



Effect of aging temperature during refluxing on the textural and surface acidic properties of zirconia catalysts



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ARTICLE INFO

Article history:

Received 22 March 2017

Received in revised form 2 May 2017

Accepted 23 May 2017

Available online 14 June 2017

Keywords:

Zirconia

Reflux

Aging temperature

Acid properties

Dehydration

ABSTRACT

Hydrous zirconia was synthesized via precipitation method, and effect of aging temperature during refluxing (30–100 °C) precursor solution was investigated. We found that the aging temperature influenced on structural and textural properties of the hydrous zirconia, with variations in the textural properties leading to changes in the surface properties of calcined zirconia, including the acid functionalities. In addition, ZrO₂ aged at 100 °C exhibited the highest specific surface area and the highest Lewis and Brønsted acidities among the samples. Finally, enhanced catalytic activity was also observed for the ZrO₂ samples prepared at higher aging temperatures in the dehydration of *iso*-propanol.

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Introduction

It is well known that pure ZrO₂ can exist in its monoclinic, tetragonal, and cubic crystalline structures at atmospheric pressure [1–3], and crystalline ZrO₂ has been extensively studied for various applications in the ceramics field, due to its high strength and fracture toughness, high melting point (~2700 °C), excellent electrical conductivity and chemical stability, superplastic behavior, and low thermal conductivity [2,4–8]. In addition, ZrO₂-based materials have been used in various applications, including optical devices [9,10], electrochemical gas sensors [11], and solid-oxide fuel cells [12]. However, the favorable properties of this material mainly originate from retention of the metastable tetragonal phase of ZrO₂ [5,6], and thus it is essential to maintain the tetragonal polymorph to ensure optimal strength and toughness in ceramic applications.

Amongst three possible crystalline structures of the ZrO₂, the monoclinic phase has been known as the most thermodynamically stable polymorph below 1100 °C, while the metastable tetragonal phase can only be obtained under suitable preparative conditions at relatively low temperatures. Therefore, the ZrO₂ is usually synthesized at relatively low temperatures as a monoclinic or a mixture of monoclinic and tetragonal forms due to thermodynamic reasons. In

addition, the ZrO₂ once synthesized with tetragonal structure undergoes an undesirable phase transformation to monoclinic polymorph with lattice expansion [5,6,13] in the presence of water or water vapor at relatively low temperatures (i.e., 65–400 °C). As such, the practical application of the tetragonal ZrO₂ has been limited [1].

Currently, two major routes exist for the synthesis of tetragonal ZrO₂ crystallites at relatively low temperatures. The first method involves the introduction of impurities such as Al₂O₃, SiO₂, CeO₂, CaO, MgO, La₂O₃, and Y₂O₃ into the ZrO₂ matrix [14,15], which results in stabilization of the tetragonal structure through increasing the oxygen vacancy concentration [1,2,5,6]. In contrast, the second method involves preparation of the tetragonal crystallites by controlling the particle size. For example, Garvie et al. [16–18] noted that particles with diameters <30 nm could be stabilized in the tetragonal phase due to their lower surface energies. Both methods resulted in suppression of the crystallization, and thus the specific surface area was normally increased. This is of particular importance, as a high specific surface area is one of the most important factors when considering the catalytic applications of such materials.

Indeed, as ZrO₂-based materials bear both acidic and basic functionalities in addition to exhibiting good hydrothermal stabilities [4], they have been studied for application as catalytic materials (i.e., as catalysts, supports, and promoters) for steam reforming [19], CO₂ reforming of methane [20], hydrodesulfurization [21], partial oxidation [22], methane combustion [23], formic acid decomposition [24], esterification [25], and the dehydration of C3–C4 alcohols [26]. However, only a few studies have focused on

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the synthesis and application of the pure ZrO₂ material with a high specific surface area. For example, Chuah et al. [3,27–30] reported that high specific surface area ZrO₂ can be synthesized via a refluxing method, and they examined the effect of the aging procedure under reflux. However, only the effects of aging temperature and time on the textural properties were examined as a material aspect.

In the context of catalytic applications, not only the specific surface area of a material but also its surface properties are closely associated with the resulting catalytic performance. In particular, surface acid sites have a large impact on the dehydration reactivity, for example, syntheses of α -olefins from alcohols, 1-butene from 2-butanamin, 1-amino-2-propanol to from allylamine [27]. In addition, the reductive amination of alcohols to alkylamines was well known that the metallic surface area of the supported metal species are closely related to the catalytic performance, however, the selectivity and the conversion can be varied depending on acid functionalities of the support [31–33]. Thus, we herein report the synthesis of ZrO₂ catalysts via a precipitation method, and examine the effect of aging temperature on variations in crystalline phase and specific surface area. In addition, the surface properties including the acid functionalities will also be characterized by X-ray photoelectron spectroscopy (XPS), pyridine-adsorbed infrared spectroscopy (Py-IR), and *iso*-propanol-temperature programmed desorption (IPA-TPD), and will be compared with the results of the IPA dehydration reaction.

