Characterization of high-surface-area zirconia aerogel synthesized from combined alcohothermal and supercritical fluid drying techniques

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Thermally stable tetragonal zirconia aerogel with a high surface area can be obtained by a novel alcohothermal route, followed by the supercritical fluid drying technique. In addition, a cheaper inorganic salt was used as raw material instead of the expensive and harmful zirconium alkoxides. The zirconia aerogel samples were characterized using X-ray diffraction, thermal analysis, N_2 adsorption measurements, diffuse reflectance infrared Fourier transform spectroscopy, and transmission electron microscopies. The results show that the resulting zirconia aerogel was composed primarily of narrowly distributed nanoparticles with loose aggregation. It is shown that the thermally stable zirconia aerogel has a high specific surface area and a well-developed textural mesoporosity with narrow pore size distribution, which is highly attractive for potential applications in heterogeneous catalysis.

KEY WORDS: zirconia aerogel; tetragonal; surface area; combined; alcohothermal; supercritical fluid drying.

1. Introduction

Zirconia is an important material that has attracted enormous interest in catalysis [1]. It is a unique material of excellent thermal stability and chemical inertness. Moreover, its surface has both acid and basic properties, as well as oxidizing and reducing properties [2,3]. Therefore, there has been continuously growing recent interest in using zirconia as a suitable material for important applications in catalytic processes such as paraffin isomerization [4], hydrogenation of olefins [5], alcohol dehydrogenation [6,7] and other technological uses. Additionally, due to its nature as an n-type semiconductor, it has been considered recently as a promising photocatalyst in photochemical heterogeneous reactions [8,9]. The use of zirconia as a support material or catalyst often requires zirconia having a high accessible specific area as well as a large and well-developed porous texture [10]. However, zirconia oxides generally have surface areas of $50\,m^2\,g^{-1}$ or less, which is rather low compared with conventional supports such as SiO_2, Al_2O_3 or TiO_2. Higher surface areas are attainable with amorphous zirconia (200–$300\,m^2/g$), but this was usually achieved at the expense of much lower thermal stability.

It was shown that the synthesis procedure as well as the subsequent thermal treatment might have a great influence on pore-size distribution, special surface area and thermal stability of the final materials of ZrO_2. A common preparation route for zirconia consists first of a precipitation of hydrous zirconia with ammonia from a zirconium salt solution and, second, subsequent thermal treatment of the hydrous zirconia precipitate [11]. This amorphous precipitate usually has a large surface area. However, an abrupt decrease of the surface area of the amorphous zirconia due to the crystallization to the monoclinic or metastable tetragonal phases takes place at temperatures around 450 °C. Extensive investigations have been carried out aimed at developing new synthetic methods that may allow the formation of a larger specific surface area of zirconia [12,13]. The synthesis of a large surface area of zirconia by calcination of a hydroxylated gel derived from precipitation, hydrolysis or decomposition of zirconium (or zirconyl) salts in various mediums has been investigated [14,15], and it has been found that the use of an appropriate organic solvent may favor the formation of a zirconia sample with a high surface area. Recently, Inoue *et al.* [16] reported that the decomposition of zirconium precursors in toluene can afford the formation of thermally stable zirconia oxide with a large surface area ($90–160\,m^2/g$) and a fairly high thermal stability, where the zirconium alkoxides were specially utilized as the zirconium sources [17]. More recently, several surfactant-templated sol–gel approaches have also been developed to synthesize mesoporous zirconia oxides with regular pore structure [18,19], which are claimed to have an extremely high surface area, up to $390\,m^2/g$. However, the preparation procedure for this process usually involves conventional hydrothermal reactions for several days, even weeks, which is therefore very elaborate and time consuming.

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Moreover, the use of expensive and harmful zirconium alkoxides or surfactants is required, which strongly limits the possible production of zirconia with desirable features at a large scale. Hence, it is highly desirable to develop a more convenient and facile methodology to prepare catalytically attractive zirconia material using cheaper inorganic salts as alternative zirconium raw materials.

