

# Development of a modified co-precipitation route for thermally resistant, high surface area ceria-zirconia based solid solutions

ALFONSINA PAPPACENA \*

**Abstract.** In this work a modified co-precipitation route for ceria-zirconia based material with a high surface area, high thermal stability and enhanced OSC properties has been developed and the importance of the addition of surfactants and  $H_2O_2$  in order to promote the stability of these materials at high temperatures has been developed.

**Key-words.** Ceria-zirconia, TWC, OSC, surface area, surfactant.

**1. Introduction.** The use of ceria-based materials in catalytic science is well established (Bernal et al. 1999, Trovarelli 2002). Ceria is presently used in a large number of industrial processes and it accounts for a large part of the rare earth oxide market. Undoubtedly its major commercial application is in the treatment of emissions from internal combustion engines where ceria-based materials have been used in the past 30 years (Kaspar & Fornasiero 2003). Its more important action in TWCs is to take up and release oxygen following variations in the stoichiometric composi-

tion of the feedstream. Typical materials currently used for the manufacture of TWC washcoats are mixtures based on aluminium oxide combined with Ce or Zr rich  $CeO_2$ - $ZrO_2$  plus additional rare earth dopants. Within the automotive exhaust gas purification there is estimated to be a future huge demand on TW catalysts when more stringent emission standards will be introduced to the market within the next years. Particularly, countries which do not have any emission standards yet are considered to give a significant contribution to the growing demand in the materials.

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\* Department of Chemistry, Physics and the Environment, University of Udine, Udine, Italy.  
E-mail: alfonsina.pappacena@uniud.it

The severe conditions to which catalysts are subjected during operations require materials with high thermal stability and this forced researchers to develop new synthesis routes in order to achieve formulations responding to the market requests for the new generation of washcoat materials (Wakita et al. 2007, Larcher et al. 2009).

The aim of this work is the design of highly stable ceria-zirconia based materials with particular attention to surface and oxygen storage properties, understanding the effect of composition and of addition of surfactant agents, the effect of pre and post treatments using  $H_2O_2$  and the effect of any variation in coprecipitation procedure.

**2. Experimental procedures.** Ceria-zirconia solid solutions were prepared by co-precipitation starting from nitrate salts precursors (Treibacher Industrie AG) with ammonium hydroxide (Aldrich) in a glass reactor (1L) equipped with a temperature-controlled chamber and four automatized pumps for adding reagents and controlling pH. A typical composition contains 20% wt. of  $CeO_2$ , 73%  $ZrO_2$ , and two dopants from the rare earth family (5%  $Nd_2O_3$  and 2%  $La_2O_3$ ). Precipitates were filtered and washed three times with 0.5L of de-mineralized water and the resulting cakes were dried at 393 K and calcined at 773 K (fresh), 1273 K (soft aging) and 1373 K (severe aging) for 4 h and they were extensively characterized by conventional techniques (XRD, TGA, BET)

for checking phase purity, textural and oxygen exchange properties. Textural properties and porosity were measured, respectively, according to the B.E.T. and BJH methods, by nitrogen adsorption/desorption at 77 K, using a Tristar 3000 gas adsorption analyzer (Micromeritics). Structural features of the catalysts were characterized by X-ray diffraction (XRD). XRD patterns were recorded on a Philips X'Pert diffractometer operated at 40 kV and 40 mA using nickel-filtered  $Cu-K_\alpha$  radiation. Spectra were collected using a step size of  $0.02^\circ$  and a counting time of 40 s per angular abscissa in the range  $20^\circ$ - $145^\circ$ . The mean crystalline size was estimated from the full width at the half maximum (FWHM) of the X-ray diffraction peak using the Scherrer equation with a correction for instrument line broadening. The OSC properties of the powders are determined in static conditions with a TGA method similar to those reported in Mamontov et al (2003). The oxidized powder is treated with 5%  $H_2/Ar$  at 923 K for 70 min and the observed weight loss, due to oxygen removal by  $H_2$  to form water, can be associated to total oxygen storage capacity at that temperature.

