

A Relation between Oxidation State of Sulfur and Acidic Property of Iron Oxide Containing Sulfur

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Five kinds of iron oxide catalysts promoted with sulfur were prepared by impregnating $\text{Fe}(\text{OH})_3$ with $(\text{NH}_4)_2\text{SO}_4$ and by treating Fe_2O_3 and $\text{Fe}(\text{OH})_3$ with H_2S and SO_2 . Changes in acidic properties of the catalysts with changes in oxidation states of sulfur were investigated by test reactions such as isomerization of cyclopropane and dehydration of 2-propanol over the oxidized or reduced catalysts. It has been found that the generation of acidic properties of the catalysts was independent of the kinds of the starting sulfur compounds, but dependent on the oxidation states of the sulfur. The sulfur in the highest oxidation state was responsible for the strongly acidic property of the catalyst.

It has been reported recently that the iron oxide catalyst promoted with SO_4^{2-} ion exhibited high catalytic activities for the isomerization of cyclopropane and the dehydration of 2-butanol.¹⁾ It was also found that this type of catalyst was quite effective for a coal liquefaction under a high hydrogen pressure and at a high temperature.²⁾ High catalytic activities in the former reactions were attributed to the enhanced acidic properties of the promoted catalysts, which originated from a strongly electrophilic nature of S=O bonds of sulfur species bound on the surface.¹⁾ In the latter reaction, however, the Fe_2O_3 - SO_4^{2-} catalyst is considered to be reduced with hydrogen to lose the high acidic property as well as the catalytic activity. Therefore, it is necessary to examine the influence of the oxidation state of sulfur on the acidic property of Fe_2O_3 containing sulfur. This report deals with whether H_2S and SO_2 , besides SO_4^{2-} , as sulfur sources are effective for enhancing the acidic property and how such a property changes when the oxidation state of sulfur is controlled.

Experimental

Catalyst Preparation. Iron oxide and hydroxide were prepared by the hydrolysis of $\text{Fe}(\text{NO}_3)_3$ with aqueous ammonia. The sulfur promoted catalysts were prepared by adsorbing inorganic sulfur compounds on iron hydroxide or oxide, followed by calcination, reduction, and oxidation. The Fe_2O_3 (A)- SO_4^{2-} catalyst was prepared by immersing $\text{Fe}(\text{OH})_3$ in an aqueous solution of $(\text{NH}_4)_2\text{SO}_4$, followed by drying at 110 °C and calcining at 500 °C. The amount of sulfur loaded was adjusted to about 2 wt% as SO_3 . The Fe_2O_3 (A)- H_2S and Fe_2O_3 (A)- SO_2 catalysts were obtained by treating $\text{Fe}(\text{OH})_3$ with 1200 Pa of H_2S and SO_2 . The Fe_2O_3 (B)- H_2S and Fe_2O_3 (B)- SO_2 catalysts were obtained by treating Fe_2O_3 instead of $\text{Fe}(\text{OH})_3$ similarly as above. Treating temperature is denoted as Fe_2O_3 (A)- H_2S -400 (Fe_2O_3 (A) treated with H_2S at 400 °C). When the catalyst was oxidized with O_2 at 500 °C, it is denoted as Fe_2O_3 (A)- H_2S -400- O_2 -500. Catalyst nomenclature is illustrated in Table 1. Prior to the reaction, some of the catalysts treated with H_2S and SO_2 were oxidized with O_2 at 400 to 500 °C for 10 min and evacuated at 500 °C, and some of the Fe_2O_3 (A)- SO_4^{2-} catalysts were reduced with hydrogen at 350—500 °C.

