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Anionic surfactant-aided preparation of high surface area and high thermal stability ceria/zirconia-mixed oxide from cerium and zirconium glycolates via sol–gel process and its reduction property

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This work is focused on the ceria zirconia mixed oxide prepared through a surfactant-introduced synthesis method. High surface area nanoparticle mesoporous ceria/zirconia-mixed oxide was successfully synthesized and characterized using various techniques. High surface area mesoporous fluorite-structured CeO_2–ZrO_2 was obtained from the elimination of surfactants upon calcination. A surface area in excess of 205.6 m^2/g was obtained after calcination at 500 °C, and dropped to 75.96 m^2/g by heating at 900 °C. Temperature-programming reduction (TPR) results showed that the lowest reduction temperature was obtained from the sample containing 40% zirconia content.

Keywords: ceria; zirconia; sol–gel process; TPR; anionic surfactant

Introduction

Recent studies report the improvement of textural properties by introducing doping elements in the CeO_2 fluorite-type lattice, and the most efficient dopant studied was zirconium, as discussed by our previous work.[1] Because of their use in the three-way catalyst (TWCs), the thermal stability required for CeO_2-based oxides has been studied over the years as converter technology continues its development.[2] Success depends on the molecular homogeneity, surface area and textural/morphological properties, which are affected by the appropriate selection of precursor, preparation methods and mixing composition[1].

Among many synthesis methods,[3–5] the sol–gel process is a versatile technique, allowing control of the texture, composition, homogeneity and structural properties of solids.[6] The surface areas of ceria–zirconia obtained by either conventional co-precipitation or sol–gel were typically in the range of 60–90 m^2/g after calcination with air at 700–800 K.[3,5]

Recently, much interest has focused on the preparation of transition metal oxides using several templating pathways to design novel high surface area materials for catalytic applications.[7,8] A few meso-structured surfactant-oxide composites have shown a regular pore structure even after calcination,[9] while the majority suffered from collapse of the regular pore structure after calcination.[10] There are some reports using a cationic surfactant as a template for ceria zirconia mixed oxide preparation,[11,12] but no reports describe the use of an anionic surfactant as a template in these mixed-oxide preparations, especially by the sol–gel method. Thus, this study aimed to improve textural, structural and chemical properties of ceria-based catalysts for environmental application using an anionic surfactant via the sol–gel route at ambient temperature. Its reduction property was also studied.

Methodology

Mixed-oxide preparation

Cerium glycolate and sodium tris(glycozirconate) precursors[13] were mixed with 1 M sodium hydroxide and aqueous sodium dodecyl sulfate (SDS) at a 1 : 2:1 mole ratio. The ratio between the metal alkoxides varied, depending on the desired compositions: $Ce_xZr_{1-x}O_2$, where $x = 0.2$–0.8. The mixture was stirred for 2 h to obtain a gel and was further kept at room temperature for 2 and 10 days to study the effect of aging time on the properties of mixed-oxides. After the aging step, the gels were washed with deionized water three times to remove the Na content generated from sodium tris(glycozirconate), the free surfactant and the NaOH added during the gelation step. The samples were then put in an oven at 110 °C for at least 12 h to let them dry before calcination at 500 or 900 °C for 2 h and at 1000 °C for 5 h, as studied by Monte and Kas'par.[14]

Characterization

X-ray spectra were determined on a Rigaku D/MAX 2000, using CuK_α radiation ($\lambda = 1.5406$ Å). The average grain size (D) was estimated according to the Scherrer equation[1] ($D = 0.94\,\lambda/\beta\cos\theta$). Lattice parameters of samples were calculated using the Vegard rule $\{a_{\text{average}} = [2(\sqrt{2}a) + c]/3;$ a and c are the lattice parameters$\}$.

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Scanning electron micrographs (SEM) were obtained on a Jeol 5200-2AE (MP15152001). Surface areas and pore sizes of powder samples were determined by N_2 adsorption at 77 K using a Quantachrome Corporation Autosorb. The thermal behavior and stability of the synthesized mixed oxides were investigated under oxygen on a Perkin-Elmer Pyris Diamond TG/DTA with a ramp rate of 10 °C/min. A Micromeritics TPD/TPR 2900 was employed for the temperatures of the thermal conductivity detector, using a furnace temperature up to 900 °C at a linear ramp rate of 10 °C/min, and 5% hydrogen in nitrogen was used as the carrier gas.

