# Preparation of Micro-Crystalline $ZrO_2$ with Monoclinic Structure and Its Strong Acid and Base Sites

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The micro-crystalline $ZrO_2$ with the monoclinic structure was prepared by the calcination at low temperature of the Zr-hydroxide obtained by the hydrolysis of Zr-alkoxide. Both the strong acid sites and the strong base sites were observed to be simultaneously generated on the monoclinic $ZrO_2$ surface.

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Monoclinic $ZrO_2$ is well-known to have a very interesting property attributed to acid and base sites; weak acid and base sites are simultaneously exhibited on the $ZrO_2$ surface.[1-3] The cooperation of acid and base sites has been reported to often produce some superior catalytic activities and selectivities.[1-3] The monoclinic $ZrO_2$ is, therefore, expected to be applied as an acid-base bifunctional catalyst. However, only weak acid and base sites have been observed on the $ZrO_2$ surface. It is very interesting to strengthen both the acid and base properties on the $ZrO_2$ surface in order to adapt to a wide variety of catalytic reactions.

Recently, the present author has reported that the acidic properties on pure metal oxides, such as $TiO_2$ and $SnO_2$, depended on the crystalline size.[4,5] The metal oxides have been observed to possess a strong acidity as well as a high catalytic activity when the metal oxides consisted of micro-crystalline particles. These characteristic properties are attributed to the co-ordinately unsaturated atoms developed on the surface of the micro-crystalline particles.[4] The purpose of the present work is to prepare the micro-crystalline $ZrO_2$ with monoclinic structure and to evaluate the acid-base catalytic properties on the surface. The author found that the very strong acid and base sites are simultaneously generated on the micro-crystalline monoclinic $ZrO_2$ obtained by the calcination at low temperature.

The $ZrO_2$ can be prepared by the thermal decomposition of Zr-hydroxide that is yielded by a hydrolysis of $Zr(NO_3)_4$, $ZrCl_4$, $ZrO(NO_3)_2$ or $ZrOCl_2$.[6-8] However, a small amount of anions, $Cl^-$ and $NO_3^-$ etc, remains in the $ZrO_2$ as contaminations. These contaminations exert some influences on the growth of crystallites as well as the acid and base catalytic properties. In this work, the $ZrO_2$ was prepared by hydrolysis of Zr-alkoxide because such anions never remained in the resulting oxides and the micro-crystalline particles were readily obtained.[5] 0.0223 mol of zirconium(IV) propoxide ($Zr(OC_3H_7)_4$, Aldrich Chemical Co.) was first dissolved in 50 mL of 1-propanol and the solution was slowly poured into 300 mL of distilled water with vigorous stirring at room temperature. The mixed solution was allowed to continue stirring for 60 min. The precipitate obtained was washed with distilled water, filtered with suction and dried at 387 K for 24 h, and then was calcined in air at the desired temperatures for 3 h.

In figure 1 are shown the X-ray diffraction spectra of the $ZrO_2$ samples calcined at various temperatures, with the BET surface areas and the crystalline sizes estimated by the use of Scherrer's equation. The very weak and broad diffraction peaks assigned to monoclinic structure with a little metastable tetragonal phase were observed in the $ZrO_2$ sample calcined at 673 K, indicating that the $ZrO_2$ is composed of the micro-crystalline particles. The intensity of diffraction peaks increased with an increase in the calcination temperatures. It is suggested that the crystallization of $ZrO_2$ is gradually induced by the calcination above 623 K though monoclinic structure is still dominant.

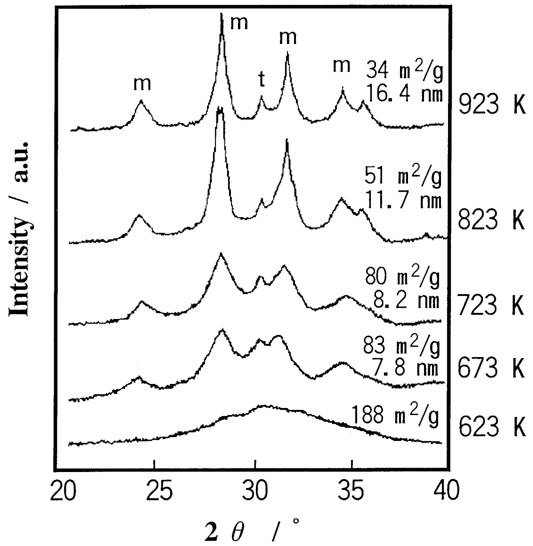

**Figure 1.** X-ray diffraction spectra, surface areas and crystalline sizes of $ZrO_2$ calcined at various temperatures. m; monoclinic, t; tetragonal.