On the other hand, it is known that the solvothermal process is a powerful technique for generating novel materials with interesting properties using cheap raw materials under mild conditions [20]. We have recently developed a novel synthetic approach utilizing combined alcohothermal and supercritical fluid drying (alcohothermal–SCFD) processes for the preparation of a large-surface-area zirconia aerogel [21]. A cheap inorganic salt of zirconium nitrate hydrate ($Zr(NO_3)_4{\cdot}5H_2O$) was used as raw material instead of zirconium alkoxides. It was previously demonstrated that this novel synthesis route can afford the convenient preparation of thermally stable zirconia aerogel with an extremely large specific surface area up to $462\,m^2/g$. In the present work, we report the detailed physicochemical characterization results that provide new insights into the interesting surface and structural properties of the zirconia aerogel samples prepared by the novel combined alcohothermal–SCFD method. The results show that the alcohothermal–SCFD method can allow the preparation of catalytically important zirconia material with several advantageous features, including a large surface area as well as pore volume and a well-developed porosity with narrow pore-size distribution in the mesoporous range.

2. Experimental

2.1. Sample preparation

The preparation of zirconia aerogel consists of two consecutive synthetic procedures involving the alcohothermal process followed by the supercritical fluid drying (SCFD) treatment [21]. Briefly, appropriate amounts of $Zr(NO_3)_4{\cdot}5H_2O$ were dissolved in 50 ml absolute ethanol to obtain a $0.3\,mol\,l^{-1}$ alcoholic solution followed by putting the solution into an autoclave of 50 ml capacity. After sealing, the autoclave was maintained at 383 K for 60 min and then allowed to cool to room temperature. A translucent alcogel was thus obtained. The alcogel was aged at room temperature for about 60 min. The resultant alcogel was then supercritically dried by 210 ml of ethanol in a 500 ml autoclave. The autoclave was pressurized (7.0 MPa) with high purity nitrogen and was heated ($\sim$2 °C/min) to 280 °C to form a supercritical ethanol (553 K, 11.0 MPa). The autoclaved sample was allowed to dry slowly (2 ml ethanol/min) under the supercritical condition for 1 h, followed by the release of the pressure in flowing N_2 to cool the sample (the second stage). After the autoclave had been cooled to room temperature, the resulting zirconia aerogel was obtained. Calcination of the SCF dried sample was conducted in a muffle oven in air for 2 h.

2.2. Characterization

The X-ray powder diffraction (XRD) of the catalysts was carried out on a Bruker D8Advance X-ray diffractometer using nickel filtered Cu K_α radiation ($\lambda = 1.5418$ Å) in the 2θ range 10–80°. The textural parameters have been measured using the BET method by N_2 adsorption and desorption at 77 K in a Micromeritics TriStar system. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization of the catalysts was performed using a Bruker Vector 22 instrument equipped with a DTGS detector and a KBr beam splitter [22]. Aerogel samples were placed in a sample cup inside a Harrick diffuse reflectance cell equipped with KBr windows and a thermocouple mount that allowed direct measurement of the sample temperature. All spectra were collected in nitrogen atmosphere at 200 °C. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) measurements were performed on a Perkin-Elmer 7 Series Thermal Analyzer apparatus in air flow (30 ml/min), using Al_2O_3 as a reference and with a heating rate of 10 K/min. For each experiment, 10–15 mg of sample was used. The morphology of the aerogel samples was observed on a high-resolution transmission electron microscope (HRTEM), JOEL 2011, using an accelerating voltage of 200 kV.