TABLE 1. CATALYSTS TREATED WITH SULFUR COMPOUNDS BY DIFFERENT METHODS

Catalyst nomenclature	Source of sulfur	Supporting method	Temperature of gas treatment/°C
Fe_2O_3	None	—	Untreated ^{a)}
Fe_2O_3 (A)- SO_4^{2-}	$(\text{NH}_4)_2\text{SO}_4$	Impregnation	Untreated ^{a)}
Fe_2O_3 (A)- SO_4^{2-} - H_2 -350	$(\text{NH}_4)_2\text{SO}_4$	Impregnation	350 with H_2
Fe_2O_3 (A)- SO_4^{2-} - H_2 -400	$(\text{NH}_4)_2\text{SO}_4$	Impregnation	400 with H_2
Fe_2O_3 (A)- SO_4^{2-} - H_2 -500	$(\text{NH}_4)_2\text{SO}_4$	Impregnation	500 with H_2
Fe_2O_3 (A)- H_2S -400	H_2S	Gas treatment	400 with H_2S
Fe_2O_3 (A)- H_2S -400- O_2 -500	H_2S	Gas treatment	400 with H_2S and 500 with O_2
Fe_2O_3 (B)- H_2S -400	H_2S	Gas treatment	400 with H_2S
Fe_2O_3 (B)- H_2S -400- O_2 -500	H_2S	Gas treatment	400 with H_2S and 500 with O_2
Fe_2O_3 (A)- SO_2 -400	SO_2	Gas treatment	400 with SO_2
Fe_2O_3 (A)- SO_2 -400- O_2 -500	SO_2	Gas treatment	400 with SO_2 and 500 with O_2
Fe_2O_3 (B)- SO_2 -400	SO_2	Gas treatment	400 with SO_2
Fe_2O_3 (B)- SO_2 -400- O_2 -500	SO_2	Gas treatment	400 with SO_2 and 500 with O_2

a) Untreated with any gas, but calcined in air at 500 °C.

The $\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_4^{2-}$ was prepared by the hydrolysis of iron alum with urea as described in our previous paper.¹⁾ The amount of sulfur loaded was 6 wt% as SO_3 . The $\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_4^{2-}$ catalyst was used for 2-propanol dehydration. For a series of the experiments, the catalyst was evacuated at 500 °C, reduced with a stream of hydrogen at different temperatures, and then evacuated again at the same temperature of reduction. In the case of the catalyst reduced below 200 °C, the final evacuation was performed at 200 °C. For the other series of experiments, the catalysts were treated as in the cases of the first series of experiments and then oxidized with flowing air at 500 °C for 1 h, followed by evacuation at 500 °C.

Measurement of Surface Area. Specific surface area was determined by the BET method using nitrogen.

Measurement of Sulfur Content. The atomic ratios of S/Fe in the catalysts reduced at different temperatures were determined by X-ray fluorescent spectroscopy on the basis of the samples of known S/Fe ratios.

Reaction Procedure. Isomerization of cyclopropane was carried out at 150 °C by use of 0.2 g of catalyst in a closed recirculation apparatus of 800 ml capacity which was equipped with a sampling manifold. A 6,670 Pa of cyclopropane was used. The reaction of 2-propanol was carried out at 200 °C in a closed recirculation apparatus of 266 ml capacity, 4,000 Pa of 2-propanol being passed through 0.2 g of a $\text{Fe}_2\text{O}_3-\text{SO}_4^{2-}$ catalyst. The product was only propene.

Results and Discussion

Isomerization of Cyclopropane. Isomerization of cyclopropane to yield propene is known to be one of

TABLE 2. CATALYTIC ACTIVITIES FOR ISOMERIZATION OF CYCLOPROPANE

Catalyst	Rate of reaction
	$10^{-5} \text{ mol min}^{-1} \text{ g}^{-1}$
Fe_2O_3	0
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_4^{2-}$	30
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_4^{2-}-\text{H}_2-350$	34
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_4^{2-}-\text{H}_2-400$	15
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_4^{2-}-\text{H}_2-500$	0
$\text{Fe}_2\text{O}_3(\text{A})-\text{H}_2\text{S}-400$	0
$\text{Fe}_2\text{O}_3(\text{A})-\text{H}_2\text{S}-400-\text{O}_2-500$	30
$\text{Fe}_2\text{O}_3(\text{B})-\text{H}_2\text{S}-400$	0
$\text{Fe}_2\text{O}_3(\text{B})-\text{H}_2\text{S}-400-\text{O}_2-500$	28
$\text{Fe}_2\text{O}_3(\text{A})-\text{H}_2\text{S}-500$	0
$\text{Fe}_2\text{O}_3(\text{A})-\text{H}_2\text{S}-500-\text{O}_2-500$	7
$\text{Fe}_2\text{O}_3(\text{B})-\text{H}_2\text{S}-500$	0
$\text{Fe}_2\text{O}_3(\text{B})-\text{H}_2\text{S}-500-\text{O}_2-500$	6
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_2-400$	0
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_2-400-\text{O}_2-500$	44
$\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_2-400$	0
$\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_2-400-\text{O}_2-500$	35
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_2-500$	0
$\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_2-500-\text{O}_2-500$	32
$\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_2-500$	0
$\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_2-500-\text{O}_2-500$	32

