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SURFACE PROPERTIES OF ZrO_2 DISPERSED ON SiO_2

Tsutomu YAMAGUCHI *, Takanari MORITA, Tarek M. SALAMA and Kozo TANABE

Department of Chemistry, Faculty of Science Hokkaido University, Sapporo 060, Japan

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Zirconium oxide microcrystals were dispersed on SiO_2 from methanol or toluene solution of corresponding zirconium compounds and the surface properties in terms of the acid-base concept was examined by means of a temperature-programmed-desorption technique. Though bulk zirconium dioxide exhibited both acidic and basic properties, surface zirconium oxide lost the basic properties.

1. Introduction

It has been reported that zirconium dioxide shows specific catalytic actions for the cleavage of a C–H bond [1] and the hydrogenation of buta-1,3-diene by a molecular hydrogen and hydrogen donor molecules such as cyclohexadiene [2–4] and high selectivities for the formation of 1-olefins from secondary alcohols [5] and of isobutane in $CO + H_2$ reaction [6]. Recently decomposition of triethylamine to yield acetonitrile, in which both dealkylation by acidic sites and dehydrogenation by basic sites were involved, was reported [7]. These characteristic behaviors of ZrO_2 are considered to be due to the acid-base bifunctional catalysis.

Zirconium dioxide is not only an interesting oxide catalyst, but is becoming even more important as a catalyst support. For instance, the Rh supported on ZrO_2 exhibits higher catalytic activity for the hydrogenation of CO and CO_2 compared with that supported on Al_2O_3, SiO_2, etc. [8,9]. In particular, the Rh/ZrO_2 catalyst shows the highest activity for the hydrogenation of CO_2 [8]. Such specific catalytic properties have also been reported over Rh carbonyl clusters impregnated onto Zr-containing silica [10,11].

Supported metal oxide catalysts can be obtained by dispersing titania on various supports. On the other hand, few papers have been published concerning

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[*] To whom all correspondence should be addressed.

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the dispersion of non-transition metal oxides such as zirconia or titania on silica support [11] and not much attention has been paid yet to investigate the surface acidity and basicity of this type of catalysts.

It is also important to see how the acid and/or base properties are developed from unimolecular, bimolecular, cluster, or crystallized states. In fact, it was shown recently that superacid properties, which were obtained by promotion of ZrO_2 dispersed on SiO_2 with sulfur compounds, have been correlated with the extent of crystallization of ZrO_2 [12].

In this article, we wish to report on the acidic and basic properties of ZrO_2 supported on SiO_2 by means of the temperature-programmed-desorption (TPD) technique.

2. Experimental

Bulk zirconium dioxide was prepared by hydrolysis of $ZrO(NO_3)_2$ or $Zr(OPr)_4$, followed by drying at 383 K, and calcining at 873 K. The resultant samples are denoted as bulk-A and bulk-B, respectively.

Supported zirconium oxide was prepared by depositing the corresponding nitrate ($ZrO(NO_3)_2$) or alkoxide ($Zr(OPr)_4$) onto SiO_2 (Fuji-Davison, Type ID; surface area = 299 m^2g^{-1}; calcined at 773 K for 3 h) from methanol solution or toluene solution, respectively, followed by filtration, hydration at 373 K, and calcination at 773 K for 5 h. The resultant samples are denoted as SZA and SZB, respectively. The sample which was prepared by the deposition of $ZrO(NO_3)_2$ from methanol solution onto another SiO_2 (Fuji-Davison, CARIACT 50; surface area = 70 m^2g^{-1}) is denoted as SZC. The amount of zirconium oxide deposited was in the range of 1 to 4 mmol g^{-1} and is labeled SZA-1.0, SZC-3.4 and so on.

TPD experiments were performed as follows [7,13]: 0.1 g of a sample was exposed to 1.33 kPa of NH_3 or CO_2 gas for 30 min, followed by the evacuation for 1 h (base pressure = 1×10^{-5} Torr; 1 Torr = 0.133 kPa) and then the TPD procedure was started by a heating rate of 10 K min^{-1}. The desorbed gas was analyzed by a NEVA NAG-515 quadrupole mass spectrometer at an ionization voltage of 90 eV. Peak intensities of desorbed gases were normalized by using Ar (ca. 0.1 Pa) as an internal standard.

