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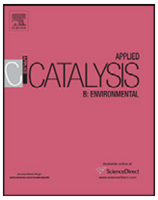

Improvement of oxygen storage capacity using mesoporous ceria–zirconia solid solutions

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ABSTRACT

Mesoporous phases of ceria (CeO_2) and ceria–zirconia solid solutions up to 50% of Zr have been synthesized using hard template method. The structures of the obtained metal oxides replicas correspond to the chosen structures of the KIT-6 and SBA-15 silica. This method allows obtaining materials with a uniform and homogenous porous size distribution as replica of the used nanotemplate. This structure facilitates the interaction with the gas molecules, their diffusivity inside the material and the porous size control. Obtained replicas were analysed using a variety of characterization techniques. TEM results reveal successful formation of the expected structures which were also supported by BET measurements. Replicas obtained applying SBA-15 and KIT-6 nanotemplates present similar behaviour although KIT-6 shows a slightly higher (about 5%) active surface with values in the range of 125 m^2/g after thermal annealing. XRD and Raman spectra confirm formation of solid solutions with cubic structure up to 20% of zirconium above which, formation of tetragonal phase was observed. Functionally, besides their high active surface, these ceria–zirconia solid solutions show significant improvement in their oxygen storage capacity (OSC). In comparison with pure mesoporous ceria, it has been found that due to the introduction of zirconium even for a few percentage of zirconium (5%) the OSC increases (more than 30 times) which is attributed to the presence of substitutional zirconium in the ceria lattice.

1. Introduction

Ceria (CeO_2) has significant oxygen ionic conduction at lower temperatures as compared to pure zirconia [1] and according to its redox properties, it has a fast Ce^{4+}/Ce^{3+} balance [2] which can be simply written as:

$$2CeO_2 \leftrightarrow Ce_2O_3 + \frac{1}{2}O_2 \tag{1}$$

As a consequence, for its use in three way catalysts, ceria can store O_2 during an oxygen-rich phase and later, feed the noble metal with oxygen when the O_2 partial pressure decreases. This capability for feeding oxygen is estimated according to the value of the oxygen storage capacity, OSC, which determines its role in the optimum CO, HC, and NO_x conversions [3]. This property is lost as the temperature increases. So, thermal stability at high temperature becomes an essential requirement taking into account that it must be applied in the flue duct of many combustion chambers or internal combustion engines with operating temperatures higher than 700 °C [4]. Likewise, the oxygen storage capacity needs to be increased since thermodynamically, solid ceria in its pure form, crystallizes in the fluorite structure co-ordinating each cerium atom with 8 neighbouring oxygens. This results in stabilization of the material, making the CO_2 reduction unfavourable. Therefore, materials should be modified in order to improve these performances. Under these restrictive boundaries, as ZrO_2 has better stability at higher temperatures, binary compounds, $Ce_xZr_{1-x}O_2$, constitutes an interesting alternative for satisfying all of these requirements, thermal stability and oxygen storage capability, in a wide operating window. In fact, introduction of some zirconium atoms in the ceria lattice by isomorphous substitution of Ce^{4+} cations (ionic radius 0.97 Å) with Zr^{4+} cations (ionic radius 0.84 Å), clearly should influence the final properties of these materials, at least, as long as the cubic structure of ceria is maintained [5,6]. This is a result of introduction of extrinsic defects associated with oxygen vacancies which in Kröger–Vink notation is stated as:

$$ZrO_2 = Zr''_{Ce} + V_O{}^{\bullet\bullet} + 2O_o^{\times} \tag{2}$$

Vacancies can also be created as a result of surface interactions with oxygen which means that surface oxygen density is a function of the oxygen partial pressure:

$$2Ce_{Ce}^{\times} + O_o^{\times} = 2Ce'_{Ce} + V_O{}^{\bullet\bullet} + \tfrac{1}{2}O_2 \tag{3}$$

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On one hand, higher oxygen bulk mobility is expected due to the zirconium presence and, on the other hand, there is a higher surface oxygen vacancy due to the lattice parameter changes. Both features are enhancing the oxygen storage capacity.

Nevertheless, it is well known that all of these properties are changed for nanocrystalline materials. For example, nanocrystalline ceria, about 10 nm or less in size, possesses greatly reduced grain boundary impedance and increased electronic conductivity [7,8]. Fundamental defect and transport properties govern these properties and, hence, the dominant role of interfacial defect formation gives rise to preferential reduction at grain boundary atomic sites of lowered oxygen vacancy formation energy. The concentration of oxygen vacancies is changed two orders of magnitude when the crystal size is increased from 4 to 60 nm. All such properties fundamentally depend on the defect thermodynamics and related electrical and mass transport properties of the polycrystalline solid that are strongly dependent on the synthesis and treatment procedures. For example, Conesa group showed that fabrication of these mixed oxides through microemulsion method can result in 2D or 3D structures with different phases (pseudo-cubic t″ phase in high concentrations of Ce) which differ in catalytic properties [9]. Therefore, the origin of many of the reported data for nanocrystalline oxides is unclear whether they are due to (i) increased interfacial area, (ii) logical extensions of conventional size scaling laws (e.g., the grain size dependence of oxygen diffusion), or (iii) the result of truly size-dependent physical properties as the oxygen vacancy enthalpy of formation [10]. So, different results have been reported for different synthesis procedures like sol–gel [11] and mechanical milling [12] pointing out the strong sensitivity of the interfacial characteristics to the obtaining procedure, especially thermal treatment, and its control.

