



## Effect of Preparation Methods on Structure, Redox Properties and CO Oxidation of $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$ Mixed Oxides

ZONG-LAN YAN\* and JUN SHI

Department of Basic Science, Tianjin Agricultural College, Tianjin 300384, P.R. China

\*Corresponding author: Tel: +86 131 94661382, E-mail: 251494227@qq.com

(Received: 28 January 2011;

Accepted: 3 November 2011)

AJC-10588

$\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxide was prepared by citrate sol-gel, decomposition of nitrate and coprecipitation methods. The effect of preparation methods on catalytic activity for CO has been investigated. The mixed oxide prepared by citrate sol-gel method has the best CO oxidation activity.

**Key Words:**  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxide, XRD, Raman,  $\text{H}_2$ -TPR, CO oxidation.

### INTRODUCTION

An oxygen-storage component is crucial for optimal performance of a three way and emission-control catalyst.  $\text{CeO}_2$  is present for the majority function in the three-way catalysts (TWC), because it has multiple effects on the catalyst state and performance. The primary function of  $\text{CeO}_2$  in the three-way catalysts is to provide oxygen-storage capacity (OSC), acting as an efficient oxygen buffer to undergo reduction/oxidation cycles by shifting between  $\text{CeO}_2$  under oxidizing conditions effective (oxygen storage) and  $\text{Ce}_2\text{O}_3$  under reducing conditions (oxygen release), respectively<sup>1</sup>. However the thermostability of pure ceria under high-temperature conditions is poor, because its oxygen storage capacity (OSC) decreases greatly<sup>2</sup>. Therefore, a great number of  $\text{CeO}_2$ -based mixed oxide systems<sup>3-7</sup> such as Ce-Zr-O, Ce-Th-O, Ce-Sn-O, Ce-Ti-O, Ce-Pr-O, etc. have been studied. Many studies have shown that the redox properties can be considerably enhanced if additional elements are introduced into the  $\text{CeO}_2$  lattice and solid solutions are formed. The present work is devoted to preparing  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxides by sol-gel, decomposition of nitrate and coprecipitation methods and to investigating their structure, reduction properties and catalytic activities for CO oxidation.

### EXPERIMENTAL

**Preparation of  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxide:**  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxides were prepared by citrate sol-gel method, decomposition of nitrate method<sup>8</sup> and coprecipitation method<sup>8</sup>. For citrate sol-gel method, an appreciate amount of citrate acid solid power was added to each pre-mixed nitrate solution of

cerium and praseodymium. The mixture was then vapourized under stirring, until it was slowly becoming transparent gel. The gel that was transparent and viscous was dried at 100 °C in an oven and obtained a solid. The solids were finally calcined at 500 °C for 4 h to obtain yellow powders.

**Characterization:** X-ray diffraction patterns were collected on a PHILIPS PW3040/60 powder diffractometer using  $\text{CuK}_\alpha$  radiation. The working voltage of the instrument was 40 kV and the current was 40 mA. The intensity data were collected at 25 °C over a  $2\theta$  range 20~100° with a scan rate of 0.1 °/s.

Raman spectra were obtained with a Renishaw RM1000 confocal microscope. The exciting wavelength was 633 nm from an He-Ne laser with a power of ca. 3 mw on the sample. The resolution is  $\pm 1 \text{ cm}^{-1}$ . In order to get the comparable data the samples were made to disk by pressing the power in a custom-made mold. The scanning rang was 1300-100  $\text{cm}^{-1}$ .

**Temperature programmed reduction:** The reduction properties of  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxides were measured by means of temperature-programmed reduction technique.  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2.8}$  mixed oxides (50 mg) were placed in a quartz reactor, which was connected to a conventional temperature-programmed reduction apparatus. The sample was reduced in a flow of  $\text{H}_2\text{-N}_2$  (5: 95) mixed gas at a heating rate of 20 °C/min up to 900 °C.

**Oxidation activity:** Catalytic activity measurements were carried out in a fixed bed reactor (6 mm i.d.) using 150 mg catalyst. The total flow rate of the feed gas was 80 mL/min. The gas consisted of 2.4 % CO and 1.2 %  $\text{O}_2$  in  $\text{N}_2$ . The analysis of  $\text{CO}_2$  and CO in the reactor effluent was performed on a gas chromatograph equipped with thermal conductivity detector.

The chromatographic columns were 13X molecular sieve and Propark Q.