the best reactions for examining acidic properties of solid acid catalysts.^{3,4)} The rates of the isomerization over the Fe_2O_3 catalysts treated with $(\text{NH}_4)_2\text{SO}_4$, H_2S or SO_2 and then with H_2 or O_2 are summarized in Table 2. The Fe_2O_3 catalyst was inactive, but became active when treated with $(\text{NH}_4)_2\text{SO}_4$ in accordance with our previous work.¹⁾ However, the activity of $\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_4^{2-}$ decreased on reduction with H_2 at 400 °C and lost the activity completely when reduced with H_2 at 500 °C. Thus, the oxidized state of SO_4^{2-} is considered to be essential for the generation of acidity of the catalyst.

In the case of Fe_2O_3 treated with H_2S or SO_2 at 400 °C, no catalytic activity was observed. However, the $\text{Fe}_2\text{O}_3-\text{H}_2\text{S}$ and $\text{Fe}_2\text{O}_3-\text{SO}_2$ catalysts exhibited almost the same activity as that of $\text{Fe}_2\text{O}_3-\text{SO}_4^{2-}$ when oxidized with O_2 . The difference between $\text{Fe}_2\text{O}_3-\text{H}_2\text{S}$ and $\text{Fe}_2\text{O}_3-\text{SO}_2$ was that Fe_2O_3 treated with H_2S at 500 °C followed by oxidation with O_2 showed a low activity ($6-7 \times 10^{-5} \text{ mol min}^{-1} \text{ g}^{-1}$), whereas Fe_2O_3 treated with SO_2 at 500 °C followed by oxidation with O_2 showed almost the same activity ($32 \times 10^{-5} \text{ mol min}^{-1} \text{ g}^{-1}$) as that of $\text{Fe}_2\text{O}_3(\text{A})-\text{SO}_4^{2-}$. Thus, the temperature of treatment with H_2S is important to generate the activity after the oxidation in the case of H_2S -treated catalysts.

The data of Table 2 clearly indicate that the introduction of any kinds of sulfur compounds causes the enhancement of the activity for the acid-catalyzed reaction, provided that the sulfur-treated catalysts are oxidized, whatever the source of sulfur is. Since the high catalytic activities of $\text{Fe}_2\text{O}_3-\text{SO}_4^{2-}$ for the acid type reactions were attributed to strong acid sites created by the electron-attracting property of S=O bonds of a sulfur species like $>\text{S} \equiv \text{O}$ on the surface,¹⁾ H_2S and SO_2 are considered to be converted into the sulfur species by oxidation. In other words, the highest oxidation state of sulfur (S^{6+} in the $>\text{S} \equiv \text{O}$) is necessary to show high catalytic activity.

Dehydration of 2-Propanol. An iron oxide catalyst containing SO_4^{2-} ions was highly active for the dehydration of 2-butanol.¹⁾ The dependency of the catalytic activity on the temperature of H_2 treatment was examined over the catalyst, $\text{Fe}_2\text{O}_3(\text{B})-\text{SO}_4^{2-}$, prepared by a urea method by use of the dehydration of 2-propanol as a test reaction. As shown by open circles in Fig. 1, when the catalyst was reduced with flowing H_2 below 100 °C, no detectable change in the activity was observed. The activity, however, abruptly decreased with increase in the reduction temperature from 100 to 150 °C. By raising the temperature from 150 °C to 400 °C, the catalytic activity decreased gradually to zero. The activities of the catalysts reoxidized at 500 °C are also shown by solid circles in Fig. 1. Recovery of the activity by oxidation was observed for all the catalysts. The extent of recovery varied

