

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Background

Carbonmonoxide (CO) is the major one of the important pollutants present in the automotive exhaust. It is a by-product of combustion caused by incomplete combustion of hydrocarbons. It has a serious effect on human and animal nervous systems even in low concentrations (Tanielyan and Augustine, 1992).

A number of investigations have been carried out on three-way catalysts (TWC) technology in recent years. The development of the TWC was dictated by the need to simultaneously convert the CO, hydrocarbons (HCs) and NO<sub>x</sub> present in the automotive exhaust into CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. The conventional TWCs employed in the late 1980s mostly contain Rh and Pt as active noble metals and CeO<sub>2</sub> (Kašpar *et al.*, 1999).

CeO<sub>2</sub> is the most significant of the oxides of rare earth elements, which have has been widely investigated in catalysis as structural and electronic promoters to improve the activity, selectivity and thermal stability of the catalysts (Alessandro *et al.*, 1999).

There are many reasons to deposit a certain amount of ceria on the surface of TWC. Firstly, ceria is known to stabilize, on its surface, well-dispersed noble metals thus favouring the amount of active surface per weight of the catalyst. Secondly, ceria is supposed to promote water-gas shift and hydrocarbon reforming reactions that play a fundamental role in the elimination of CO and HCs in reduction conditions, as well as CO oxidation in oxidizing conditions. And last but not least, ceria presents an interesting ability to act as a store of oxygen due to its low reduction potential, thus

increasing the conversion of CO and HCs in reducing conditions and, particularly, the conversion of NO in oxidizing conditions (Kašpar *et al.*, 1999).

The role of CeO<sub>2</sub> as an efficient “oxygen buffer” is directly related to its capability to undergo effective reduction and re-oxidation under rich and lean conditions, respectively. By storing and releasing oxygen, CeO<sub>2</sub> keeps the reductant/oxidant ratio in the exhaust close to the stoichiometric value where the highest conversions of all the pollutants are attained. Moreover, transient but highly productive exhaust conversion was observed for reduced CeO<sub>2</sub> containing TWCs. All these factors point to the importance of the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox couple in improving the TWCs performances (Vidmar *et al.*, 1997).

The enhancement of oxygen storage and release is occurred, by shifting between CeO<sub>2</sub> under oxidizing conditions and Ce<sub>2</sub>O<sub>3</sub> under reducing conditions, respectively. Among these functions, high OSC of a TWC is an important property in vehicle application, since it allows one to enlarge the operating air/fuel (A/F) window, thereby making the catalyst less sensitive to small temporary variations of A/F. Furthermore, the oxygen vacancies associated with reduced ceria in the proximity of noble-metal particles have been suggested as promoting sites for CO conversion (Fornasiero *et al.*, 1995).

Recently, Fornasiero *et al.* (1995) reported that CO is effectively decomposed at the Ce<sup>3+</sup> sites in the Rh- and Pt-loaded Ce-containing materials, suggesting a direct participation of the reduced support in the CO conversion. It was also observed that upon incorporation of ZrO<sub>2</sub> into a solid solution with CeO<sub>2</sub>, the reducibility of the Ce<sup>4+</sup> is strongly enhanced compared to pure CeO<sub>2</sub> both in the unsupported and metal-loaded samples. As a matter of fact, in the presence of H<sub>2</sub>, a Rh/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> sample was reduced in the bulk at temperatures as low as 400°C. This suggest that such a system, when operating in a reducing environment such as the fuel-rich conditions, could

effectively decompose CO at the  $\text{Ce}^{3+}$  sites which results in an enhanced CO removal efficiency of the catalyst in the low-temperature regimes. CO decomposition occurred indeed at temperature as low as 200°C.

