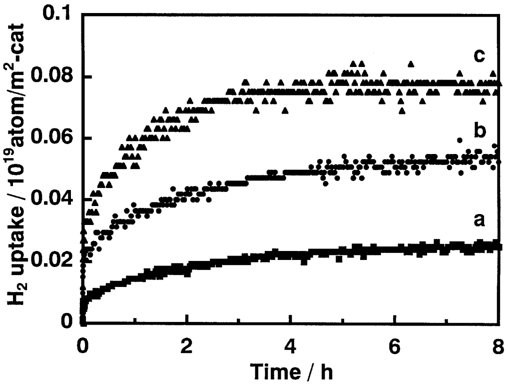

Figure 8. Variations of hydrogen uptake on unit surface area as a function of time for Pt/ZrO_2 with different fraction of crystalline phases: (a) Pt/ZrO_2 with monoclinic phase 63% and tetragonal phase 37%, (b) Pt/ZrO_2 with monoclinic phase 22% and tetragonal phase 78%, (c) Pt/ZrO_2 with monoclinic phase 7% and tetragonal phase 93%.

to the reported results for different catalysts discussed later, water preadsorption on Pt/SO_4^{2-}–ZrO_2 decreased the hydrogen uptake to a considerable extent.

3.2.4. *Effect of crystal structure of ZrO_2*

Since the addition of Na to Pt/SO_4^{2-}–ZrO_2 caused a decrease in the hydrogen uptake (figure 5) as well as an increase in the fraction of monoclinic ZrO_2, the effect of the crystal structure of ZrO_2 on hydrogen uptake was examined. Hydrogen adsorption was measured for Pt supported on ZrO_2 with different ratios of tetragonal phase to monoclinic phase. The surface areas were greatly different, and, therefore, the comparison is better based on the unit surface area. Figure 8 shows the variations of hydrogen uptake on a unit surface area basis as a function of time for Pt/ZrO_2 with different monoclinic to tetragonal ratios. The hydrogen uptake was much larger for the sample rich in monoclinic phase than for the sample rich in tetragonal phase. It should be noted that the hydrogen uptake on a unit surface area basis was higher for Pt/SO_4^{2-}–ZrO_2 than for all Pt/ZrO_2 samples. The presence of SO_4^{2-} enhanced hydrogen uptake.

3.3. *Catalytic activity for cyclohexane isomerization*

The addition of Na and preadsorption of pyridine should poison the active sites on Pt/SO_4^{2-}–ZrO_2. The degree of poisoning was estimated by the activity for cyclohexane isomerization to methylcyclopentane, which is known to be an acid-catalyzed reaction. The time dependencies of the conversion of cyclohexane are shown in figure 9 for the Na-added catalysts, and in figure 10 for the pyridine-preadsorbed catalysts.

The activity was decreased to about 70% of the original activity by addition of 0.1 wt% Na, while the activity was completely eliminated by the addition of 0.5 wt% Na.

Preadsorption of pyridine completely poisoned the active sites for cyclohexane isomerization even after the adsorbed pyridine was outgassed at 558 K.

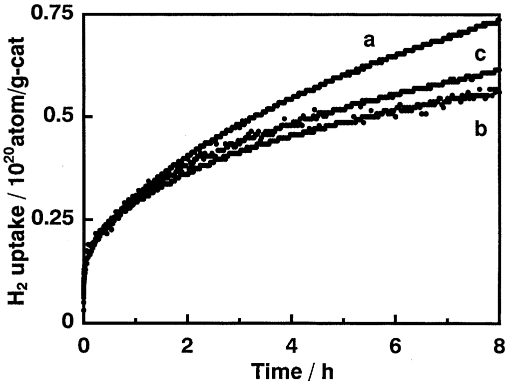

Figure 7. Variations of hydrogen uptake as a function of time for water-preadsorbed Pt/SO_4^{2-}–ZrO_2: (a) Pt/SO_4^{2-}–ZrO_2 without preadsorption of water, (b) Pt/SO_4^{2-}–ZrO_2 exposed to water followed by outgassing at 523 K, (c) Pt/SO_4^{2-}–ZrO_2 exposed to water followed by outgassing at 548 K.

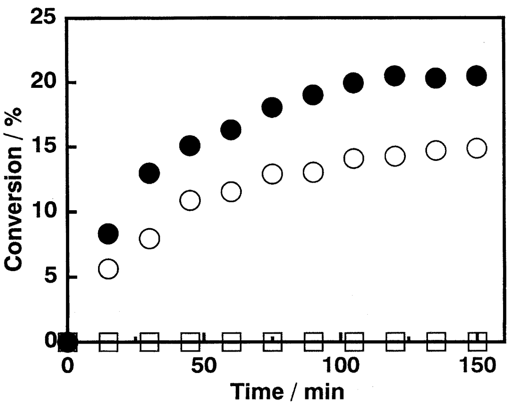

Figure 9. Time dependences of the conversion of cyclohexane for Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na: ●, Pt/SO_4^{2-}–ZrO_2; ○, 0.1Na–Pt/SO_4^{2-}–ZrO_2; □, 0.5Na–Pt/SO_4^{2-}–ZrO_2.

