Microporous and Mesoporous Materials 143 (2011) 357–361

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Fabrication and stabilization of nanocrystalline ordered mesoporous MgO–ZrO_2 solid solution

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ARTICLE INFO

Article history:
Received 18 November 2010
Received in revised form 11 March 2011
Accepted 13 March 2011
Available online 21 March 2011

Keywords:
Ordered mesoporous structure
MgO–ZrO_2
Solid base
High stability

ABSTRACT

The crystalline mesoporous MgO–ZrO_2 solid solutions have been fabricated by a simple evaporation induced self assembly procedure with zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and magnesium nitrate tetrahydrate ($Mg(NO_3)_2 \cdot 4H_2O$) as metal precursors and triblock co-polymer of Pluronic P123 as templating agent. Small-angle X-ray diffraction (SXRD) and transmission electron microscopy (TEM) results showed that ordered mesoporous structure and worm-like mesoporous structure were obtained under different calcine temperatures. Wide angle X-ray diffraction (WXRD) indicated that the formation of homogeneous solid solutions were responsible for the stable tetragonal phase. All MgO–ZrO_2 solid solutions were endowed with strong basicity ($H\_ = 9.3–12.2$) and high water resistance. The Mg^{2+} doped into zirconia lattice could stabilize the tetragonal phase and prevent zirconia crystals from excessive growth. This kind of structure could also inhibit basic sites dissolve in water in the reaction and effectively improve the thermal stability of products.

1. Introduction

Solid base is an important variety of catalyst which was widely applied to synthesize fine chemicals particularly in respect of substituting homogeneous base catalyst such as NaOH and KOH. In recent years, the researchers of the solid base catalyst have attracted much attention in view of environmental and economical reasons. This is mainly due to the distinct advantage of solid base catalysts, such as non-corrosiveness and fewer disposal problems. However, solid base such as single or binary alkali earth oxide (e.g. CaO and MgO) possesses low specific area and water resistant, which to some extent limited the production efficiency in practical application [1–3]. In order to increase the specific area of base catalysts, many approaches were developed for fabricating porous alkali earth metal oxide. But simple porous MgO or CaO still showed poor stability as employed in the solvent. Thus selecting appropriate carrier for the solid base catalyst was quite significant. Zeolites were used to utilize as the support to produce strong base through alkali oxide or alkali earth oxide modification [4–6]. But the drawback of small pore openings prevented bulky molecules from reaching the active sites. Hence the use of earth oxide as guest, direct generation of basicity on mesoporous silica SBA-15 has also been proposed [7,8]. However, the relatively low loading rate of earth oxide and water resistance of solid solution strictly limited sufficient utilization of solid base. Meanwhile the novel solid base namely CaO–ZrO_2 [9] solid solution has been reported in recent years. Obviously, the acidic–basic surface and redox properties of zirconia played an important role to make it to be an excellent support. The formation of solid solution efficiently prevented the active component from lixiviating into the reaction medium. So Liu et al. [10] subsequently prepared mesoporous CaO–ZrO_2 as the solid base and revealed the prospect of transesterification of esters with methanol. However, the preparation suffered from the tedious post treatment. Moreover, the distinct worm-like mesoporous structure and amorphous framework walls were disadvantageous to mechanical and thermal stability. Ordered mesoporous structure of MgO–ZrO_2 solid solution as a promising solid base has been scarcely reported so far.

In the present work, we prepared ordered mesoporous MgO–ZrO_2 solid solution with a simple method, characterized its structure and measured its basicity and stability. The crystalline wall of MgO–ZrO_2 can efficiently improve the thermal and mechanical stability. Based on the view above, this new type of solid base was found to be highly stable and activity.

