Enhanced Catalytic Activity of Specially Prepared Fe_2O_3 for the Isomerization of But-1-ene and Cyclopropane and the Dehydration of Butan-2-ol

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Summary Ferric oxide prepared from iron alum by hydrolysis with urea exhibited enhanced activities compared with Fe_2O_3 prepared by other methods; in particular, the activity for the dehydration of butan-2-ol was found to be 2000 times higher than that of Fe_2O_3 prepared from iron alum by hydrolysis with aqueous ammonia.

IT has been reported recently that the catalytic activities of TiO_2,[1,2] ZrO_2,[3] and Fe_2O_3[4] were remarkably increased by the addition of a small amount of sulphate ion. We now report the change in activity of Fe_2O_3 caused by different methods of preparation, *i.e.* different starting materials (iron nitrate and alum) and different reagents for precipitation (ammonia and urea).

Fe_2O_3 (A) and Fe_2O_3 (B) were prepared by hydrolysis of iron nitrate [$Fe(NO_3)_3.9H_2O$; G.R., Wako Pure Chemicals Ind. Ltd.] with aqueous ammonia (28%) and an excess of urea, respectively; the precipitates were washed with distilled water, dried, and calcined in air at 500 °C. Fe_2O_3 (C) and Fe_2O_3 (D) were prepared by hydrolysis of iron alum [$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$; G.R., Nakarai Chemicals, Ltd.] with aqueous ammonia (28%) and an excess of urea, respectively, followed by the same procedure as above. Details of precipitation with urea have been described previously.[1]

Double-bond isomerization of but-1-ene, ring-opening isomerization of cyclopropane, and dehydration of butan-2-ol were carried out independently at 100—200 °C in a closed recirculation reactor. The products were analysed by gas chromatography with a 5 m column of VZ-7 or a 1 m column of TCP.

The Table shows the catalytic activities [reaction rates, mol min^{-1} (g of catalyst)$^{-1}$] and the surface areas of the four kinds of iron oxide. Fe_2O_3 (D), prepared from iron alum with urea, exhibited high catalytic activities for the three reactions compared with the other iron oxides prepared by different methods. In particular, the activity of Fe_2O_3 (D) was extremely high for the isomerization of cyclopropane and the dehydration of butan-2-ol. In the latter case, the activity of Fe_2O_3 (D) was about 2000 times higher than that of Fe_2O_3 (C) prepared from the same starting material (alum) with aqueous ammonia and about 300 times higher than that of Fe_2O_3 (B) prepared from iron nitrate with urea. The surface areas of Fe_2O_3 (D) and the other oxides differ only by a factor of 4—5 (Table).

According to gravimetric analysis, the content of SO_4^{2-} was 2 wt. % for Fe_2O_3 (D), but 0 wt. % for Fe_2O_3 (A), (B), and (C). Thus, the sulphate ion seems to be important for the production of pronounced catalytic activity, as reported

TABLE. Catalytic activities of iron oxides (A)—(E) prepared by different methods.

			Catalytic activities					
				Cyclopropane isomerization				
Fe_2O_3 catalyst	Starting materials	Precipitating reagents	But-1-ene isomerization[a] Rate[b]	Reaction temp./°C	Rate[b]	Butan-2-ol dehydration[c] Rate[b]	Surface area/ m^2 g^{-1}	SO_4^{2-} content/ wt %
(A)	Nitrate	Ammonia	12·3	200	0	0·018	13·0	0
(B)	Nitrate	Urea	5·56	200	0	0·074	18·0	0
(C)	Alum	Ammonia	12·6	200	0	0·011	11·3	0
(D)	Alum	Urea	101	100	81·5	21·5	53·5	2
(E)	Nitrate + $(NH_4)_2SO_4$	Ammonia	90·3	100	44·2	4·04	37·4	2

[a] Reaction temperature, 100 °C. [b] 10^{-5} mol min^{-1} g^{-1}. [c] Reaction temperature, 200 °C.

also by Hino and Arata[4] for the dehydration of ethanol. However, Fe_2O_3 (E) which contained 2 wt. % of sulphate ion (prepared from a mixture of iron nitrate and ammonium sulphate with aqueous ammonia; the resultant precipitate was dried, but not washed, and was calcined at 500 °C) was found to be less active than Fe_2O_3 (D) for the three reactions. For the dehydration of butan-2-ol, the activity per unit surface area of Fe_2O_3 (D) was four times higher than that of Fe_2O_3 (E) which contained the same amount of sulphate ion. Therefore, it should be realized that not only the content of sulphate ion, but also the use of urea as a precipitating reagent is important for the preparation of a very active iron oxide catalyst for particular reactions.

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