3. Results and discussion

The XRD patterns of the zirconia aerogel obtained by the combined alcohothermal–SCFD route, as well as the calcined samples, are given in figure 1(a)–(c). Figure 1(a) shows the typical XRD patterns recorded for the zirconia aerogel derived by an alcohothermal–SCFD method. These broad diffraction patterns are characteristic of nanoparticles of tetragonal zirconia with a low crystallinity. The mean crystalline size of the zirconia aerogel, deduced from the full width at half-maximum, is reported in table 1. The calculated mean crystalline size (D_{hkl}) for the as-synthesized aerogel sample was about 1.1 nm. After calcination at 673 K for 2 h, a sharpening of the diffraction peaks for the zirconia sample was observed in figure 1(b), reflecting a slightly crystallite growth of the zirconia sample. Moreover, several new weak diffraction bands corresponding to monoclinic phase concentration of $\sim$14 wt% were also observed in figure 1(b), suggesting the occurrence of a slight transformation of the tetragonal to monoclinic phase in the 673 K calcined sample. Further calcination of the sample at 773 K results in progressive sharpening of the

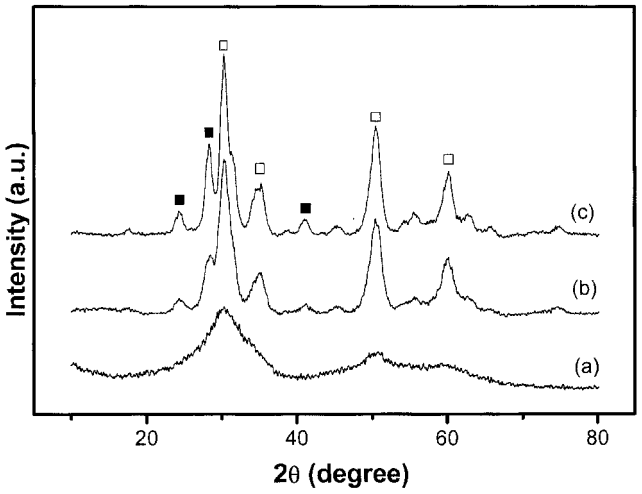

Figure 1. XRD patterns of the zirconia aerogel samples obtained by the combined alcohothermal–SCFD approach: (a) as synthesized, (b) calcined at 673 K for 2 h, (c) calcined at 773 K for 2 h. ■, monoclinic phase; □, tetragonal phase.

diffraction peaks corresponding to two phases (monoclinic phase concentration of ~27 wt%), indicating the further enlargement of the crystallite size with the increase of the calcination temperature.

It should be noted that the freshly derived zirconia aerogel obtained by the present alcohothermal–SCFD method is shown to be gray in color. After calcination in air at temperature above 673 K, a white colored sample can be readily obtained. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy has been employed to follow the variation of the surface properties of the alcohothermal–SCFD derived zirconia samples as a function of calcination temperature. The DRIFT spectra in the region of 2400–4000 cm^{-1} for the alcohothermal–SCFD derived zirconia aerogel and calcined samples are presented in figure 2. The IR spectrum of the original sample (figure 2(a)) shows three strong absorption hands at 2968, 2937 and 2883 cm^{-1} in the range 2400–4000 cm^{-1}, corresponding to C–H stretching modes of ethoxy moiety capped on the surface of the aerogel sample. In comparison, the spectrum in figure 2(b) shows only very weak vibrational features

Table 1
Physicochemical properties of the as-derived zirconia aerogel and calcined samples. The phase concentration (wt%) of the zirconia samples as a function of annealing temperature is also included

Processing temperature	S_{BET} ($m^2 g^{-1}$)	V [a] ($cm^3 g^{-1}$)	D [b] (nm)	D_{hkl} (nm)	Phase concentration (wt%)	
					Tetragonal	Monoclinic
As-synthesized	462	2.90	20.42	1.1	100	0
673 K for 2 h	270	0.89	21.71	2.0	86	14
773 K for 2 h	206	0.79	22.72	3.0	73	27

[a] BJH adsorption pore volume.
[b] BJH adsorption average pore diameter.