At the same time, ceria presents an important problem that prevents its use directly as a catalytic support in TWC converter because the significant conversions are attained only at high temperatures in the driving conditions. Enhanced catalytic activities at low temperatures are highly desirable. In order to minimize vehicle emissions during the cold start, the majority of vehicle applications utilize close-coupled catalyst locations. This results in extreme catalyst temperatures at high driving speeds. When the temperatures exceed about 900°C or above-that can be reached easily by the catalyst in normal operation-it has a tendency to deactivate the catalyst due to sintering and lose its porous structure. As soon as significant sintering of  $\text{CeO}_2$  particles occurs, both OSC and metal-support interactions appear inhibited because of the changes in the pore structure and the crystallite growth, and highly porous structure of the catalytic support is necessary for an adequate dispersion of the active phase (González-Velasco *et al.*, 1999).

The industrial research has spent significant efforts on finding the solution for improving the thermal stability both by modification of the  $\text{CeO}_2$  synthesis and by looking for different types of promoters and stabilizers. Doping with cations such as  $\text{Zr}^{4+}$ ,  $\text{Al}^{3+}$  or  $\text{Si}^{4+}$  may effectively improve the stability of the surface area of ceria at high temperature. Among different systems tested,  $\text{ZrO}_2$  appears to be the most effective thermal stabilizer of  $\text{CeO}_2$ , particularly when it forms a mixed oxide with ceria. Recently, a new generation of mixed oxides containing  $\text{CeO}_2$  and  $\text{ZrO}_2$  has been developed. In addition to enhanced redox properties, these mixed oxides exhibit good thermal resistance (Colón *et al.*, 1999).

## 2.2 Literature Review

According to the ceria content, the  $\text{CeO}_2\text{-ZrO}_2$  solid solutions exist in three different structures, namely monoclinic, tetragonal and cubic. Ozawa and Loong (1999) shown that the dimensions of the unit cell decreased linearly with decreasing the ceria content from 100 to 50 mol %. At the same time, from density measurements, a decrease in the number of atoms present in the cell was observed, which denotes the presence of structural defects. The bulk of the material was involved in the reduction-oxidation cycles, structural dependence of the OSC may be expected.

Several methods have been used to prepare the above mixed oxides, which are loaded with metal, such as precipitation or co-precipitation, impregnation, ion exchange and sol-gel technique.

In the early reports, the addition of  $\text{ZrO}_2$  to  $\text{CeO}_2$  is made in an uncontrolled way, mostly by impregnation, in which the mixed oxides is contacted with a solution which contains the metal to be deposited on the mixed oxides. A suspension is initially formed. This suspension is heated under continuous mixing in order to evaporate the solvent and to disperse the metal on the mixed oxides.

The next method is the ion exchange, which consists in exchanging either hydroxyl groups or protons from the support with cationic or anionic species in solution. In this method, it is important to adjust the pH in order to maximize the electronic interaction between the mixed oxides and the metal precursor. Knowledge of the isoelectric point is essential if meaningful dispersions are to be obtained.

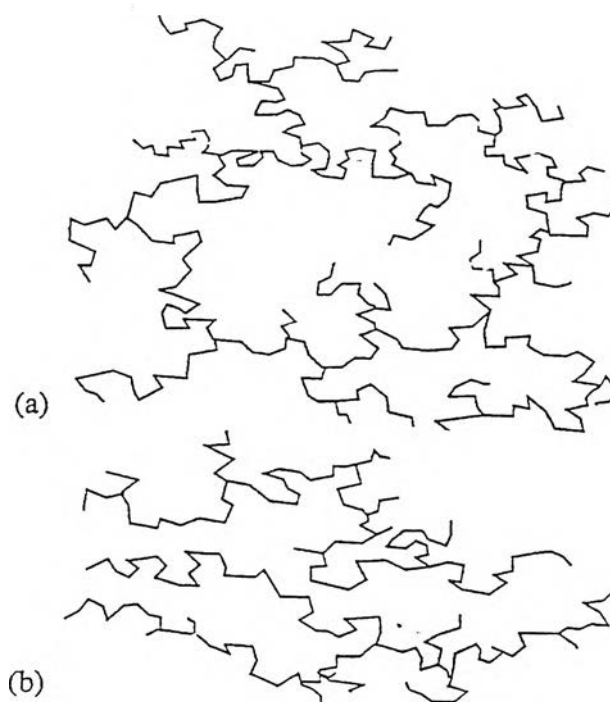
In the precipitation or co-precipitation method, one or more soluble salts, which contain the metal of interest, are neutralized through the addition of a base (usually ammonia) to form a precipitate or co-precipitate of the corresponding metal oxide gels.

