Characterization of Sulfur on Pt–Alkali metal/Al_2O_3 Catalysts Treated with H_2S by a Temperature-Programmed Reaction Using Deuterium and Its Role in the Dehydrogenation of Isobutane

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This paper discusses the promotion of isobutane dehydrogenation due to sulfur species adsorbed on Pt–alkali metal (Li, Na, or K)/Al_2O_3 catalysts. A treatment with hydrogen sulfide at 833 K increased the selectivity to isobutene on all Pt–alkali metal/Al_2O_3 catalysts. The promotion effect of sulfurization was most significant on a Pt (1 wt%)–Na_2O (3 wt%)/Al_2O_3 catalyst; the selectivity increased from almost 0 for a reduced catalyst to 75% for a sulfurized catalyst. The effect on the selectivity of the addition of alkali metals increased in the order sodium > potassium > lithium. Temperature-programmed reaction (TPR) experiments, conducted by flowing deuterium onto the sulfurized catalysts, were used to characterize the sulfur species that easily desorbed with hydrogen. The results indicated that HS^- is the major species on the catalysts and that the adsorbed HS^- bridges the PtS_{ir} and the Na_2S_{ir} particles. Re-reduction of the sulfurized Pt–Na_2O/Al_2O_3 catalyst to remove the HS^- decreased the selectivity from 75 to 8%, implying that HS^- is effective in enhancing the selectivity.

Increased demand for isobutene, used for the production of methyl *t*-butyl ether, has generated interest in the catalytic conversion of isobutane to isobutene. Currently, isobutene is predominantly obtained from C4 fractions of ethylene plants or FCC units. However, since the supply of isobutene from these sources depends on the demand for the primary products, other processes have been investigated. We have noted the dehydrogenation of isobutane on Pt/Al_2O_3 catalyst. In the dehydrogenation of isobutane to isobutene on Pt/Al_2O_3 catalyst, the isobutene yield is lowered due to the occurrence of such by-reactions as cracking, coking, and skeletal isomerization.[1] In the present work, we attempted to enhance the selective dehydrogenation to isobutene by inhibiting these by-reactions.

Sulfur is generally considered to poison a catalyst. However, at low concentrations it acts as a modifier to selectivity, or even, in some case, as an activator.[2] The addition of sulfur in a Pt–Re/Al_2O_3 reforming catalyst reduces the carbon deposition on the catalyst and increases the reaction rate.[3] These promotion effects have been explained by both changes in the electronic properties and a geometric limitation on the active sites.[4] However, the addition of an alkali metal is considered to inhibit by-reactions over acid sites on alumina. Therefore, Pt–alkali metal (Li, Na, or K)/Al_2O_3 catalysts were prepared and treated with hydrogen sulfide, and used in the dehydrogenation of isobutane. The purpose of the present work was to clarify the influence of the kind of alkali metals and the reaction temperature on isobutane dehydrogenation.

It is known that Pt/Al_2O_3 catalyst treated with a sulfide, such as hydrogen sulfide, has two kinds of adsorbed sulfurs. Sulfur that is easily removed by a hydrogen treatment is called "reversibly adsorbed sulfur"; sulfur not so removed is called "irreversibly adsorbed sulfur".[5—7] We characterized the reversibly adsorbed sulfur by temperature-programmed reaction experiments (TPR) flowing deuterium as $S_{ad}+D_2 \rightarrow D_2S$ and $HS_{ad}+D_2 \rightarrow HDS$, where S_{ad} and HS_{ad} signify sulfur in reversibly adsorbed states. This paper describes the role of reversibly and irreversibly adsorbed sulfurs in isobutane dehydrogenation.

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 a H_2PtCl_6 aqueous solution, which was then dried at 373 K for 24 h. Pt–Li_2O/Al_2O_3, Pt–Na_2O/Al_2O_3, and Pt–K_2O/Al_2O_3 catalysts were prepared by the impregnation of dried Pt/Al_2O_3 catalyst with $LiNO_3$, $NaNO_3$, and KNO_3 aqueous solutions, respectively. A Na_2O/Al_2O_3 catalyst was also prepared by using γ-alumina and $NaNO_3$ aqueous solution. All of the catalysts were dried at 273 K for 24 h and then calcined at 923 K for 4 h. The Pt loading was 1 wt%, and those of the alkali metals 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.

