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CATALYTIC ACTIVITY OF IRON OXIDE TREATED WITH SULFATE ION FOR DEHYDRATION OF 2-PROPANOL AND ETHANOL AND POLYMERIZATION OF ISOBUTYL VINYL ETHER[1)]

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The catalytic activity of Fe_2O_3 for the title reactions was remarkably enhanced by exposing $Fe(OH)_3$ or Fe_2O_3 prior to the crystallization to 0.1-1 N H_2SO_4 or $(NH_4)_2SO_4$ and then calcining in air at 500°C, its activity for the dehydration of ethanol being much higher than that of SiO_2-Al_2O_3.

Recently, it was reported that the catalytic activity of TiO_2 for isomerization of 1-butene and dehydration of 2-propanol was promoted by an addition of ammonium sulfate.[2,3)] Previously we found that iron sulfates heat-treated at high temperature were exceedingly active for the polycondensation of benzyl chloride[4)] and the polymerization of vinyl alkyl ethers.[5)] Thus in the present work, we studied the catalytic effect of sulfate ion on solid acid catalysts, and found that remarkable increases in the surface acidity and in the catalytic activity of Fe_2O_3 result from the sulfate ion treatment, followed by a heat-treatment, of $Fe(OH)_3$ or Fe_2O_3 prior to the crystallization. The reactions investigated were dehydrations of 2-propanol and ethanol, well-known acid-catalyzed reactions,[6)] and the polymerization of isobutyl vinyl ether (IBVE), which is generally promoted by Lewis catalysts such as BF_3·etherate and $TiCl_4$.[7)]

$Fe(OH)_3$-I and Fe_2O_3 were supplied from Kokusan Chemical Works, Ltd. and Wako Pure Chemical Co., respectively, and dried at 100°C for 24 h before use. $Fe(OH)_3$-II and -III were precipitated by hydrolyzing iron(III) nitrate and chloride, respectively, with aqueous ammonium hydroxide. They were washed and then dried at 100°C for 24 h. The treatment of the catalysts with sulfate ion was performed by pouring 30 ml of aqueous sulfuric acid or ammonium sulfate solution to 2 g of the dried materials on a filter paper. After drying, the material was powdered below 100 or to 32-60 mesh, and then it was calcined in a Pyrex glass tube in air for 3 h. The prepared catalyst was sealed in an ampoule until use. Dehydrations of 2-propanol and ethanol were carried out at 170 and 250°C, respectively, by using a microcatalytic pulse reactor (flow rate of He for carrier gas : 30 ml/min, catalyst amount : 30 and 20 mg, pulse size : 0.4 and 1.0 μl, for reactions of 2-propanol and ethanol, respectively). Effluent products were directly introduced into a gas chromatographic column for analysis (Porapak R 2-m, 128°C). The percentage conversion was evaluated by averaging the conversions obtained from the 6th to the 10th pulse reaction.

Table 1. Dehydration of 2-Propanol and polymerization of Isobutyl Vinyl Ether

Run	Catalyst	Treatment	Calcination temp. after treatment °C	Conversion, %		SO_3 content, wt % b)
				Dehyd. of 2-propanol a)	Polym. of IBVE	
1	$Fe(OH)_3$-I	without treatment	300	0	0	
2	$Fe(OH)_3$-I		500	0		
3	Fe_2O_3		500	0	0	
4	Fe_2O_3	1 N H_2SO_4	500	9	0	
5	$Fe(OH)_3$-I	1 N H_2SO_4	500	54	70	2.33
6	$Fe(OH)_3$-I	1 N $(NH_4)_2SO_4$	500	58	62	2.06
7	$Fe(OH)_3$-I	1 N H_2SO_4	550	17		0.89
8	$Fe(OH)_3$-I	1 N H_2SO_4	600	0	0	0
9	$Fe(OH)_3$-II	0.5 N H_2SO_4	500	85		3.43
10	$Fe(OH)_3$-II	1 N H_2SO_4	500	79	93	4.80
11	$Fe(OH)_3$-II	1 N $(NH_4)_2SO_4$	500	68		2.46

a) Product was only propylene.

b) Estimated from weight decrease at 500-800°C in TGA.

