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In-Situ XPS Study of Zirconium Oxide Promoted by Platinum and Sulfate Ion

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In-situ X-ray photoelectron spectroscopy (XPS) and infrared (IR) study of adsorbed CO were performed to characterize the states of the platinum particles supported on the sulfate ion-treated zirconium oxide (SO_4^{2-}–ZrO_2) after reduction with hydrogen. Presence of the sulfate ion strongly suppressed the reducibility of the platinum particles as well as the chemisorptive capacity for CO. The platinum particles consisted mainly of platinum cations (mixture of platinum oxide and platinum sulfate) after reduction with hydrogen at 673 K; the concentration of metallic platinum phase was low. The low reducibility of the dispersed platinum particles present as platinum cations on the SO_4^{2-}–ZrO_2 support is interpreted by the redox metal–support interaction (RMSI), which is caused by the acidic properties of the SO_4^{2-}–ZrO_2 support and results in a slow nucleation of the platinum particles. The states of sulfur were also measured by XPS, and the partial conversion of the S^{6+} (sulfate ion) to S^{2-} species on hydrogen treatment is concluded to occur by the metal-catalyzed mechanism involving spiltover hydrogen atoms resulting from the dissociation of a hydrogen molecule on the metallic platinum. © 1992 Academic Press, Inc.

INTRODUCTION

In previous papers (*1, 2*), it has been reported that the addition of platinum on the SO_4^{2-}–ZrO_2 enhances the catalytic activity for acid-catalyzed reactions such as skeletal isomerization of alkanes. The characteristic feature is that the activity of the catalyst (Pt/SO_4^{2-}–ZrO_2) for skeletal isomerization is high and persists for a long period only when the reaction is carried out in the presence of molecular hydrogen. This hydrogen promotion effect on the catalytic activity for acid-catalyzed reactions could be interpreted by the generation of protonic acid sites originating from molecular hydrogen (*2, 3*). It is postulated that the hydrogen molecule dissociates on the supported platinum to spillover onto the support where atomic hydrogen converts to protons which act as a catalytic site. Another important characteristic feature of the Pt/SO_4^{2-}–ZrO_2 catalyst is a lack in the alkane hydrogenolysis and alkene hydrogenation abilities of the supported platinum. Thus, the state of platinum in the Pt/SO_4^{2-}–ZrO_2 should be different from the usual supported platinum metal. The platinum on the support should be in such a state as to dissociate molecular hydrogen but not to hydrogenate alkanes or to catalyze hydrogenolysis (*2*).

In our previous paper, we discussed the states of platinum in the Pt/SO_4^{2-}–ZrO_2 and presented two possible states (*2*). One is in the "Strong Metal–Support Interaction" (*4–9*) state and the other is in such a state that the platinum surface is covered by the sulfur which originates from hydrogen sulfide evolution during the hydrogen treatment of the catalyst. A subtle modification of the electronic state of the dispersed metal should be involved in both cases. The tech-

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nique which could monitor the changes in the electronic properties due to the metal–support interaction is X-ray photoelectron spectroscopy (XPS) (*10–16*).

In this study, *in-situ* XPS measurements for a reduced Pt/SO_4^{2-}-ZrO_2 sample were performed to clarify the state of the platinum. In addition, to observe the electronic states of the platinum, attention was paid to measure the states of the sulfur species on the Pt/SO_4^{2-}-ZrO_2 sample after reduction, because the existence of sulfur on the metal is well known to modify the catalytic activity of the metal (*17*).

EXPERIMENTAL METHODS

Catalyst Preparation

The sulfate ion treated $Zr(OH)_4$ was prepared by the impregnation of $Zr(OH)_4$ with 1*N* H_2SO_4 aqueous solution followed by filtration and drying at 383 K. The $Zr(OH)_4$ was obtained by the hydrolysis of $ZrOCl_2 \cdot 8H_2O$ with 25% aqueous ammonia followed by filtration. The gel thus obtained was washed with distilled water until no Cl^- ions could be detected. The Pt/SO_4^{2-}-ZrO_2 sample (5.0 wt% Pt) was prepared by impregnation of SO_4^{2-}-$Zr(OH)_4$ with 1% H_2PtCl_6 aqueous solution followed by drying at 383 K and calcination at 873 K in air. The amount of S that remained in the resulting catalyst was 1.5 wt%, determined by XRF. The Pt/ZrO_2 was prepared by the impregnation of $Zr(OH)_4$ with 1% H_2PtCl_6 aqueous solution followed by drying at 383 K and calcination at 873 K.

