

## The Preparation and Surface Characterization of Zirconia Polymorphs

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**Abstract**—Zirconium hydroxides were obtained by precipitation of zirconium chloride with aqueous ammonia at constant pH followed by hydrothermal treatment. The effect of thermal activation of the zirconium hydroxide on physical properties, and the effect of crystalline phase on the surface properties of zirconia were studied. The pressure during the hydrothermal treatment of zirconium hydroxide affected the surface area, particle growth, and phase transformation of the zirconia product. Hydrothermally treated zirconia under atmospheric pressure (LP) shows higher surface area than that under high pressure (HP) and untreated (UT). HP zirconia shows a mixture of tetragonal and monoclinic phase after hydrothermal treatment due to the higher solubility and reprecipitation rate, whereas LP sample shows a tetragonal crystal structure from 600 to 1,050 °C. Monoclinic phase zirconia shows greater CO<sub>2</sub> and NH<sub>3</sub> surface adsorption than amorphous and tetragonal phase zirconia. This suggests that the crystal structure of zirconia strongly affects the amount and strength of the surface adsorption site.

Key words: Monoclinic Zirconia, Hydrothermal Treatment, Surface Property, TPD

### INTRODUCTION

For twenty years, extensive investigations have been devoted to the utilization of zirconium oxide (zirconia) as a low toxicity ceramic, thermal barrier, automotive catalyst, electroceramic, pigment, filler, and oxygen sensor because of its interesting thermal and mechanical properties [Yamaguchi, 1994]. Zirconia is known to possess surface acidity and basicity as well as high thermal stability, which are important for applications as a catalyst or catalyst support in petroleum chemistry [Fujitani et al., 1994]. It by itself is active in the synthesis of methanol and isobutene from CO and hydrogen [He and Ekerdt, 1984], and hydrogenation of CO [Ekerdt and Karles, 1992] and dehydration of alcohol [Chokkaram and Davis, 1997]. In addition zirconia is a very stable support that can be used at low pressures, under a reducing atmosphere, or photo irradiation [Moles, 1992].

In an effort to develop more effective zirconia catalysts or catalyst supports, the relationships between textural properties (surface area, particle size and crystalline structure) and chemical reactivity have been studied. Factors influencing the surface area and the phase transformations of zirconia have attracted interest because commercially available zirconia has less than 50 m<sup>2</sup>/g while silica and alumina has 100-600 m<sup>2</sup>/g. Supercritical drying method (SCD) was employed to make zirconia with high surface areas and large pore volumes. Klabunde and Bedilo [1997] prepared zirconia aerogels from zirconium alkoxide with the surface area of 565 m<sup>2</sup>/g after drying and above 100 m<sup>2</sup>/g after calcination at 500 °C for 2 h. By using CO<sub>2</sub>-SCD, Ko and Ward [1993] studied structural transformation of zirconia at low temperature. Pajonk and ElTanany [1992] have synthesized a tetragonal phase zirconia aerogel with a surface area of 200 m<sup>2</sup>/g at 430 °C. Ciesla et al. [1999a, b] reported meso-

porous zirconia with a surface area of 390 m<sup>2</sup>/g at 500 °C could be prepared by using post-synthetic treatment with surfactants. However, these zirconia samples show drastic loss of surface area on thermal sintering. This is a severe drawback for applications in catalytic processes, which have to be conducted at relatively high temperatures.

Zirconia has three stable polymorphs at atmospheric pressure: monoclinic, tetragonal, and cubic structure [Mercera, 1991]. Garvie and Chan [1988] proposed that the sum of free energy from surface, bulk, and strain effects determine the stability of single-phase zirconia. An abrupt tetragonal to monoclinic phase transition occurs upon heating as the crystal size grows above 30 nm because the surface energy should dominate the bulk term. Stichert and Schuh [1998] also reported that the phase transition was attributed to changes in crystallite size during the calcination. Zirconia is often combined with cation dopants (Y<sub>2</sub>O<sub>3</sub>, MgO, Cr<sub>2</sub>O<sub>3</sub>, CaO or La<sub>2</sub>O<sub>3</sub>), anionic elements (SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, or CO<sup>-</sup>) because these additives retard sintering and crystallization [Clearfield et al., 1994; Chuah, 1999]. Water vapor and sodium ions in zirconia gel affect the formation of monoclinic and tetragonal phase, respectively [Murase and Kato, 1983; Chauh et al., 1998].

Several workers have reported that texture properties are affected by the preparation conditions for the hydroxide [Awate et al., 2001; Lee et al., 1999; Suh et al., 2000; Torralvo et al., 1984; Wright et al., 1983]. Mamott et al. [1991] suggested that the pH of the solution used during the precipitation directly influences the rate of polymerization and therefore the degree of localized order within the hydroxide units. Benedetti et al. [1991] also showed that the surface area was strongly related to pH of the zirconium hydroxide. Corma et al. [1994] reported that the pH of precipitation of the precursor Zr(OH)<sub>4</sub> has a strong influence on the structure of crystalline zirconia under hydrothermal treatment. Because of the high solubility, a dissolution/precipitation mechanism and association of tetrameric zirconyl species are dormant at low pH [Clearfield et al.,

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1994]. In a neutral medium, varying amounts of both monoclinic and tetragonal phases were obtained. In this region, the solubility of zirconium hydroxide is small and they precipitate first followed by in-situ hydrothermal crystallization of the amorphous phase into tetragonal and monoclinic phase. In high pH regime, zirconium hydroxides have high hydroxyl content and lower water content, which would aid the dewatering process. Dehydration occurs which results in the higher energy tetragonal phase during the hydrothermal treatment.