Co-precipitation method has been used to prepare the CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution. The study of Daniela *et al.* (1998) aimed at developing doped-ceria catalysts with improved textural, structural and chemical properties for environmental applications. Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> and Ce<sub>0.80</sub>Zr<sub>0.20</sub>O<sub>2</sub> were prepared by reaction of a cationic surfactant (cetyltrimethylammonium bromide was used) with the hydrous mixed oxide produced by co-precipitation under basic conditions, which the cationic surfactants effectively incorporated into hydrous oxides of ceria and zirconia. The presence of cerium inhibited the action of alkyl-trimethyl-ammonium salts as true templating agents and there was no formation of a regular pore structure. The elimination of surfactants upon calcination gave rise to the formation of high surface area, fluorite-structured CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution characterized by a fairly good compositional homogeneity. Surfactants could be added to the pore liquid to reduce the interfacial energy and thereby decrease the surface tension of water contained in the pores. This reduced the shrinkage and collapse of the network during drying and calcination, which could help to maintain high surface areas.

Sol-gel techniques, which was chose to be a method to prepare the CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides in this thesis, have been recommended to be a interesting route to prepare the mixed oxide catalysts. The term of sol-gel describes the technique fairly accurately, with sol meaning a colloidal solution. A colloid is an intermediate state between being a solution and a suspension, in which the particles of the solute are large enough to scatter light, but to small to settle, generally in the range of between one and one thousand nanometers (Purcell, 1997). Also, the word of gel means a dispersion of a solid substance in a fluid medium that behaves like elastic solid or a semi-solid rather than a liquid. These techniques have several promising advantages over the above methods because they can “tailor make” catalysts to fit particular applications. Advantages include: (i) superior homogeneity