Infrared Spectroscopy

IR spectra were recorded on an FT/IR-7000 infrared spectrometer (Japan Spectroscopic Co., Ltd.) at room temperature. A self-supported wafer placed in an *in-situ* IR cell with CaF_2 windows was pretreated at 623 K in a hydrogen flow for 1.5 h. The sample was cooled to room temperature in a hydrogen flow and then evacuated. CO (5 Torr, 1 Torr = 133.3 Nm^{-2}) was adsorbed and IR spectra were measured.

X-ray Photoelectron Spectroscopy

The XPS measurements were done by two different methods. One was *in-situ* XPS measurements and the other the conventional method which involves exposure of the sample to air for a few minutes to set on the sample holder. XPS measurements were conducted by a MODEL-5500 MT (ULVAC-PHI Co., Ltd.) at Kyoto University with Mg*Kα* X rays (1253.6 eV) for the measurements of oxidized samples and reduced Pt/ZrO_2. The oxidized samples were the samples calcined at 873 K as described above.

For Pt/ZrO_2, the sample was placed in a recirculation reactor and treated with recirculating hydrogen (ca. 200 Torr) at 623 K for 1 h, then the sample was evacuated at the same temperature. This treatment was repeated three times. During hydrogen treatment, a liquid nitrogen trap was used to remove water from the reactor. Before the XPS measurements, the treated sample was exposed to air at room temperature for a few minutes in order to place it on the sample holder.

For Pt/SO_4^{2-}-ZrO_2, the *in-situ* XPS measurements were performed on a VG Scientific ESCALAB Mk II at Hokkaido University with Mg*Kα* X rays. The sample was pretreated in a hydrogen flow (1 atm) at the desired temperature for 1.5 h. The sample was cooled down to room temperature in a H_2 flow and evacuated, then transferred into the XPS measurement stage. After measurement of the XPS spectrum, the sample was transferred back to the gas reaction chamber for hydrogen treatment at different temperatures. The pretreatment temperature was increased stepwise in 50-K increments.

The binding energy was calibrated using the Zr 3*d* (182.3 eV). The separation of the Pt 4*f* XPS peaks for both platinum oxide and metal was performed using an intensity ratio of Pt $4f_{7/2}$ to Pt $4f_{5/2}$ of 4/3, and a peak separation, 3.3–3.4 eV (*18, 19*). The separation of the peaks was done on a VGS5250 System. The background subtraction was performed

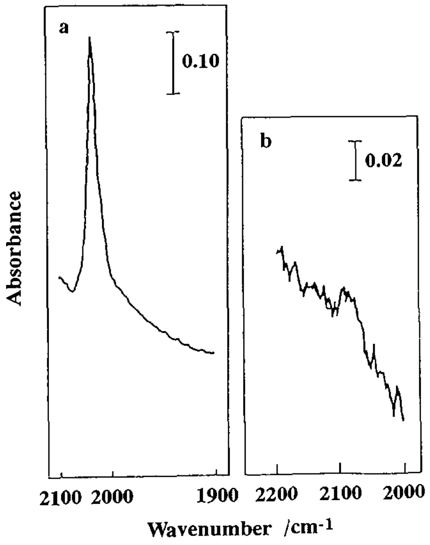

FIG. 1. IR spectra of adsorbed CO on the samples treated with hydrogen at 623 K. (a) Pt/ZrO_2 and (b) $Pt/SO_4^{2-}-ZrO_2$.

using Shirley's method (*20*). The peaks were separated by using a Gaussian/Lorentzian product function (*21*). According to this separation method, the peaks could be fitted by a mixing ratio of 85–90% contribution of the Gaussian shape.