A variety of processes have been reported for preparation of ceria–zirconia solid solutions [13,14]. In this work, we report a procedure based on the use of mesoporous silica as a hard template for the synthesis of mesoporous ceria–zirconia solid solutions. The use of templates is an attractive alternative to overcome the abovementioned difficulties concerning the fabrication control and its influence on the interfacial properties as nanoparticle properties become related to the used template. Nevertheless, the soft-template methods, based on the use of surfactants, were initially discarded because the template is removed before annealing and this introduces difficulties for preventing the material agglomeration. In contrast, in the hard-template methods, the template is removed afterwards, and this ensures a good control of the particle size since the template acts as a physical barrier to coalescence of the crystals during the calcination process. The hard-template method also offers several additional advantages. Firstly, it allows obtaining a porous network that depends on the nanotemplate structure, selected among a wide variety, such as MCM-41, SBA-15, KIT-6, and SBA-16. Secondly, the replication process using silica templates is easy to scale-up. This is an advantage compared with other hard-templates such as anodized aluminum oxides (AAO) membranes [15]. Thirdly, mesoporous silica templates offer good thermal stability for the synthesis of metal oxides compound even at relatively high temperatures [16].

2. Experimental

2.1. Synthesis of nanotemplates

Mesoporous silica was synthesised using a non-ionic triblock copolymer surfactant ($EO_{20}PO_{70}EO_{20}$, Pluronic P123 from BASF$^{®}$) as a structure directing agent. In this work, we have used two different structures of mesoporous silica: SBA-15 (two-dimensional hexagonal *p6mm* symmetry) and KIT-6 (three-dimensional cubic *Ia3d* symmetry).

For the preparation of SBA-15 [16,17], 6 g of P123 were dissolved in 60 g of HCl (6 M) and 165 g of deionized H_2O, stirring for 4–6 h at constant temperature of 38 °C in a thermal bath. Then, 12.49 g of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added drop wise. The resulting mixture was stirred again for 24 h at 38 °C in the thermal bath. A hydrothermal treatment was performed on the product through putting the sample in an oven already heated up to 100 °C for another 24 h. Samples were then filtered and cleaned with purified water. This step was followed by a drying process in oven at 50–60 °C for 24 h. Resulting nanopowder was finally calcined at 550 °C for 4 h using a heating ramp of 4 °C/min.

Similarly, KIT-6 [16,18] was prepared in the same way through mixing 6 g of P123 with 24 g HCl and 208 g H_2O. Here, after 2 h of stirring at 36 °C, 6 g of 1-butanol was added followed by 3 h of stirring. Then, 12.49 g TEOS was added and the agitation was continued for another day at 36 °C. Hydrothermal treatment was performed at 90 °C for 24 h. The rest of the process was the same as the one used for SBA-15.

2.2. Synthesis of mesoporous ceria and ceria–zirconia

Solid solutions of ceria–zirconia were prepared by a two-step impregnation method where the previously synthesised silica templates were impregnated with aqueous solutions of its nitrate salts [16].

First, proper amounts of cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) and zirconium oxynitrate ($ZrO(NO_3)_2{\cdot}6H_2O$) were dissolved in purified water in order to make 0.1 M solutions. In the first impregnation step, 0.15 g of silica template (SBA-15 or KIT-6) was mixed with the adequate volumes of ceria and zirconia solutions in order to have 1 mmol of total metal ions. The metal ratio $[Zr^{4+}]/([Zr^{4+}]+[Ce^{3+}])$ was varied between 0 and 0.5. The mixture was stirred for 30 min, dried at 50 °C and calcined at 350 °C for 4 h with a heating rate of 4 °C/min. In the second impregnation step, 0.5 mmol of metal ions ($[Zr^{4+}]+[Ce^{3+}]$) with the same metal ratio were added to the resulting powder, stirred, dried and calcined to the final calcination temperature (600 °C, 800 °C or 1000 °C).

To remove the template, products were hot-etched using NaOH. Powders were introduced in a 2 M NaOH solution and stirred for 24 h at 70 °C. Products (ceria and ceria–zirconia powders with mesoporous structure) were recovered by centrifugation and cleaned several times with purified water until reaching a neutral product (pH 7). They were finally washed with ethanol for two times and oven-dried for 12 h in air.

2.3. Characterization

XRD analysis was performed on Siemens D500 and Bruker D4 X-ray Powder diffractometers, working with the Cu Kα radiation with Bragg Brentano geometry. TEM characterization was carried out using a Philips CM30 SuperTwin electron microscope operating at 300 keV. BET (Brunauer–Emmett–Teller) analysis was performed using a Micromeritics Tristar 3000 surface area analyzer, degassing the samples at 150 °C before doing the experiment. Raman spectra were recorded at room temperature using a Jobin Yvon T64000 spectrograph equipped with a bidimensional charge-coupled device (CCD) detector and an Ar^+ Coherent INNOVA 300 laser ($\lambda = 514$ nm) as excitation source. The laser power onto the sample was 3 mW.

Oxygen storage capacity was measured by thermogravimetric analysis (TG) [11], using a thermobalance TGA-SDTA 851e/SF/1100 from Mettler Toledo. 15 mg of mesoporous ceria or ceria–zirconia powder was heated up to 600 °C in nitrogen (50 mL/min) in order to release oxygen from the sample. After 10 min of stabilization, synthetic air was introduced resulting to an increase in sample weight due to the uptake of oxygen from air. This weight change