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Hydrogen spillover and structural defects in a PdO/zirconia nanophase synthesized through a surfactant-templated route

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Abstract

Nanosized zirconia with structural defects was synthesized by using surfactant-templated method. The average crystallite size, phase composition, cationic defect concentration and structural microstrain in the monoclinic phase of zirconia annealed at 800 °C were quantitatively determined by the Rietveld refinement. An unusual behaviour of hydrogen reversibly storing into/releasing from the PdO/ZrO_2 nanophases was observed, which related to formation/decomposition of a hydride phase β-$PdH_{0.76}$ and to hydrogen storage in the cationic defects of zirconia nanophases by means of hydrogen spillover from Pd metals to zirconia support.

Keywords: Zirconia; Surfactant-templated synthesis; Structural defects; Hydrogen spillover

1. Introduction

Zirconium oxide is an important catalyst support used for many catalytic reactions, such as for methanol conversion to hydrocarbons, Fischer–Tropsh synthesis and hydrocracking [1,2]. Sulfated-promoted zirconia (SO_4^{2-}/ZrO_2) was recognized as superacid, and is an active catalyst for *n*-butane isomerization at room temperature [3,4]. Zirconia has a defective crystalline structure that makes it possible to be used as solid oxide fuel cell [5–7]. Because of the attractive applications, a considerable amount of work has been devoted to zirconia synthesis and characterization [8,9].

An interesting synthesis route on the basis of mesoporous MCM-41 synthesis was reported to obtain zirconia in acidic conditions by using surfactant as template or pseudo-template [10–12]. As a result, a mesostructured zirconia with enhanced surface area was obtained. Since the surfactants are incorporated into the network of the solid in the synthesis procedure, when the surfactant cations are removed by calcination, the surface or bulk structure of zirconia may be strongly modified, for example, producing some cationic or anionic defects in the crystals, which is very interesting for catalytic reactions or other applications like hydrogen storage [13]. However, details of the surface and bulk defective structure of nanosized zirconia prepared by using surfactant-templated method have not been reported yet. This work attempts to prepare zirconia nanophases via a surfactant-templated route in a base condition and to study the possible relationship between the structural defects and the surface reduction properties of a PdO loaded zirconia nanophases, aiming to developing new functional material.

2. Experimental

The 51.9 g of $ZrOCl_2{\cdot}8H_2O$ was dissolved in one container with 500 ml deionized water to form a zirconium solution. This solution was, drop by drop, added into a 3500 ml vessel that contains a solution of 10 g of surfactant (cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}N(CH_3)_3Br$, as molecular template). The ratio of surfactant/Zr was about 1.2 and the pH of the mixture was controlled at 11 by adding ammonia (28%). During the addition, a proper agitation was operated to disperse the droplets before local concentrations become excessive. After aging for 24 h, the precipitate was filtered and washed with water and methanol, and then dried at 80 °C for 2 days and calcined at 200, 400, 600 or 800 °C for 4 h in air.

The PdO loaded ZrO_2 sample was prepared by impregnating the ZrO_2 support which was calcined at 800 °C, with an aqueous solution of $Pd(NO_3)_2{\cdot}2H_2O$.

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The 3 wt% PdO/ZrO_2 material was dried at 120 °C for 5 h and the dried sample was calcined at 800 °C in air for 4 h with a heating rate of 10 °C/min. Finally, the 3 wt% PdO/ZrO_2 was obtained.

The X-ray power diffraction patterns of the samples packed in a glass holder were obtained at room temperature with Cu Kα radiation in a Bruker Advanced D-8 diffractometer having a θ–θ configuration and a graphite secondary beam monochromator. Diffraction intensities were measured between 10° and 110°, with a step of 0.02° for 2.3 s per point. Crystalline structures were refined with the Rietveld technique by using FULLPROF98 code [14]. For refinement of crystalline structure by the Rietveld method, the zirconia structures were fitted with a tetragonal unit cell with space group $P4_2/nmc$ and a monoclinic unit cell with a symmetry described by space group $P2_1/c$. Peak profiles modeled with pseudo-Voigt functions contained average crystalline size as one of its characteristic parameters [15,16]. The standard deviations of the structural refinements, which show the last figure variation of a number, are given in parentheses.