**3. Results and discussion.** The optimization of synthesis parameters was done by working on pre- and post-treatment variables such as introduction of reflux, addition of  $H_2O_2$  (Djuričić & Pickering 1999, Yu et al. 2006, Larcher et al. 2009) and/or surfactant and by varying pH during precipitation. The synthesis route was

Table 1. Textural morphological and OSC properties of materials.

	average pore size (nm)				SA <sub>BET</sub> (m <sup>2</sup> /g)			OSC <sub>923K</sub> (μmol-O <sub>2</sub> /g-CeO <sub>2</sub> )			crystallite size (Å)		
	773	773	1273	1373	773	1273	1373	773	1273	1373	773	1273	1373
<b>Ageing temperature (K)</b>													
CZ	26	72	0	0	1059	822	699	54	133	168			
rCZ	30	112	7	0	957	841	175	55	137	265			
hCZ	43	93	19	1	1002	987	943	71	147	196			
r,hCZ	46	111	18	1	1027	958	638	55	142	242			

modified step by step evaluating the effect of each variable on the surface area, porosity and OSC of materials. The sample prepared by the traditional co-precipitation (i.e. without reflux and with no addition of H<sub>2</sub>O<sub>2</sub> and surfactant) is identified as CZ.

The reflux post-treatment for 20 h (rCZ) induces an increase of the surface area of the material and its role decreases by increasing the temperature of thermal treatment (Table 1). On the contrary, the pre-treatment with H<sub>2</sub>O<sub>2</sub> (hCZ, using [H<sub>2</sub>O<sub>2</sub>]/[metal]=3) shows an important role (correlated with its capability to induce the precipitation of ceria at acid pH [Djuričić & Pickering 1999]), enhancing the surface area up to 19 m<sup>2</sup>/g at 1273 K. It is interesting to observe that the reflux positively affects the surface area of fresh samples, while the pre-treatment with H<sub>2</sub>O<sub>2</sub> significantly improves the thermal stability at 1273 K and a combination of the two treatments (r,hCZ) produces a material showing high surface area under fresh and aged conditions. The calcination at 1373 K induces a dramatic drop in surface area for all

the samples, but nevertheless the use of H<sub>2</sub>O<sub>2</sub> improves the oxygen storage capacity also after thermal treatment. From Table 1 it appears that while the reflux post-treatment slightly affects the properties of the samples, the pre-treatment with H<sub>2</sub>O<sub>2</sub> is a key parameter to increase the surface area and the OSC and for these reasons in the optimization of the synthesis only the H<sub>2</sub>O<sub>2</sub> treatment was maintained.

The synthesis procedure was further modified with the introduction of a surfactant post-precipitation treatment adding the lauric acid (Aldrich), directly in solid form to the batch, as “soft templating” agent (Zhang et al. 2009) (commonly used in the preparation of mesoporous structures [Terribile et al. 1998]); the resulting solution is kept under stirring 4 h, then the slurry is filtered and washed as describe above. The role of the surfactant agent is to modify the surface morphology of the material inducing a mesoporous structure. Varying the total metal ions/surfactant molar ratio ([metal]/[lauric acid]) affects the pore size distribution of samples and, as shown in Fig-

ure 1, the thermal stability after aging at 1373 K is strictly correlated with the average pore size. The higher the average pore size, the higher the surface area after severe aging treatment (the better results is obtained for the molar ratio of 1/0.25 with a surface area of 14 m<sup>2</sup>/g). Summarizing, the post-treatment with lauric acid results a key parameter in order to obtain materials with high surface area and coupling the pre-treatment with H<sub>2</sub>O<sub>2</sub> and the post-treatment with lauric acid the thermal stability was dramatically improved.

A very interesting result is obtained by studying the effect of the pH on the final properties of the materials.

The precipitation was interrupted at different pH values, from 6 to 11, and then the precipitate was treated with lauric acid (all the samples were pre-treated with H<sub>2</sub>O<sub>2</sub>). The value of pH affects the interaction between the surfactant and the precipitate, influencing not only the surface area, but also the porosity of materials; higher values of the pH of precipitation are correlated with higher porosity of the catalysts and enhanced thermal stability (Figure 2). This effect is probably due to the  $\zeta$ -potential of the precipitate that drives the interaction with the amphiphilic molecules (Terribile et al. 1998, Ozawa & Hattori 2006). The porosity results to be very important in order to maintain elevated surface area, indeed our study pointed out that fresh samples with higher pore size show higher thermal stability.