## RESULTS AND DISCUSSION

**Effect of preparation methods on structure of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxides:** Fig. 1 shows the XRD patterns of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxides prepared by different methods. From Fig. 1 it can be seen that the structure of all samples is fluorite-like and the diffraction peaks are very close to each other. This is because the  $Ce^{4+}$  ionic radius (0.097 nm) is very similar to that of  $Pr^{4+}$  (0.096 nm). The diffraction peaks of the sample prepared by sol-gel method are stronger than the samples prepared by decomposition of nitrate method and coprecipitation method. It indicates that the sample prepared by sol-gel method is well crystallized. The diffraction peaks of sample prepared by decomposition of nitrate method have little difference with the sample prepared by coprecipitation method.

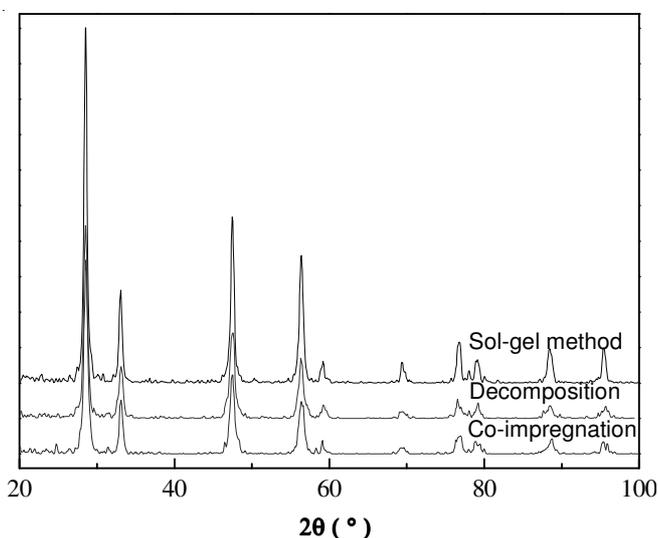


Fig. 1. XRD patterns of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods

Fig. 2 shows the Raman spectra of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods. From Fig. 2 it can be seen that there are two obvious bands at  $465\text{ cm}^{-1}$  and  $570\text{ cm}^{-1}$ . The sharp single band near  $465\text{ cm}^{-1}$  has  $F_{2g}$  symmetry and can be viewed as a symmetric breathing mode of the oxygen atoms around each cation. McBride *et al.*<sup>5</sup> pointed out that for  $Ce_{1-x}RE_xO_{2-y}$  sample, Raman peak near  $570\text{ cm}^{-1}$  are caused by oxygen vacancy in  $Ce_{1-x}RE_xO_{2-y}$  mixed oxides. For every two  $Ln^{3+}$  ion that replace two  $Ce^{4+}$  ion, one oxygen vacancy is needed to balance the charge. In the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide, the new Raman peak in the spectrum at  $580\text{ cm}^{-1}$  can also be attributed to oxygen vacancies.

For Raman spectra, the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by sol-gel method has the strongest peak intensity, especially for the band near  $570\text{ cm}^{-1}$ . The peak intensity of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by decomposition of method is a little larger than that of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by coprecipitation method. Combined with the XRD patterns in Fig. 1, it can be suggested that  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by sol-gel method can form the more perfect crystallite and

the oxygen vacancies arrange more orderly in the solid solutions.

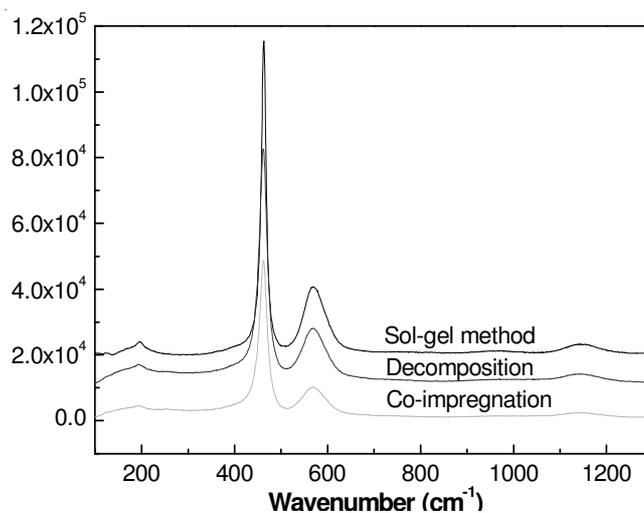


Fig. 2. Raman spectra of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods

**Effect of preparation methods on redox properties of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxides:** Fig. 3 shows the temperature-programmed reduction profiles of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods. From Fig. 3 it can be seen that, there are three obvious redox peaks in the measuring range. The low temperature redox peak in  $400\text{ }^{\circ}\text{C}$  to  $600\text{ }^{\circ}\text{C}$  is generally attributed to the reduction of the surface region and the peak at  $>860\text{ }^{\circ}\text{C}$  is ascribed to the reduction of the bulk.<sup>8</sup> The redox peak area of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by decomposition of method has little difference with that of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by coprecipitation method. The  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by sol-gel method has the smallest redox peak area. The redox temperature  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by decomposition of method is higher than that of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared with decomposition of method. But the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared with sol-gel method has the lowest redox temperature.

