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The Structure of Sulfur Adsorbed on Pt–Na_2O/Al_2O_3 Catalyst and Its Influence on Isobutane Dehydrogenation

Junya Kobayashi,* Takashi Shimizu, and Takanori Mizushima†

Hakodate National College of Technology, Tokura-cho, Hakodate, Hokkaido 042-8501

†Department of Material Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580

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The structures of the sulfur species on a sulfurized Pt–Na_2O/Al_2O_3 catalyst were characterized by Extended X-ray Absorption Fine Structure (EXAFS) and temperature-programmed reaction (TPR) experiments. EXAFS indicated that PtS_2 is formed on a surface of Pt particles. A TPR experiment using deuterium indicated that HS^- is the major species on the catalyst and that the HS^- bridges the PtS_2 and Na_2S particles. This HS^- was effective in enhancing the selectivity for isobutane dehydrogenation.

In the dehydrogenation of isobutane to isobutene on Pt/Al_2O_3 catalyst, the yield of isobutene is lowered due to the occurrence of by-reactions such as cracking, coking, and skeletal isomerization.[1] We have attempted to enhance the selective dehydrogenation to isobutene by inhibiting these by-reactions. In previous papers,[2,3] we demonstrated that a H_2S treatment and the addition of sodium enhance the selectivity to isobutene.

The Pt–Re/Al_2O_3 catalyst used as a reforming catalyst is also pretreated with a sulfide. This pretreatment decreases the carbon deposition and increases the reaction rate.[4] It is known that Pt/Al_2O_3 and Pt–Re/Al_2O_3 catalysts pretreated with a sulfide, such as hydrogen sulfide, has two kinds of adsorbed sulfurs. On the Pt/Al_2O_3 catalyst, sulfur that is easily desorbed by a hydrogen treatment is called "reversibly adsorbed sulfur", and sulfur not so desorbed is called "irreversibly adsorbed sulfur".[5—7] The irreversibly adsorbed sulfur, which does not exist on pure alumina, would interact with platinum metal. Surface studies using low-energy electron diffraction (LEED)[8] and ultraviolet photoelectron spectroscopy (UPS)[9] showed that the Pt–S bond is essentially a covalent one. These papers merely indicated that the Pt–S bond is attributed to the PtS formation on the surface of a platinum particle.

Regarding the structure of the reversibly adsorbed sulfur, Koestner et al. noted the presence of HS^- and H_2S at low temperature on (111) monocrystalline platinum.[10] Ultraviolet-visible reflectance spectroscopy for Pt/Al_2O_3 catalyst showed that the reversibly adsorbed species were made of neutral sulfur and polysulfide.[11] The dissociative chemisorption for H_2S was observed by an IR experiment, even on an Al_2O_3 support. On MgO, Tench et al. suggested the following reaction :

$$H_2S+(O^{2-})_{surface}\rightarrow H_2O+(S^{2-})_{surface}.$$

We characterized the irreversibly and reversibly adsorbed sulfurs by a extended X-ray absorption fine structure (EXAFS) and a temperature programmed reaction (TPR), respectively, flowing deuterium as follows: $S_{ad}+D_2\rightarrow D_2S$ and $HS_{ad}+D_2\rightarrow HDS$, where S_{ad} and HS_{ad} signify sulfur in reversibly adsorbed states. Further, this paper describes the role of the reversibly and irreversibly adsorbed sulfurs in isobutane dehydrogenation.

In this paper, the reversibly adsorbed sulfur is defined by the following reaction:

$$\begin{aligned} H_2S &\rightleftarrows S_{ad}+H_2 \\ H_2S &\rightleftarrows HS_{ad}+\frac{1}{2}H_2 \\ H_2S &\rightleftarrows H_2S_{ad} \end{aligned}$$

Consequently, the irreversibly adsorbed sulfur is defined as sulfur species remaining on the catalyst under a hydrogen atmosphere at high temperature.

Experimental

Preparation of Catalysts. A Pt/Al_2O_3 catalyst was prepared by the impregnation of γ-alumina (Sumitomo Chemical, BET surface area = 150 $m^2\,g^{-1}$) with an H_2PtCl_6 aqueous solution, which was then dried at 273 K for 24 h. Pt–Na_2O/Al_2O_3 catalyst was prepared by the impregnation of dried Pt/Al_2O_3 catalyst with $NaNO_3$ aqueous solutions. A Na_2O/Al_2O_3 catalyst was also prepared by using γ-alumina and a $NaNO_3$ aqueous solution. All of the catalysts were dried at 373 K for 24 h and then calcined at 923 K for 4 h. For the isobutane dehydrogenation and TPR experiments, Pt loading was 1 wt%, and those of Na varied from 0 to 5 wt% as the oxide formed. For example, it is represented as Pt–$Na_2O(3)/Al_2O_3$ catalyst in this paper. The EXAFS experiments used catalyst loadings of 2.5 wt% Pt.