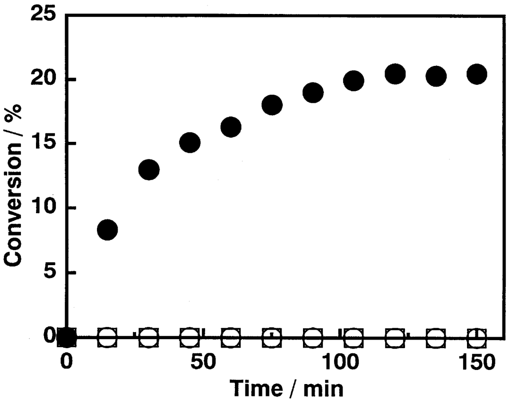

Figure 10. Time dependences of the conversion of cyclohexane for pyridine-preadsorbed Pt/SO_4^{2-}–ZrO_2: ●, Pt/SO_4^{2-}–ZrO_2 without preadsorption of pyridine; ○, Pt/SO_4^{2-}–ZrO_2 exposed to pyridine followed by outgassing at 543 K; □, Pt/SO_4^{2-}–ZrO_2 exposed to pyridine followed by outgassing at 558 K.

4. Discussion

The hydrogen adsorption on Pt/SO_4^{2-}–ZrO_2 was suppressed by the addition of Na, preadsorption of pyridine, and preadsorption of water. The hydrogen adsorption on Pt/ZrO_2 was also affected by the presence of SO_4^{2-} ions and the crystal phase of ZrO_2. Although the quantities of pyridine and water adsorbed on Pt/SO_4^{2-}–ZrO_2 were unknown, it would be helpful for picturing the state of the surface to compare the surface concentrations of Na, SO_4^{2-}, and hydrogen uptake on a unit surface area basis. The concentrations of Na, S, and hydrogen uptake in 8 h are summarized in table 2.

The concentrations of hydrogen uptake in 8 h were in the range from 0.27 atom/nm^2 for 0.5Na–Pt/SO_4^{2-}–ZrO_2 to 0.62 atom/nm^2 for Pt/SO_4^{2-}–ZrO_2. The concentrations of S were about 2.6 atom/nm^2 for Pt/SO_4^{2-}–ZrO_2 samples containing different amounts of Na. The concentrations of Na were 0.22 atom/nm^2 for 0.1Na–Pt/SO_4^{2-}–ZrO_2 and 1.13 atom/nm^2 for 0.5Na–Pt/SO_4^{2-}–ZrO_2. Considering that the hydrogen uptake was still increasing in an adsorption time of 8 h, the surface concentrations of Na, SO_4^{2-}, and the capacity of hydrogen uptake were all within the same order of magnitude.

Comparing Pt/ZrO_2 with Pt/SO_4^{2-}–ZrO_2, hydrogen uptake was about 3.5 times larger for Pt/SO_4^{2-}–ZrO_2 than for Pt/ZrO_2. Without addition of SO_4^{2-}, the surface shows no acidic properties. The adsorption of hydrogen on Pt/ZrO_2 may involve spillover and surface diffusion of spiltover hydrogen, but the spiltover hydrogen may not be stabilized on the surface. This is different from the adsorption of hydrogen on Pt/SO_4^{2-}–ZrO_2 where spiltover hydrogen is stabilized in the form of a proton on the oxygen atom near the Lewis acid site to which the spiltover hydrogen donates an electron [1,2]. It seems plausible that the presence of Lewis acid sites enhances the hydrogen uptake by stabilizing spiltover hydrogen.

The decrease in the hydrogen uptake caused by addition of Na to Pt/SO_4^{2-}–ZrO_2 is interpreted by a decrease in the Lewis acid sites on Pt/SO_4^{2-}–ZrO_2. As shown in figure 5, both protonic acid sites and Lewis acid sites decreased on addition of Na to Pt/SO_4^{2-}–ZrO_2. Although the decrease was more extensive for protonic acid sites than for Lewis acid sites, it is evident that Lewis acid sites also decreased. More exactly, the number of strong Lewis acid sites which are able to retain pyridine against outgassing at 673 K decreased. Some of the strong Lewis acid sites were weakened by addition of Na. This was supported by the shift of S=O stretching band to a lower frequency for Na-added samples as shown in figure 3. The results of ammonia TPD also indicated that the strong acid sites were weakened by addition of Na. It is therefore suggested that the decrease in the number of the strong Lewis acid sites caused a decrease in hydrogen uptake for Na-added Pt/SO_4^{2-}–ZrO_2.