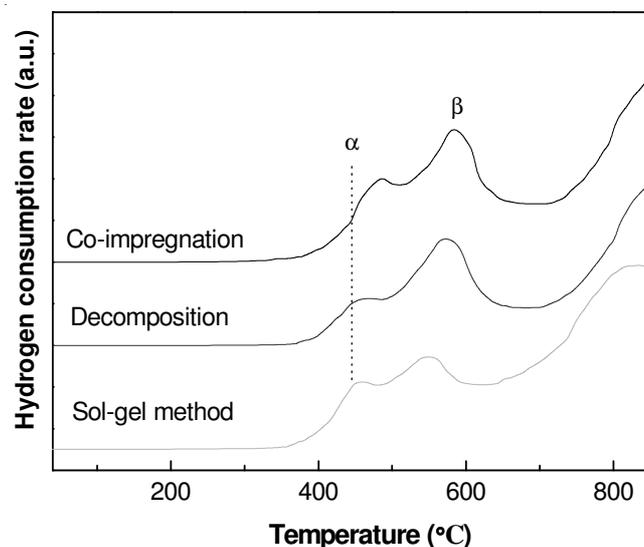


Fig. 3. Temperature-programmed reduction profiles of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods

**Effect of preparation methods on CO oxidation of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxides:** Fig. 4 shows the activity of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods for CO oxidation. From Fig. 4 it can be seen that the preparation method has great effect on the CO oxidation of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxides. The  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by sol-gel method has the highest CO oxidation. The CO oxidation of the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by decomposition of method is higher than  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  sample prepared by decomposition of method. Combined with XRD result in Fig. 1 and Raman result in Fig. 2, it can be pointed out that the CO oxidation has some relationship with the oxygen vacancies existing. The more oxygen vacancies in the  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide, the higher CO oxidation activity occurs. Combined with temperature-programmed reduction result in Fig. 3, it can be seen that the redox temperature is related to CO oxidation. Lower the redox temperature, higher is the CO oxidation activity. Moreover it has no obvious relationship with the redox peak area.

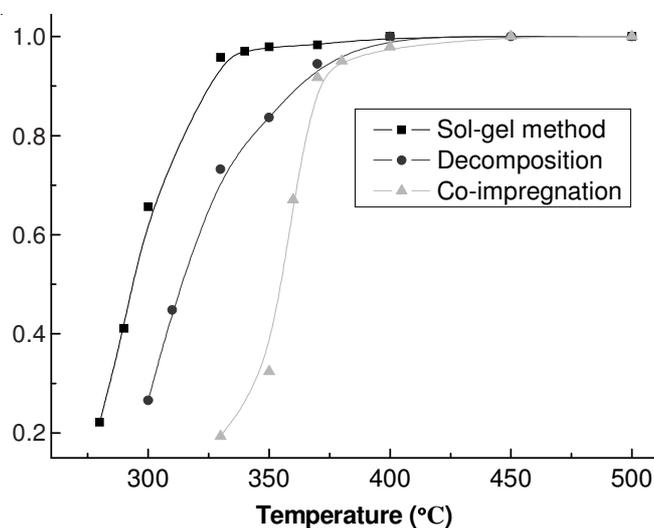


Fig. 4. Activity of  $Ce_{0.9}Pr_{0.1}O_{2-\delta}$  mixed oxide prepared by different methods for CO oxidation

## REFERENCES

1. W.-D. Wang, P.-Y. Lin, Y.-L. Fu and G.-Y. Cao, *Catal. Lett.*, **82**, 19 (2002).
2. J.E. Kubsh, J.S. Rieck and N.D. Spender, *Stud. Surf. Sci. Catal.*, **71**, 109 (1994).
3. A. Trovarelli, *Catal. Rev.-Sci. Eng.*, **38**, 439 (1996).
4. Y.-J. Zhong, R. Lin, M.-F. Luo and W.-P. Liu, *React. Kinet. Catal. Lett.*, **79**, 53 (2003).
5. J.R. McBride, K.C. Hass, B.D. Poindexter and W.H. Weber, *J. Appl. Phys.*, **76**, 2435 (1994).
6. R.K. Usman, G.W. Graham, W.L.H. Watkins and R.W. McCabe, *Catal. Lett.*, **30**, 53 (1995).
7. M.-F. Luo, Z.-L. Yan, L.-Y. Jin and M. He, *J. Phys. Chem. B*, **110**, 13068 (2006).
8. M.-F. Luo, R. Lin, M. Chen, X.-X. Yuan and X.-M. Zheng, *J. Rare Earths*, **18**, 35 (2000).