Hydrothermal methods have been widely applied for the synthesis of a variety of materials because this technique yields well-shaped and isolated, fine metal oxide particles, while solid-state calcination strongly affects the morphology and particle size due to the sintering effect [Jung et al., 1997; Jung and Shul, 1998]. The hydrothermal method is, therefore, preferred in the production of fine zirconia particles for use in advanced ceramics.

For catalytic applications of zirconia, the effect of surface area and different crystalline phase with the same surface area on the surface properties need to be studied. Up to now, there have been no reports on this area because of many variables, which affects for surface area, and crystalline phase as discussed above. In this study, the two main parameters to deal with are (1) the preparation of single-phase zirconia by different preparation techniques, and (2) the characterization of surface reaction of crystalline zirconia with the same surface area. For these, we made zirconium hydroxide at the same pH (=10) to exclude the effect of pH on the crystalline phase and to obtain high physical properties. After zirconium hydroxide was made, hydrothermal treatment under high, autogeneous, pressure (HP) and under low, atmospheric, pressure (LP) was applied to elucidate the pressure effect during the preparation of zirconia. Finally, the effect of crystalline phase and surface area on the surface properties was also discussed.

## EXPERIMENTAL

### 1. Catalyst Preparation

Zirconium oxyhydroxide [ $\text{ZrO}_x(\text{OH})_{4-2x}$ ] was prepared by hydrolysis of a 0.5 M zirconyl chloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , Aldrich) solution using dropwise addition of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) at pH 10. This pH was chosen based on the previous studies. The authors suggested that maximum mesoporosity, surface area, and total pore volume could be obtained at a pH of 10 [Khodakov et al., 1998]. The pH of the solution was continuously monitored with a glass electrode system, thus enabling samples to be precipitated at pH 10. To study the effect of pressure during the hydrothermal treatment on the zirconia phase, each batch of precipitated slurries was divided into three equal volumes. First, one portion was placed into a 23 cm<sup>3</sup> static, Teflon (PTFE)-lined, stainless steel autoclave (Parr Co.), and heated in an oven at 110 °C. Following a specified period of heating (240 h), the autoclave was removed from the oven and cooled to room temperature. Hereafter, we will refer to this sample as the HP sample [hydrothermal treated sample at high (autogeneous) pressure]. The second volume was transferred to a hydrothermal treatment reactor at atmospheric pressure and heated to 100 °C under reflux. Additional ammonia was added to maintain the pH during the reaction for 240 h. Hereafter, we will refer to it as the LP sample (hydrothermal treated sample at low, atmospheric,

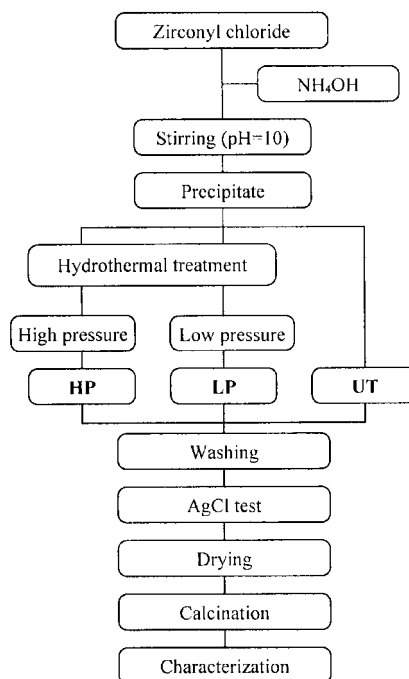


Fig. 1. Experimental scheme for the preparation of zirconia.

pressure). The third one (UT) was left untreated and allowed to age at room temperature for the same reaction time to compare with hydrothermally treated samples. In all cases, the hydrous zirconia was recovered via vacuum filtration after the reaction for 240 h. They were washed repeatedly by redispersion in water in order to remove residual chlorine. After each wash, a few drops of  $\text{AgNO}_3$  solution were added to the filtrate liquid until  $\text{AgCl}$  was not detected. Zirconium hydroxide obtained was dried at 100 °C in oven for 24 h. These samples were studied both in the freshly prepared state and after calcination. Calcination was carried out in oxygen flow in a tube furnace at various temperatures. The temperature was increased at a rate of 10 °C/min to the final temperature and held for 5 h. The overall schematic diagram for the preparation is shown in Fig. 1.

### 2. Physico-Chemical Characterization

X-ray powder diffractometer (XRD) patterns were recorded in a Siemens D5000 with graphite monochromator by using  $\text{Cu-K}\alpha$  radiation. Scans were made in the  $2\theta$  range from 23° to 37° with a scanning rate of 0.005°/s. The Scherer relationship was used to calculate crystal size by using the integral line width ( $B_{hkl}$ ) of the monoclinic and tetragonal pattern-resolved reflections and a shape factor (S) equal to 0.9. Thermogravimetric (TG) and differential thermal analysis (DTA) of the samples were carried out at a temperature of up to 900 °C with heating rate of 10 °C/min. During the measurements oxygen was used as a purging gas. An Autosorb gas adsorption system was used to obtain nitrogen adsorption/desorption isotherms. Surface area, pore volume, and pore size were determined from the corresponding isotherms at -196 °C. Before analysis, all samples were outgassed for 1 h under vacuum at 100 °C (non-heat treatment) or 250 °C (other samples). From the 80-point adsorption and desorption isotherms, BET surface area (taken at  $P/P_0 \sim 0.3$ ), and pore size distribution (BJH) were calculated.