Results and Discussion

The reaction time of 2 days provides non-homogeneity of solid solutions, probably due to an incomplete exchange reaction between the hydroxyl groups of the hydrous oxide and the surfactant.[12] The mixed oxides show a good compositional homogeneity and thermal stability after aging for 10 days.

The average particle sizes calculated by the Scherrer equation for $Ce_xZr_{1-x}O_2$ powders are listed in Table 1. The average particle sizes of mixed oxides are increased with the doping of CeO_2 and after calcination at high temperature due to the sintering process. However, the particle size decreases as the aging time increases because mixed oxides, which have longer aging time, are more difficult to sinter, while the pure oxides are easier to sinter, especially CeO_2.

The average lattice parameter *a* is considered in the case of the cubic symmetry.[12,14] The six main reflections are typical of fluorite-like structured material with a fcc cell, corresponding to the {111}, {200}, {220}, {311}, {222} and {400} planes. Values of *a* in the range 0.52–0.54 nm were obtained from the mixed-oxide catalysts. These results are in agreement with those obtained from Ce–Zr–O prepared by other routes.[15]

Table 1. Surface areas and particle sizes of ceria/zirconia-mixed oxides

Sample no.	Ce : Zr	Aging time (day)	Calcination temperature (°C)	Average particle size XRD (nm)	Surface area (m^2/g)
1	ZrO_2	2	500	9.03	80.00
2			900	17.98	20.12
3	2 : 8		500	8.15	98.06
4			900	14.23	28.44
5	4 : 6		500	7.93	99.87
6			900	13.12	32.68
7	6 : 4		500	6.85	107.65
8			900	12.09	35.76
9	8 : 2		500	5.19	105.12
10			900	11.65	28.85
11	CeO_2		500	9.65	92.35
12			900	18.96	20.13
13	ZrO_2	10	500	9.02	100.65
14			900	17.42	30.05
15	2 : 8		500	8.02	110.22
16			900	14.01	37.26
17	4 : 6		500	7.12	120.47
18			900	12.95	42.9
19	6 : 4		500	6.06	205.6
20			900	11.83	75.96
21	8 : 2		500	4.94	192.17
22			900	10.96	62.23
23	CeO_2		500	9.21	105.14
24			900	18.14	29.44

Table 1 also includes the N_2 adsorption/desorption data, showing the minimum calcination temperature of 500 °C. At this temperature, all the organic residues were removed and detected using TGA (not shown). BET surface areas of the mixed oxides calcined at 500° and 900 °C are higher than those of pure oxides and decrease as the crystallite size increases after calcining at higher temperature.

Figure 1 shows the thermal stability of the mixed oxides. It increased when increasing the amount of zirconia up to 40%. This can be explained as follows: the addition or incorporation of zirconia to ceria as mixed oxides can enhance the thermal stability of CeO_2, resulting in better resistance of the sintering and deactivation processes. It is clear that CeO_2 undergoes a rapid crystallite growth process since BET surface areas of both catalysts using aging times of 2 and 10 days decrease significantly more than those of the mixed-oxide samples. Therefore, the crystallite growth process is retarded by the incorporation of Zr ion into the CeO_2 matrix.[1] The results also show that, when aging time is increased, the obtained surface area and thermal stability increase, probably due to the complete exchange reaction between the hydroxyl groups of the hydrous oxide and the surfactant in the samples after aging for 10 days. These results also indicate that the surfactant-aided preparation yields a ceria/zirconia-mixed oxide of higher surface area and higher thermal stability than those reported by many researchers.[11,12,16–18] The highest surface area and thermal stability were obtained from the $Ce_{0.6}Zr_{0.4}O_2$ aged for 10 days. Its N_2 isotherms were type IV, indicating that mesoporous structure and average pore diameter increased from 3.61 to 6.13 nm after calcining at higher temperature (not shown).

The TGA profile (Fig. 2) of synthesized $Ce_{0.6}Zr_{0.4}O_2$ aged for 10 days showed the loss of the water (35–150 °C) as well as the decomposition of organic residues. Upon further heating in air, we observed sharp exothermic peaks at 200–500 °C, attributed to the loss of surfactant and organic ligands in the mixed oxide.