In general, the $ZrO_2$ particles exhibit some different crystal structures according to the temperature of the calcination.[6] The tetragonal structure is known to be normally formed from the amorphous phase at the temperature around 607 K and to be transformed to monoclinic structure above 923 K.[6] Therefore, the preparation of monoclinic single phase $ZrO_2$ is usually required at least to be calcined at the temperature higher than 923 K. In this work, the monoclinic crystals were, however, observed to be preferentially formed in the $ZrO_2$ samples prepared from Zr-propoxide in spite of the calcination at very low temperature of 673 K and to be directly produced from the amorphism, as shown in figure 1.

The Zr-hydroxides obtained by the hydrolysis of Zr-salts have three different types of the structures; $\alpha$, $\beta$ and $\gamma$-types. Murase et al.[9] have suggested that the monoclinic crystals of the $ZrO_2$ are often given by the thermal decomposition of the $\gamma$-type hydroxides with a small amount of hydroxyl groups around Zr ions, whereas the $\alpha$-type hydroxides under highly hydrated conditions are readily crystallized to the tetragonal structure. In the case of Zr-propoxide, the $\gamma$-type hydroxides are, probably, mainly produced by the hydrolysis.

Figures 2 and 3 show the strengths and the amounts of acid

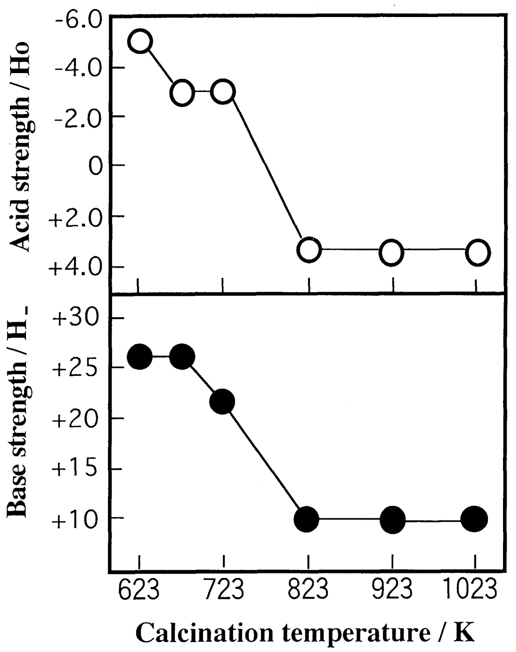

**Figure 2.** Changes in the acid and base strengths on the $ZrO_2$ with the calcination temperatures.

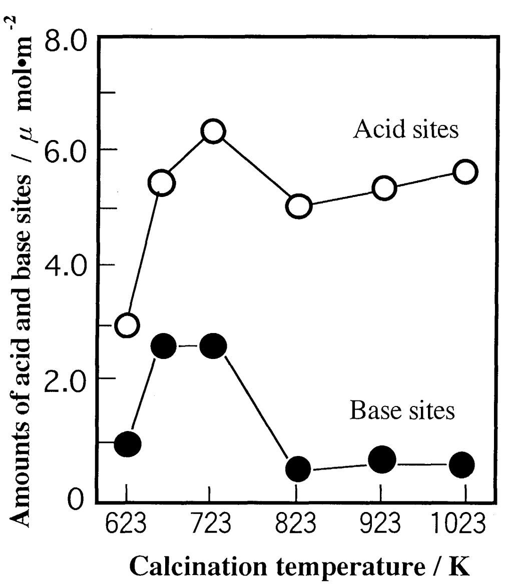

**Figure 3.** Change in the acid and base amounts on the $ZrO_2$ with the calcination temperatures.

and base sites on the $ZrO_2$ samples calcined at various temperatures. The acid and base strengths on the $ZrO_2$ were determined by the observation of the changes in color of indicators dissolved in benzene.[10] These sample powders were treated with an evacuation at 673 or 623 K for 1 h, prior to the measurements of the strengths of the acid and base sites. The amounts of acid and base sites were estimated from the amounts of ammonia and carbon dioxide adsorbed at 423 K, respectively, on the $ZrO_2$ samples which are recalcined in flowing He at 673 or 623 K.