Catalytic surface properties were measured by  $\text{CO}_2$  and  $\text{NH}_3$  tem-

perature-programmed desorption with analysis by mass spectrometry (TPD-MS). The zirconia samples (0.025–0.05 g) were placed in an adsorption reactor and preheated under oxygen flow at 300 °C for 1 h. After cooling to room temperature, CO<sub>2</sub> (or NH<sub>3</sub>) was introduced into the reactor and contacted with zirconia samples for 1 h. Physically adsorbed material was then removed by flushing the samples with He gas for 2 h at adsorption temperature. The TPD was run up to 600 °C at a linear rate of 10 °C/min. Composition of the desorbed gases was monitored by injecting gas samples into a UTI 100 quadrupole mass spectrometer. All gases were purified prior to use. He gas was passed through an oxysorb (CrO<sub>2</sub>) trap to remove O<sub>2</sub> and then a molecular sieve trap (3 Å Davidson grade 564) to remove water. CO<sub>2</sub> was passed through a hopcalite trap (80% MnO<sub>2</sub> + 20% CuO) to remove CO and a molecular sieve trap to remove water. Purified gases were delivered to the TPD reactor via Tylan Model FC-280 mass flow controllers. Electrical resistance heaters heated the reactor and an Omega Series CN-2010 programmable temperature controller controlled the cell temperature.

## RESULTS

### 1. Crystalline Structure

Fig. 2 shows the effect of preparation method on the XRD patterns. Monoclinic ((111-) and (111)) and tetragonal phase ((111)) zirconia are determined from peaks of 28.0° and 31.4°, and 30.2°, respectively. Despite the same pH (=10) used for zirconium hydroxide precipitation, different XRD patterns were obtained. The XRD patterns of hydrothermal treated samples at high pressure (HP) show a mixture of tetragonal and monoclinic phase even after drying at 100 °C, while hydrothermal treated samples at low pressure (LP) and untreated sample (UT) are amorphous under the same condition. In general, the preparation of monoclinic phase zirconia usually requires calcination at temperatures higher than 650 °C at the solid state reaction [Tanabe et al., 1978]. However, monoclinic crystals were observed to be formed in the HP sample after drying, and the relative portion of monoclinic phase increased with increasing

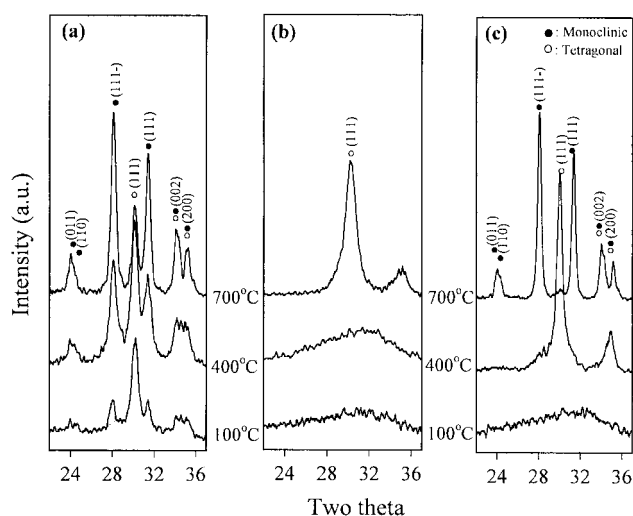


Fig. 2. Effect of preparation method on the crystalline structure of zirconia as a function of calcination temperature. (a) HP, (b) LP, and (c) UT

temperature as shown in Fig. 2a. After the calcination of LP sample at the temperature of 400 °C and below, no sign of a crystal phase could be observed but a very broad peak was observed. Based on the broad peak, it can be assumed that a very short-range ordering of the reaction products was obtained by hydrothermal treatment under atmospheric pressure. After calcination at 700 °C, broad diffraction lines of tetragonal phase zirconia appear and their intensities increase. This result suggests that the tetragonal phase apparently is stabilized by the hydrothermal treatment at atmospheric pressure while, in general, the zirconia particles exhibit different crystal structures according to the calcination temperature in these ranges [Tanabe et al., 1978]. UT sample shows a hybrid crystalline phase between HP and LP. The tetragonal crystals are observed to be directly produced from the amorphous phase and to be preferentially formed from 400 °C as shown in Fig. 2c. They directly transformed into the monoclinic phase. The tetragonal phase zirconia in the UT transformed into monoclinic phase zirconia more easily than that of HP and LP samples because the UT sample does not have rigid porous networks which form during the hydrothermal treatment and retard sintering and crystallization [Chuah et al., 1996].

During the calcination, crystal sizes increased with calcination temperature in all cases as shown in Fig. 3. The crystal size of the monoclinic phase in HP and UT abruptly increased with increasing treatment temperature, while the particle size of tetragonal phase increased slightly by 16–24% of the initial particle size of tetragonal phase zirconia. If we consider the particle size change of monoclinic phase (230%), it can be assumed that the particle size of the tetragonal phase does not change. The tetragonal phase particle size was also affected by the hydrothermal treatment pressure and increased in the following order of LP < HP < UT.