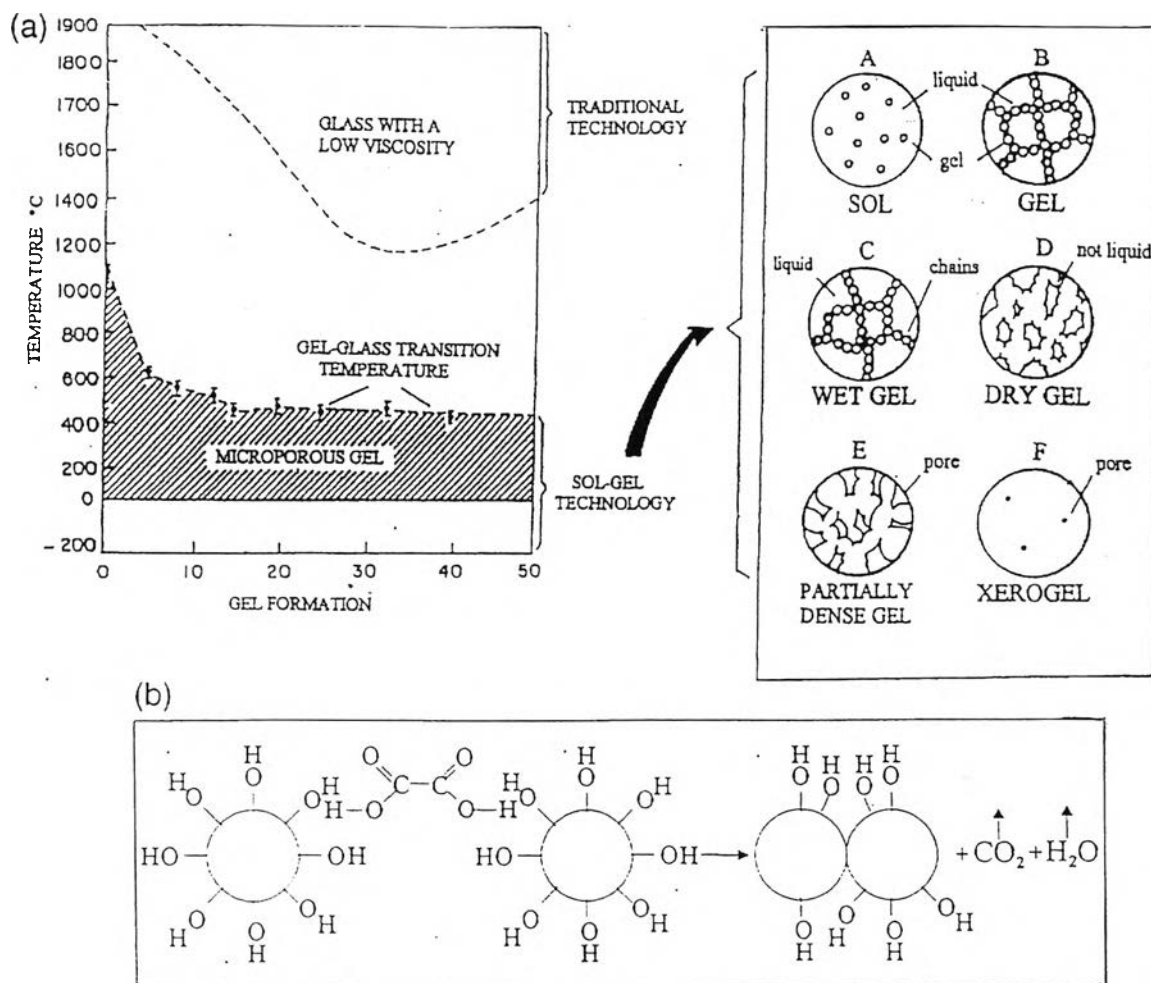
and purity; (ii) better microstructural control of metallic particles; (iii) higher BET surface area; (iv) improved thermal stability of the supported metals; (v) well-defined pore size distributions; (vi) the ease with which additional elements can be added; (vii) inorganic chain-structures can be generated in solution; and (viii) a finer degree of control over the hydroxylation of the support can be obtained. Moreover, the interestingly advantages of the sol-gel methods are the occurring of non-agglomerated, nanometer-sized particles (Cauqui and Rodriguez-Izquierdo, 1992).

In the sol-gel preparations, a metal alkoxide is used as the starting material. The alkoxide in an organic medium is first hydrolyzed by addition of water, follow by polymerization of the hydrolyzed alkoxide through



**Figure 2.1** Schematic diagram showing differences between gels of polymers with significant branching and cross-linking (a) vs. little branching and cross-linking (b) (adopted from Gonzalez *et al.*, 1997)

condensation of hydroxyl and/or alkoxy groups. When the extent of polymerization and cross-linking of polymeric molecules become extensive, the entire solution becomes rigid and a solid gel is formed. The size and the degree of branching of the inorganic polymer, and the extent of cross-linking have strong influence on porosity of this gel, and later, the surface area, pore volume, pore size distribution, and thermal stability of the final oxide after calcination. In general, if the gel contains polymeric chains with significant branching and cross-linking, the gel has large void regions, is structurally quite rigid, and the resulting oxide after calcination has mostly macropores and mesopores. If the gel contains polymeric chains with little branching and



**Figure 2.2** Gelation stage (a), densification (b) of the sol-gel (adopted from Gonzalez *et al.*, 1997)

cross-linking, the gel has smaller void regions, is structurally weak, and thus collapses readily upon calcination. The resulting oxide has mostly micropores and low surface area (Gonzalez *et al.*, 1997).