RESULTS

Figure 1 shows the infrared spectra of adsorbed CO on the (a) Pt/ZrO_2 and (b) $Pt/SO_4^{2-}-ZrO_2$ pretreated with hydrogen at 623 K. For Pt/ZrO_2 catalyst, a single and sharp peak was observed at 2070 cm^{-1}. On the other hand, no band was appreciably observed when CO was adsorbed on the $Pt/SO_4^{2-}-ZrO_2$ catalyst. The relative intensity of the adsorbed CO on $Pt/SO_4^{2-}-ZrO_2$ to that of Pt/ZrO_2 was less than 1/100.

Because the observed band position (2070 cm^{-1}) on the reduced Pt/ZrO_2 sample is similar to that of linearly adsorbed CO on metallic platinum sites (*22*), the surface state of the platinum particle on the reduced Pt/ZrO_2 is thought to be metallic. The drastic decrease in the IR absorption peak of adsorbed CO on the reduced $Pt/SO_4^{2-}-ZrO_2$ suggests that the surface state of the platinum particles on the $SO_4^{2-}-ZrO_2$ are either not metallic, or are surface metallic states which cannot adsorb CO molecules. In either case, the presence of sulfate ion on the support drastically modifies the states of the supported platinum particles. The decrease in the peak intensity of adsorbed CO by the sulfate ion is the same order of magnitude as the decrease in the propene hydrogenation activity, which was reported previously (*2*).

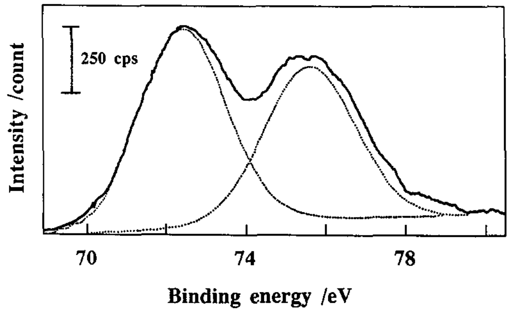

FIG. 2. Pt 4*f* XPS spectra (solid line) of the oxidized $Pt/SO_4^{2-}-ZrO_2$. The separation curves are shown by dotted lines.

Figure 2 shows the Pt 4*f* XPS spectra of the oxidized $Pt/SO_4^{2-}-ZrO_2$. These peaks are due to the platinum oxide phase. The peak parameters of the spectra are tabulated in Table 1 together with those for the oxidized Pt/ZrO_2. It should be noted that the peak position and the FWHM (Full Width at Half Maximum) of the supported platinum oxide particles changes in the presence of the sulfate ions.

The Pt 4*f* XPS spectra of the

TABLE 1

Peak Parameters of Platinum Oxide Particles of Oxidized Samples

Sample	Position (eV)		Spin orbit separation (eV)	FWHM (eV)	
	$4f_{7/2}$	$4f_{5/2}$		$4f_{7/2}$	$4f_{5/2}$
Pt/ZrO_2	72.1	75.3	3.20	2.35	2.43
$Pt/SO_4^{2-}-ZrO_2$	71.7	74.9	3.20	2.56	2.70

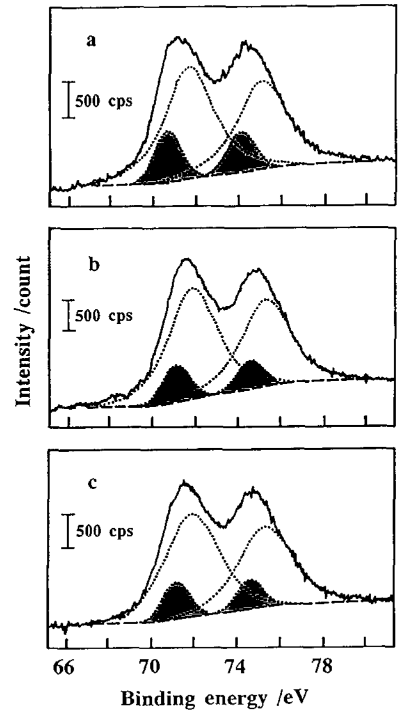

FIG. 3. Pt 4*f* XPS spectra (solid line) of the $Pt/SO_4^{2-}-ZrO_2$ sample after (*in-situ*) hydrogen treatment at (a) 573 K, (b) 623 K, and (c) 673 K. The separation curves are shown by dotted lines. The background is shown by a dashed line. Shaded parts represent platinum metallic phase. Note that the hydrogen pretreatment temperature was raised stepwise in 50-K increments.