### 2. Thermal Analysis

Thermogravimetric analysis (TGA) of the hydrous zirconia was used to determine the degree of hydroxylation as shown in Fig. 4. The HP sample shows two stages of weight loss. The first stage is from room temperature to 90 °C, which undoubtedly corresponds to desorption of physically adsorbed water. The second loss of weight, due to the desorption of chemisorbed water, continuously decreases and completes at about 760 °C. The observed weight loss is entirely

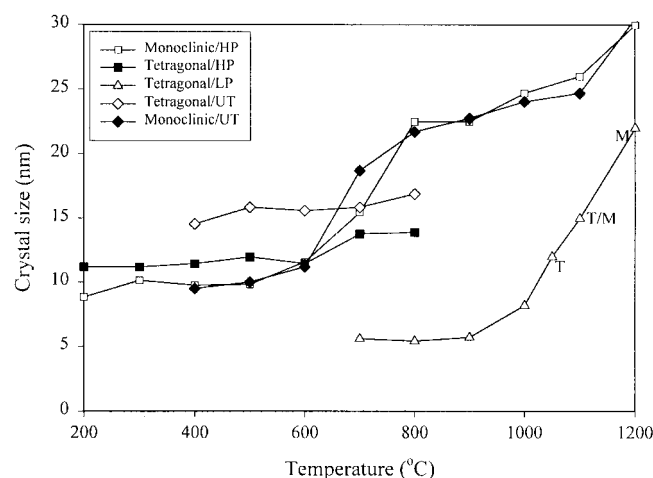
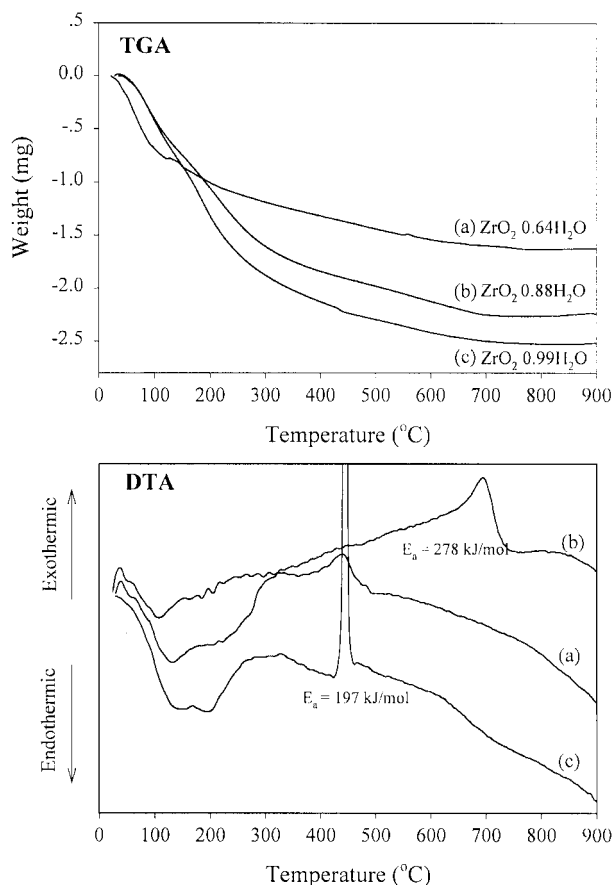


Fig. 3. Effect of preparation method on the particle size of zirconia as a function of calcination temperature.



**Fig. 4. Thermal analysis results of zirconium hydroxide and zirconia catalysts.**

(a) HP, (b) LP, and (c) UT

due to the removal of water, dehydroxylation [Tanabe et al., 1978]. Based on the weight loss from room temperature to 1,100 °C, water contents in the zirconium hydroxide are calculated. UT has the formula  $\text{ZrO}_2 \cdot 0.99\text{H}_2\text{O}$ . However, hydrothermal treated samples show lower water content [ $\text{ZrO}_2 \cdot 0.64\text{H}_2\text{O}$  (HP), and  $\text{ZrO}_2 \cdot 0.88\text{H}_2\text{O}$  (LP)] than that of UT. As shown in the XRD results (Fig. 2), an increase in pressure during the hydrothermal treatment brings about changes in the structure of the hydrous zirconia and leads to the formation of crystalline products which may be related to the lower weight loss.

A DTA measurement was performed to study the possible influence of the pressure of hydrothermal treatment on crystallization temperature. The DTA curves of LP and UT show two broad endotherms from room temperature up to about 280 °C, which correspond to the desorption of physisorbed and chemisorbed water. The relative amount of chemisorbed water associated with HP and LP is smaller than that of UT, which suggests that hydrothermal treatment decreases the amount of chemisorbed water, as mentioned in connection with the TGA results. The exotherm for HP and UT appeared at about 450 °C, while that for the LP sample occurred at about 670 °C. This exotherm was accompanied by a small weight loss due to the surface hydroxylation. These exotherms, known as "glow exotherm phenomena," were observed by other studies and attributed to the crystallization of zirconia [Mercera, 1991; Clearfield et al., 1994; Chauh, 1999]. According to XRD results (Figs. 2b and

2c), it is certain that the exothermic peak can be assigned to the crystallization of LP and UT. However, for the HP sample, a mixture of tetragonal and monoclinic phases was observed after drying the zirconium hydroxide at 100 °C as shown in Fig. 2a. This indicates that the exotherm peak for HP is not related to its crystallization but to the phase transition from tetragonal phase to monoclinic phase as shown by the XRD results. If we consider that the exothermic peak is absent when the hydrous oxide is already crystalline or when the final oxide is amorphous, another possibility is crystallization of the remaining amorphous zirconium hydroxide in the HP sample. The crystallization peak for the LP sample is about 220 °C higher compared to that for the UT.