The inorganic salts are the other starting materials for the preparation of catalyst, which is prepared by the sol-gel methods. Cauqui and Rodriguez-Izquierdo (1992) proposed a method to prepare monodispersed colloidal particles of rare-earth oxides, particularly CeO<sub>2</sub>, starting from inorganic salts, such as chloride or nitrates by reaction with urea in aqueous media at 70°C. The pH, temperature and aging time were the factors controlling the particle size and the degree of homogeneity of the powders, which could be obtained in this way.

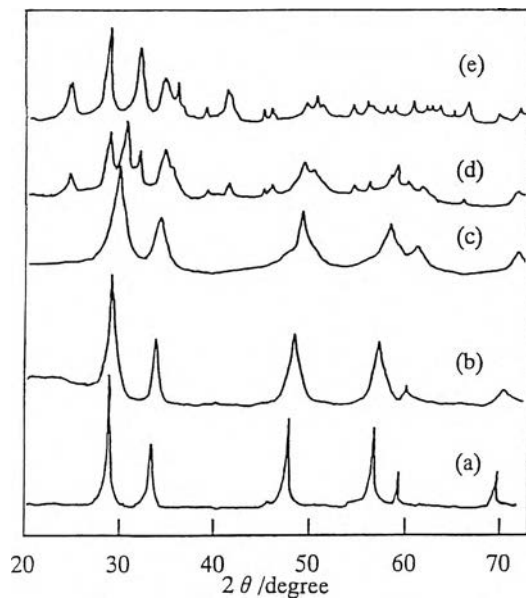
A preparation of mixed oxide catalysts by sol-gel technique is the interesting study. Meeyoo and Wright (1999) studied the preparation of Ce/Zr and Ce/Y mixed oxide catalysts, which were achieved via the hydrolysis of urea. The results indicated that the resultant particles were highly uniform and possess solid solution even at low preparation temperature (ca 100°C). It was found that urea concentration had an effect on the production yield. The suitable urea concentration for the hydrolysis of mixed metals salt solution was 0.4 M. Urea did not show a distinct effect on the production rate. On the other hand, the temperature had a pronounced influence on the production rate. The optimum temperature was reported at 100°C. The results indicated the evidence of precipitation as the reaction was carried out at temperature above 100°C. The products obtained at these temperatures were found to be rather heterogeneous.

In the recent years, there are many researchers who are interested in the oxygen-storage properties of ceria in three-way automotive catalysts, which were promoted and stabilized by mixing with zirconia. In the present study, this promotion was investigated by using model catalysts in which ceria films were vapor deposited onto  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> polycrystalline ZrO<sub>2</sub>. The results

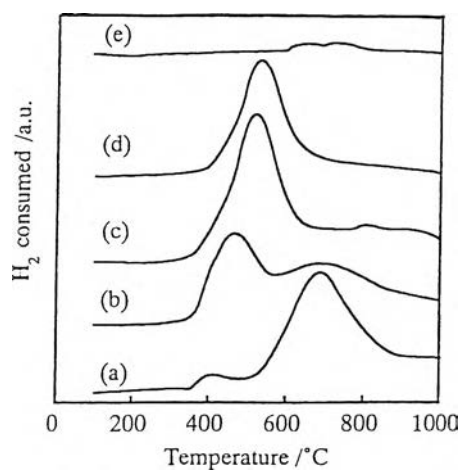


deposition of Pd, both TPD of CO and steady-state CO-oxidation kinetics suggested that the ceria films on the zirconia-based substrated were much more easily reduced than films on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. CO oxidation studies have shown that, following high-temperature calcination, ceria-zirconia model catalysts showed higher activities toward promotion of the ceria-mediated mechanism than did ceria samples. The enhanced activity and thermal stability of the ceria-zirconia samples appear to result primarily from structural modification of the ceria in contact with the zirconia (Putna *et al.*, 1999).