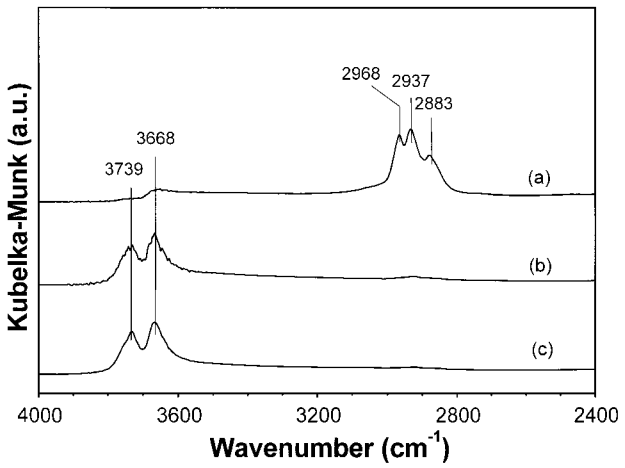

Figure 2. DRIFT spectra of the calcined zirconia aerogel synthesized by the alcohothermal–SCFD method: (a) as-synthesized, (b) calcined at 673 K for 2 h, (c) calcined at 773 K for 2 h.

around 3000 cm^{-1}, suggesting the presence of only a trace amount of carbonaceous residues on the 673 K calcined aerogel sample. The strong IR bands at 3739 and 3668 cm^{-1} shown in figure 2(b) are attributed to the terminal and bridged OH species present on the calcined zirconia aerogel sample, respectively [23]. Further calcination at 773 K results in the total disappearance of the absorption features around 3000 cm^{-1} as well as an increase in intensity of the bands at 3739 and 3668 cm^{-1} in the spectrum of figure 2(c), demonstrating unambiguously the clean surface nature for the aerogel sample calcined at 773 K for 2 h. The DRIFT results demonstrate clearly that the present combined alcohothermal–SCFD synthetic method can allow the convenient preparation of highly pure zirconia materials without carbonaceous contamination for attractive applications in heterogeneous catalysis.

The above XRD results reveal that the calcination only causes a slightly crystallite growth (up to 3.0 nm) and only a slight transition of the tetragonal to monoclinic phase. This point can be further demonstrated by the thermal analyses (figure 3) results of the zirconia

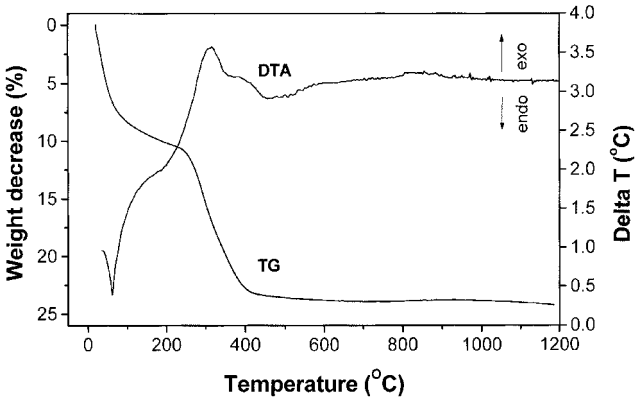

Figure 3. Thermal analysis (TG/DTA) profile of the zirconia aerogel obtained by the alcohothermal–SCFD method: heating rate 10 °C min^{-1} in a 40 ml min^{-1} flow of dry air; reference sample α-alumina.

aerogel sample, as shown in figures 3(a) and (b). The TG diagram of the zirconia aerogel presents two weight decrease processes at 70 °C and at about 300 °C, respectively. The former process was associated with endothermic response in DTA and is attributed to the desorption of physisorbed species related to losses of water. On the other hand, the latter process centered at 300 °C was highly exothermic and is due to the combustion of the covalently anchored ethoxy groups over the surface of the sample. Similar results have been reported on the zirconia precipitates obtained by thermal decomposition of zirconium alkoxides in organic media [14–16], where small amounts of alkyl groups covalently bonded to the surface oxygen atoms of the zirconia particles have been detected.