The transformation temperature corresponds to the maximum rate of reaction, and the apparent activation energy,  $E_a$ , is related to the heating rate by the Redhead equation based on the temperature-programmed reaction theory [Falconer and Schwartz, 1983]:

$$E_a = RT_f [\ln(vT_f/\beta) - 3.64]$$

where  $v$  is taken as  $10^{13} \text{ s}^{-1}$ ,  $R$  is gas constant,  $T_f$  the maximum temperature of exothermic peak, and  $\beta$  is heating rate. Using this equation, an apparent activation energy of crystallization for UT of 197 kJ/mol is calculated which is similar to the result when compared to those of other samples with activation energies ranging from 180 to 200 kJ/mol [Chauh, 1996]. After the hydrothermal treatment, the apparent activation energy of crystallization is 278 kJ/mol for LP sample.

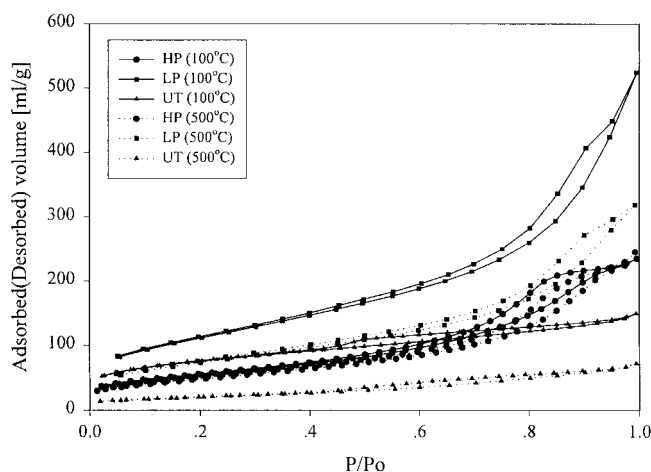
### 3. Physical Properties

The effect of preparation method on the surface area and crystalline structure of zirconia is summarized in Table 1. It is seen that the hydrothermal pressure has a strong influence on the surface area. The surface area of LP sample is 325  $\text{m}^2/\text{g}$  at 400 °C, a surface area higher than any other previously reported for zirconia [Mercera, 1991; Clearfield et al., 1994; Chauh, 1999]. To obtain the single tetragonal phase zirconia, we calcined LP sample at higher temperature and prepared a tetragonal phase zirconia which shows its phase up to 1,050 °C with the surface area of 20  $\text{m}^2/\text{g}$ . Upon calcining at progressively higher temperatures, the UT samples have lower sur-

**Table 1. Sample preparation conditions of zirconia for TPD measurement**

Preparation method	Calcination temperature (°C)	BET surface area ( $\text{m}^2/\text{g}$ )	Crystalline phase
Hydrothermal treatment at atmospheric pressure (LP)	100	404	Am
	400	325	
	700	187	T
	1050	20	
Untreated sample (UT)	100	259	Am
	400	150	T>>M
	700	19	M
Hydrothermal treatment at autogeneous pressure (HP)	100	195	T>>M
	400	132	T>M
	700	55	T=M

Am: amorphous phase zirconia. T: tetragonal phase zirconia. M: monoclinic phase zirconia.

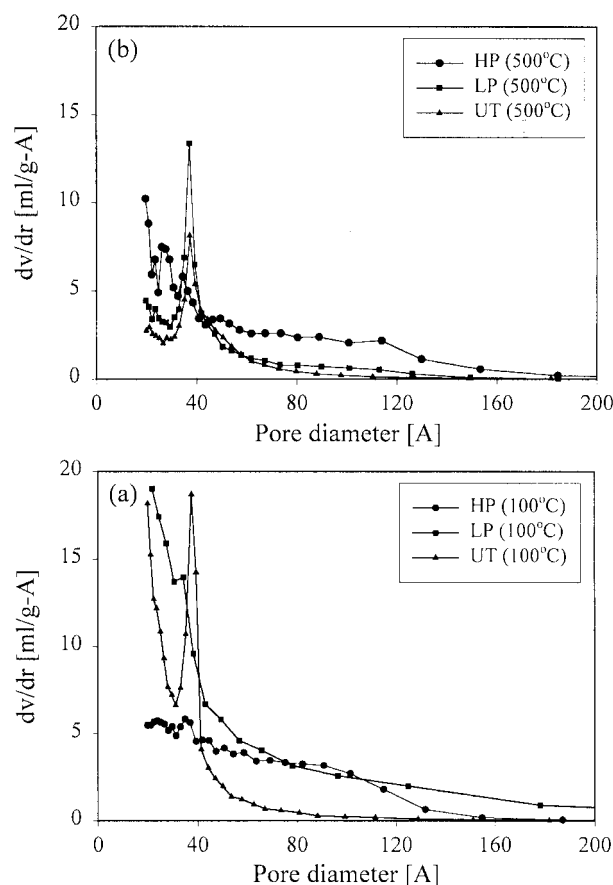


**Fig. 5. Nitrogen adsorption-desorption isotherms at  $-196^{\circ}\text{C}$  for zirconia as a function of preparation method.**

face area than that of LP. A similar dependence of surface area on the calcination temperature was found for the HP samples because of phase transition from tetragonal phase to monoclinic phase. The initial surface area obtained at  $100^{\circ}\text{C}$  decreases. The relative amount of decreasing surface area up to  $500^{\circ}\text{C}$  is in the following order: LP (27%) < HP (43%), and UT (61%) zirconia. These results suggest low thermal stability of UT sample.