$Pt/SO_4^{2-}-ZrO_2$ pretreated with hydrogen at different temperatures are shown in Fig. 3. The separation curves are also shown in Fig. 3 by dotted lines. The shaded parts represent the Pt 4*f* peaks of the metallic phase. The unshaded parts of the separation peaks represent the Pt 4*f* peaks of platinum cations. The peak parameters of the XPS Pt 4*f* spectra for the $Pt/SO_4^{2-}-ZrO_2$ pretreated with hydrogen at different temperatures are tabulated in Table 2. The peak intensity ratio of Pt 4*f* (platinum cation) to the Zr 3*d* after pretreatment with hydrogen at 573 K was 0.045. For the oxidized $Pt/SO_4^{2-}-ZrO_2$ sample, the ratio was 0.052.

TABLE 2

Peak Parameters of Pt 4*f* XPS Spectra of the $Pt/SO_4^{2-}-ZrO_2$ Sample Pretreated with Hydrogen at Different Temperatures (*in-Situ*)

Pretreatment temperature (K)	Peak position (eV)				Relative area cation/metal[a]
	metal		cation		
	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	
573	70.8 (1.48)	74.2 (1.48)	71.8 (2.79)	75.1 (2.79)[b]	4.5
623	71.0 (1.48)	74.3 (1.48)	71.7 (2.76)	75.1 (2.76)	6.1
673	71.1 (1.48)	74.5 (1.48)	71.8 (3.12)	75.2 (3.12)	6.1

Note. Binding energy was calibrated using the Zr 3*d* peak (182.3 eV).
[a] ($4f_{7/2}$ + $4f_{5/2}$ of cation)/($4f_{7/2}$ + $4f_{5/2}$ of metal).
[b] In parenthesis are given FWHM in eV.

The surprising result from the Pt 4*f* XPS spectra is a high cation/metal peak ratio (4.5), even after pretreatment (*in situ*) of the $Pt/SO_4^{2-}-ZrO_2$ sample with hydrogen at 573 K. The platinum cation/metal peak ratio for the Pt/ZrO_2 sample pretreated at 573 K was ca. 0.3 even after exposure of the reduced sample to air before the XPS measurement (Fig. 4). Thus, the small fraction of the metallic phase observed for the $Pt/SO_4^{2-}-ZrO_2$ sample after *in-situ* reduction at 573 K strongly suggests the presence of a large fraction of unreduced platinum oxide particles on the $SO_4^{2-}-ZrO_2$. By increasing the hydrogen pretreatment temperature from 573 to 673 K, the cation/metal

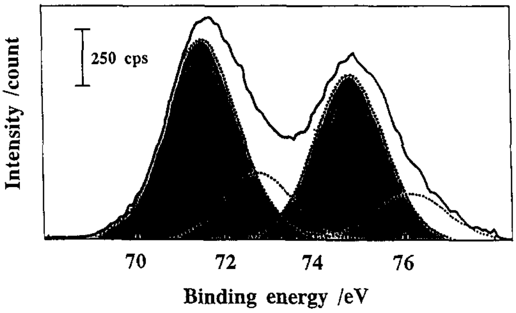

FIG. 4. Pt 4*f* XPS spectra (solid line) of the Pt/ZrO_2 sample after hydrogen pretreatment at 623 K (before XPS measurement, the sample was exposed to air for a few minutes to set on the sample holder). The separation curves are shown by dotted lines. Shaded parts represent platinum metallic phase.

peak ratio did not change much. It means that the reduction of the platinum oxide to the platinum metal scarcely occurs on raising the hydrogen treatment temperature from 573 to 673 K. The presence of the sulfate ion is considered to inhibit the reduction of the dispersed platinum oxide particles.