The present TG weight loss curve is quite different from the observation found with a hydrous zirconia gel obtained by conventional methods, where dehydration occurs continuously over the whole range of temperatures studied [13]. On the other hand, it is known that zirconia always undergoes a strong exothermal transition, easily observable in a DTA measurement, which is generally attributed to the crystallization of zirconia or the tetragonal monoclinic transformation. The DTA data for the alcohothermal–SCFD-derived zirconia aerogel do not show any distinct endotherms or exotherms/glow exotherms which are associated with crystallization of the amorphous phase, indicating that the substantial transition of an amorphous phase into crystalline modification of zirconia or the significant transformation of $t \rightarrow m$ phase did not take place. This result is different from the phenomenon reported by Inui *et al.* [14], who observed that the surface area rapidly decreased with further rising of the calcination temperature (>773 K) due to crystal growth of the tetragonal phase and transformation to the stable monoclinic phase. Based on suggestions by Garvie [24] and by Garvie and Goss [25], the tetragonal phase is believed to be stable below the transformation temperature (*i.e.* 1447 K) when the crystallite size is smaller than the critical crystallite size (about 10–15 nm). Garvie and co-workers thus attributed the stabilization to the surface and strain energy effect. This can well account for the experimental fact that a high thermal stability has been achieved for the present alcohothermal–SCFD-derived tetragonal zirconia aerogel.

The morphological properties of the ZrO_2 aerogel samples have been studied by TEM. It was noted that upon calcination at elevated temperature in air, the zirconia aerogel samples undergo a significant morphology change from a high degree of cross-linked texture to loosely aggregated nanoparticles with an increase in average size. Figure 4(a) shows the TEM image of the original zirconia aerogel derived through an alcohothermal–SCFD route. A fine polymeric structure in sub-nanometer scales and 2-nm polymeric aggregates were observed in aerogels obtained from the alcohothermal–SCFD route. It can be seen that the as-prepared

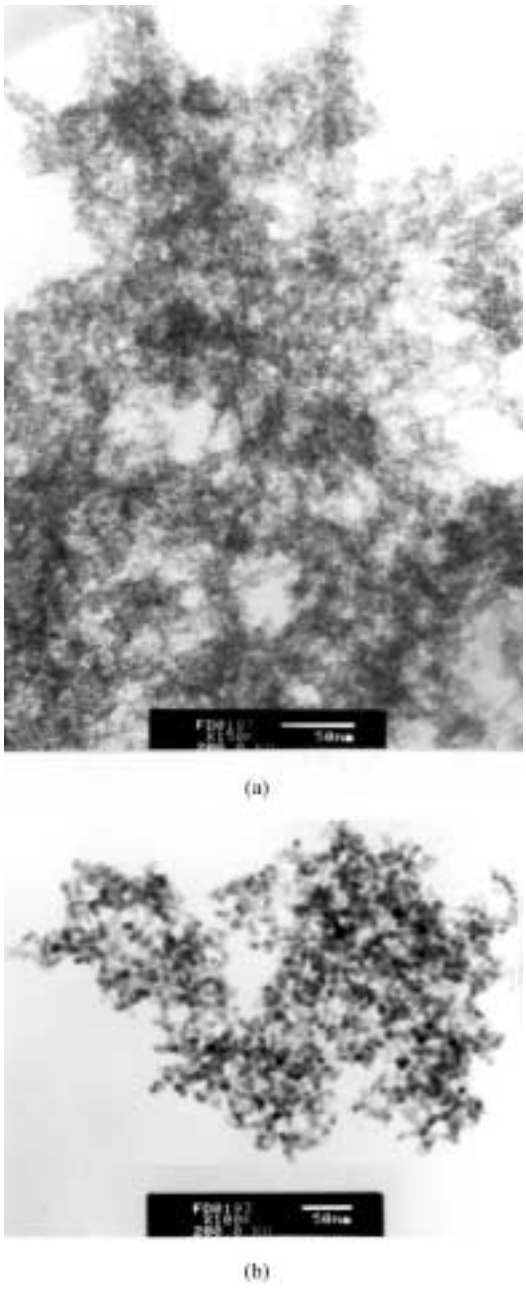

Figure 4. TEM microscopy of (a) the as-prepared zirconia aerogel, and (b) sample calcined at 773 K for 2 h.