Pretreatment of Catalysts. Before isobutane dehydrogenation and TPR, the catalysts were pretreated with hydrogen and hydrogen sulfide contained in 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 containing 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".

Isobutane Dehydrogenation. After 0.15 g of catalyst was pretreated, hydrogen sulfide and hydrogen in a quartz reactor were replaced by flowing helium (50 ml min^{-1}) at 833 K for 2 h. The reactor was set to reaction temperatures of 673, 723, 773, and 823 K; then, 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.

Characterization of Adsorbed Sulfurs by Temperature Programmed Reaction. The characterization of adsorbed sulfurs was carried out using TPR flowing deuterium as follows:

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

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

The reaction apparatus is shown in Fig. 1. 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 (C in Fig. 1) was used to control the pressure in the mass spectrometer. However, each experiment was carried out under a different pressure, due to a difficulty of 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.

Results and Discussion

Effects of Sulfurization, the Addition of Alkali Metal, and the Reaction Temperature. Table 1 shows the effect of sulfurization on the conversion and selectivity for various catalysts. For the results shown in Table 1 and throughout this paper, the following definitions hold:

$$\text{Conversion \%} = 100 \times \text{mol isobutane reacted} / \text{mol isobutane injected},$$

$$\text{Selectivity \%} = 100 \times \text{mol isobuteneproduced} / \text{mol isobutane reacted},$$

where the reacted mol isobutane was calculated from the difference between the injected and unreacted isobutane in the first pulse.

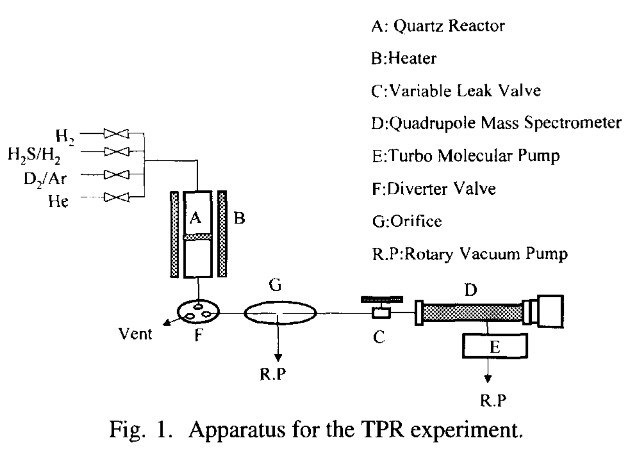

Fig. 1. Apparatus for the TPR experiment.

Table 1. Effects of Sulfurization and Reduction Isobutane Dehydrogenation Activities

Catalysts	Reduced		Sulfurized	
	Conv. %	Sel. %	Conv. %	Sel. %
Pt–Li_2O/Al_2O_3	99	0	51	52
Pt–Na_2O/Al_2O_3	98	0	30	75
Pt–K_2O/Al_2O_3	98	0	29	70
Pt/Al_2O_3	100	0	78	0
Na_2O/Al_2O_3	< 1	Trace	12	51

The activities of the first pulse were listed. Concentrations of platinum and alkali oxides are 1 wt% and 3 wt%, respectively.