Pretreatment of Catalysts. Before isobutane dehydrogenation and TPR, the catalysts were pretreated with hydrogen and hydrogen sulfide with hydrogen in a flow system with a fixed quartz glass reactor (8 mm i.d.). The catalysts (16—32 mesh size) were reduced by flowing hydrogen at 50 $ml\,min^{-1}$ at 833 K for 3 h, and then sulfurized by flowing hydrogen with 7 vol% hydrogen sulfide at 50 ml min^{-1} at 833 K for 1 h. We simply called the above treatment the "H_2S-treatment".

The pretreatment for the EXAFS experiment was performed in an in situ glass cell. This glass cell was similar to an in situ IR cell, except that it had attached beryllium windows. The catalyst (disk 20 mm ϕ in diameter) was heated at 373 K for 1 h under reduced pressure, reduced at 833 K in 400 Torr of hydrogen (1 Torr = 133.322 Pa), and then sulfurized at 833 K in 400 Torr of hydrogen with 7 vol% hydrogen sulfide. The cell was evacuated with a vacuum pump for 1 h, and cooled to room temperature.

Characterization of Adsorbed Sulfurs by Temperature Programmed Reaction. The characterization of adsorbed sulfurs was carried out using TPR flowing deuterium and EXAFS. The TPR experiment used the following reactions:

$$S_{ad} + D_2 \rightarrow D_2S \uparrow$$
$$HS_{ad} + D_2 \rightarrow HDS \uparrow$$

A flow system with a quadrupole mass spectrometer was shown in our previous paper.[12] After 0.075 g of the catalyst was pretreated, hydrogen sulfide and hydrogen in a quartz reactor were replaced by flowing helium (50 ml min^{-1}) at 833 K for 5 h. The catalyst was then cooled to room temperature in flowing helium. Argon containing 4.86 vol% deuterium was flowed at a flow rate of 60 ml min^{-1} and the reactor was heated to 1073 K at a rate of 10 K min^{-1}. Desorbed sulfur-containing gases were monitored with an on-line quadrupole mass spectrometer. A variable leak valve was used to control the pressure in the mass spectrometer. However, each experiment was carried out under a different pressure, due to a difficulty in controlling the opening of the variable leak valve. As a result, it was impossible to control the intensity for a particular peak of each catalyst, although good reproducibility of the desorbed temperature was obtained.

Characterization of Adsorbed Sulfurs by EXAFS. EXAFS measurements were performed by an in-house EXAFS system (Rigaku, R-EXAFS 2000), which consisted of a high-power X-ray generator, a spectrometer with a curved Ge(400) crystal, a sealed proportional counter for I_0, and a scintillation counter for I. The X-ray source with a Mo target was operated at 23 kV and 200—330 mA in order to minimize the effect of higher order reflections.

Isobutane Dehydrogenation. After 0.15 g of the catalyst was pretreated, hydrogen and hydrogen sulfide in a quartz reactor were replaced by flowing helium (50 ml min^{-1}) at 833 K for 2 h. The reactor was set to a reaction temperature of 773 K. 6 vol%-isobutane/nitrogen was admitted by injecting pulses of 1 ml into the helium carrier, and hence to the catalyst. Isobutene; by-products such as methane, propylene, and 2-butenes; and unreacted isobutane were analyzed using an on-line gas chromatograph (VZ-10 column) with a thermal conductivity detector.

Results and Discussion

Characterization of Irreversibly Adsorbed Sulfur by EXAFS Analysis. In this paper, we regard the irreversibly adsorbed sulfur species as the sulfur remaining on the catalyst at the temperature of re-reduction (833 K), because only little desorption of H_2S (or D_2S, HDS) at 833 K was detected by a TPR experiment.

It has been reported that the H_2S-treated Pt/Al_2O_3 catalyst has irreversibly adsorbed sulfur.[5—7] The reaction between H_2S and platinum have previously been reported as:

$$Pt + H_2S \rightarrow PtS_{ir} + H_2,$$

where S_{ir} signifies sulfur in an irreversibly adsorbed state.[7] We attempted to characterize the irreversibly adsorbed sulfur by an EXAFS analysis.

The EXAFS data were analyzed using standard samples with known structure. The Pt–Pt and Pt–S contributions were extracted from the EXAFS data for a Pt foil and PtS_2, respectively. A cubic spline background subtraction was performed to extract EXAFS data for severely treated catalysts and the reference. The resulting patterns were normalized by dividing the edge height. These EXAFS signals are shown in Figs. 1 and 2; a k^3-weighted Fourier transformation was performed (Figs. 3 and 4). Table 1 lists the structural parameters calculated by considering the phase factors. The coordination number and the Pt–Pt distance of the reduced Pt/Al_2O_3 and $Pt–Na_2O/Al_2O_3$ catalysts were calculated to be almost 12 and 2.78 Å, respectively, comparable to those of a Pt foil. After sulfurization, the coordination number of Pt–Pt decreased, while a peak appeared for Pt–S. The coordination number and the distance for Pt–S in both catalysts were consistent with those for PtS_2, rather than those for PtS ($N = 4$, $R = 2.312$ Å), listed as a reference. The signal for Pt–Pt remained after sulfurization. These sulfurization behaviors can be explained on either of the following. Only the surfaces of the platinum particles were sulfurized, or platinum particles were divided into two areas, PtS_2 and Pt metal particles. In the former case, the decrease in the coordination number of Pt–Pt indicates that platinum remained inside the platinum particles. In the latter case it suggests that the PtS_2 particles were isolated from the platinum particles. We judged that it is impractical to divide into two areas; hence, only the surface of a platinum particle was sulfurized. After re-reduction at 833 K for 5 h in 400 Torr, the PtS_2