High resolution transmission electron microscopy (HRTEM) observations of ZrO_2 crystals were carried out in a JEOL 4000 EX electron microscope equipped with a pole piece with spherical aberration coefficient of $C_s = 1.00$ mm. The ZrO_2 powder sample was grounded softly in an agate mortar and dispersed in isopropylic alcohol in an ultrasonic bath during several minutes. Some drops were deposited on 200 mesh copper grids covered with a holed carbon film. Electron micrographs were recorded in electron negative films and in a digital PC system attached to the electron microscope.

The hydrogen reduction behaviour of the PdO/zirconia sample was evaluated by using temperature-programmed reduction (TPR) technique in a temperature range between 20 and 800 °C on a TPD/TPR-2900 analyser (Micromeritics). A 10% H_2 in Ar was used as reducing agent with 99.9% He as carrier. The 0.1 g of sample placed in a quartz tube was first thermally treated under a current of He at 400 °C for 1 h to remove the adsorbed species on the sample, and then it was cooled down to 20 °C. Afterwards, the 10% H_2 in Ar was allowed into the U-type tube with a flow rate of 75 ml/min for the TPR experiment. The temperature was increased at a rate of 10 °C/min. The TPR signal was recorded by a thermal conductivity detector (TCD).

3. Results and discussion

The XRD patterns of the zirconia solid calcined at various temperatures are shown in Fig. 1 and a Rietveld refinement plot of the zirconia sample annealed at 800 °C is shown in Fig. 2.

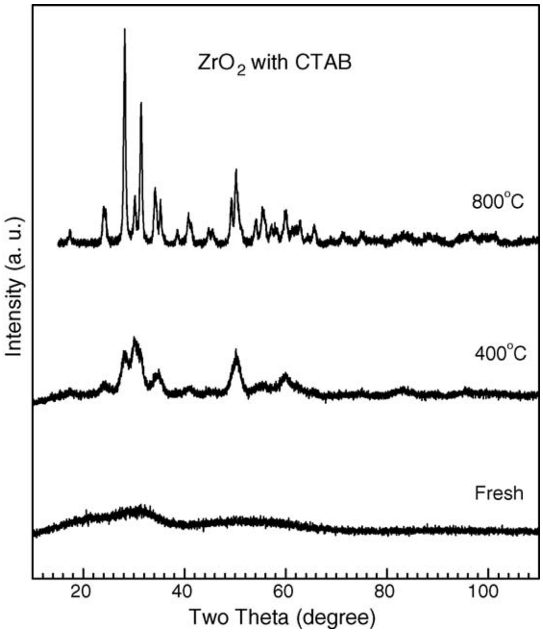

Fig. 1. XRD patterns of the ZrO_2 solid calcined at different temperatures.

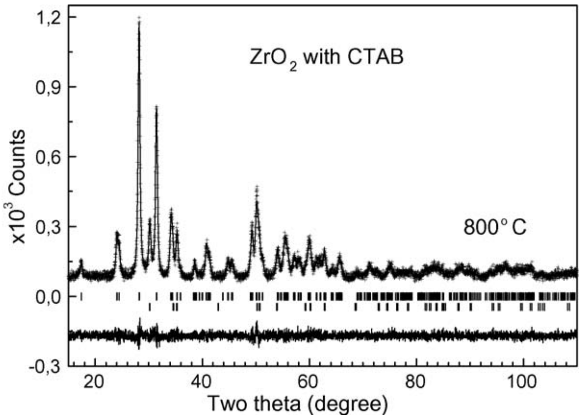

Fig. 2. A Rietveld refinement plot of ZrO_2 solid calcined at 800 °C. Experimental data are indicated by crosses while the calculated curve obtained after the refinement is indicated with a continuous line. Upper tick masks correspond to monoclinic zirconia. The lower one to the tetragonal phase. The continuous curve under the tick marks represents the difference between the experimental and the calculated data.