The results show that the sulfurization of Pt–alkali metal/Al_2O_3 catalysts increases the selectivity to isobutene, while it decreases the conversion. Cracking products such as methane, ethane, ethylene, and propene were detected on the H_2S-treated and reduced catalysts. On the Pt/Al_2O_3 catalyst, sulfurization results in a decrease in the conversion without increasing the selectivity, indicating that the H_2S only acts as a poisoning material. The result in which no dehydrogenation occurred on the reduced Pt/Al_2O_3 catalyst differs from that of previous literature.[8] The selectivities in these were higher than that in our Pt/Al_2O_3 catalyst. The difference in the reaction conditions, such as the reaction temperature and atmosphere, would be responsible for the higher selectivity reported in the literature. Only a slight reaction on the Na_2O/Al_2O_3 catalyst occurred without sulfurization. However, the conversion and selectivity after sulfurization increased to 12 and 51%, respectively. The results on Pt–alkali metal/Al_2O_3 catalysts and the Na_2O/Al_2O_3 catalyst suggest that the sulfur adsorbing on alkali species is related to the increase in selectivity. The characterization of the structures of the sulfur species is discussed in a following section.

For H_2S-treated Pt–alkali metal/Al_2O_3 catalysts, the orders of conversion and selectivity were Pt–Li_2O/Al_2O_3 > Pt–Na_2O/Al_2O_3 > Pt–K_2O/Al_2O_3, and Pt–Na_2O/Al_2O_3 > Pt–K_2O/Al_2O_3 > Pt–Li_2O/Al_2O_3, respectively. No clear explanation for the measured orders can be offered at the present time, although the order of conversion seems likely to be related to the order of area occupied by alkali sulfides on the alumina support and/or the ionic radius of the alkali metals. The formation of Na_2S was described in our previous paper.[9]

Skeleton isomerization products, *n*-olefins (1-butene, *cis* and *trans* 2-butenes), were also formed on the reduced and the H_2S-treated Pt/Al_2O_3 catalysts, but not on the Pt–alkali metal/Al_2O_3 and Na_2O/Al_2O_3 catalysts. This indicates that alkali metals inhibited the skeleton isomerization of isobutane on strong acid sites of the alumina support. No hydrogen sulfide was detected in the products in any of the experiments. In subsequent pulses of isobutane, the conversion of the H_2S-treated Pt/Al_2O_3 catalyst decreased, while the conversion of the H_2S-treated Pt–Na_2O/Al_2O_3 and Na_2O/Al_2O_3 catalysts was almost equal. This suggests that the decrease in conversion is attributable to the deposition of coke on acid sites. The isobutene selectivity in subsequent pulses for all catalysts remained unchanged.

On the basis of this result, subsequent experiments were mainly carried out on $Pt–Na_2O(3)/Al_2O_3$ catalyst.

Figure 2 shows the effect of the reaction temperature on the dehydrogenation of isobutane. The selectivity changed little with temperature up to 773 K, but decreased abruptly at 823 K, while the conversion increased with temperature. Dehydrogenation and cracking are endothermic reactions that attend an increase in the number of molecules. Hence, raising the reaction temperature is preferable for both reactions. A remarkable decrease in selectivity at 823 K was attributed to the fact that cracking rose to predominance over dehydrogenation. During subsequent pulses of isobutane, the conversion of the H_2S-treated Pt/Al_2O_3 catalyst decreased, while conversion of the H_2S-treated $Pt–Na_2O/Al_2O_3$ and Na_2O/Al_2O_3 catalysts was almost equal. This suggests that the decrease in conversion is attributable to the deposition of coke on acid sites.

Characterization of Adsorbed Sulfur. It has been reported that H_2S-treated Pt/Al_2O_3 catalyst has both reversibly and irreversibly adsorbed sulfurs.[5—7] The irreversibly adsorbed sulfur in the Pt/Al_2O_3 catalyst suggested a covalent bonding of sulfur to Pt; a surface study using LEED showed that the sulfur adsorbed on the platinum surface was probably bonded more strongly than that in the bulk metal sulfide.[10,11] Our previous XRD and XPS experiments showed that the H_2S-treated Pt/Al_2O_3 and $Pt–Na_2O/Al_2O_3$ catalysts had PtS and Na_2S, respectively.[12] Thus, we propose that the irreversibly adsorbed sulfurs in these catalysts correspond to Pt–S and Na–S.