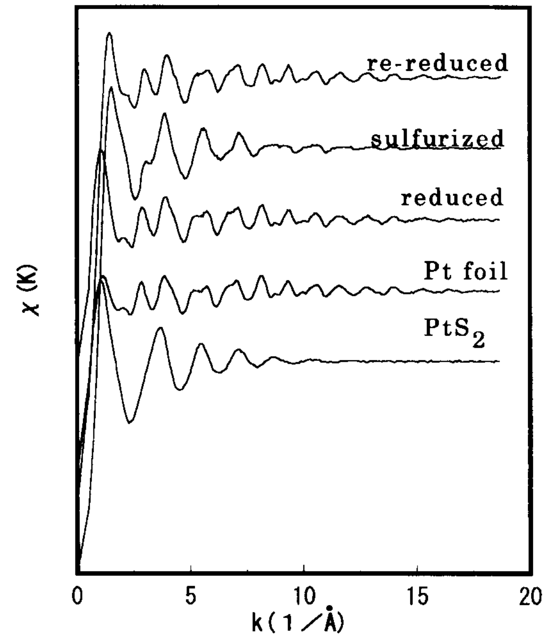

Fig. 1. EXAFS patterns of the variously treated Pt/Al_2O_3 catalysts and standard samples.

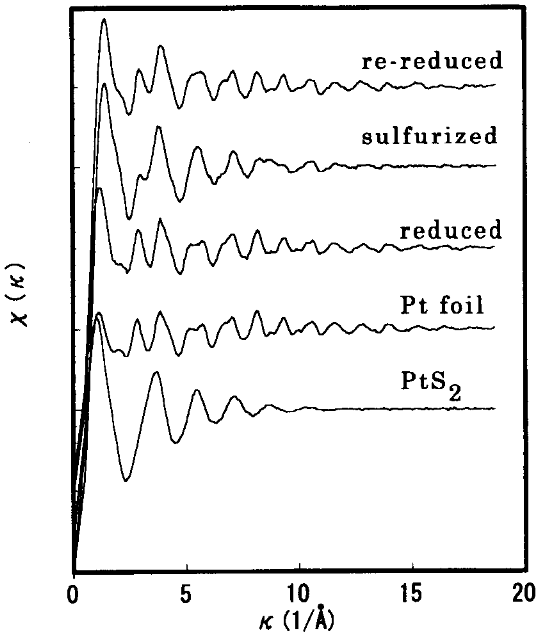

Fig. 2. EXAFS patterns of the variously treated Pt–Na_2O/Al_2O_3 catalysts and standard samples.

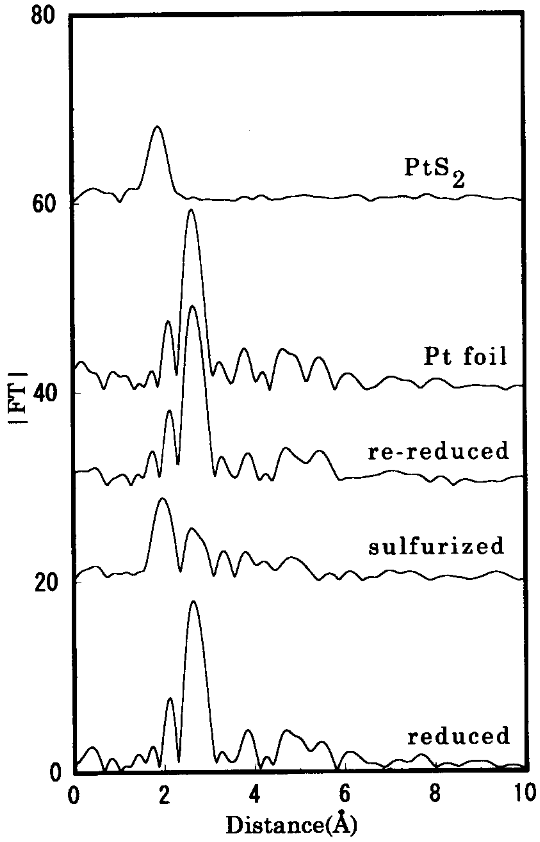

Fig. 3. Fourier transform patterns for the EXAFS patterns of the variously treated Pt/Al_2O_3 catalysts and standard samples.