Both the acid strength and the base strength on the $ZrO_2$ were found to depend on the calcination temperatures; these strengths greatly increased with a decrease in the calcination temperature below 723 K, as shown in Figure 2. Although the highest acid strength of pure $ZrO_2$ particles has been reported to be very weak of $H_0$=+1.5 at most,[11] the very strong acidity of $H_0$=-5.6, which is equal to the acid strength of strong solid acids[11] such as $SiO_2$-$Al_2O_3$ and $TiO_2$-$SiO_2$, was detected on the micro-crystalline $ZrO_2$ sample obtained by the calcination at 623 K. Moreover, this $ZrO_2$ sample was also observed the presence of very strong base sites with $H_-$=+26.5. The acid and base amounts per unit surface area also show the maximum values when the $ZrO_2$ samples were calcined at 673-723 K, as shown in Figure 3. These results indicate that the strong acid and base sites are generated in quantity on the micro-crystalline $ZrO_2$ obtained at moderately low temperatures. In addition, the rate of 1-butene isomerization on the micro-crystalline $ZrO_2$ sample calcined at 673 K was proved to be a noticeably higher value of 13.2 μmol/min · $m^2$ (the ratio of *cis*-2-butene to *trans*-2-butene was 2.9) at the reaction temperature of 413 K, though even those on the $ZrO_2$-$TiO_2$ and $TiO_2$-$SiO_2$ having very strong acidities were 1.7 μmol/min · $m^2$ (*cis*/*trans*=2.0) and 1.5 μmol/min · $m^2$ (*cis*/*trans*=1.8), respectively.

The micro-crystalline oxides obtained by the calcination at low temperature have a large number of the imperfection sites of crystallographic structure on the surface.[4] The imperfections due to metal or oxygen vacancies developed by the release of hydroxyl groups from γ-type hydroxides cause the local charge imbalances on the surface. The acid sites and the base sites on the $ZrO_2$ seem to be individually affected by the local imbalances of the negative and positive charges, respectively. Of course, it will be necessary to reveal the reason why the strong acid sites are generated together with the strong base sites without a compensation on the surface of the micro-crystalline monoclinic $ZrO_2$.

## References

1 T. Yamaguchi, *Catal.Today*, **20**, 199 (1994).

2 T. Yamaguchi and M. Ookawa, *Shokubai (Catalysts & Catalysis)*, **38**, 260 (1996).

3 T. Yamaguchi, *Sekiyu Gakkaishi*, **36**, 250 (1993).

4 H.Nakabayashi, N.Kakuta, and A.Ueno, *Bull.Chem.Soc.Jpn.*, **64**, 2428 (1991).

5 K. Nishiwaki, N. Kakuta, A. Ueno, and H. Nakabayashi, *J. Catal.*, **118**, 498 (1989).

6 "Metal oxide and Binary oxide," ed by K.Tanabe, T.Seiyama, and K.Fueki, Kodansha Scientific, Tokyo (1978), Chap.10, p.119.

7 Raũl A.Comelli, Carlos R.Vera, and Josẽ M.Parera, *J.Catal.*, **151**, 96 (1995).

8 T.Tatsumi, H.Matsuhashi, K.Arata, *Bull.Chem.Soc.Jpn.*, **69**, 1194 (1996).

9 Y. Murase and E. Kato, *Nippon Kagaku Kaishi*, **1978**, 367.

10 K. Tanabe, "Solid Acids and Bases," Kodansha, Tokyo (1970) p.38.

11 K. Shibata, T. Kiyoura, J. Kitagawa, T. Sumiyoshi, and K. Tanabe, *Bull.Chem.Soc.Jpn.*, **46**, 2985 (1973).