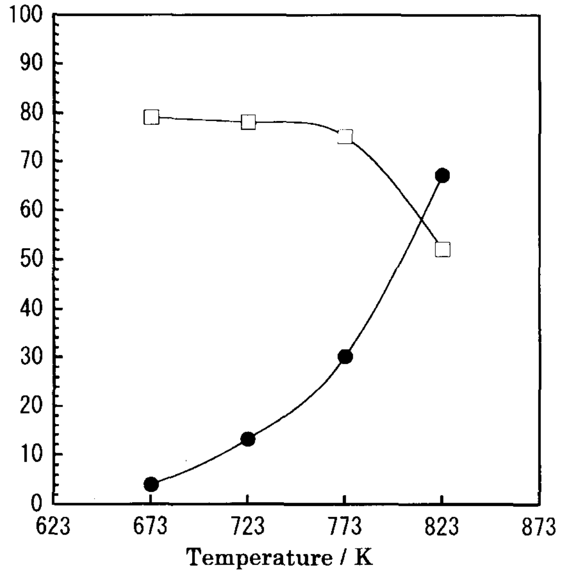

Fig. 2. Effect of reaction temperature on conversion (●) and selectivity (□). $Pt–Na_2O(3)/Al_2O_3$ catalyst was used.

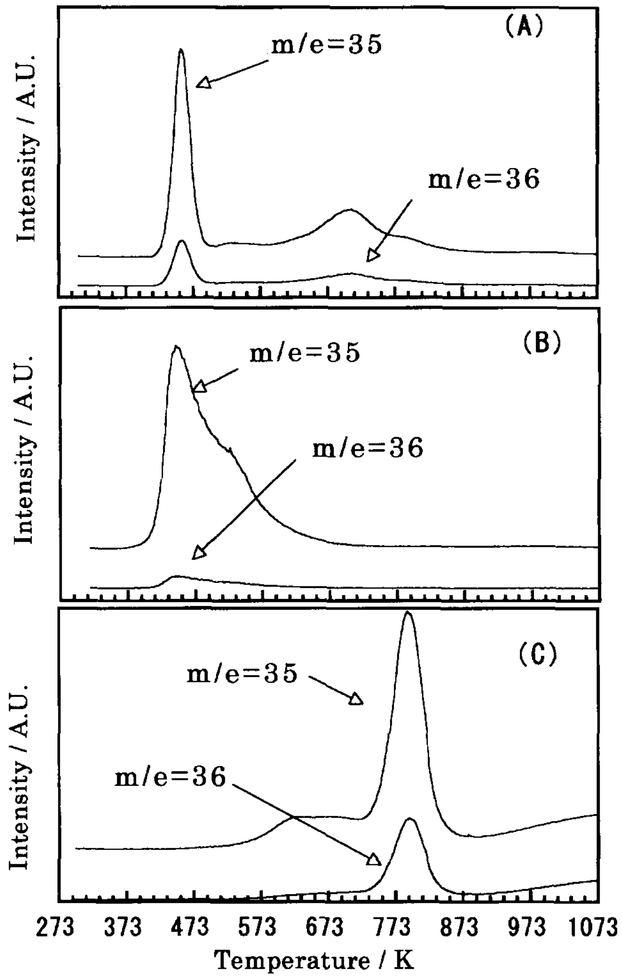

Fig. 3. TPR patterns of (A): $Pt–Na_2O/Al_2O_3$, (B): Na_2O/Al_2O_3, (C): Pt/Al_2O_3 catalysts.

The structure of reversibly adsorbed sulfur was clarified by a TPR experiment using deuterium. Figure 3 shows the patterns of $m/z = 35$ and $m/z = 36$ assigned to the desorbed HDS and D_2S, respectively. In all of the catalysts, the intensity of HDS is higher than that of D_2S, which implies that the reversibly adsorbed sulfur tends to form HS^- rather than S^{2-}. The reaction between H_2S and platinum have been reported as

