



CHAPTER I INTRODUCTION

Pollution is one of the major problems for mankind nowadays. Since the second half of 1990s, stringent emission regulations, for example, EURO5, LEVII, and J-SULEV, have been introduced around the world to control pollution level. The development of more efficient catalysts for abatement of exhaust emissions is essential [Morikawa *et al.*, 2008].

Automotive three-way catalyst (TWC) is one of the mechanisms to control the pollution level. The development of the TWCs was dictated by the need to simultaneously convert the three main pollutants in the automotive exhaust, i.e., carbon monoxide (CO), hydrocarbons (HCs), and nitrogen oxides (NO_x) to CO₂, H₂O and NO₂, respectively. Highest conversion of the pollutants is attained close to the stoichiometric conditions, while excursions to fuel-rich (net reducing) or fuel-lean (net oxidizing) air-to-fuel (A/F) ratios severely decrease the efficiency of the TWCs. Such excursions may represent a serious limitation for a TWC since the A/F significantly oscillates around the stoichiometric value $A/F = 14.6$ [Talor, 1984].

Cerium oxide is widely used as a promoter for TWCs due to its good oxygen storage capacity (OSC), which is the ability of CeO₂ to maintain constant the oxygen partial pressure through the redox process. CeO₂ releases oxygen during rich conditions and is converted to Ce₂O₃. During lean conditions, Ce₂O₃ is oxidized back to CeO₂. This property of CeO₂ helps the catalyst to cope with the oscillations of the composition of the gas stream, and thus, the efficiency of the converter remains high. Beside its role as OSC, ceria also promotes water gas shift reaction and dispersion of precious metals as well as inhibits the sintering of alumina support [Trovarelli, 1996].

A major problem of the TWC converters is that significant conversions are attained only at high temperatures (>600 K). As a result, during the cold-start of the engine, the emissions of the pollutants, particularly the HC, are quite high until

the converter reaches the operating temperature.

Accordingly, inclusion of the cold-start in the engine test and the remarkably low limits required in the near future for the HC emissions demanded for the development of the close-coupled catalyst (CCC). This converter is mounted directly on the engine exhaust manifold, which exposes the catalyst to temperatures as high as 1373 K. Such high temperatures together with the required durability (over 120,000 miles) represent a strong challenge in the development of thermally stable catalytic materials. Sintering of the noble metal and deactivation of the OSC function due to CeO₂ particle growth have long been recognized as major TWC deactivation pathways [Talor, 1984].

The addition of zirconium and especially the formation of Ce-Zr mixed oxides have been found to be effective in preventing the ceria from sintering [Cuif *et al.*, 1997]. Moreover, the incorporation of ZrO₂ into the CeO₂ lattice has been found to strongly promote the reducibility of the mixed oxide [Fornasiero *et al.*, 1995].

Transition aluminas with high porosity and surface are widely used as catalyst support materials, especially in automotive catalytic converter [Valentini *et al.*, 2001 and Ozawa *et al.*, 1996] and high temperature catalytic fuel combustion applications [Thevenin *et al.*, 1994 and Liotta *et al.*, 1997]. Therefore, the usage of Ce-Zr mixed oxides as additives in alumina supported noble catalyst is of great technological importance.

The successful enhancement depends on the molecular homogeneity, surface area and textural/morphological properties, which are affected by the appropriate selection of precursor, preparation methods and the mixing composition. In generally, finely dispersed particles of CeO₂ can be obtained by calcination of Ce(NO₃)₃ impregnated on a support such as Al₂O₃, however, this creates an intimate contact between Al₂O₃ and the highly dispersed CeO₂ particles, facilitating the interaction between them. Upon aging, this easily leads to formation of CeAlO₃ that deactivates the OSC component [Miki *et al.*, 1988].

There are many different synthesis methods that have been applied to prepare

CeO₂-ZrO₂ and related mixed oxides, including conventional precipitation, high-energy ball milling, and sol-gel [Hori *et al.*, 1998]. The sol-gel process is a versatile technique, allowing control of the texture, composition, homogeneity, and structural properties of solids. The properties of the final products were found to be dependent on the temperature and the hydrolysis catalysts [Bokhimi *et al.*, 1998].

The surface areas of ceria-zirconia obtained by either conventional co-precipitation or sol-gel were typically in the range of 60-90 m²/g after calcination under air at 700-800 K [Leitenburg *et al.*, 1996].

The use of a templating technique for the synthesis of mesoporous solids has recently opened up new opportunities in the design of novel high surface area materials for catalytic applications. Much interest is being focused on the preparation of transition metal oxides using several templating pathways [Kresge *et al.*, 1992 and Huo *et al.*, 1994].

Several meso-structured surfactant-oxide composites have been synthesized by this approach, and a few of these composites showed a regular pore structure even after calcination while the majority suffered from collapse of the regular pore structure after calcinations [Huo *et al.*, 1994].

Zirconia is currently under extensive investigation in this area and several different approaches have been developed using cationic [Hudson and Knowles, 1996], anionic [Larsen *et al.*, 1996] or amphoteric routes [Kim *et al.*, 1997], to expand the range of surface areas achievable.

The uses of cationic surfactant as a template for ceria-zirconia mixed oxide preparation have been reported by many researchers, but none of the reports describes the use of an anionic surfactant as a template in these mixed oxide preparations, especially by the sol gel method.

A number of catalysts have been investigated in the past decades. Among them, supported noble metal catalysts have given promising results, because of their activity, good hydrothermal and resistance to impurities such as SO₂ [Obuchi *et al.*, 1993]. However, the employment of noble metal catalysts is limited due to their scarcity and

expensiveness, and the substitution by the cheap metals for the noble metals has attracted much interest recently [Parvulescu *et al.*, 1998].

Copper-contained catalysts show a potential activity for the treatment of exhaust gas from automobiles and have been extensively investigated during the past decades [Bocuzzi *et al.*, 1994]. Copper oxide has been demonstrated to be a very active species among the base-metal oxides as oxidation catalysts, in which the catalysts based upon CuO-Al₂O₃ oxides have been used in a variety of processes in chemical industry [Knozinger, 1976]. In addition, special attention has also been paid to this system as a substitute for noble metal containing catalysts in the automotive post-combustion recently [Lin *et al.*, 1995].

Due to the needs of high surface area, high catalytic activity and high thermal stability catalysts for using in the TWCs, this research work was performed with the following objectives:

- To obtain higher surface area and characterize the properties, including the reduction property, of CeO₂-ZrO₂ mixed oxides prepared by sol-gel process at ambient temperature, the influences of the composition, aging time and heat treatment on the texture, structure, reduction property and catalytic activity for CO oxidation of the samples were investigated and discussed.

- To synthesize a series of high-surface-area nanosized Cu-Ce-Zr catalysts by the sol-gel method at ambient temperature and tested for their catalytic activities for CO oxidation reaction. The copper species in the catalyst were distinguished, and the main active phase for CO oxidation was investigated.

- To study the effect of thermal stability enhancement of Ce-Zr solid solution using aluminum.