Nitrogen adsorption-desorption isotherms for zirconia sample both after drying at  $100^{\circ}\text{C}$  and calcination at  $500^{\circ}\text{C}$  are illustrated in Fig. 5. In all cases the isotherms are of Type IV, a well-developed mesoporous system in the BET classification. These results suggest that the isotherm type is not affected by the hydrothermal treatment pressure under which formation of hydrous zirconia and zirconia occur. All samples dried at  $100^{\circ}\text{C}$  exhibit larger hysteresis loops than that of calcined samples. In addition, the shape of the hysteresis loops of UT sample changes gradually from that of type E to type A (following the classification of De Boer et al. [1958]) in the high relative pressure ( $P/P_o$ ) with hydrothermal treatment. E-type hysteresis is often associated with “ink-bottle” pores, spheroidal cavities or voids between close-packed spherical particles; on the other hand, A-type hysteresis is characteristic of cylindrical pores. These results mean that UT having mesoporous and spherically shaped pores (E-type hysteresis) changed into cylindrically shaped pored pore (A-type hysteresis) by thermal treatment. Calcination at  $500^{\circ}\text{C}$  led to the uptake of a smaller amount of nitrogen than that of the dried sample of LP and UT. However, a slight difference is observed in HP between drying at  $100^{\circ}\text{C}$  and calcination at  $500^{\circ}\text{C}$ .

The mesopore size distribution for each sample was calculated from the desorption branch of the isotherms following the BJH method. Figs. 6a and b show the effect of calcination at  $500^{\circ}\text{C}$  on the development of the mesopore size distribution of hydrous zirconia samples. From these figures, it is evident that uncalcined LP and UT exhibit unimodal and narrow pore size distributions having a maximum pore size of about  $40\text{ \AA}$ . On calcining at  $500^{\circ}\text{C}$ , the pore size distribution, and maximum pore value does not shift toward higher value for UT. However, for the LP sample, there is a formation of a peak at about  $40\text{ \AA}$  indicating the development of pore size. The order of maximum peak intensity was changed between



**Fig. 6. Pore size distribution for zirconia as a function of preparation method.**

(a) before calcination, (b) after calcination

both samples. However, there is no big difference in the pore size distribution for the HP sample before and after calcination at  $500^{\circ}\text{C}$ , compared to other samples. HP samples show a broad pore size distribution resulting from the formation of crystalline phase prior to the calcination.

#### 4. Surface Properties

In order to understand the relationship between the phase and the surface properties, we selected the single-phase zirconia samples based on our results (Table 1). Amorphous ( $325\text{ m}^2/\text{g}$ ), tetragonal phase with high surface area ( $187\text{ m}^2/\text{g}$ ), tetragonal phase with low surface area ( $20\text{ m}^2/\text{g}$ ) were obtained by calcination of LP sample at  $400$ ,  $700$ , and  $1,050^{\circ}\text{C}$ , respectively. Monoclinic phase zirconia ( $19\text{ m}^2/\text{g}$ ) was made by calcining UT at  $700^{\circ}\text{C}$ . The mixture phase between tetragonal and monoclinic zirconia was obtained by HP with the surface area of about  $80\text{ m}^2/\text{g}$ .

Temperature-programmed desorption of  $\text{CO}_2$  and  $\text{NH}_3$  has been proposed as a measure of the strength of the adsorbent-adsorbate interactions, i.e., basicity and acidity amount and strength distribution in solid [Bianchi et al., 1995]. Figs. 7 and 8 show the TPD profiles after adsorption of  $\text{CO}_2$  and  $\text{NH}_3$  on zirconia at various temperatures, respectively. The interpretation of these variations in the TPD peaks is not easy. However, the shape of the peaks is related to the amount and/or the energetic distribution of surface adsorption sites on the various zirconia samples. It can be seen that the  $\text{CO}_2$ -TPD curves corresponding to the true basic center in zirconia

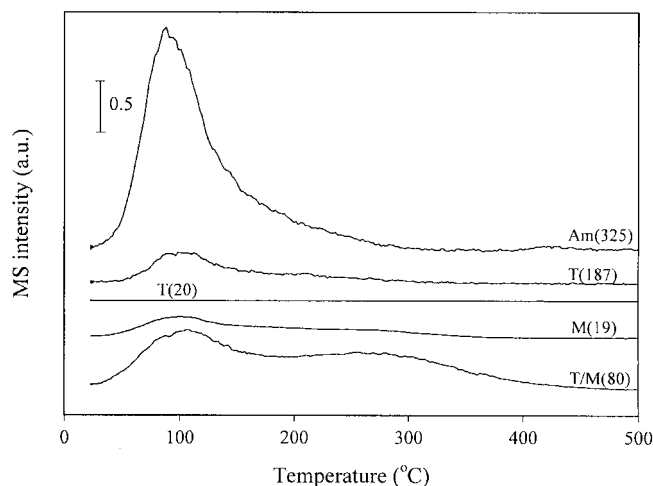


Fig. 7. Effect of preparation method on the CO<sub>2</sub> desorption MS spectra.