zirconia sample is highly porous in nature and consists of narrowly distributed nanoclusters of cross-linked particles smaller than 1 nm. This observation is in good agreement with the results obtained from XRD. An increase in the average particle size after calcination has been monitored by the TEM measurements. A representative TEM image of the zirconia aerogel calcined at 773 K is shown in figure 4(b). The absence of the amorphous phases and the small crystalline particle sizes are clearly confirmed through TEM studies. One can see that the calcined zirconia aerogel sample consists of loose agglomerates of very small and round

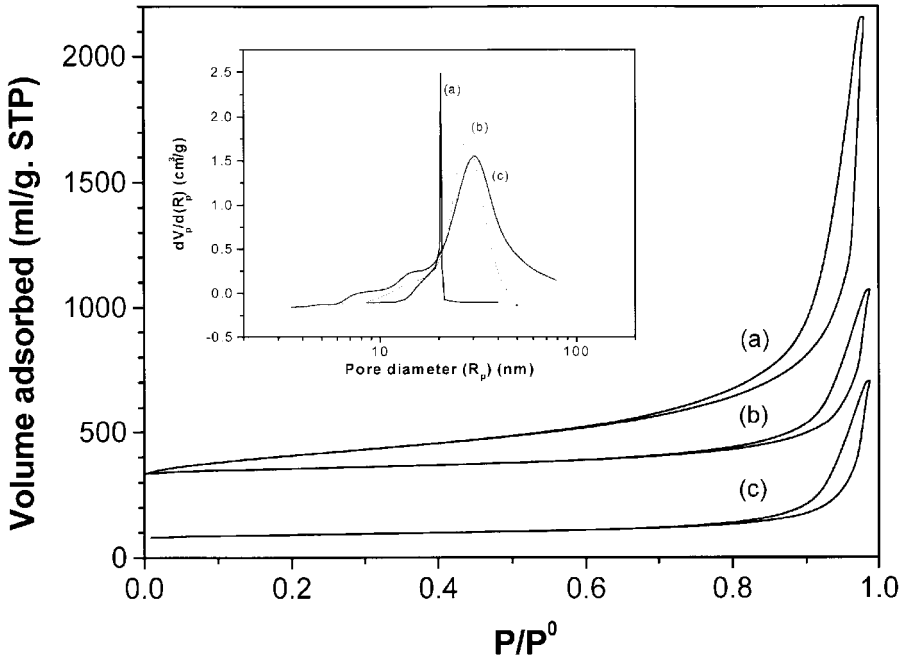

Figure 5. Nitrogen adsorption–desorption isotherms for (a) as-prepared zirconia aerogel, (b) sample calcined at 673 K for 2 h and (c) sample calcined at 773 K for 2 h. The inset plots the BJH pore-size distribution (PSD) for corresponding zirconia samples.

primary particles having diameters of ~6 nm, in good consistency with the XRD data.

Table 1 presents the values for the surface area, pore volume and average pore radius for the alcohothermal–SCFD derived zirconia as well as the samples calcined at higher temperatures. The temperature causes severe loss of surface area [11] and pore volume, as seen in table 1, as well as transformation in the structure of the sample, as demonstrated by XRD experiments. The as-synthesized zirconia sample has a very large surface area and pore volume of up to $462\,m^2\,g^{-1}$ and $2.90\,cm^3\,g^{-1}$, respectively. Upon calcination at 673 K, the zirconia sample presents a surface area of $270\,m^2\,g^{-1}$ and a reduced pore volume of $0.89\,cm^3\,g^{-1}$. When calcination temperature goes to 773 K, the sample still retains a rather high surface area of $206\,m^2\,g^{-1}$.

The N_2 adsorption–desorption isotherms for zirconia aerogel obtained from the alcohothermal–SCFD method, as well as the calcined samples, are shown in figure 5, indicative of a Type V isotherm with an H3 hysteresis loop based on IUPAC classifications [26]. The appearance of a well-defined hysteresis loop associated with irreversible capillary condensation in the mesopores in the P/P_0 region from 0.5 to 1.0 suggests the presence of substantial textural mesoporosity arising from non-crystalline intra-aggregate voids and spaces formed by interparticle contacts in the aerogel samples. It is also noted from figure 5 that the freshly-derived zirconia aerogel affords more textural porosity relative to that for calcined samples. The calcination in air at temperatures above 673 K results in substantial loss of the textural porosity in the zirconia samples.