XRD peaks of the samples calcined at 500 and 900 °C in Fig. 3, as expected, become sharper with increasing calcination temperature, indicating an increase in the crystallite size and crystallization of the amorphous phase due to partial sintering.[15]

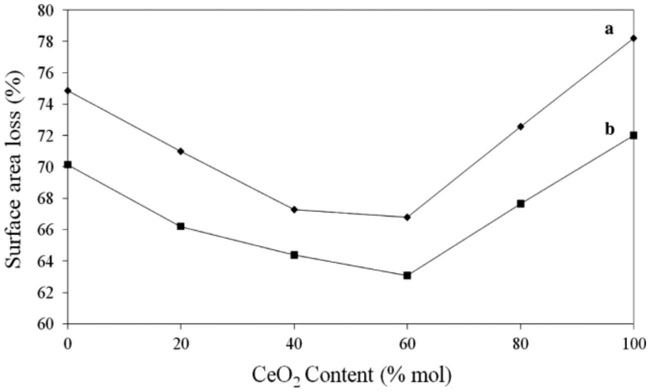

Figure 1. Loss of surface areas for ceria/zirconia mixed oxides at the aging time of (a) 2 and (b) 10 days.

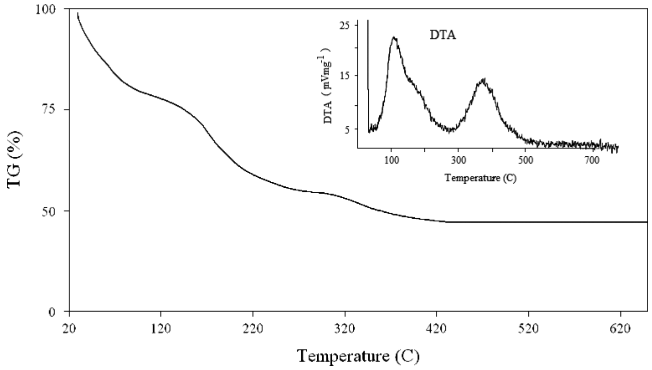

Figure 2. Thermogram and its derivative (TGA/DTA) of the synthesized $Ce_{0.6}Zr_{0.4}O_2$ aged 10 days.

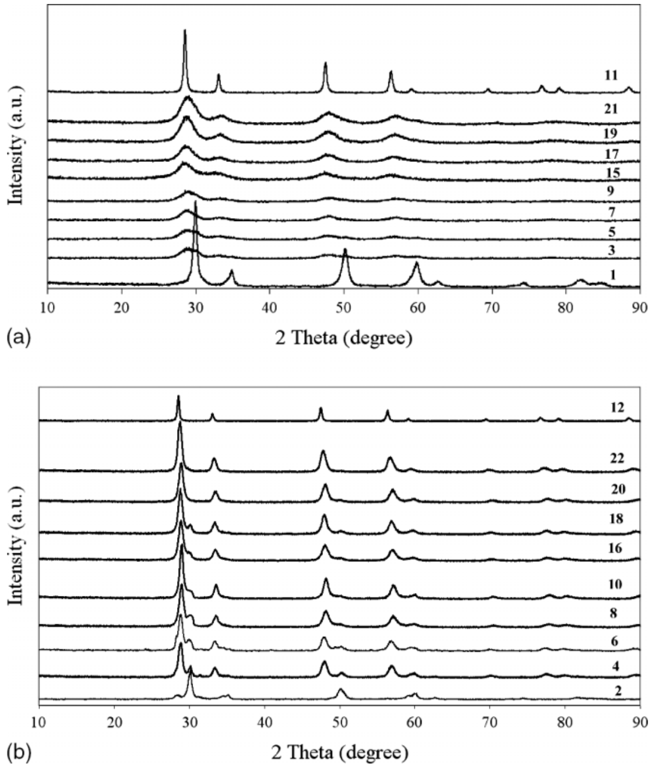

Figure 3. XRD patterns for ceria/zirconia-mixed oxides calcined for 2 h at (a) 500 °C (sample nos 1, 3, 5, 7, 9, 11, 15, 17, 19 and 21) and (b) 900 °C (sample nos 2, 4, 6, 8, 10, 12, 16, 18, 20 and 22).