The polymerization of IBVE was carried out with 5 ml of IBVE, 45 ml of toluene and 40 mg of catalyst (below 100 mesh) at room temperature for 30 min. The conversion for polymerization of IBVE was obtained on the basis of the unreacted monomer content obtained by a gas chromatography with benzene as an internal standard. The analysis was carried out at 95°C using a 1 m column of tricresyl phosphate on Celite 545.

The catalytic activities of various iron oxides with or without the sulfate treatment for the reactions of 2-propanol and isobutyl vinyl ether are summarized in Table 1. Both reactions did not occur at all over the catalysts prepared by calcining $Fe(OH)_3$ and Fe_2O_3. On the other hand, the Fe_2O_3 catalyst which was exposed to 1 N H_2SO_4 and calcined at 500°C gave 9 % conversion for the dehydration of 2-propanol (Run 4). Similarly, 4 % conversion was obtained in the IBVE polymerization over the $Fe(OH)_3$-I catalyst treated at 500°C, followed by an analogous treatment. More interesting fact is that the $Fe(OH)_3$-I catalyst treated with 1 N H_2SO_4 (before calcination at 500°C) showed unexpectedly high activities for both reactions (Run 5). The treatment with ammonium sulfate also enhanced the activity to the same extent as that with sulfuric acid. By X-ray diffraction experiments, $Fe(OH)_3$-I calcined at 500°C and Fe_2O_3 were found to be crystallized iron(III) oxides, while the degree of crystallization of $Fe(OH)_3$-I was low.

The catalytic activity of the treated $Fe(OH)_3$-I decreased on raising the calcination temperature (Run 7 and 8). TGA data of the catalysts treated with sulfate ion showed a weight decrease at 550-750°C. This decrease would probably be caused by the decomposition of sulfate to form SO_3. Thus, the catalytic activity is

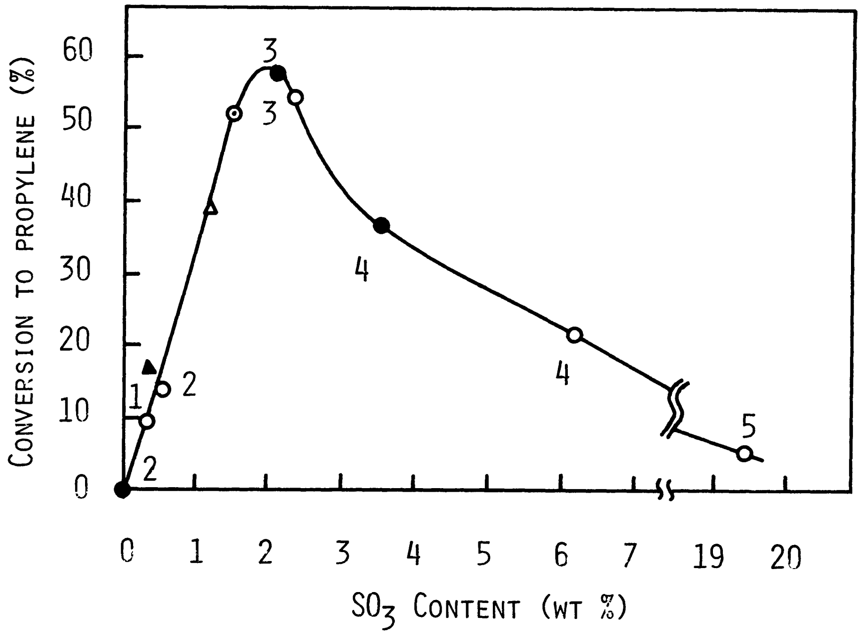

Fig. 1. Relation Between Catalytic Activity of Fe(OH)$_3$-I Treated with Various Sulfur Compounds for Dehydration of 2-Propanol and SO_3 Content. Treated with H_2SO_4(○), $(NH_4)_2SO_4$(●), SO_2(⊙), H_2S(△) and SO_3(▲). Concentration of sulfate ion : 0.1, 0.5, 1, 3 and 6 N for 1, 2, 3, 4 and 5, respectively.

considered to be related with the amount of sulfate adsorbed on the surface of Fe_2O_3.

