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The Catalytic Activity of Hydrous Zirconium Oxide Calcined at Several Temperatures

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Synopsis. Hydrous zirconium oxide is an amorphous solid and has several catalytic activities. The oxide was changed to crystalline zirconia by calcination at a high temperature, and the catalytic activities were lowered. The correlation between the surface property and the catalytic activity was investigated on hydrous zirconium oxide calcined at several temperatures; the best activity was obtained in the oxide calcined at 300 °C.

In previous papers, we reported that hydrous zirconium oxide serves as an excellent catalyst for the reduction of aldehydes and ketones with 2-propanol,[1] the formylation of amines with *N*,*N*-dimethylformamide,[2] the amidation of carboxylic acids with amines,[3] the esterification of carboxylic acid with alcohols,[4] and the reduction of carboxylic acid with 2-propanol.[5] The hydrous zirconium oxide is known as an amorphous solid possessing an ion-exchange ability[6,7] and is differentiated from crystalline zirconium dioxide, that is, zirconia. In fact, the catalytic activities of zirconia on all of the reactions described above were very small compared with those of the hydrous zirconium oxide. This difference was caused by the distinct surface properties, which were in turn caused by the difference in the preparation methods, especially the heat-treatment temperatures. The solid-state chemistry[8] of the hydrous zirconium oxide is very complex, and few data on the surface properties have been reported in the literature.[7]

In this paper, we will report that the surface properties and the catalytic activity of the hydrous zirconium oxide changes with its calcination temperature, and that the highest activity is achieved by calcination at 300 °C.

Experimental

Materials and Instrument. Into a solution of zirconium(IV) dichloride oxide ($ZrOCl_2 \cdot 8H_2O$) (200 g of a solid in 10 dm^3 of deionized water) was slowly added an aqueous solution of sodium hydroxide (1 mol dm^{-3}) at room temperature. A constant gentle stirring was maintained, and the addition was continued until the pH of the resulting solution reached 6.80. The solution was then allowed to stand for 48 h at room temperature. The resulting product was filtered and washed until the supernatant became free from chloride ions. The gel was spread on a glass plate and dried in air at room temperature for 10 h and then at 80 °C for 2 h. Fifty-four grams of hydrous zirconium oxide were thus obtained in the form of granules. The calcination of the oxide was carried out in a muffle furnace at 110—900 °C for 5 h in air.

X-Ray photoelectron spectroscopy (XPS, ESCA) was measured by means of Shimadzu Electron Spectrometer ESCA-750. Thermal gravimetric analyses were performed with a Shimadzu TGA-40 apparatus. X-Ray diffraction (XRD) analyses were performed with Rigaku Geigerflex RAD equipment. The surface area and the pore distribution were measured by means of Shimadzu micrometrics AccuSorb equipment.

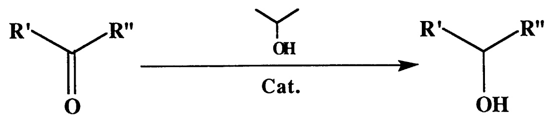
The quantity of surface acidic or basic sites was measured by the butylamine- or trichloroacetic acid-titration method respectively, using various Hammett indicators.

Reaction. In a 25-cm^3 round-bottom flask equipped with a reflux condenser was placed 1.0 or 2.0 g of hydrous zirconium oxide, 5 mmol of an aldehyde or a ketone, and 10 cm^3 of 2-propanol, plus 0.5 mmol of a hydrocarbon as the internal standard. The contents were heated under a gentle reflux. The reaction mixture was collected at appropriate times, and the concentrations of the products were analyzed by means of GLC (a capillary column PEG 20 M 30 m).

Results and Discussion

The ESCA analyses of hydrous zirconium oxides calcined at several temperatures showed that their chemical shifts of Zr$^{3d_{5/2}}$ were in the range from 182.5 to 183.4 eV. This indicates that the surface species on

Table 1. Specific Surface Areas and Catalytic Activities of the Hydrous Zirconium Oxide Calcined at Varying Temperatures[a)]



Calcination temp/°C	Specific surface area/m$^2 \cdot$g^{-1}	Rate constant (×10^{-4} s^{-1}) Cyclohexanone	Hexanal	Acetophenone[b)]
110	272	3.45	0.34	0.34
200	251	5.12	0.42	0.44
300	207	7.19	0.97	0.68
400	112	2.86	0.41	0.050
600	43	2.12	0.069	0.076
900	14	0.47	0.019	0.020

a) Catalyst: 1.0 g, aldehyde or ketone: 5 mmol, 2-propanol: 10 cm^3, reaction temperature: 82 °C. b) Catalyst: 2.0 g.