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

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

where S_{ir} and S_r signify sulfur in irreversibly and reversibly adsorbed states, respectively.[13] However, the results of TPR experiments show that $PtS_{ir}(HS)_r$ in the reversibly adsorbed state also takes place. Pt/Al_2O_3 catalyst has a sharp peak at 793 K and a broad peak in the temperature range 553—733 K, suggesting two different $Pt–(HS)_r$ bonds. Heegeman et al.[14] investigated the surface structures of sulfur on the (100) and (111) faces of Pt. Two adsorption states were found on each surface, referred to as α and β layers. β layers, characterized by a lower order, were desorbed in the temperature range around 573—673 K. The well-ordered α layer was stable to a heat treatment up to 873 K. Chang et al. have assigned these peaks as desorption of chemisorbed H_2S (lower temperature) and reduction of the bulk PtS (higher temperature).[15] In our experiments, however, the intensity for desorbed H_2S ($m/z = 34$) was very weak. In addition, concerning the signal of

$m/z = 34$, it is necessary to consider DS^- resulting from a fragment of the HDS. Therefore, we considered that the desorption peak at 793 K resulted from a well-ordered –SH layer and from the reduction of a part of PtS_{ir}, and that the peak in the range 553—733 K resulted from –SH having a lower order. The desorption from $PtS_{ir}(HS)_r$ is considered to proceed as

$$PtS_{ir}(HS)_r + 1/2D_2 \rightarrow PtS_{ir} + DSH \uparrow .$$

Na_2O/Al_2O_3 catalyst has a peak at 453 K with a shoulder at 533 K. Sodium before a H_2S treatment is thought to be supported as Na_2O, and $-O^-Na^+$ is replaced with hydrogen in an acidic hydroxyl group. Some of the respective sodium species are considered to be sulfurized according to the following reactions:

$$Na_2O \rightarrow Na_2S_{ir} \rightarrow Na_2S_{ir}(HS)_r,$$

$$-O^-Na^+ \rightarrow Na_2S_{ir} + -O^-H^+ \rightarrow Na_2S_{ir}(HS)_r.$$

Thus, the peaks at 433 K are considered to have occurred according to the following reaction:

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

The Na_2S_{ir} comprised many adsorption sites, which would lead to a broadening of the desorption peak.

The TPR pattern of $Pt-Na_2O(3)/Al_2O_3$ catalyst, in comparison with Pt/Al_2O_3 and Na_2O/Al_2O_3 catalysts, is non-additive. The pattern of $Pt-Na_2O(3)/Al_2O_3$ catalyst has two peaks, at 453 and at 713 K. Judging from the pattern of Na_2O/Al_2O_3 catalyst, the peak at 453 K is considered to desorb from the $Na_2S_{ir}(HS)_r$. However, the peak at 713 K is lower than the desorption peak at 793 K for the $PtS_{ir}(HS)_r$ in the Pt/Al_2O_3 catalyst. It seems that the addition of sodium shifted the desorption temperature for the $(HS)_r$ in $PtS_{ir}(HS)_r$ to a lower temperature. We consider that contact with platinum and sodium caused a shift of the desorption peak to a temperature between those of Na_2O/Al_2O_3 (453 K) catalyst and Pt/Al_2O_3 (793 K) catalyst. If the peak at 713 K were attributed to desorption from a new adsorption site formed by contact between the PtS_{ir} and the Na_2S_{ir}, both the 453 and 793 K peaks would remain. However, the desorption peaks at 793 K for Pt/Al_2O_3 and a shoulder at 533 K for Na_2O/Al_2O_3 catalyst almost disappear. Furthermore, in XPS experiments, signals of Pt4f7/2 and Na1s for $Pt-Na_2O/Al_2O_3$ catalyst were almost equal to those for Pt/Al_2O_3 and $Na_2O(3)/Al_2O_3$ catalysts, suggesting that a new adsorption site was not formed by contact with the PtS_{ir} and the Na_2S_{ir}. Therefore, $(HS)_r$, which is strongly adsorbed in comparison to the H_2S-treated Na_2O/Al_2O_3 catalyst and is weakly adsorbed in comparison to the H_2S-treated Pt/Al_2O_3 catalyst, is expected. We assume that $(HS)_r$ bridges between Na_2S_{ir} and PtS_{ir} due to their interaction. This is shown schematically in Fig. 4. $Pt-Na_2O(3)/Al_2O_3$ catalyst has shoulders at both sides of higher and lower temperature than the main desorption peak at 713 K, which implies a stronger interaction between $(HS)_r$ with either PtS_{ir} or Na_2S_{ir} particles. The desorption peak is observed at 453 K, suggesting that the Na_2S_{ir} and PtS_{ir} are far apart, and that not all of the $(HS)_r$ bridged between the Na_2S_{ir} and the PtS_{ir}.