Below 200 °C of calcination, the zirconia were armorphous. When the calcination temperature was increased to 400 °C, the crystallization of the solid took place, producing 69 wt% monoclinic zirconia and 31 wt% tetragonal zirconia. Further increasing the calcination temperature lead to the phase transformation from tetragonal to monoclinic zirconia, for example, the solid annealed at 800 °C consisted of 91 wt% monoclinic and 9 wt% tetragonal zirconia phases, being the monoclinic one the main phase. The average crystallite size of the monoclinic phase annealed at 800 °C was approximately 27 nm (Table 1).

The Rietveld refinement reveals that not only the zirconium occupancy number in the crystalline structure of monoclinic phase is smaller than the value 1.000 that corresponds to cation occupancy number in a perfect monoclinic crystal of zirconia, but also the ratio of occupancy number of zirconium/oxygen is less than the stoichiometric value. These are clear indications that the monoclinic phase contains cationic lattice defects in its crystalline structure. After 800 °C of calcination in monoclinic crystal, the zirconium occupancy number is 0.8325 which corresponds to 0.63 cationic defects per lattice cell. Formation of the structural defects was also directly observed in the HRTEM micrograph (Figs. 3 and 4). Electron diffraction recorded from

Table 1
Data of average crystallite size, phase concentration, cation occupancy number, and zirconium defect number per unit cell in the monoclinic phase of zirconia (m-ZrO_2) annealing at 800 °C

Average crystallite size (nm)	27 (0.5)
Monoclinic concentration (%)	91 (6)
Average crystal microstrain (%)	1.2 (1)
Zr atom occupancy number	0.8325 (1)
Number of Zr defect per lattice cell	0.63
Cell parameter	
a (nm)	0.51315 (5)
b (nm)	0.5316 (1)
c (nm)	0.53143 (7)

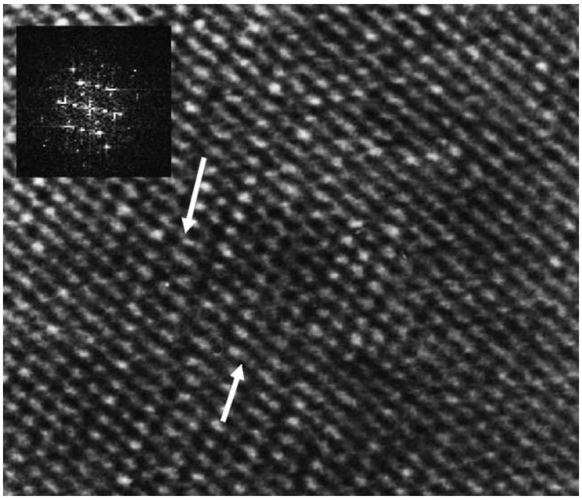

Fig. 3. A HRTEM micrograph of the zirconia solid calcined at 800 °C. Dislocations and structural defects like the white arrowed are commonly found in the sample. The Fourier transform in the inset comes from the whole HRTEM micrograph presented.

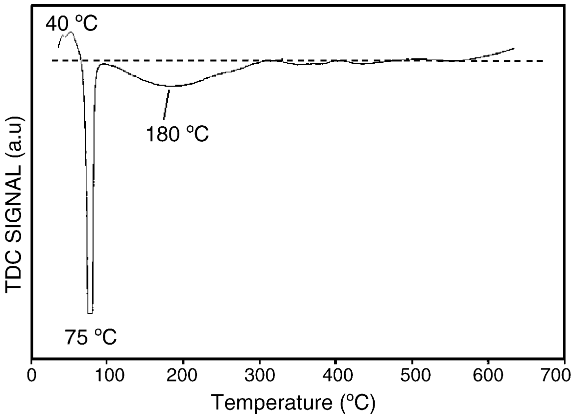

Fig. 5. A profile of temperature programmed reduction of the PdO/ZrO_2 nanophases calcined at 800 °C.

the upper section in Fig. 3 displays a spotted pattern that corresponds to the monoclinic phase of zirconia. Lattice line defects in the m-ZrO_2 structure were observed, as indicated with arrows in Fig. 3. Many lattice defects appeared in the boundaries of the crystals as shown in Fig. 4.