The insert to figure 5 shows the pore-size distribution plots calculated using the BJH (Barrett–Joyner–Halenda) equation from the adsorption branch of the isotherm. The pore-size distribution (PSD) measurements show that the zirconia aerogel had pronounced mesoporosity in the range 10–100 nm with a relatively narrow pore-size distribution. It is noticeable that the PSD of the original zirconia aerogel exhibits a well-defined mesostructure with an extremely narrow pore-size distribution in the mesoporous range 20–22 nm. It can be seen that no micropores exist in the sample. The pore volume (V_{cum}) as well as the most frequent pore radius ($R_{P(max)}$) for the freshly-derived zirconia aerogel are $2.90\,cm^3/g$ and 20 nm, respectively, which are much larger than those of the zirconia prepared by the co-precipitation method, decomposition of zirconium isopropoxide in toluene and other methods. The PSD of the 673 K calcined sample shows a broader PSD peak in the range 10–60 nm, with the maximum centered around 27 nm pore radii. The pore-size distribution of the 773 K calcined sample shows that the pore distribution and the most frequent pore radii ($R_{P(max)}$) shift toward even higher values. The most frequent pore radius ($R_{P(max)}$) for the 773 K calcined zirconia aerogel is ~30 nm, significantly larger than that for the freshly-derived aerogel sample. The pore-size distribution for the 773 K calcined sample is located in the range 20–40 nm, much broader than the narrow one for the freshly-derived aerogel. Based on these data, the present alcohothermal–SCFD-obtained zirconia aerogel can be described as a porous material with well-developed mesoporous textural structure and a narrow pore-size distribution.

It is well documented that zirconia generally has a surface area of 100 m^2/g or less, which is small compared to the typical silica or alumina catalysts and supports. Using only the simple salt of zirconium nitrate ($Zr(NO_3)\cdot 5H_2O$) as a zirconium precursor, we have demonstrated that the thermally stable nanocrystalline zirconia with a large BET surface area as well as pore volume could be conveniently obtained in several hours at a much lower cost, as compared with the conventional route from alkoxide precursors. The zirconia aerogel had pronounced mesoporosity in the range 10–100 nm with a relatively narrow pore-size distribution. We suggest that the extremely large surface area and pore volume obtained in the present case may be attributed to the zirconia alcogel formation process using the alcohothermal route. This particular process allows the generation of clear and firm zirconia alcogels to have a rigid porous framework with better thermal stability, which has the structural rigidity required for subsequent supercritical drying.

Although zirconia aerogels were first obtained over two decades ago, they have attracted considerable interest only more recently due to the unique properties of zirconia. Despite a number of excellent papers on their preparation, the effect of process variables is known to have a marked influence on gel pore texture and morphology of the aerogels obtained from alkoxide precursors [27,28]. Apparently, the zirconia aerogel synthesized using the present combined alcohothermal–SCFD approach has a number of attractive advantages in heterogeneous catalytic applications. The synthesis procedure is simple and convenient, providing a new promising cost-reduction approach for the production of large-surface-area zirconia aerogel materials.

4. Conclusions

In summary, thermally stable zirconia aerogel can be synthesized by a novel synthetic approach using a combined alcohothermal and supercritical fluid drying (SCFD) method with low cost precursors. The phases, morphology, particle size and microstructure of the derived zirconia aerogel samples were characterized using combined techniques of X-ray diffraction (XRD), thermogravimetric (TG) and differential thermal analyses (DTA), N_2 adsorption measurements, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and high-resolution transmission electron microscopy (HRTEM). The results showed that the as-prepared zirconia aerogel has a high accessible specific surface area and a well-developed textural mesoporosity, whereas the calcined samples were composed primarily of narrowly distributed nanoparticles with loose aggregation. The large surface area as well as pore volume and a well-developed porosity in the mesoporous range of the alcohothermal–SCFD-derived zirconia aerogel render it a promising material for potential catalytic applications.

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