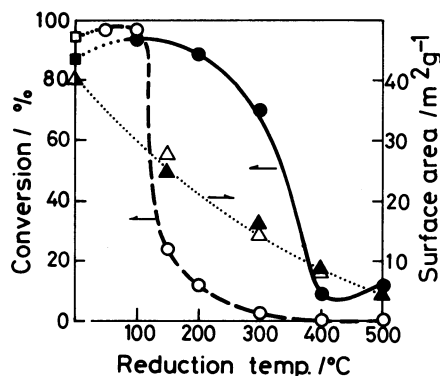


Fig. 1. Decomposition of 2-propanol at 200°C over Fe₂O₃ (B)-SO₄²⁻ (△,○; Fe₂O₃ (B)-SO₄²⁻ evacuated at 500°C for 2 h was reduced with hydrogen for 2 h, followed by evacuation for 1 h at each temperature indicated in the figure. In the case of below 200°C of reduction temperature, the catalyst was evacuated at 200°C for 1 h.

▲,●; The above catalyst was oxidized with air at 500°C for 2 h, followed by evacuation at 500°C for 2 h.

□; Fe₂O₃ (B)-SO₄²⁻ evacuated at 500°C for 2 h was oxidized with air at 500°C for 2 h.

■; Fe₂O₃ (B)-SO₄²⁻ evacuated at 500°C for 2 h was oxidized with air at 500°C for 2 h, followed by evacuation at 500°C for 2 h.

△; Fe₂O₃ (B)-SO₄²⁻ evacuated at 500°C for 2 h.

with the reduction temperatures. A catalyst reduced at 200°C recovered the original activity after the reoxidation and a catalyst reduced at 300°C recovered about 80% of its original activity. The catalysts reduced above 400°C, however, restored the activity to a small extent. Recovery by the oxidation indicates that the active sites are related with a higher oxidation state of sulfur.

State of Sulfur. It is pointed out that the activity loss by reduction at lower temperatures may arise from the removal of surface oxygens. An X-ray diffraction analysis revealed that the reduction of Fe₂O₃ took place to yield Fe₃O₄ phase around 250°C.⁵⁾ Therefore, below 300°C, the reduction may occur *via* a removal of the oxygens bridged to both S and Fe. Such a removal of the oxygens will result in the loss of the catalytic activity in the low temperature range and the lost activity is easily restored by reoxidation in agreement with the case of the isomerization of cyclopropane.

Figure 2 shows the change in the sulfur contents measured by X-ray fluorescent spectroscopy with reduction temperature. The amount of sulfur gradually decreased with an increase in the reduction temperature. Loss of sulfur by raising the reduction temperature from 300 to 400°C was not significant as

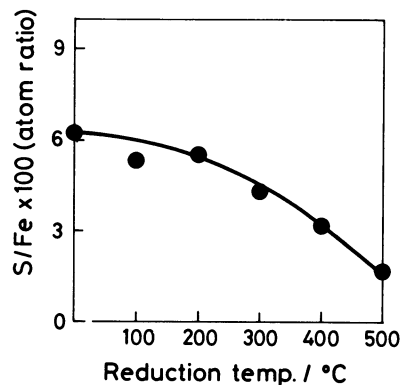


Fig. 2. Variation of S/Fe ratio in Fe₂O₃ (B)-SO₄²⁻ with reduction temperature.

compared with a large decrease in the activity. Thus, the marked decrease in catalytic activity observed when reduction temperature was raised from 300 to 400°C can not be attributed to the removal of the sulfur.

Changes in the surface area by reduction and reoxidation at various temperatures are also shown in Fig. 1. Although these changes are not coincide with the changes in the catalytic activities, poor recovery of the activity for the catalyst reduced at 400°C is considered to be partly due to a decrease in surface area.

XPS results indicated the reversible change between S²⁻ and S⁶⁺ states by reduction and reoxidation above 400°C.⁶⁾ This suggests that catalytically inactive iron sulfide is formed by reduction and it is changed to catalytically active sulfate complex by reoxidation. Thus, another reason for the poor recovery is considered to be due to the decrease in the number of sulfur species on the surface by its migration to the bulk on reduction above 400°C.

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