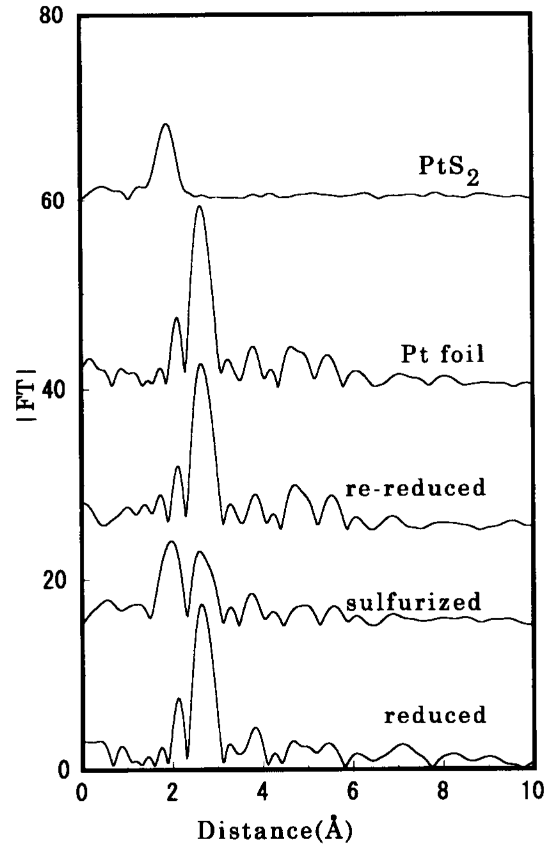

Fig. 4. Fourier transform patterns for the EXAFS patterns of the variously treated Pt–Na_2O/Al_2O_3 catalysts and standard samples.

reduced to Pt metal. However, sulfur was detected by X-ray Photoelectron Spectroscopy: XPS and Electron Probe Micro Analysis: EPMA experiments on the re-reduced Pt/Al_2O_3 and Pt–Na_2O/Al_2O_3 catalysts. The reason why these experiments conflicted with EXAFS is considered as to be follows. The coordination numbers for Pt–Pt in the reduced catalysts and platinum foil were mostly 12, implying that the platinum particles in the reduced catalysts were bulky, as for platinum foil. The fraction of platinum atoms occupying surface positions was therefore very small. In addition, the sulfur would only exist on an extremely thin surface of the platinum particles, because most of it was removed by the re-reduction. As a result, the amount of Pt–S structure would be less than the identification limit for the EXAFS experiments. We conclude that the irreversibly adsorbed sulfur on Pt is a Pt–S bond in PtS_2.

Although EXAFS spectra for Pt/Al_2O_3 and Pt–Na_2O/Al_2O_3 catalysts obtained after the H_2S treatment indicate the formation of PtS_2, our previous X-ray powder diffraction (XRD) experiments have indicated that PtS forms.[3] We considered the cause of the contradiction between the EXAFS and XRD results in relation to the dispersion of platinum measured by hydrogen and carbon monoxide adsorption methods. Catalysts with 2.5 and 5 wt% platinum loadinds were used with EXAFS and XRD experiments, respectively. The H/Pt (CO/Pt) values of Pt(2.5)/Al_2O_3 and Pt(5)/Al_2O_3 catalysts were 0.21(0.19) and 0.061(0.069), respectively. These H/Pt and CO/Pt values suggest that the platinum particles in the Pt(2.5)/Al_2O_3 catalyst was smaller than that in the Pt(5)/Al_2O_3

Table 1. Structural Parameters of Pt Metal, PtS_2, Pt/Al_2O_3, and $Pt–Na_2O/Al_2O_3$ Catalysts

Sample	Treatment	Shell					
		Pt–Pt			Pt–S		
		R(Å)	N	σ	R(Å)	N	σ
Pt	–	2.774	12	0.06			
PtS_2	–				2.402	6	0.06
Pt/Al_2O_3	Reduced	2.77	12.2	0.062			
	H_2S-treated	2.78	3.8	0.063	2.43	6.5	0.054
	Re-reduced	2.78	12.4	0.061			
$Pt–Na_2O/Al_2O_3$	Reduced	2.78	12.0	0.063			
	H_2S-treated	2.77	6.0	0.065	2.43	6.6	0.052
	Re-reduced	2.78	12.4	0.063			

R: Average absorber-backscatterer distance. N: Coordination number for the absorber-backscatterer pair. σ: Debye–Waller factor.

catalyst and tended to be sulfurize. Therefore, it is estimated that the platinum particles in the $Pt(2.5)/Al_2O_3$catalyst were sulfurized until PtS_2 was formed.