In the separation of the Pt 4*f* spectra of the Pt/SO_4^{2-}–ZrO_2 pretreated at 573 K and 623 K, the platinum cation peaks could be fitted with ca. 2.75–2.79 eV FWHM, which are close to the FWHM values (2.6–2.7) obtained for the oxidized Pt/SO_4^{2-}–ZrO_2 sample. However, the platinum cation peak for the Pt/SO_4^{2-}–ZrO_2 pretreated at 673 K could not be fitted without using a larger FWHM value (3.1 eV). The increase in the FWHM value for the platinum cation peak with the increase in the reduction temperature suggests that a qualitative change of the platinum cation occurs by the pretreatment with hydrogen between 623 and 673 K.

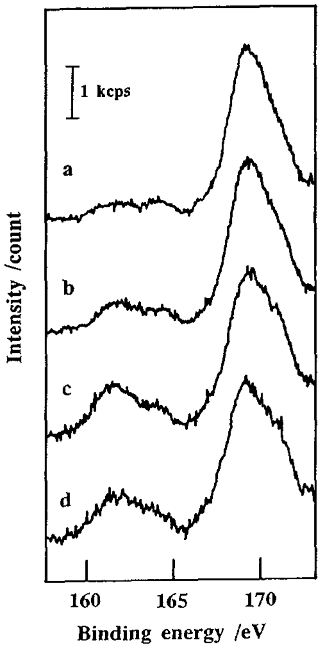

FIG. 5. S 2*p* XPS spectra of Pt/SO_4^{2-}–ZrO_2 after (*in-situ*) hydrogen pretreatment at (a) 573 K, (b) 623 K, and (c) 673 K; (d) after exposure to air at room temperature. X-ray satellites were subtracted. Note that the hydrogen pretreatment temperature was raised stepwise in 50-K increments.

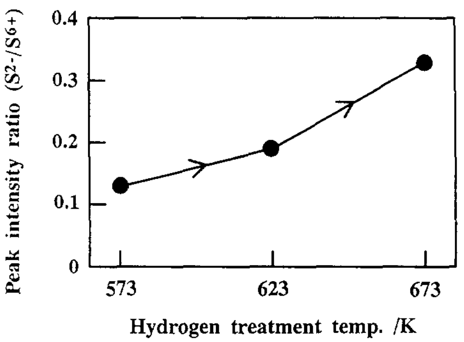

FIG. 6. The variation of the relative S 2*p* XPS peak area (S^{2-}/S^{6+}) of Pt/SO_4^{2-}–ZrO_2 with increasing hydrogen pretreatment temperature. Note that the hydrogen pretreatment temperature was raised stepwise in 50-K increments.

The S 2*p* XPS spectra of the Pt/SO_4^{2-}–ZrO_2 samples pretreated with hydrogen at different temperatures are shown in Fig. 5. In the figure, X-ray satellites have been subtracted. For the Pt/SO_4^{2-}–ZrO_2 sample pretreated at 573 K, the single peak at ca. 169 eV was observed. This S 2*p* peak is due to sulfur with oxidation number 6+ (*19*). By increasing the pretreatment temperature to 623 K, a new peak appeared at ca. 162 eV. This newly formed S 2*p* peak is due to the sulfur with oxidation number 2−. The observed peak separation between 6+ and 2− was 7.4–8.0 eV, which is higher than the reported value of 7.2 eV for $Fe(SO_4)$ and FeS (*19*).The peak intensity for S^{2-} increased on raising the pretreatment temperature to 673 K. The peak intensity of the S^{2-} was not influenced by exposure of the pretreated sample to air at room temperature after the XPS measurement. The peak intensity ratio S^{2-}/S^{6+} is plotted against the pretreatment temperature in Fig. 6. The formation of S^{2-} species is facilitated at a higher pretreatment temperature.

The O 1*s* XPS core level spectra of the Pt/SO_4^{2-}–ZrO_2 sample pretreated at different temperatures are shown in Fig. 7 together with separation peaks (dotted lines).