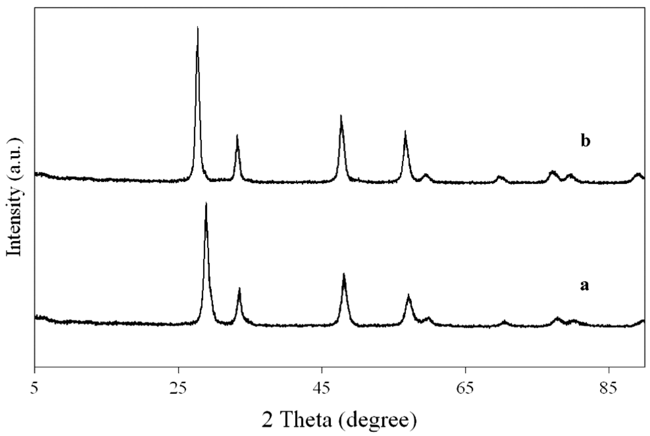

Figure 4. XRD patterns for (a) $Ce_{0.6}Zr_{0.4}O_2$ and (b) $Ce_{0.8}Zr_{0.2}O_2$ aged for 10 days and calcined at 1000 °C for 5 h.

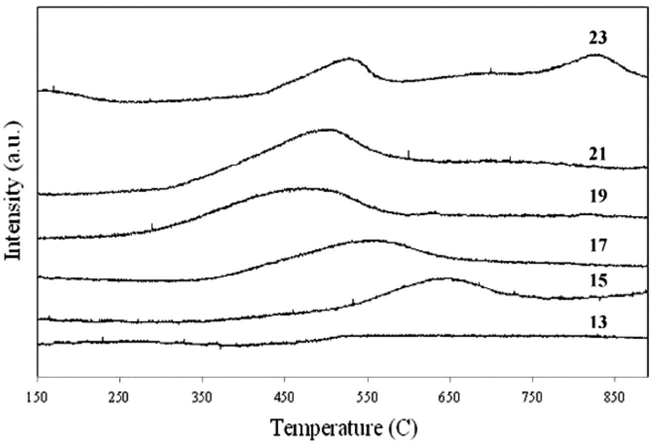

Figure 5. TPR profiles of ceria/zirconia-mixed oxides aged for 10 days and calcined at 500 °C for 2 h (sample nos 23, 21, 19, 17, 15 and 13).

The pure oxide peaks indicate cubic CeO_2 and tetragonal ZrO_2 after heating at 500 °C for 2 h. Additional monoclinic phase ZrO_2 appears with the peaks at $2\theta = 28$ and 31° after heating at 900 °C for 2 h. In other words, the monoclinic phase is preferable at higher temperature, which is in good agreement with the results reported elsewhere.[19] The sample aged for 10 days and calcined at 1000 °C for 5 h (Fig. 4) gave the single-phase mixed oxides in the ceria-rich region.

The reactivity of lattice oxygen in ceria/zirconia mixed oxide catalysts towards H_2 was investigated by TPR (Fig. 5). The two-peak pattern, due to surface (low temperature peak) and bulk reduction (high temperature peak) is clearly seen in CeO_2.[20] These two peaks are merged together in the solid solutions, suggesting that the whole ceria component, including the bulk part, in the solid solutions is subjected to the reduction in a single stage. The single stage reduction of the solid solutions can be explained in terms of the ease with which the migration of oxygen ions in the CeO_2-ZrO_2 lattice occurs.[21] The variation in temperature profile seems to be related to the ZrO_2 content in the sample and may have some structure dependency as well.[22] The H_2 consumption of the mixed oxide is higher than that of the CeO_2 alone, meaning that the presence of ZrO_2 improves the reduction property of CeO_2. The reduction of the bulk lattice oxygen in the solid solution becomes easier because of the distortion of the structure, which is caused by the partial substitution of Ce^{4+} (ionic radius 0.97 Å) with Zr^{4+} (ionic radius 0.84 Å) in the sol–gel technique. As a result, reduction of the bulk lattice oxygen must occur simultaneously with the reduction of the surface oxygen. This occurs through the structural modifications of the fluorite-type lattice of ceria. The effect of this substitution is to decrease cell volume, lowering the activation energy for oxygen-ion diffusion within the lattice, and consequently favoring the reduction. The introduction of zirconium also enhances the formation of structural defects, which are expected to play an important role in determining the reduction/oxidation behavior. This result is in agreement with many previous works.[19] It is clearly shown from the TPR results that the mixed oxides have better reduction properties than many