Experimental

Catalyst preparation

The ZrO₂ catalysts were synthesized via a precipitation method using a ZrOCl₂·8H₂O (98%, Sigma–Aldrich) precursor. The zirconium precursor was completely dissolved in deionized water (0.5 M final concentration) at room temperature with vigorous stirring. Subsequently, NH₄OH solution (28 wt%, SK Chemical) was added dropwise to the zirconium solution until the pH reached 9.5. The resulting solution was then aged for 48 h at the desired temperature (30–100 °C). The aging procedure was carried out under reflux condition to prevent the NH₄OH vaporization and composition change of mother liquid during the aging process. After completion of the aging procedure, the white solid precipitate was filtered and washed exhaustively with deionized water. The product was then dried at 60 °C overnight, and calcined at 600 °C for 6 h. The final product was labeled as ZrO₂ (x), where x denotes the aging temperature.

Characterization

To estimate the specific surface areas, total pore volumes, and average pore diameters of the calcined ZrO₂ samples, N₂-sorption isotherms were recorded using a Micromeritics ASAP 2020. Prior to obtaining the isotherms, the samples were degassed at 250 °C for 5 h under vacuum. To identify the crystalline structures of the calcined ZrO₂ samples, X-ray diffraction (XRD) was carried out using a Siemens D5005 X-ray diffractometer with Cu K α radiation. From the XRD patterns, the crystallite size (D, nm) was calculated using the Scherrer equation (Eq. (1)):

$$D = k\lambda / \beta \cos\theta \quad (1)$$

where k is the shape factor of the particle (0.89), λ is the X-ray wavelength (0.15406 nm), β is the corrected full width at half maximum in radian, and θ is the Bragg diffraction angle in degree. The volume fraction of the tetragonal phase (V_T) was estimated using the following empirical formulas (Eqs. (2)–(4)) [24,34,35]:

$$V_M = 1.311X_M / (1 + 0.311X_M) \quad (2)$$

$$X_M = [I_M(111) + I_M(-111)] / [I_M(111) + I_M(-111) + I_T(011)] \quad (3)$$

$$V_T = 1 - V_M \quad (4)$$

where V_M is the volume fraction of the monoclinic phase, and I_M and I_T are the peak intensities of the monoclinic and tetragonal phases, respectively.

Thermo-diagrams of the hydrous zirconia samples were obtained by thermogravimetric-differential thermal analysis (TG-DTA, TA Instruments SDT 2960). Prior to the TG-DTA measurements, the sample was pretreated at 80 °C for 3 h under a flow of air. The heating rate and total flow rate of air during the TG-DTA measurements were 10 °C/min, and 110 cm³/min, respectively. Field emission scanning electron microscopy (FESEM) images were obtained using an Ultra Plus (Carl Zeiss). In addition, the surface chemical states of the calcined ZrO₂ catalysts were identified by XPS using an ESCALAB 210 photoelectron spectrometer (Al K α radiation; $h\nu = 1486.6$ eV), and the XPS data were calibrated using the binding energy of adventitious carbon (i.e., C 1s, 284.6 eV) as a standard. To determine the peak areas and positions, the deconvolutions of the O 1s and Zr 3d_{5/2} spectra were carried out using a Gaussian–Lorentzian curve-fitting method after background subtraction by the Shirley method (see the Supplementary data for the fitting parameters and error margins, Table S1).

All IPA-TPD experiments were carried out using a quadrupole mass spectrometer (Pfeiffer vacuum, GSD301). In each case, the sample (0.05 g) was loaded into a U-shaped quartz reactor using quartz wool. The sample was pretreated at 300 °C for 1 h under a stream of Ar (30 cm³/min), prior to cooling to room temperature. After cooling, the sample was exposed to 4.5 kPa of IPA for 0.5 h, and then purged with Ar for 0.5 h to remove the physically adsorbed IPA. Subsequently, the temperature was elevated to 600 °C with a heating rate of 10 °C/min under a flow of Ar (30 cm³/min).

Finally, Py-IR was performed using a Thermo Nicolet 6700 Fourier transform (FT) IR spectrometer. We carried out the cleaning by degassing at 500 °C under vacuum for 1 h to remove the chemicals (pyridine) and moisture in the cell. Prior to analysis, a sample of the catalyst (30 mg) was pressed into a self-supported wafer. For the calibrations, the ZrO₂ catalysts were pretreated at 300 °C for 1 h under vacuum, and a background spectrum was collected at 300 °C. Following the injection of pyridine (5 μ L) at 150 °C, the sample cell was saturated for 15 min, and then evacuated for 0.5 h under vacuum. All Py-IR spectra were recorded with 32 scan numbers and 4 cm⁻¹ resolution. From the Py-IR measurements, quantitative analysis of Lewis and Brønsted acid densities was conducted with vibration bands at 1444 and 1640 cm⁻¹, respectively. The acid densities were calculated by following empirical formula according to literature [36] where it was assumed that all Brønsted acid sites processed the same integrated molar extinction coefficient (integrated molar extinction coefficient: 2.22 and 1.67 cm²/mol for Lewis and Brønsted acid sites, respectively).

$$C(\text{pyridine on Lewis acid sites}) = 1.42 \cdot IA(L) \cdot R^2 / W$$

$$C(\text{pyridine on Brønsted acid sites}) = 1.88 \cdot IA(B) \cdot R^2 / W$$

where C is acid density (mmol/g_{cat}), and IA (L, B) is integrated absorbance of Lewis and Brønsted band (cm⁻¹), and R and W are radius of catalyst disk (cm) and weight of disk (mg), respectively.

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