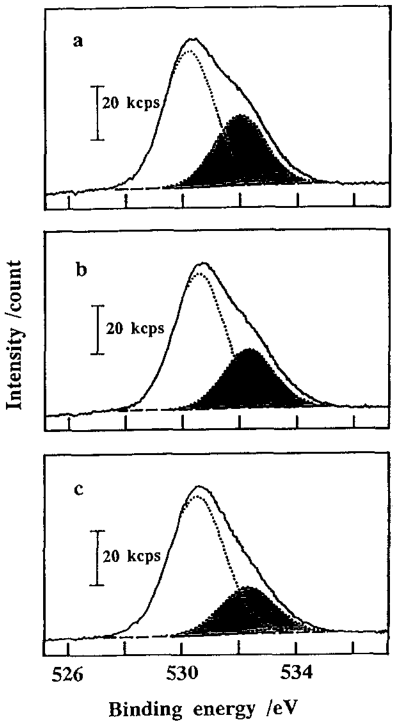

FIG. 7. O 1*s* XPS spectra of $Pt/SO_4^{2-}-ZrO_2$ after (*in-situ*) pretreatment with hydrogen at (a) 573 K, (b) 623 K, and (c) 673 K. The shaded part represents O 1*s* XPS spectra of O^{2-} in the SO_4^{2-} ion. The background is shown by a dashed line. Note that the pretreatment temperature was raised stepwise in 50-K increments.

The observed O 1*s* peak for the $Pt/SO_4^{2-}-ZrO_2$ sample pretreated at 573 K can be fitted with three peaks at 530.5, 532.5, and 533.5 eV. The main O 1*s* peak (530.5 eV) is attributed to the O^{2-} of zirconium oxide. The second O 1*s* peak (532.5 eV) was not observed for the Pt/ZrO_2 sample pretreated with hydrogen at 623 K. Thus, the O 1*s* peak at 532.5 eV is attributed to the O^{2-} of the sulfate ion (SO_4^{2-}). The O 1*s* peak at the higher binding energy (533.5 eV) is due to the O^{2-} of adsorbed water (*19*). By increasing the reduction temperature, the relative peak intensity of the O 1*s* peak at 532.5 eV decreased stepwise, 33% (573 K) → 29% (623 K) → 24% (673 K). The peak at 533.5 eV kept almost the same intensity on increasing the pretreatment temperature from 573 to 623 K, but disappeared by the pretreatment with hydrogen at 673 K. Unfortunately, the O 1*s* peak for the O^{2-} of platinum oxide was not separable from the O^{2-} of the zirconium oxide support.

DISCUSSION

Obviously, the reduction of S^{6+} to S^{2-} requires hydrogen. TPR (temperature-programmed reduction) experiments showed that hydrogen consumption for the $SO_4^{2-}-ZrO_2$ (without platinum) reaction occurred above 873 K (*23*). Occurrence of the reduction even at 573 K for $Pt/SO_4^{2-}-ZrO_2$ suggests that the presence of platinum facilitates the reduction of S^{6+} to S^{2-}. Hydrogen molecules dissociate on the metallic platinum to form hydrogen atoms which react with S^{6+} (SO_4^{2-}) to form S^{2-}. In other words, a metal-catalyzed reaction is involved in the conversion of S^{6+} to S^{2-}:

$$SO_4^{2-} + 4H_2 \rightarrow S^{2-} + 4H_2O. \qquad (1)$$

Two possible locations of S^{2-} are on the zirconium oxide support and on the platinum particles dispersed on the support. In the latter case, platinum sulfide (PtS) phase will form. The conversion of metal to sulfide usually shows up as an increase in the core electron binding energies of the metal (*24*). The Pt 4*f* peak for PtS appears at a higher binding energy than that of metallic Pt and is close to that of platinum oxide. The peak position and FWHM value for the $Pt/SO_4^{2-}-ZrO_2$ samples pretreated with hydrogen at 573 and 623 K are close to those of the oxidized sample (Table 1). Therefore, it is suggested that the platinum cations observed for the $Pt/SO_4^{2-}-ZrO_2$ samples are due mainly to platinum oxide. The presence of PtS could not be confirmed by the XPS measurement of Pt 4*f*. The low peak intensity of S^{2-} for the sample pretreated at 573 K also favors the absence of PtS, though the presence of PtS could not be excluded.