Creation of the lattice defects in the structure is suggested to mainly associate to the incorporation of the cationic surfactant in the solid during the synthesis by strong interactions between the deprotonated hydroxyl groups and positively charged surfactant headgroups. At a proper calcination temperature, these incorporated surfactant species were combusted, generating some lattice defects in the corresponding locations. The zirconia structures show strong distortion due to the presence of cationic defects that gives rise to microstrain generation in the crystals, for example, after 800 °C of calcination, the average crystallite microstrain reached 1.2%.

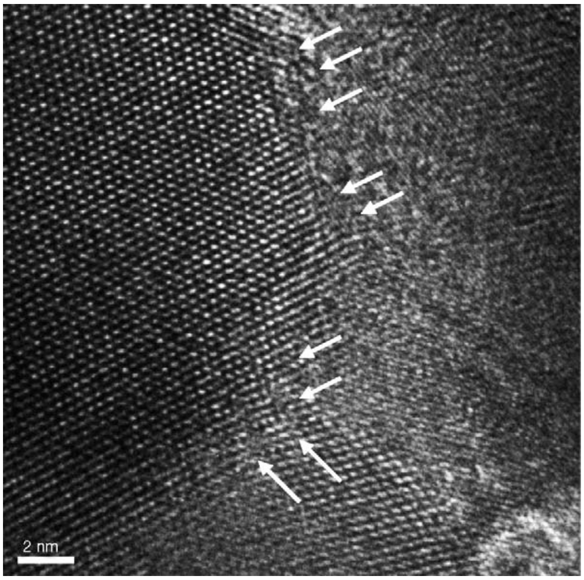

Fig. 4. A HRTEM micrograph of the zirconia solid calcined at 800 °C. Many structural defects in the boundaries as indicated by white arrows are observed.

The surface reduction properties of the PdO loaded zirconia nanophase were studied by using temperature-programmed reduction technique. Fig. 5 shows a TPR profile of the 3 wt% PdO/ZrO_2 solid calcined at 800 °C. A sharp, negative peak with a minimum at approximately 75 °C was observed. In the temperature between 100 and 300 °C, a wide, negative peak was also detected. We also observed a similar TPR behaviour in the PdO/ZrO_2 samples prepared by using other surfactants like myristyltrimethylammonium bromide and octadecytrimethylammonium bromide as templates and in the materials of PdO/CeO_2 and PdO/$Ce_xZr_{1-x}O_2$ ($0.2 < x < 0.8$) prepared by using the same surfactant as template (cetyltrimethylammonium bromide) [17,18]. The negative peak in the TPR profile indicates that molecular hydrogen is delivered during the TPR procedure. Ozkan et al. once reported that PdO supported on TiO_2 could be reduced even at subambient temperature to form palladium hydride which was decomposed to release hydrogen at 95 °C [19]. By using in situ X-ray absorption spectroscopy, McCaully also observed the formation of β-PdH_x phase on the PdO/C and PdO/γ-Al_2O_3 catalysts when being treated by hydrogen [20]. Based on those studies, the first negative peak centered at 75 °C in Fig. 5 is assigned to hydrogen generation due to decomposition of palladium hydride (β-PdH_x) where $x = 0.76$. It is likely that palladium oxide was first reduced to palladium atoms at a temperature 20–50 °C, simultaneously, some hydrogen was dissociatively adsorbed on the palladium crystals to form a new compound Pd hydride phase (β-PdH_x), which was unstable, and it then decomposed to release molecular hydrogen when the temperature was raised to about 70 °C, thus a sharp, negative peak in the TPR profile was produced. These steps can be expressed by Eqs. (i)–(iv):

$$\text{PdO reduction by hydrogen}: \quad PdO + H_2 = Pd + H_2O \tag{i}$$

$$\text{Hydrogen dissociation on Pd metals}: \quad H_2 = 2H \tag{ii}$$

$$\text{Pd-hydride phase formation}: \quad xH + Pd = \beta\text{-}PdH_x \tag{iii}$$