2. Experimental

2.1. Synthesis of mesoporous MgO–ZrO_2

In preparation of mesoporous MgO–ZrO_2, a delicate procedure was designed. Typically, 0.7 g P123 was dissolved ultrasonically

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doi:10.1016/j.micromeso.2011.03.015

in 12.5 ml of the absolute ethanol. As the surfactant was completely dissolved, 4 mmol zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$) and 1 mmol magnesium nitrate tetrahydrate ($Mg(NO_3)_2{\cdot}4H_2O$) were added (the molar ratio of Mg/Zr was 0.25). Upon rapid stirring at room temperature at least 2 h, the resulting transparent-sol mixture underwent solvent evaporation under controlled relative humidity (RH = 50%) at 40 °C in air for two days and subsequently dried in the oven at 100 °C for one day. Then the as-prepared samples were heated at a ramping rate of 15 °C/min to 500 °C or 600 °C in the air for 3 h. Under the desired temperature and humidity conditions, the additional synthesis of MgO–ZrO_2 solid solution with Mg/Zr = 0.5 and 1.0 (molar ratio) was similar to that described above, in which 2 mmol and 1 mmol of zirconyl chloride octahydrate were added.

2.2. Characterization

The structure of the materials were characterized by small-angle X-ray diffraction (SXRD) using a Philips X'pert diffractometer with Cu Ka radiation (40 kV, 50 mA) and 0.02° step size with a speed of 3°/min in the range of $0.5° < 2\theta < 10°$. Transmission electron microscopy (TEM) images were collected on a (JEOL 2000 EX) electron microscope operating at an accelerating voltage of 200 kV. The phase identification were performed by wide-angle X-ray diffraction (WXRD) recorded with a Rigaku D/max-ßB diffractometer using a Cu Ka radiation source ($\lambda = 0.15432$ nm). The specific surface areas of the samples were measured by Micromeritics ASAP2020 apparatus at liquid nitrogen (77 K). Before measurement, the samples were first degassed at 200 °C under vacuum for a minimum of 24 h. Thermogravimetry (TG) and differential scanning calorimetry analysis (DSC) of the samples were performed at a Setaram Setsy 16/18 thermoanalyzer with a heating rate of 10°/min in air flow.

The base strength was detected using a series of Hammett indicators. The samples were activated in a N_2 flow with 30 ml/min at 500 °C for 2 h. About 200 mg of sample was shaken with 10 ml methanol solution of the Hammett indicator and left for 1 h to achieve equilibration. 0.02 mol/L phenolphthalein ($H\_ = 9.3$), 2, 4, 6-dinitroaniline ($H\_ = 12.2$), 2, 4-nitroaniline ($H\_ = 15.0$) were used for Hammett indicators. The water resistance measurement was performed as follows: 0.1 g sample was added into the 20 ml boiling purified water and then vigorously stirred for 48 h. The supernatant was collected after centrifugation and then titrated by 0.2 M HCl with phenolphthalein as an indicator to determine the concentration of base which was dissolved in the water.

3. Results and discussion

Mesoporous MgO–ZrO_2 solid solution would be denoted as xMgZrO in the following discussion, in which x ($x = 0.25$–1.0) was represented Mg/Zr molar ratio. Fig. 1 shows the small-angle XRD (SXRD) patterns of xMgZrO. When the calcined temperature was 500 °C (Fig. 1(a)) one diffraction peak at around $2\theta = 1.0$–$1.4°$ was appeared gradually with the Mg/Zr molar ratio increasing from 0.5 to 1.0. The presence of reflections at pseudo-small angles always means a large and repeated lattice structure. This result indicated that the samples have highly regularly ordered structure. With the calcined temperature increasing to 600 °C (Fig. 1(b)), the diffraction peak became broader and almost disappeared which implied the damage of mesoporous structure. The results suggested that higher temperature and low Mg/Zr molar ratio exerted a negative effect on the mesoporous framework of MgO–ZrO_2 solid bases.