(A): A is BET surface area [m<sup>2</sup>/g]

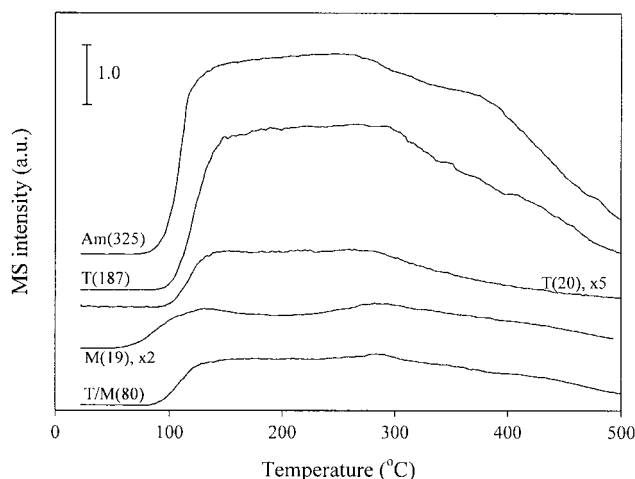


Fig. 8. Effect of preparation method on the NH<sub>3</sub> desorption MS spectra.

(A): A is BET surface area [m<sup>2</sup>/g]

show two desorptions at the temperature of 100 and 290 °C corresponding to weak and strong basicity, whereas CO is not detected and neither is hydrogen like other researchers [Bianchi et al., 1995]. All TPD results confirm the correlation between the total desorption amount of CO<sub>2</sub> and surface area, and the monoclinic structure of zirconia bring about stronger surface adsorption sites than the tetragonal structure. Interestingly, the tetragonal phase calcined at 1,050 °C (20 m<sup>2</sup>/g) does not desorb any CO<sub>2</sub>.

In contrast to CO<sub>2</sub>, the desorption peak of NH<sub>3</sub> shows poorly resolved peaks and shoulders due to various surface species having gradually increasing activation energies of desorption. The amount of NH<sub>3</sub> desorption decreases when the temperature of the desorption increases from the 300 °C as shown in Fig. 8. Three desorption ranges can be differentiated: three broad peaks at 100-150, 280-300, and about 400 °C. These peaks can be assigned to acid sites with strength in the low, medium, and strong. All spectra show similar relative intensity of desorption peaks. In relation to the tetragonal phase zirconia, the monoclinic phase zirconia provides a rela-

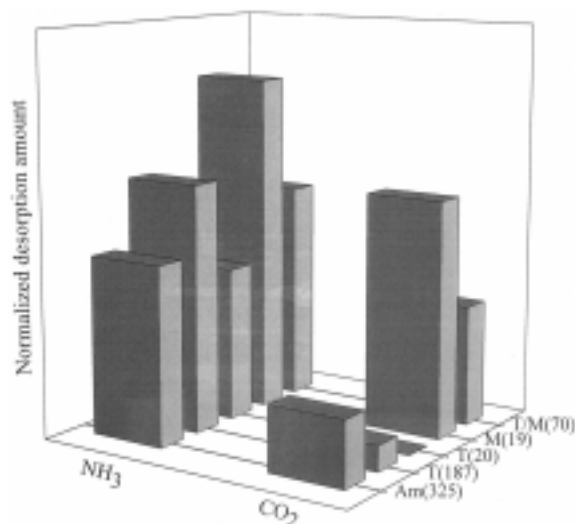


Fig. 9. Effect of crystalline phase and BET surface area of zirconia on the normalized amount of CO<sub>2</sub> and NH<sub>3</sub> desorption. Normalized amount means the amount of CO<sub>2</sub> (NH<sub>3</sub>) desorption was divided by its BET surface area.

(A): A is BET surface area [m<sup>2</sup>/g]

tively higher concentration of medium acid sites and is more differentiated, exhibiting two maxima at temperatures of about 120 and 290 °C. From these results, the surface area and texture of the sample also affect the strength of the surface adsorption site for a given crystallographic structure.

Fig. 9 shows the normalized amount of CO<sub>2</sub> and NH<sub>3</sub> desorption as a function of crystalline phase with various surface areas. Normalization means that the amount of total desorption of CO<sub>2</sub> (or NH<sub>3</sub>) for each sample is given per square meter of surface area. For the CO<sub>2</sub>, the order of normalized desorption was in the order of monoclinic>amorphous>tetragonal phase zirconia. Meanwhile, desorption of NH<sub>3</sub> decreased in the order of monoclinic>tetragonal>amorphous phase zirconia. The normalized desorption amount of NH<sub>3</sub> is higher than that of CO<sub>2</sub> for all zirconia samples. It is clearly seen that both the acidity and the basicity on the zirconia were found to depend on the crystalline structure. Both techniques (CO<sub>2</sub> and NH<sub>3</sub> TPD) concur in the order of the amount of desorption and the density of adsorption site (monoclinic>tetragonal).

## DISCUSSION

While general relationships between preparation and final properties have been previously appreciated, we have for the first time been able to demonstrate directly that the pressure during the hydrothermal treatment of zirconium hydroxide considerably affects both the physical and chemical properties. In addition, the crystallographic structure is the main factor determining the nature and density of the surface sites involved in the adsorption of CO<sub>2</sub> and NH<sub>3</sub>.