Sodium before the H_2S treatment is thought to have been supported as Na_2O, and $-O^-Na^+$ was replaced with hydrogen in an acidic hydroxyl group. Our previous EPMA and XPS experiments indicated that the Na_2S_{ir} formed in the H_2S-treated Na_2O/Al_2O_3 catalyst.[3] Some of the respective sodium species are considered to be sulfurized according to the following irreversible reactions:

$$Na_2O + H_2S \rightarrow Na_2S_{ir} + H_2O,$$
$$-O^-Na^+ + \frac{1}{2}H_2S \rightarrow -OH + \frac{1}{2}Na_2S_{ir}.$$

We conclude that the irreversibly adsorbed sulfurs on the $Pt–Na_2O/Al_2O_3$ catalyst were the Pt–S bond in PtS_2 and the Na–S bond in Na_2S, respectively.

Characterization of the Reversibly Adsorbed Sulfur by Temperature-Programmed Reaction Using Deuterium. Figures 5, 6, and 7 show the patterns of $m/e = 35$ and $m/e = 36$ assigned to the desorbed HDS and D_2S from H_2S-treated catalysts, respectively. Saur et al. reported the adsorbed sulfur species, such as Al–OH$\cdots$$SH_2$ and Al–O$\cdots$HSH, on alumina treated with H_2S.[13] These adsorption species involve a hydrogen bond between a surface oxygen atom and the hydrogen atom of the HS bond. However, the signals of $m/e = 34$, 35, and 36 were not detected on the H_2S-treated alumina support alone. This suggests that these adsorption species were desorbed by passage through helium at 833 K for 5 h. Thus, we do not consider the role of sulfur species on an alumina support in later sections.

In all of the catalysts, the intensity of HDS was higher than that of D_2S. This implies that the reversibly adsorbed sulfur tended to form HS^-, rather than S^{2-}. The reactions between H_2S and platinum or sodium species would proceed as follows:

$$PtS_2 + H_2S \rightleftarrows PtS_2(HS) + \frac{1}{2}H_2,$$
$$Na_2S_{ir} + H_2S \rightleftarrows Na_2S_{ir}(HS) + \frac{1}{2}H_2.$$

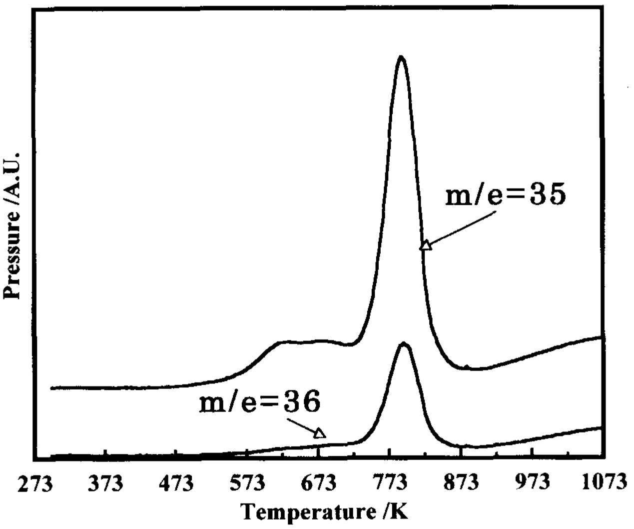

Fig. 5. TPR patterns of sulfurized Pt/Al_2O_3 catalyst.

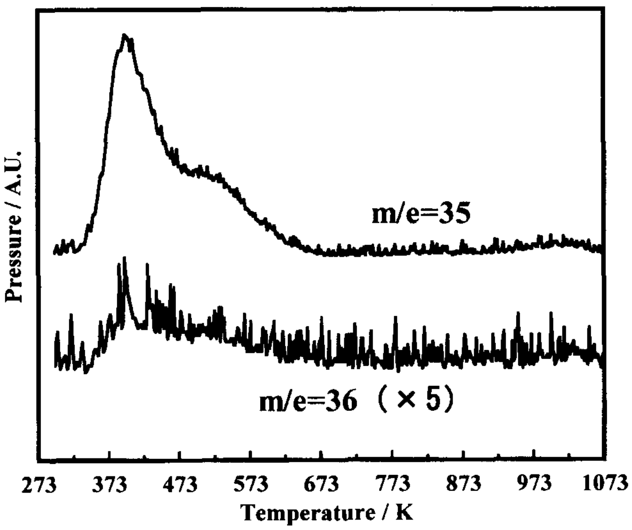

Fig. 6. TPR patterns of sulfurized Na_2O/Al_2O_3 catalyst.