Considering TWC catalysts, the

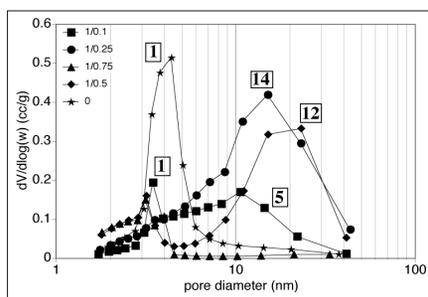


Figure 1. Pore size distribution of fresh materials prepared with H<sub>2</sub>O<sub>2</sub> and surfactant with different [M<sup>+</sup>]/[C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>] molar ratio (in the label the SA values for samples calcined at 1373K).

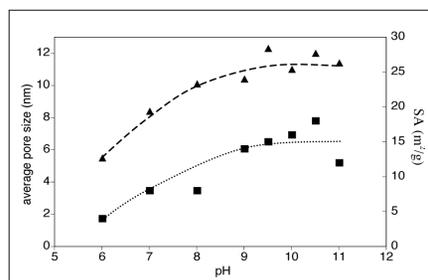


Figure 2. Dependence of average pore size ( $\blacktriangle$ , fresh samples) and surface area ( $\blacksquare$ , aged samples) against pH (surfactant ratio 1/0.25).

deterioration of the OSC (Wakita et al. 2007), due to the aging processes, is another critical property to evaluate. Figure 3 shows the dependence of OSC deterioration (% drop of OSC following thermal treatments) against pH; the graph assumes an inverse volcano plot profile with the best results obtained at pH 9.5.

The interaction time of the surfactant with the precipitate (1 or 4 hour) influenced in different way the ther-

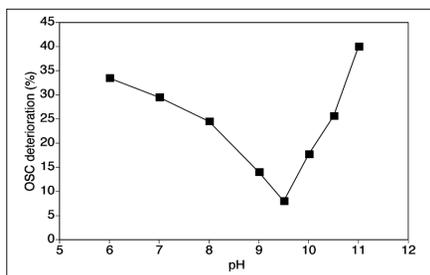


Figure 3. Deterioration of OSC due to thermal ageing.

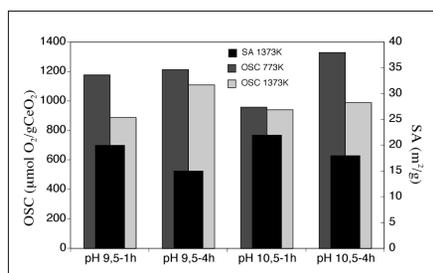


Figure 4. OSC properties and surface area of materials prepared with different interaction time with the templating agent.

mal stability and the OSC of the materials; indeed, lower interaction time affects positively the surface area (Figure 4), while higher times of interaction are correlated to a better

OSC. The best result was obtained for pH 10.5 with 1 hour of interaction being the surface area of the sample 22 m<sup>2</sup>/g and with almost no deterioration of OSC (2%).

**4. Conclusion.** In this work a modified co-precipitation route for ceria-zirconia based material with a high surface, high thermal stability and enhanced OSC properties has been developed.

While the reflux post-treatment slightly affects the properties of the samples, the pre-treatment with H<sub>2</sub>O<sub>2</sub> and the post-treatment with lauric acid improved dramatically the thermal stability after ageing up to 1373 K for 4 hours with a surface area of 22 m<sup>2</sup>/g against ca. 1-2 m<sup>2</sup>/g for the unmodified synthesis. Another important variable in order to achieve highly stable materials is the pH of precipitation; an increase of the pH affects the porosity of the materials, with important effects on stability and oxygen storage/release properties. In summary, it seems that modified co-precipitation with addition of surfactants and H<sub>2</sub>O<sub>2</sub> strongly promotes stability of these materials at high temperatures.

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