Fig. 2 demonstrated the wide angle XRD pattern of xMgZrO solid bases at different calcined temperatures. It was obvious that all the samples showed the typical diffraction peaks ascribed to the tetragonal ZrO_2 crystal (please refer to JCPDS no. 14-0534) in the range 2θ from 26° to 70° (Fig. 2). With the increase of Mg/Zr molar ratio ranging from 0.25 to 1.0, the diffraction peaks became broad and weak. According to Scherrer formula $D = k\lambda/(b\cos\theta)$, the crystallite sizes were 5.97 nm, 4.0 nm and 3.67 nm, respectively. This result suggested that the t-ZrO_2 crystal size was extremely small. The shift of diffraction peak with respect to pure ZrO_2 was a result of Mg^{2+} incorporation. It was of interest that no diffraction peak corresponding to MgO crystallites was observed at 0.25MgZrO. The absence of diffraction lines of MgO indicated that Mg^{2+} ions substituted for Zr^{4+} ions in the host lattice and then homogeneous MgO–ZrO_2 solid solution formed. Conventionally, zirconia exists in monoclinic phase at temperatures below 1170 °C, and tetragonal phase is metastable which tends to be transformed into the monoclinic as temperatures elevated to a certain range [11,12]. However, in the present study, t-ZrO_2 nanocrystals were quite stable up to 600 °C. The stability of tetragonal phase could be ascribed the doping effect of Mg^{2+} and the small crystal size. It was reported that when MgO was added to ZrO_2, MgO either simply stayed on the surface or incorporated into the ZrO_2 lattice to form solid solution, depending on the preparation procedure [13]. When excessive $Mg(NO_3)_2$ added to the system, such as the case of 05MgZrO and 1.0MgZrO, reflection peaks at 2θ of 43° were appeared, which suggested the formation of free MgO nanocrystals in the system.

The mesoporous framework of the xMgZrO solid bases was also confirmed by TEM (see Fig. 3). The TEM images showed that with the increase of Mg/Zr molar ratio (from 0.5 to 1.0) the degree of ordered mesoporous channel increased. Fig. 3(a) exhibited regular and parallel pore structure of 0.25MgZrO sample. However the degree of order was very low which indicated performance of the local order structure. For the Fig. 3(b) the regular ordered structure with parallel channels and cylindrical channels were clearly observed which can be inferred for the synthesis of hexagonal mesoporous structure of 0.5MgZrO sample. The pore size was about 4 nm. Fig. 3(c) implied TEM image of 1.0MgZrO powder. Ordered pore structure was clearly visible and widely distributed which showed long-range ordered structure. When the calcined temperature increased to 600 °C (Fig. 3(d)), the ordered mesoporous structure was almost damaged and worm-like mesopores could be found. As mentioned above, the thermal stability of mesoporous zirconia was very poor [14] i.e. the framework tended to collapse and the mesopore structure disappeared along with the increase of calcined temperature. However, as-prepared xMgZrO mesoporous structures exhibited remarkable resistivity to calcinations. Even after heated up to 600 °C, the mesoporous framework was well preserved. The high thermal stability of MgO–ZrO_2 nano-oxides could be crucially attributed to the substitute of Mg^{2+} for Zr^{4+} in the host lattice and the formation of homogeneous MgO–ZrO_2 solid solution.

The textural property of xMgZrO sintered at 500 °C was determined by N_2 adsorption–desorption. As can be seen from Fig. 4, the isotherms of all samples were typically IV type with large hysteresis loops, which suggested the existence of mesoporous framework. A BJH analysis (inset in Fig. 4) of the desorption branch of the isotherm indicates that 0.25MgZrO, 0.5MgZrO and 1.0MgZrO with mesoporous structure possess a mean pore size of 4.0 nm, 4.0 nm and 3.54 nm with pore volume bearing 0.13 cm^2/g, 0.18 cm^2/g and 0.22 cm^2/g respectively. The new solid base exhibited relatively high specific surface area and the BET surface areas are 93.5 $m^2\ g^{-1}$, 118.9 $m^2\ g^{-1}$ and 170.79 $m^2\ g^{-1}$ respectively. We deduce that the increase of the specific surface area among the as-synthesized mesoporous xMgZrO samples can be ascribed to the