Little $m/e = 34$ signal was detected. This means the absence of reversibly adsorbed H_2S. Ponitzsch[9] reported that

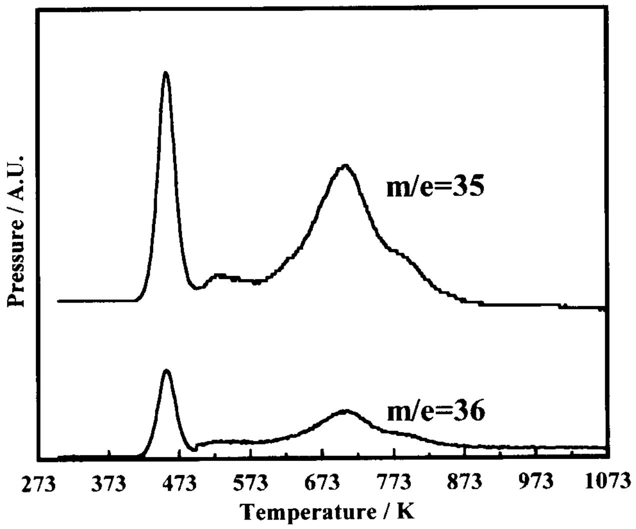

Fig. 7. TPR patterns of sulfurized Pt–Na_2O/Al_2O_3 catalyst.

chemisorbed H_2S produces a transformation into an elementary sulfur in a helium atmosphere. Therefore, it is necessary to consider that a part of the $m/e = 36$ signal resulted from a reaction between deuterium and elementary sulfur.

Pt/Al_2O_3 catalyst has a sharp peak at 793 K and a broad peak in the temperature range 553—773 K, suggesting the desorption of HDS and D_2S from PtS_2 (HS) and from the bulk PtS_2, respectively:

$$\begin{aligned} PtS_2(HS) + \frac{1}{2}D_2 &\rightarrow PtS_2 + HDS, \\ PtS_2 + 2D_2 &\rightarrow Pt + 2D_2S. \end{aligned}$$

The Na_2O/Al_2O_3 catalyst has a peak at 453 K with a shoulder at 533 K. The peak at 453 K is considered to have resulted from the following reaction:

$$Na_2S_{ir}(HS) + \frac{1}{2}D_2 \rightarrow Na_2S_{ir} + HDS.$$

The Na_2S_{ir} is comprised of many adsorption sites derived from the difference in the supporting states of sodium, which would lead to a broadening of the desorption peak and producing the shoulder.

The TPR pattern of the Pt–Na_2O/Al_2O_3 catalyst, in comparison with Pt/Al_2O_3 and the Na_2O/Al_2O_3 catalyst, is non-additive. A comparison of the Pt–Na_2O/Al_2O_3 catalyst with the Na_2O/Al_2O_3 catalyst indicates that the peak at 453 K is desorbed from $Na_2S_{ir}(HS)$, but the ratio of $m/e = 36$ and $m/e = 35$ signals from the Pt–Na_2O/Al_2O_3 catalyst was higher than that from Na_2O/Al_2O_3 catalyst. It is probable that the platinum changed the properties on the Na_2S_{ir} surface. It is clear that the majority of desorbed species from both catalysts at 453 K was, in any event, HDS. The desorption peak at 793 K for the $PtS_2(HS)$ in the Pt/Al_2O_3 catalyst was weakened, whereas a new peak at 713 K appeared. It seems that adding sodium caused a change in the adsorption states of HS^- or the formation of a new adsorption site. It does not appear that the addition of sodium created a new adsorption site, because in XPS experiments, the binding energies of $Pt_{7/2}$ for both H_2S-treated Pt(5)–Na_2O/Al_2O_3 catalyst and Pt(5)/Al_2O_3 catalyst were almost equal (71.9 eV). Therefore, HS^-, which is strongly adsorbed in comparison with H_2S-treated Na_2O/Al_2O_3 and weakly adsorbed in comparison with H_2S-treated Pt/Al_2O_3 catalyst, is expected. We consider that HS^- bridged between the PtS_2 and the Na_2S_{ir} particles. The desorption peak observed at 453 K for the Pt–Na_2O(3)/Al_2O_3 catalyst suggests that the Na_2S_{ir} particles covered a part of the PtS_2 surface, and thus the HS^- adsorbed on Na_2S_{ir} without bridging with the PtS_2 and Na_2S_{ir} particles. We can not rule out the possibility that HDS was formed by desorbing D_2S and a surface –OH group. Although IR spectra for the H_2S-treated Na_2O/Al_2O_3 catalyst only displayed the H–S stretching mode at 2593 cm^{-1}, no H–S–H bending mode was detected. This would be evidence that many HS^- exist. Because the desorbed HDS is probably related, at least in part, to the reaction between the surface HS^- and $(1/2)D_2$, in this paper we did not consider the reaction between D_2S and the surface –OH group.

The influence of the sodium concentration on the desorption peak ($m/e = 35$) is illustrated in Fig. 8. Pt–Na_2O(1)/Al_2O_3 had a desorption peak related to the PtS_2 particles, compared with the Pt/Al_2O_3 catalyst, but no peak at 453 K was observed related to $Na_2S_{ir}(SH)$. These facts reflect that all of the Na_2S particles interacted with the PtS_2 particles, while isolated PtS_2 particles existed. The Pt–Na_2O(5)/Al_2O_3 catalyst has a broad peak at 413 K. The desorption temperature agreed with that from the Na_2O/Al_2O_3 catalyst. Our previous experiment on hydrogen adsorption showed that the Pt–Na_2O(5)/Al_2O_3 catalyst had a structure in which the PtS_2 particles were completely covered with Na_2S particles, because the amount of adsorbed hydrogen was almost zero.[3] However, the D_2S peak desorbed from the Pt–S structure was also observed. We presume that the desorbed D_2S re-