The Fe(OH)$_3$-II catalyst subjected to the similar treatment showed higher activity and higher SO_3 content (determined by TGA) than the Fe(OH)$_3$-I catalyst. The activity and the SO_3 content were found to depend greatly on the calcination temperature of the hydroxide before the treatment. Namely, the catalysts prepared by pre-calcining Fe(OH)$_3$-II at 100, 200, 300, 400 and 500°C, then treating each with 0.5 N H_2SO_4 and finally calcining at 500°C gave 85, 63, 55, 45 and 11 % conversions for the dehydration of 2-propanol and 3.43, 2.29, 1.78, 1.70 and 0 wt % for the SO_3 contents, respectively. DTA of Fe(OH)$_3$-II showed that this material crystallizes at 430°C. X-ray analysis revealed that Fe(OH)$_3$-II heated at 100°C is completely amorphous, and the material calcined at 500°C is the crystalline Fe_2O_3. Therefore, it is considered that sulfate ion is not adsorbed on the crystallized oxide, but on the amorphous or especially hydroxide form, and hence the amount of adsorbed anion is closely related with the catalytic activity.

The catalytic action of the materials treated with sulfate ion of different concentrations was examined, and the results are shown in Fig. 1, where the catalyst used was Fe(OH)$_3$-I. The maximum activity was observed at 2 % of the SO_3 content or 1 N concentration of both H_2SO_4 and $(NH_4)_2SO_4$. The material treated with sulfate ion of 1 N concentration showed IR absorption bands at 980-990, 1030-1060, 1120 and 1220 cm^{-1}, which are assigned to the bidentate sulfate coordinated to metal elements,[3) while the samples treated with 3 and 6 N showed the IR spectra quite similar to those

Table 2. Dehydration of Ethanol

Catalyst	Treatment	Conversion, %[a)]
$Fe(OH)_3$-II	0.1 N H_2SO_4	45
$Fe(OH)_3$-II	0.5 N H_2SO_4	59
$Fe(OH)_3$-II	1 N H_2SO_4	48
$Fe(OH)_3$-II	1 N $(NH_4)_2SO_4$	38
$Fe(OH)_3$-III	0.1 N H_2SO_4	49
$Fe(OH)_3$-III	0.5 N H_2SO_4	40
SiO_2-Al_2O_3[b)]		12[c)]

a) Product and selectivity : 57-67 % ethyl ether and 33-43 % ethylene.

b) Al_2O_3 : 15 wt %, N631(L) of Nikki Chemical Co.

c) 10 % of ethyl ether and 2 % ethylene.

of iron sulfate. It is of interest that the treatments with SO_2, H_2S and SO_3[8)] also promoted the catalytic activity, the activity *vs.* SO_3 content relationships falling on a curve of those with the H_2SO_4 and $(NH_4)_2SO_4$ treatments as shown in the Figure.

The present catalysts were applied to the dehydration reaction of ethanol as shown in Table 2. The $Fe(OH)_3$-II and -III catalysts treated with 0.1-1 N H_2SO_4 or $(NH_4)_2SO_4$, followed by calcining at 500°C, showed quite high activities, much higher than that of SiO_2-Al_2O_3 which is well known as one of the catalysts with the highest surface acidity.

SiO_2-Al_2O_3 and TiO_2-ZrO_2, which bear acid sites stronger than $Ho = -8.2$,[6)] were inactive for the polymerization of IBVE. The present catalysts were completely poisoned by an addition of small amount of pyridine (inactive for the reactions of 2-propanol and IBVE). Since the catalyst is itself colored, the acidity measurement by using Hammett indicator was carried out with SiO_2-Al_2O_3 as a reference for the determination of the end-point in the n-butylamine titration. In this manner, the acidity of the $Fe(OH)_3$-I catalyst treated with 1N H_2SO_4 and calcined at 500°C was found to be 0.14 mmol/g for $Ho \leqq -3.0$, while the acidity of the sample without the treatment was found to be 0.05 mmol/g for $Ho \leqq 4.8$ and zero for $Ho \leqq 1.5$.

References and Notes

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8) $Fe(OH)_3$-I was exposed to H_2S, SO_2 and SO_3 for 5 and 10 min for two of the latter, respectively, at room temperature. The treated sample (0.5 g) was then washed with 30 ml of water on a filter paper and calcined at 500°C for 3 h.

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