Table 2. Acid or Base Amounts of Hydrous Zirconium Oxide Calcined at Varying Temperatures

Calcined temp/°C	Amount/mol g^{-1} $H_0\leq-8.0$	$H_0\leq-5.6$	$H_0\leq-3.0$	$H_0\leq1.5$	$H_0\geq9.3$	$H_0\geq15.0$
200	0	5.0×10^{-6}	4.5×10^{-4}	9.0×10^{-4}	1.0×10^{-5}	0
300	0	8.0×10^{-6}	5.0×10^{-4}	1.4×10^{-3}	7.5×10^{-5}	0
400	0	1.0×10^{-6}	4.6×10^{-4}	1.2×10^{-3}	2.0×10^{-4}	0
600	0	0	0	7.0×10^{-5}	4.0×10^{-5}	0
900	0	0	0	1.0×10^{-5}	2.0×10^{-5}	0

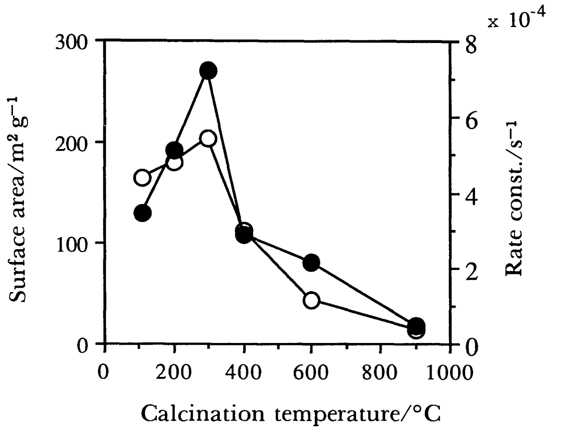


Fig. 1. Correlation between the surface area given by the sum of pore areas larger than 8 Å and the catalytic activity. ○; Surface area given by sum of pore areas larger than 8 Å. ●; Rate constant of the reduction of cyclohexanone.

the oxides is Zr^{4+} and that the change in the valence of zirconium does not occur upon calcination in air. The thermal gravimetric analyses of the oxides were carried out under an atmosphere of helium. In the case of the oxide calcined at lower temperatures (≤300 °C), rapid weight losses were observed at 460 °C, although none were observed in the samples calcined at higher temperatures. These weight losses were interpreted as being the result of rapid crystallization accompanied by the loss of water. In fact, X-ray diffraction analysis showed the oxide calcined under 300 °C to be amorphous, and the other, to be crystal. The specific surface areas of the oxide calcined at several temperatures are listed in Table 1. The specific surface area was lowered with the calcination temperarure.

The reduction of cyclohexanone, hexanal, or acetophenone with 2-propanol was carried out over hydrous zirconium oxide calcined at several temperatures. These reactions showed a first-order dependence on the concentration of aldehyde or ketone; the rate constants of the oxides calcined at several temperatures are listed in Table 1. In every case, the oxide calcined at 300 °C had the highest catalytic activity. The catalytic activity was proportional to the surface area in the cases of the oxide calcined at higher temperatures; however, it was inversely proportional in the cases of the oxide calcined at lower temperatures. These results suggest that the oxides calcined at lower temperarures have pores which are too small to show catalytic activity. Using the results of the pore distribution, the best correlation between the activity of the reduction and the surface area were obtained by using the surface area given by the sum of the surface areas due to pores larger than 8 Å, as is shown in Fig. 1.

Table 2 shows the acid or base amounts of the hydrous zirconium oxide calcined at several temperatures. The amount of acid was slightly correlated to the catalytic activity; however, the base amount was not.

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8) The solid states of the oxide have been reported to be hydrate, amorphous, a metastable tetragonal system, a monoclinic system, a tetragonal system, a cubic system, and a fused state when treated at 250, 430, 650, 1000, 1900, and 2715 °C respectively.[7]