NH_3 and CO_2 were purified under vacuum by repeated freeze-thaw cycles before use.

3. Results and discussion

X-ray diffraction analysis revealed that the crystal structure of bulk ZrO_2 was monoclinic regardless the preparation processes, while that of SZA, SZB, and SZC was ill-crystallized tetragonal, though lower amounts of deposition resulted

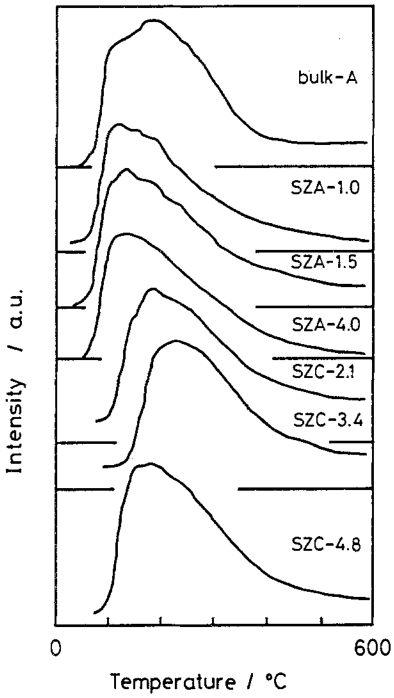

Fig. 1. NH_3-TPD profiles of bulk-A, SZA and SZC.

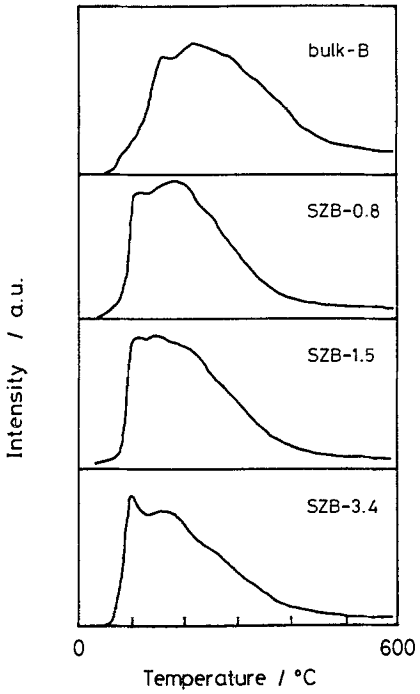

Fig. 2. NH_3-TPD profiles of bulk-B and SZB.

in an amorphous state. Thus the transformation of the tetragonal form to a monoclinic one was retarded by the deposition. It has been reported [14] that the existence of the tetragonal form in microcrystals at temperatures below the normal transformation temperature could be explained by a crystallite size effect; smaller crystallites tend to keep the tetragonal form.

Figures 1 and 2 compare the NH_3-TPD profiles of bulk-A, bulk-B ZrO_2 with SZA, SZB, and SZC ZrO_2 series. Profiles of bulk ZrO_2 samples do not show any significant difference. This clearly indicates that the preparation processes do not influence the acidic properties much. This seems true on the deposited oxides. Though there is a slight decrease in the desorption rate of the high-temperature component, TPD profiles are essentially the same as those of bulk ZrO_2. Thus it can be concluded that the acidic properties that were indicated by TPD profiles of NH_3 have been retained by changing the preparation method on both bulk and dispersed ZrO_2.

The situation was different on the TPD profiles of CO_2. As shown in figs. 3 and 4, although the profiles obtained on bulk-A and -B resemble each other, those of the dispersed ZrO_2 were completely different from bulk ZrO_2. The high temperature component which was observed in the bulk one was completely missing in SZA, SZB, and SZC. This suggests that the strong basic sites of bulk ZrO_2 have been lost when zirconium oxide was dispersed on SiO_2.

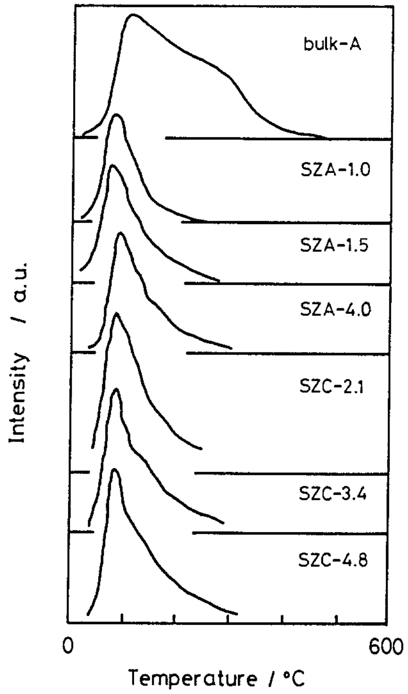

Fig. 3. CO_2-TPD profiles of bulk-A, SZA and SZC.