Otsuka *et al.* (1999) studied about a series of CeO<sub>2</sub>-ZrO<sub>2</sub> composite oxides (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>), which was characterized and tested for the gas-solid reaction with methane (CH<sub>4</sub>) in the absence of gaseous oxidant. Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> was prepared by a co-precipitation method. A sufficient amount of oxalic acid was added to a mixed aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub> and ZrOCl<sub>2</sub> under continuous stirring. After the sample was washed, the precipitate was dried at 100°C; the powder thus obtained was calcined at 800°C for 5 h in air. A solid solution with fluorite structure was formed for the samples with Zr content below 50 % ( $x \leq 0.5$ ). For Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> both desorption of O<sub>2</sub> and reduction by H<sub>2</sub> took place at lower temperatures as compared with that for CeO<sub>2</sub> alone. The conversion of CH<sub>4</sub> to H<sub>2</sub> and CO could be achieved at a temperature as low as 500°C by using Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> in the presence of Pt. Figure 2.3 shows the XRD patterns for Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> mixed oxides. Figure 2.4 and Table 2.1 show the TPR profiles and results obtained for Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> ( $x = 0, 0.2, 0.5, 0.8$  and  $1.0$ ) and the summary of TPR results, respectively.



**Figure 2.3** XRD patterns for  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  mixed oxides.  $\text{CeO}_2$  (a),  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  (b),  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (c),  $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$  (d) and  $\text{ZrO}_2$  (e) (adopted from Otsuka *et al.*, 1999)



**Figure 2.4**  $\text{H}_2$ -TPR profiles for  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  mixed oxides.  $\text{CeO}_2$  (a),  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  (b),  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (c),  $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$  (d) and  $\text{ZrO}_2$  (e) (adopted from Otsuka *et al.*, 1999)

**Table 2.1** Summary of H<sub>2</sub>-TPR profiles for Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> mixed oxides (adopted from Otsuka *et al.*, 1999)

Zr content (%)	Temperature (°C)		Degree of reduction (%)
	Peak I	Peak II	
0	410 (4)	690 (96)	14
20	470 (57)	700 (43)	14
50	517 (89)	802 (11)	13
80	528 (100)	-	7
100	-	-	1

<sup>a</sup>Values in parenthesis indicate proportion (in percentage)

Recently, there have been several researchers trying to study the CO oxidation on Pd/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts. Bekyarova *et al.* (1998) investigated the cooperative effect of CeO<sub>2</sub>-Pd on the kinetics of CO oxidation over Pd/CeO<sub>2</sub>-ZrO<sub>2</sub>. It was found that under reducing-to-moderately oxidizing conditions, a zero-order O<sub>2</sub> pressure dependence could be interpreted on the basis of a mechanism involving a reaction between CO adsorbed on Pd and surface oxygen from the support. They chose Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> as a support for Pd-based catalysts because among the solid solution contained 40-60 mol % of CeO<sub>2</sub> gave the highest degree of support reduction and the lowest reduction temperature. Pd was a metal of choice in the TWCs due to its ability to promote CO removal during a cold start of the engine. The Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> had a BET surface area of 70m<sup>2</sup>g<sup>-1</sup>. The N<sub>2</sub> adsorption isotherm at 77 K was of type IV with H3 hysteresis according to IUPAC classification, which was characteristic of a well-developed mesoporous texture. The Raman spectrum shown a strong peak centered around 475 cm<sup>-1</sup>, which was characteristic of a cubic fluorite phase. In summary, Pd-loaded Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> showed the important characteristics with respect to CO oxidation. They were an initial high surface area, a high OSC value, which was closely associated with the reduction behaviour of the support, a high degree of bulk reduction at low

temperatures, and a strong effect of the supported Pd on the redox behaviour, which was not deactivated by redox aging.