The addition of Na to Pt/SO_4^{2-}–ZrO_2 increased the fraction of monoclinic phase of ZrO_2. As shown in figure 8, hydrogen uptake per unit surface area of Pt/ZrO_2 increased as the fraction of monoclinic phase increased. Therefore, the decrease in hydrogen uptake by addition of Na is not caused by the change in crystal structure of ZrO_2.

Preadsorption of pyridine also suppressed hydrogen uptake. The Pt/SO_4^{2-}–ZrO_2 that adsorbed pyridine followed by outgassing at 558 K adsorbed 5.8×10^{19} hydrogen atom/g, while the 0.1Na–Pt/SO_4^{2-}–ZrO_2 adsorbed 4.2×10^{19} hydrogen atom/g. The suppressive effect of preadsorption of pyridine was not so severe on hydrogen uptake as compared to Na addition. On the contrary, the effects of preadsorption of pyridine were much stronger on the catalytic activity and interaction with surface SO_4^{2-} than the effects of Na addition. The catalytic activity of Pt/SO_4^{2-}–ZrO_2 was completely

Table 2
Surface concentrations of Na, S, and hydrogen uptake in 8 h

Sample	Concentration of Na (atom/nm^2)	Concentration of S (atom/nm^2)	H_2 uptake (atom/nm^2)
Pt/SO_4^{2-}–ZrO_2	–	2.66	0.62
0.1Na–Pt/SO_4^{2-}–ZrO_2	0.22	2.62	0.36
0.5Na–Pt/SO_4^{2-}–ZrO_2	1.13	2.58	0.27

eliminated by preadsorption of pyridine, but only 30% of the activity was lost by addition of 0.1 wt% Na. The IR band at about 1390 cm^{-1} that shows the existence of strong Lewis acid sites disappeared on adsorption of pyridine, but still existed to a considerable extent for 0.1Na–Pt/SO_4^{2-}–ZrO_2. It is suggested that the preadsorbed pyridine covered the surface of Pt/SO_4^{2-}–ZrO_2 more extensively than the added Na.

In spite of the extensive coverage of the surface by pyridine, the suppressive effect of pyridine preadsorption was mild on the hydrogen uptake. This may be interpreted as follows. Pyridine molecules that are adsorbed on Lewis acid sites are converted into pyridinium ions when hydrogen is adsorbed above 473 K as evidenced by IR studies [1,2]. This indicates that spiltover hydrogen atoms are able to interact with the Lewis acid sites on which pyridine has been already adsorbed. A spiltover hydrogen donates an electron to the Lewis acid site and forms a proton which is stabilized on the oxygen atom near the Lewis acid site. The pyridine molecule that was adsorbed on the Lewis acid site moves to the protonic acid site to form a pyridinium ion. A second spiltover hydrogen reacts with the electron donated to the Lewis acid site to form a hydride, and the hydride is stabilized on the Lewis acid site. Therefore, hydrogen adsorption takes place on the pyridine-covered surface, and preadsorption of pyridine does not cause a severe suppressive effect on hydrogen uptake. Cyclohexane, however, may not replace pyridine adsorbed on the active site, and, therefore, cannot undergo isomerization on the pyridine-preadsorbed Pt/SO_4^{2-}–ZrO_2.

Preadsorption of water also suppressed hydrogen uptake, though the suppressive effect was not so extensive. The hydrogen uptake in 8 h on the water-preadsorbed Pt/SO_4^{2-}–ZrO_2 followed by outgassing at 523 K was 5.6×10^{19} hydrogen atom/g, which is 77% of the hydrogen uptake on the original Pt/SO_4^{2-}–ZrO_2. The suppressive effect of water preadsorption on hydrogen uptake is opposite to the results reported for other types of catalysts. Promotional effects of water adsorption on hydrogen uptake were reported for a mixture of Pt and WO_3 [12], and Pt/Al_2O_3 [13]. There are reports that stressed an important role of the hydroxyl group in hydrogen spillover on Pt/Al_2O_3 [14] and zeolite-supported Pt [15]. In particular, Miller *et al.* reported that acidic OH groups facilitate the hydrogen spillover step more effectively than neutral OH groups on zeolites [15].

Preadsorption of water on Pt/SO_4^{2-}–ZrO_2 should convert Lewis acid sites into protonic acid sites. It is not certain as to whether protonic acid sites or acidic OH groups promote hydrogen spillover and hydrogen uptake on Pt/SO_4^{2-}–ZrO_2, but the Lewis acid sites are possibly decreased by preadsorption of water and lose the ability to stabilize spiltover hydrogen. Even if there is a promotive effect of the protonic acid sites, the negative effect caused by elimination of Lewis acid sites surpasses the positive effect on hydrogen uptake.

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