### 1. Crystalline Structure and Physical Properties

For the LP sample, the crystallite sizes of monoclinic phase zirconia are bigger than those of tetragonal phase zirconia in accordance with the postulation of Garvie and Chan [1988] that the tetragonal phase zirconia is stabilized for small sizes due to their surface energy. Denkwicz et al. [1990] also proposed a model of mono-

clinic zirconia and tetragonal zirconia crystallization. According to their model, crystallization occurs by structural rearrangement of zirconium hydroxide and the product is tetragonal zirconia while monoclinic phase zirconia can be attributed to the phase transition from tetragonal phase zirconia. Based on our results the crystallization of the tetragonal phase resulted from the aggregation of small crystallites to larger crystallites as shown in Fig. 3. However, for HP and UT, the particle size of monoclinic crystallites is smaller than that of tetragonal up to below 600 °C although it is reversed from 700 °C. This result shows that the monoclinic particles can exist without needing to be generated by the transformation of the tetragonal phase when its crystals grow. In other words, the monoclinic particle stability is not restricted by the size, while factors other than crystallite size govern tetragonal phase stability. For the order of particle size of tetragonal crystallites, our results imply that hydrothermal treatment decreases the particle size of tetragonal phase crystallites because of the high solubility, which in turn hinders grain growth during the calcination under hydrothermal treatment. For HP samples, higher solubility, reprecipitation and crystallization rate than those of LP and UT lead to the increase of particle size of tetragonal phase and the formation of the thermodynamically stable monoclinic phase by in-situ hydrothermal crystallization.

Clearfield et al. [1994] and Chauh [1999] suggest that hydrothermal treatment under atmospheric pressure which resulted in the more dehydrated zirconium hydroxide in turn leads to the high surface area zirconia after calcination. We would like to draw attention to the work of Murase et al. [1978]. They suggested three types of zirconium hydroxide ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) can be obtained by the hydrolysis of zirconium salts by taking the original model of Zaitsev. According to him, the monoclinic crystals of the zirconia are often given by the thermal decomposition of the  $\gamma$ -type hydroxide with a small amount of hydroxyl group around Zr ions [Tanabe, 1978; Murase and Kato, 1978]. If we recall the results of particle size calculated by XRD (Fig. 3) and TG-DTA (Figs. 4), hydrothermal treated samples (LP and HP) show a higher amount of dehydration and smaller particle size than that of the untreated one. These results coincide with the fact that hydrothermal treatment led to the increase of dehydroxylation and decrease of the particle size [Clearfield et al., 1994; Murase and Kato, 1978]. Especially, in our conditions, the high pressure and the long reaction time during the hydrothermal treatment increase the rate of collision between the particles so that a stabilized network is formed via condensation of hydroxyl groups. The interpretation of our results by the model of Murase suggests that high pressure treatment brings about a modification of the structure from an  $\alpha$ -type to an  $\beta$ -type, and finally  $\gamma$ -type by the loss of OH groups. Highly dehydrated  $\gamma$ -type hydroxides are mainly produced by hydrothermal treatment at high, autogeneous, pressure and then they are transformed to the monoclinic zirconia after hydrothermal treatment. This result can be confirmed by the fact that HP sample shows large amount of volume fraction of monoclinic phase than that of UT as shown [Jung and Bell, 2000].

## 2. Surface Properties

The basicity and acidity depends on the preparation procedure, the hydration-dehydration degree and mainly the calcination temperature [Morterra et al., 1993]. Nishiwaki et al. [1989] reported that the acidic properties of pure metal oxides, such as  $\text{TiO}_2$  and  $\text{SnO}_2$ , depended on the crystalline size. Based on our results, if we

consider the calcination temperature, which can affect the surface properties of the zirconia, the normalized  $\text{CO}_2$  desorption amount of monoclinic zirconia of  $19 \text{ m}^2/\text{g}$  should be similar to tetragonal phase zirconia of  $187 \text{ m}^2/\text{g}$  because of the same calcination temperature. However, monoclinic zirconia has nine times larger amount than that of tetragonal phase. For the effect of crystallite size, there is no correlation between monoclinic zirconia of  $19 \text{ m}^2/\text{g}$  and tetragonal zirconia  $20 \text{ m}^2/\text{g}$  which shows almost the same crystallite size (8-12 nm). These results suggest that normalized  $\text{CO}_2$  desorption amount is not directly related to the calcination temperature and crystallite size in our experimental conditions. Thus, it can be inferred that the crystallographic structure is the main factor determining the nature and density of the surface sites involved in the adsorption of  $\text{CO}_2$  and  $\text{NH}_3$ .

Because the cooperation of acid and base sites has been reported to produce some superior catalytic activities and selectivities, our results are very important for catalytic applications [Yamaguchi, 1994]. In the next paper, we will discuss the effect of both acidity and basicity of the zirconia on the crystallographic structure and surface hydroxyl group [Jung and Bell, 2000, 2001]. Further investigations into the crystalline structures and catalytic activity are underway.

## CONCLUSIONS

1. The hydrothermal treatment greatly affected the crystalline structure, thermal property, and physical property. The atmospheric pressure during the hydrothermal treatment affects the thermal stability of tetragonal phase zirconia and gives the higher surface area.

2. Monoclinic phase zirconia shows higher  $\text{CO}_2$  and  $\text{NH}_3$  desorption amount than that of amorphous and tetragonal phases zirconia. This suggests that the crystallographic structure is the main factor determining the nature and density of the surface sites involved in the adsorption of  $\text{CO}_2$  and  $\text{NH}_3$ .

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