Another study of the redox behaviour and catalytic properties of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ -supported palladium catalysts, which used for CO oxidation, was performed by Luo and Zheng (1999). The  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  solid solution was prepared by evaporating an aqueous solution of the mixed metal nitrates containing an equivalent amount of citric acid to obtain a gel, followed by decomposition at  $950^\circ\text{C}$  for 4 h. Its BET surface area was  $11\text{ m}^2\text{g}^{-1}$ . The redox behaviour of these catalysts was investigated by using  $\text{H}_2$ -TPR and CO-TPR. The shape and temperature of TPR peaks depended on the nature of reducing agent. Two peaks were observed when  $\text{H}_2$  was used as reducing agent for the fresh catalyst, while three peaks were observed when CO was used as reducing agent. The presence of Pd improved the reduction of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  support, which was attributed to hydrogen spillover. The reduced catalyst was easily oxidized. After re-oxidation treatments, the PdO reduction process split into two peaks. On the basis of the catalytic activity and CO-TPR results, the activity of CO oxidation was related to the Pd hydroxide or/and finely dispersed PdO, which a maximum in activity enhancement was observed at a Pd concentration of 0.25%.

New Zirconia-Ceria materials were prepared by soft chemistry with thermal treatments at temperatures below  $1000^\circ\text{C}$ . For the preparation, cerium nitrate and different zirconia precursors were used: zirconyl nitrate or chloride for co-precipitation and zirconium propoxide for the modified sol-gel method. Both the structure and the texture of those solids depended on the procedure and the zirconium precursor. By this modified sol-gel method a new cubic phase,  $\text{Zr}_{0.25}\text{Ce}_{0.75}\text{O}_2$  with a surface area of  $60\text{ m}^2\text{g}^{-1}$  was obtained while an orthorhombic zirconia phase was identified for solids prepared either by co-precipitation or sol-gel methods. The sol-gel method was particularly efficient for preparation of Ce-Zr-O mixed oxides with high cerium contents. OSC

values were significantly higher than in the case of co-precipitated oxides. This work showed that general  $\text{ZrO}_2\text{-CeO}_2$  systems, with different structures, might be prepared using different zirconia precursors. The specific area of these materials was about  $50 \text{ m}^2\text{g}^{-1}$  and did not depend on the mode of the preparation and the ceria percentage. Preparation of materials by soft chemistry led to the synthesis of a stable phase at temperatures below  $1000^\circ\text{C}$ . The formation of an orthorhombic  $\text{ZrO}_2$  phase above  $300^\circ\text{C}$  and its transformation into a monoclinic phase at  $1000^\circ\text{C}$  was also observed. For  $\text{Zr}_{1-x}\text{Ce}_x\text{O}_2$  mixed oxides, the sol-gel method allowed the synthesis of a  $\text{Zr}_{0.25}\text{Ce}_{0.75}\text{O}_2$  stable phase, this solid solution was for cerium-rich mixed oxides appeared as good candidates for improving thermal stability and promoting OSC. Preparation of  $\text{CeO}_2\text{-ZrO}_2$  mixed oxides by soft chemistry represented a very promising method to obtain stable materials with high oxygen mobility (Rossignol *et al.*, 1999).

Other modifiers have been studied in 1997 by Vidmar *et al.* They carried out the experiment to determine the effect of trivalent dopants on the redox properties of  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  mixed oxide. The high surface area  $\text{Ce}_{0.6}\text{Zr}_{0.4-x}\text{M}_x\text{O}_{2-x/2}$  ( $\text{M} = \text{Y}^{3+}, \text{La}^{3+}, \text{Ga}^{3+}, x = 0.01\text{-}0.10$ ) was synthesized. The present investigation had identified an important role of trivalent dopants in improving the oxygen exchange at low temperatures in the  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  mixed oxide, compared to the undoped system. This effect was clearly shown in the sample subjected to extensive sintering induced by redox cycles. The addition of an appropriate trivalent cation affected the textural properties and, most importantly, it favored the homogeneity of the cubic phases. Use of citrates was indicated as an efficient route for an efficient cation insertion into the host  $\text{CeO}_2$  lattice.

The future trend of research on the role of mixed oxide catalyst would appear to offer most chances of improved the CO conversion during the oxidation reaction of CO.