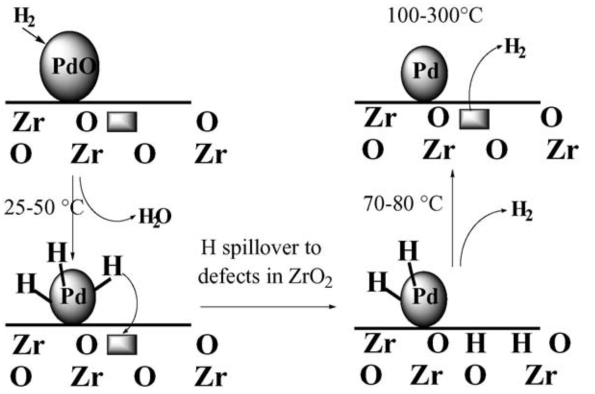

Fig. 6. Mechanism of hydrogen spillover, storage and release from the PdO/ZrO_2 nanophases.

Thermal decomposition of β-PdH_x to release H_2 :

$$\beta\text{-PdH}_x = \text{Pd} + 0.5x\text{H}_2 \tag{iv}$$

According to Eq. (i), there should appear one TPR peak corresponding to hydrogen consumption by the reduction of the PdO crystals, and this positive TPR peak must appear before the negative one. However, since the reaction (i) occurs near room temperature, it is difficult, in some time, to be observed by TPR starting from room temperature. Indeed, in our TPR experiment, one may find one positive peak located at about 35 °C in the TPR spectrum, which characterizes PdO reduction. This observation further consolidates the above postulation.

The broad, negative peak in the temperature range between 100 and 300 °C in the TPR profile must correspond to evolution of another kind of hydrogen from the sample. As shown above, the crystalline structure of zirconia contains cation lattice defects, oxygen ions in the defect location were not fully bounded, and therefore showed electron-rich character. These defects probably served as acceptors for storage of hydrogen species. However, the TPR experiment for bare zirconia seems to not support this assumption because no hydrogen generation or consumption was detected during the TPR experiment in the temperature range between 30 and 600 °C, indicating that pure zirconia is not capable of storing hydrogen and its lattice oxygen is hardly to be reduced. With respect to the TPR behaviours and structure features of both ZrO_2 and PdO/ZrO_2, it is postulated that apart from hydrogen reacting with PdO to form β-PdH_x, some other hydrogen species that adsorbed dissociatively on Pd crystals may spill over to zirconia support on which they are stored in zirconium lattice defects. In this process, the metallic palladium plays a key role in the hydrogen spillover because when Pd metals are absent, hydrogen spillover to the zirconia support does not take place. It is probably due to the ability of metallic Pd to dissociate molecular hydrogen into atomic hydrogen species that make it possible to migrate to the defects of the zirconia. The above mechanism is shown in Fig. 6.

4. Conclusions

Zirconia synthesized by the surfactant-templated method in a base condition shows nanocrystallites that contain many cationic defects in its crystalline structure. Hydrogen may be stored into or released from the PdO loaded zirconia nanophases. This is postulated to be related to the formation and decomposition of β-PdH_x hydride and hydrogen, which stores into the cationic defects of zirconia nanophases by means of hydrogen spillover from Pd clusters to the zirconia support. The nanophases of palladium supported zirconia with cationic lattice defects and ability to reversibly store/release hydrogen would be potentially used as hydrogen storage media at nearly room temperature, or used as a material for solid fuel cells and membrane reactors; it can also be used as catalyst for many catalytic reactions involving hydrogen transport.

Acknowledgments

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