For the $Pt/SO_4^{2-}-ZrO_2$ sample pretreated with hydrogen at 673 K, however, the existence of PtS is highly plausible. The FWHM value of 3.12 eV for the sample pretreated at 673 K was significantly larger than the values 2.76–2.79 eV obtained for the sample pretreated at 573 and 623 K. The large FWHM value is considered to be due to the superposition of contributions from the Pt cations of PtO and PtS.

The formation of surface PtS is considered to proceed by the reaction of S^{2-} with either PtO or metallic Pt. The plausible form of the S^{2-} to react is H_2S, and the formation of PtS may proceed by one of the following reactions:

$$PtO + H_2S \rightarrow PtS + H_2O \qquad (2)$$

$$Pt + H_2S \rightarrow PtS + H_2. \qquad (3)$$

If the reaction (2) proceeds, the ratio of Pt cation/Pt^0 will not change on hydrogen treatment, while the ratio will increase if reaction (3) proceeds. The ratio Pt cation/Pt^0 kept almost constant values of 4.5 ~ 6.1 on raising the temperature from 573 to 673 K. The reduction of S^{6+} to S^{2-} proceeded to a considerable extent on raising the treatment temperature from 573 to 673 K (Fig. 6). It is, therefore, suggested that PtS is formed in consumption mainly of PtO (reaction (2)).

The existence of a large fraction of Pt cations after pretreatment with hydrogen at 573–673 K is the feature which distinguishes the $Pt/SO_4^{2-}-ZrO_2$ sample from the Pt/ZrO_2 sample. The platinum oxide particles on the $SO_4^{2-}-ZrO_2$ are difficult to reduce with hydrogen to form metallic Pt. For the reduction of metal oxide particles, an autocatalyzed reduction mechanism is generally accepted (*25*). In the mechanism, the reduction rate of metal oxide particles is proposed to depend on both the rate of the metal nuclei formation and the rate of hydrogen diffusion through the produced nuclei to the interface between the nuclei and the metal oxide. In case of slow hydrogen diffusion, the reduction rate decreases with an increase in the metal oxide particle size.

According to Vis *et al.* (*26*), the reduction rate of supported noble metal oxide particles is limited by the nucleation rate; hydrogen diffusion through the metal particle is fast. In other words, the reduction rate of supported noble metal oxide particles does not depend on the particle size, but depends on the rate of metal nuclei formation. In the present study, the low reducibility of the $Pt/SO_4^{2-}-ZrO_2$ sample could be explained by a slow nucleation rate.

The nucleation rate is proposed to vary with the metal–support interaction (*25*). The metal–support interaction depends strongly on the nature of the support (*4–9, 27, 28*). Turlier *et al.* (*29*) proposed a type of metal–support interaction "Redox Metal–Support Interaction" (RMSI). According to them, the acidic properties of the support suppress the nucleation rate because of the low affinity of the support for the protons which is produced by the reaction between metal oxide and hydrogen ($M^{n+} + n/2H_2 \rightarrow M^0 + nH^+$). It is well known that the support $SO_4^{2-}-ZrO_2$ used in the present study is strongly acidic (*30–32*). Therefore, it is considered that the RMSI between platinum metal oxide particles and the $SO_4^{2-}-ZrO_2$ causes to lower the nucleation rate. As a result, a large fraction of platinum oxide particles remained on the $SO_4^{2-}-ZrO_2$ support after pretreatment with hydrogen at 573–673 K.

In our previous paper (*2*), we reported that the $Pt/SO_4^{2-}-ZrO_2$ catalyst pretreated with hydrogen at 623 K showed little activity for propene hydrogenation, and no activity for butane hydrogenolysis, though the catalyst was able to dissociated hydrogen molecule. In the present study, it is shown that the catalyst scarcely chemisorbs CO molecules. These properties are not observed for usual supported platinum catalysts. Based on the XPS study in the present paper, it is suggested that the unique properties of the $Pt/SO_4^{2-}-ZrO_2$ catalyst arise from the fact that a large fraction of the platinum remains in the state of cation in the form of PtO and PtS, and the metallic fraction is low.

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