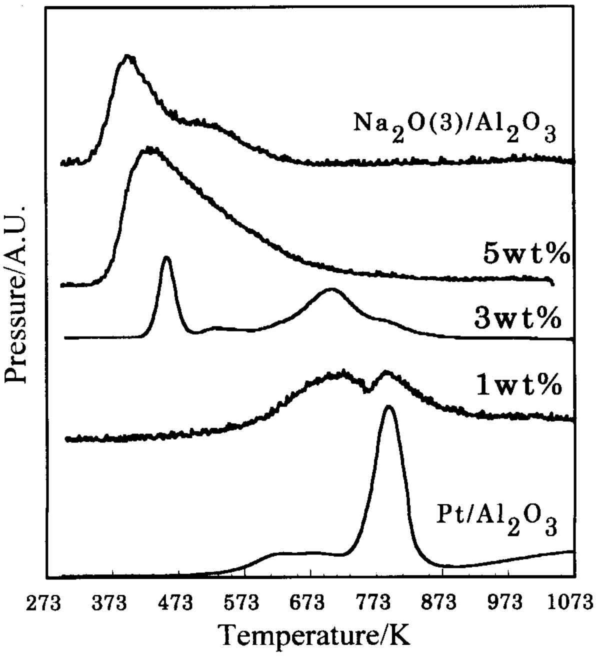

Fig. 8. Influence of Na_2O concentration in Pt–Na_2O/Al_2O_3 catalyst on TPR pattern ($m/e = 35$).

adsorbed on Na_2S_{ir}. However, the pronounced tailing suggests that the TPR pattern comprised many desorption peaks. Accordingly, the tail of the peak may include a desorption peak from the Pt–S structure.

We propose a schematic model for the H_2S-treated catalysts, as shown in Fig. 9. The Pt–$Na_2O(3)/Al_2O_3$ catalyst has shoulders on both sides of higher and lower temperatures than the main desorption peak at 713 K, which implies a stronger interaction between HS^- with either PtS_2 or Na_2S_{ir} particles. The desorption peak at 453 K suggests that the Na_2S_{ir} particles do not neighbor with the PtS_2 particles, and that not all of the HS^- are bridged between the Na_2S_{ir} and PtS_2 particles.

We conclude that most of the reversibly adsorbed sulfur on the Pt–Na_2O/Al_2O_3 catalyst was HS^- bridging between the PtS_2 and the Na_2S_{ir} particles.

Role of Adsorbed Sulfurs in the Dehydrogenation of Isobutane. Table 2 lists the conversion of isobutane, the selectivity to isobutene, and the S/Metal ratio. The amounts of sulfur, platinum, and sodium were measured with X-ray fluorescence. The S/Metal ratio for the Pt–Na_2O/Al_2O_3 catalyst is S/(Pt+Na) as an atomic ratio. Although the selectivity for the reduced Pt/Al_2O_3 and Pt–$Na_2O(3)/Al_2O_3$ catalysts was almost 0%, high conversion was obtained. Most of the products were C_1–C_3 compounds resulting from a cracking of isobutane. The Pt/Al_2O_3 catalyst also produced a few butenes. The conversion for the reduced Na_2O/Al_2O_3 was almost zero, resulting from a replacement of the hydrogen of acid sites by sodium. Compared with the reduced Pt/Al_2O_3 catalyst, the conversion of H_2S-treated catalyst decreased from 100 to 78%, but the selectivity remained unchanged. However, a H_2S-treatment of the Pt–Na_2O/Al_2O_3 catalyst resulted in a remarkable increase in selectivity and a decrease in conversion, because of a decrease in the cracking products. The conversion and selectivity for the H_2S-treated Na_2O/Al_2O_3 catalyst increased. The results of TPR experiments indicate that all of the reversibly adsorbed sulfurs can be considered to be desorbed by re-reduction. However, it was confirmed from EXAFS, XPS and EPMA that the irreversibly adsorbed sulfur on the platinum and the sodium remained. The conversions for the re-reduced Pt/Al_2O_3 and Pt–Na_2O/Al_2O_3 catalysts were lower than those for the reduced catalysts, which implies that the irreversibly adsorbed sulfur on the platinum surface only acts as an inhibitor for isobutane adsorption. For the Na_2O/Al_2O_3 catalyst, both the reversibly and irreversibly adsorbed sulfurs promote selectivity. The conversions for the re-reduced Pt–$Na_2O(3)/Al_2O_3$ catalyst increased, whereas the selectivity decreased com-