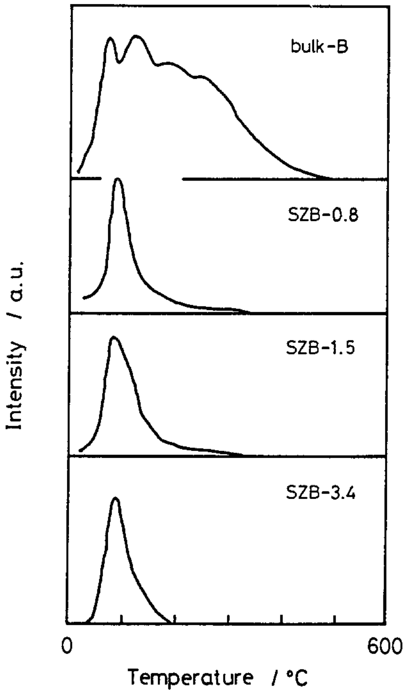

Fig. 4. CO_2-TPD profiles of bulk-B and SZB.

The catalytic properties of SZA were examined by using the hydrogenation of buta-1,3-diene and the dehydration of 2-butyl alcohol as test reactions to elucidate the contribution of basic sites for these reactions. As was reported earlier [2,3], bulk zirconium dioxide catalyzes the hydrogenation of olefins and dienes. In fact the present result confirmed this observation; 44.1% conversion with trans-2-butene as a major product in a 75 min reaction at 323 K. On the other hand, SZA showed quite low activity for this reaction, since the conversion to olefins was only 1.4% in a 26 h reaction at 373 K.

Bulk ZrO_2 catalyst catalyzes the dehydration of secondary alcohol to yield 1-olefin selectively (more than 90% selectivity) [5]. However, the selectivity to 1-butene in the dehydration of 2-butyl alcohol on SZA was only 25% at 623 K.

These results clearly indicate that the loss of basic properties from bulk zirconium dioxide resulted in the remarkable change in the catalytic performance.

From these results we may conclude the following:

(1) Acid and base properties are conserved regardless the preparation method, especially starting materials.

(2) Only acidic properties are conserved when the oxide was dispersed on the SiO_2 support; basic sites are lost by the deposition. The sequence of the starting material, the solvent, and the support does not influence this observation.

The concept of the structure sensitivity in catalysis which was introduced by Boudart [15] was successfully applied to the supported metal catalyst system and was expanded further to single crystal studies. Different crystal planes have different reactivities. Recent reports claim that this concept is also applicable to metal oxide systems. ZnO has three fundamental faces, namely (0001) (a Zn-polar plane), $(000\bar{1})$ (an O-polar plane), and $(10\bar{1}0)$ (a non-polar plane). Kung et al. showed that these planes exhibit different reactivities towards methanol, formaldehyde, formic acid, etc. [16].

A monoclinic form of zirconium dioxide usually exposes its (111) or $(\bar{1}11)$ faces. However, chemical vapor deposition (CVD) of Zr(acac) with water vapor on Si substrates resulted in the growth of the monoclinic ZrO_2 phase by the crystallographic orientation of (020) and (200) planes [17].

The surface electronic structure of ZrO_2/SiO_2 was investigated by the discrete vibrational X_α cluster model calculation [18] and the results showed that the Si–O bond of Si tetrahedra neighboring Zr tetrahedra became stronger and that the Bronsted acid site located on the SiO_4 unit exhibited stronger acidity. The change of basic property was not discussed here.

From these arguments, we may point out the reason why the acid-base properties have changed by depositing zirconium oxide on SiO_2 surface as follows:

(1) change of the surface electronic states by an electronic interaction between surface zirconium oxide and supporting SiO_2

(2) change of the exposed face by the different crystallographic orientations during the growth of zirconium oxide microcrystals on SiO_2.

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