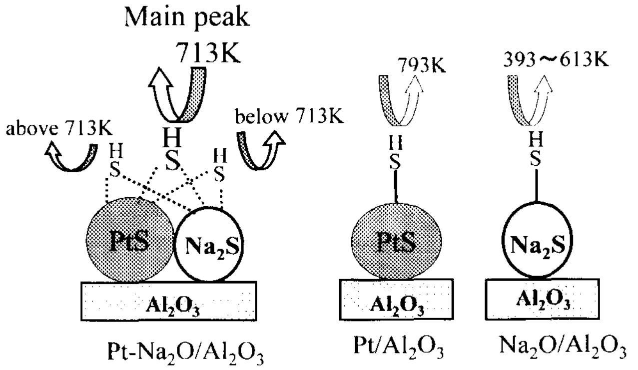

Fig. 4. Scheme of H_2S-treated catalysis.

Although adsorbing sulfurs on an alumina, such as Al-SH has been reported,[16] no TPR pattern for only alumina powder was observed. This means that the sulfur species were completely desorbed by a helium purge at 833 K.

We can not rule out the possibility that HDS was formed by a desorbing D_2S and a surface OH group. In the IR spectra of the H_2S-treated Na_2O/Al_2O_3 catalyst, the SH stretching band was observed at 2593 cm^{-1}, whereas the H–S–H deformational vibration band was not detected. This indicates that the HS groups (not H_2S) existed on the catalyst. The desorbed HDS is probably related, or at least partly related, to the reaction between $(HS)_r$ and $1/2D_2$; thus, in this study we did not consider the reaction between D_2S and the surface OH group. Because of the low transmittance of the Pt/Al_2O_3 catalyst, the obtained IR spectra were not clear.

Role of Adsorbed Sulfurs in Dehydrogenation. Table 2 lists the activities of a physically mixed catalyst. The conversion for 75 mg of catalyst was estimated from Table 1 and the yield was calculated based on the assumption that selectivity to isobutene remains unchanged. The selectivity of the physically mixed catalyst was calculated from the sum of the conversions and yields, implying no interaction between the sodium and platinum species. However, the observed selectivity of 31% is much larger than the calculated value of 13%, indicating that an interaction occurred.

Figure 5 shows the TPR patterns of the physically mixed catalyst. The desorption peak is observed at 713 K, which indicates the existence of bridging $(HS)_r$. We conclude that the increase in the observed selectivity compared with the

Table 2. Calculated and Observed Activities of Physically Mixed Catalyst

Catalysts	Conversion %	Selectivity %	Yield %
Pt/Al_2O_3 (75 mg)	39	0	0
Na_2O (3)/Al_2O_3 (75 mg)	6	51	3.1
Pt/Al_2O_3 + Na_2O (3)/Al_2O_3 (150 mg)			
Caluculation	45	14.0	*3.1*
Observation	56	31	*17.3*