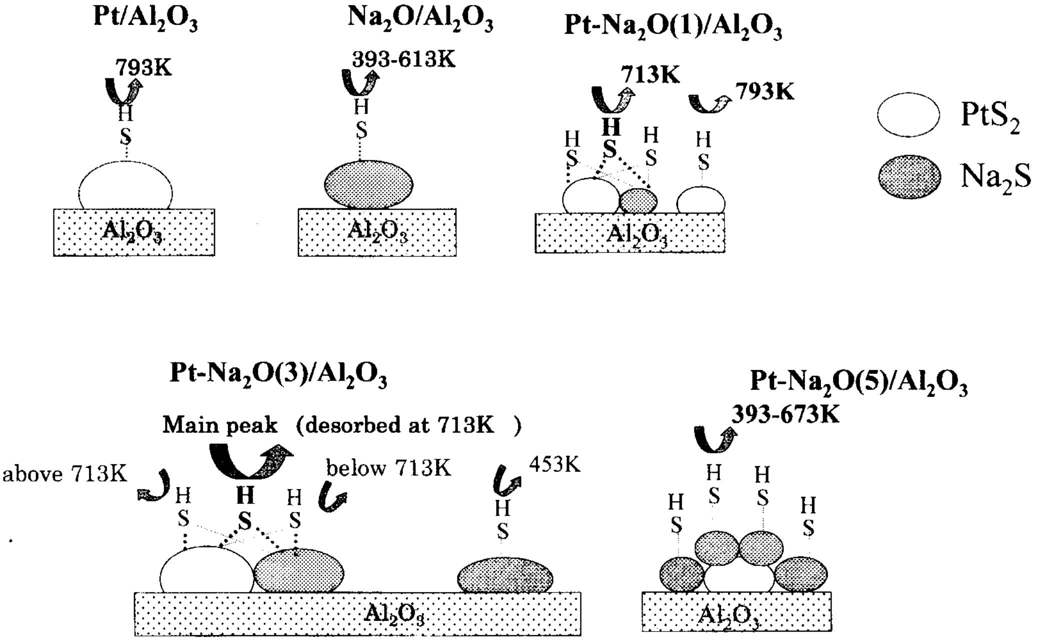

Fig. 9. Schemes of H_2S-treated catalysts.

Table 2. Isobutane Dehydrogenation Activities and S/Me Ratios

Catalysts	Reduced		H_2S-treated			Re-reduced		
	Conv.	Sel.	Conv.	Sel.	S	Conv.	Sel.	S
	%	%	%	%	Me	%	%	Me
Pt/Al_2O_3	100	0	78	0	2.0	90	0	0.4
$Na_2O(3)/Al_2O_3$	<1	Trace	12	51	0.01	4	42	3×10^{-3}
Pt-$Na_2O(3)/Al_2O_3$	98	0	30	75	0.02	64	6	5×10^{-3}

S/Me: Atomic ratio of S/Pt, S/Na, and S/(Pt+Na) for each catalyst.

pared with that of the H_2S-treated Pt–$Na_2O(3)/Al_2O_3$ catalyst. This means that the bridging (SH) increases the selectivity, while it inhibits the adsorption of isobutane. The conversion of H_2S-treated Pt/Al_2O_3 was higher than that of the Na_2O/Al_2O_3 catalysts, indicating that isobutane is adsorbed on platinum species in the Pt–Na_2O/Al_2O_3 catalyst. However, dehydrogenation from the adsorbed isobutane does not occur in the absence of the bridging HS^-, because the selectivity for the H_2S-treated Pt/Al_2O_3 is zero. The hydrogen in the adsorbed isobutane would then be attracted by the sulfur of the bridging HS^-, which would lead to, or assist, dehydrogenation.

The concentration of irreversibly adsorbed sulfur corresponds to the S/Me for re-reduced catalysts. The resulting S/Pt ratio of 0.4 for the re-reduced Pt/Al_2O_3 catalyst is lower than the ratio of 0.5 made by Apesteguia.[4] This was because the re-reduced temperature for this experiment (833 K) was high compared to the experiment by Apesteguia (773 K). The S/Na ratio of the H_2S-treated Na_2O/Al_2O_3 catalyst was lower than that of the ratio estimated from stoichiometry for Na_2S ($S/Na = 0.5$). This suggests that the supported Na_2O and/or $-O^-Na^+$ would be more difficult to sulfurize completely; therefore, a part of their sodium species remained unsulfurized. However, judging from the activity for the reduced Na_2O/Al_2O_3 catalyst, no dehydrogenation occurs on the Na_2O and/or $-O^-Na^+$. The difference between the S/(Pt+Na) ratios of the H_2S-treated and the re-reduced Pt–Na_2O/Al_2O_3 catalysts does not imply the amount of the bridging (SH), because the difference is implicit in the desorption of the sulfur from the Pt–S structure.

Conclusion

Irreversibly adsorbed and reversibly adsorbed sulfurs, respectively, were characterized by EXAFS and TPR experiments using deuterium. These clarified that PtS_2 was formed, and that most of the reversibly adsorbed sulfur was HS^-, suggesting that the reversibly adsorbed sulfur bridged between the PtS_2 and the Na_2S_{ir}. The factor that increased the selectivity would correlate with the bridging HS^-.

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