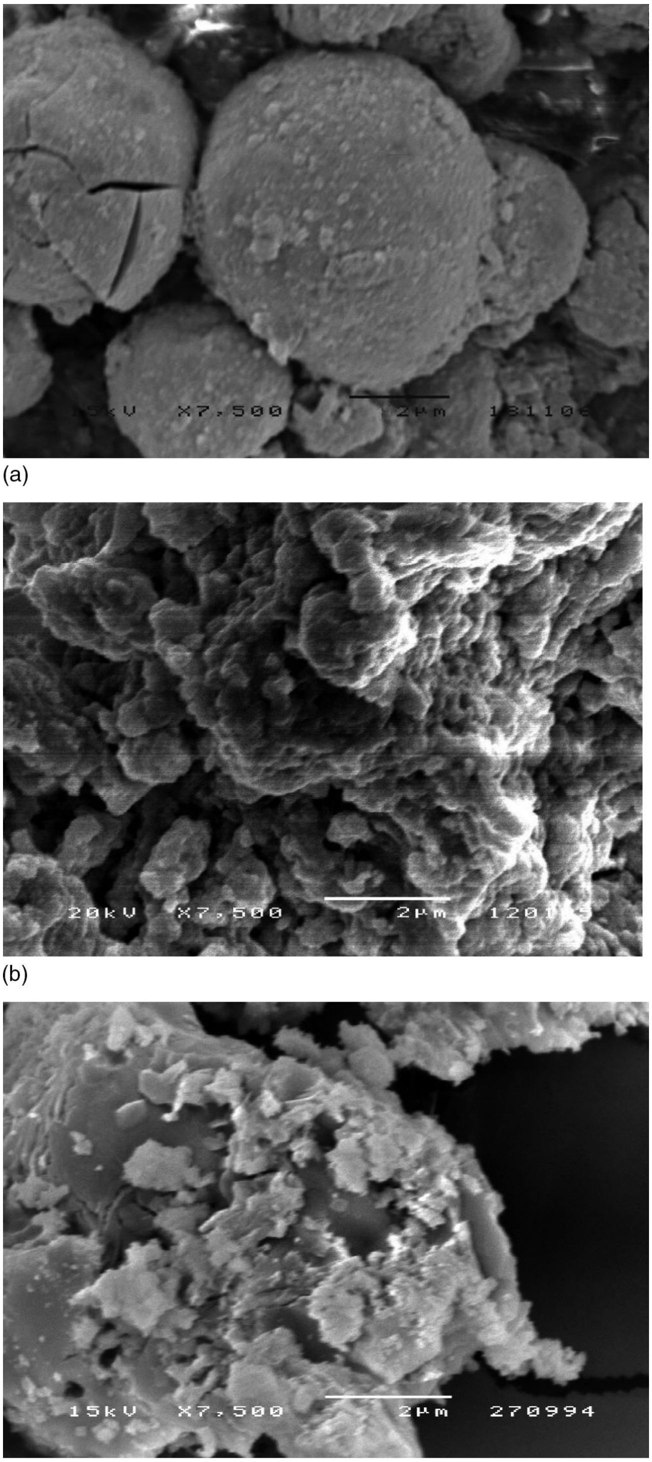

Figure 6. SEM micrographs of $Ce_{0.6}Zr_{0.4}O_2$ aged 10 days: (a) before and (b, c) after calcination for 2 h at 500 and 900 °C, respectively.

research studies[23,24] and the lowest reduction temperatures are observed in $Ce_{0.6}Zr_{0.4}O_2$.

The SEM images of $Ce_{0.6}Zr_{0.4}O_2$ aged for 10 days (Fig. 6) reveal the effect of heat treatments on morphology (7500×). The picture shows sphere-shaped and small-sized particle aggregates before calcining. After calcining at 500 and 900 °C, the particles become irregular shaped and larger sized due to the collapse in structure after heat treatment.

Conclusions

The influences of various synthesis parameters were investigated. The sample using Ce : Zr equal to 6 : 4 and aged for 10 days gave the highest surface area (205.6 m^2/g). Aging time had a significant effect on the texture and the structure of the mixed oxides. Calcinations of the mixed-oxide gels at 500 and 900 °C crystallized the mixed oxide domains and strongly affected the surface areas for these pore–solid nanoarchitectures. Heat treatment reduced the surface area and increases the average grain size and pore diameter.

Acknowledgments

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