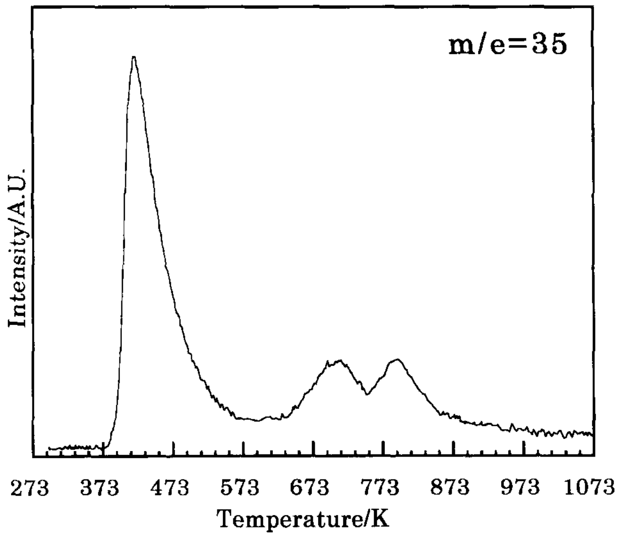

Fig. 5. TPR patterns of physically mixed catalyst (Pt/Al_2O_3+Na_2O/Al_2O_3 catalysts).

Table 3. Effect of Re-reduction on Activities

Catalysts	H_2S-treated		Re-reduction	
	Conv. %	Sel. %	Conv. %	Sel. %
Pt/Al_2O_3 [a]	78	0	90	0
$Pt-Na_2O(3)/Al_2O_3$ [a]	30	75	64	6
$Na_2O(3)/Al_2O_3$ [b]	12	51	4	42

a) Re-reduced at 833 K. b) Re-reduced at 713 K.

calculated value relates to the bridging $(HS)_r$. The selectivity on $Pt-Na_2O(3)/Al_2O_3$ catalyst was higher than that on the physically mixed catalyst, indicating that the frequency of contact between the PtS_{ir} and the Na_2S_{ir} particles in the $Pt-Na_2O(3)/Al_2O_3$ catalyst is larger than that in the physically mixed catalyst.

Table 3 shows the activities for re-reduced catalysts at 833 K ($Pt-Na_2O/Al_2O_3$ and Pt/Al_2O_3) and 713 K (Na_2O/Al_2O_3) for 5 h. Figure 3 indicates that all of the reversibly adsorbed sulfurs can be considered to be desorbed by re-reduction. However, it was confirmed from XPS and EPMA that irreversibly adsorbed sulfur on the platinum and the sodium remained. The conversions for the re-reduced catalysts increased, whereas their selectivities decreased compared with the H_2S-treated catalysts. This means that the reversibly adsorbed sulfur increases the selectivity, while it inhibits the adsorption of isobutane. The conversions for re-reduced Pt/Al_2O_3 and $Pt-Na_2O/Al_2O_3$ catalysts were lower than those for the reduced catalysts, which indicates that the irreversibly adsorbed sulfur on platinum only acts as an inhibitor for isobutane adsorption. For Na_2O/Al_2O_3 catalyst, both the reversibly and irreversibly adsorbed sulfurs promote selectivity.

A comparison between the conversions of the H_2S-treated Pt/Al_2O_3 and Na/Al_2O_3 catalysts indicates that isobutane is adsorbed on the PtS_{ir} or bridging $(HS)_r$. However, dehydrogenation from isobutane adsorbed does not occur in the absence of the bridging $(SH)_r$, 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 $(HS)_r$, which leads to, or assists, dehydrogenation.

Conclusion

The isobutane dehydrogenation selectivity on reduced $Pt-Li_2O/Al_2O_3$, $Pt-Na_2O/Al_2O_3$, and $Pt-K_2O/Al_2O_3$ catalysts was increased by a treatment with hydrogen sulfide. The orders of selectivity were $Pt-Na_2O/Al_2O_3 > Pt-K_2O/Al_2O_3 > Pt-Li_2O/Al_2O_3$. The optimum reaction temperature for increasing the selectivity was 773 K, because at temperatures above the optimum, a cracking reaction preferentially took place. The reversibly adsorbed sulfur was characterized by TPR experiments using deuterium. This clarified that most of the reversibly adsorbed sulfur is HS^-, and suggested that the reversibly adsorbed sulfur bridges between the PtS_{ir} and the Na_2S_{ir}. The factor that increased the selectivity would correlate with the bridging sulfur species and interact with the hydrogen in the adsorbed isobutane.

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