

CHAPTER I INTRODUCTION



Rare earth oxides have been widely investigated in catalysis as structural and electronic promoters in order to improve the activity, selectivity and thermal stability of catalysts. The most significant oxide of rare earth elements in industrial catalysis is certainly CeO_2 . Ceria has an important role in two of the most important commercial catalytic processes in terms of economic relevance and tonnage: three-way catalysis (TWC) and fluid catalytic cracking (FCC).

The importance of CeO_2 in catalysis is also demonstrated by the number of industrial and academic publications which have appeared on the topic over the last few years. It indicates that there are several emerging applications or processes for which cerium oxide is currently being actively investigated. Specifically, CeO_2 has potential uses for the removal of soot from diesel engine exhaust, for the removal of organics from wastewaters (catalytic wet oxidation), and as a promoter of catalysts in environmental clean-up and fuel cell technologies. In addition to these applications, much effort has been dedicated recently to study the role of ceria in well-established industrial processes such as FCC, TWCs, and ethylbenzene dehydrogenation, where CeO_2 is a key component in catalyst formulation.

A detailed analysis of publications in the year 1997 reveals that about 50 % of contributions dealt with the use of ceria-based compounds in the treatment of emissions from mobile and stationary sources, and the majority of articles dealt with the application of ceria in TWCs and novel technologies for the treatment of emissions from diesel and spark-ignited internal combustion engines (Alessandro *et al.*, 1999). This also explains the increase in the number of patent applications between 1984 and 1992, when more stringent environmental legislation came into force in all the industrialized countries. It was during this period that the CeO_2 -based MgAl_2O_4 spinel catalyst for SO_x removal and novel CeO_2 -based catalysts for auto-exhaust treatment were first developed.

As mentioned above, the main uses of ceria are in the depollution of noxious compounds from gaseous streams origination either from stationary or mobile sources. In these applications and related studies, CeO_2 is seldom used alone but it is often employed in combination with other oxides or in conjunction with active metals (generally noble metals) and thermally stable supports. Therefore, strictly speaking, ceria may function either as a structural/electronic promoter or as a co-catalyst, depending on the type of application, but not as a true catalyst, although the amount of cerium oxide which is used in certain catalyst formulations may easily exceed 20-30 wt%

The main reason why CeO_2 alone is of comparatively little interest as a support or catalyst is its textural stability, which is not high enough to meet the requirements of several gas-phase catalytic applications such as FCC and TWCs. The surface area of CeO_2 generally drops to a few square meters per gram at around 1000-1100 K, depending on preparation procedure and type of treatment, although a high degree of textural stability can be obtained by doping and modifying the preparation procedure. Another factor which discourages the use of pure ceria is its cost, which is higher than that of more common supports like Al_2O_3 and SiO_2 . Much effort has therefore been directed in recent years to finding catalyst formulations which can enhance the thermal stability of ceria without diminishing its special features, such as its redox/oxidation properties and its high oxygen mobility. The main catalyst formulations studied contain ceria spread over a thermally stable support or thoroughly mixed with other oxides in mixed-oxide formulations. In both cases, noble metals can be used to improve catalyst activity. Catalysts of this type are those currently used in the de-Sox process from FCC units and in the treatment of auto-exhaust.

In all commercial applications, stability of textural properties and resistance to sintering after aging play an important role. Several methods have recently been described for the preparation of CeO_2 for catalyst applications. These range from the high-temperature firing or high-energy milling, to conventional co-precipitation and sol-gel techniques.

Much effort has therefore been directed in recent years to find the way to enhance the thermal and texture stabilities: an example is to study the formulations of catalyst containing ceria spread over a thermally stable support or thoroughly mixed with other oxides in mixed-oxide formulations. Therefore strictly speaking, ceria may function either as a structural/electronic promoter or as a co-catalyst, depending on the type of application, but not as a true catalyst, although the amount of cerium oxide which is used in a certain catalyst formulation may easily exceed 20-30wt%

Some of the approaches that have been recently applied to prepare powdered cerium oxide are homogeneous precipitation technique with different precipitating agents and additives, hydrothermal synthesis, spray pyrolysis methods, inert gas condensation of Ce followed by oxidation, thermal decomposition of its carbonate, microemulsion, and electrochemical methods. In all these cases, cerium oxides with the surface area of not exceeding 100 m²/g at lowest calcination temperature (T<773K) were reported, and only in a few cases surface areas close to 200 m²/g were observed.

From that worthy knowledge, it brings up an idea to study how to improve the special features, such as its redox/oxidation properties and its high oxygen mobility. Key point is how to increase specific surface area with homogeneous distribution of pore size.

Sol-gel processing may be the answer of the above question. Many previous researches showed that this process influenced the microstructure, allowed homogeneous distribution of components, large pore volume, and increased of surface area. Furthermore, the product after sol-gel processing and sintering is easy to be prepared in different forms such as powder, monoliths, thin film and membranes.

Although much of the work done to characterize the sol-to-gel transition has used spectroscopic techniques, most of these techniques do not provide information about molecular weights. On the other hand, rheological measurements are sensitive to the structural and textural evolution of gels and are complementary to spectroscopic experiments.

Most of the rheological studies concern silica based sol-gel system. Furthermore these studies have been mainly limited to steady shear viscosity

measurements, which are not suited to monitor the development of the gelation process, since shear tends to break down the growing gel network. It is more useful to carry out rheological dynamic tests because the small deformation applied does not interfere with the gelation process. Therefore, focus has recently been placed on viscoelasticity as a direct probe of the change from liquid-like to solid-like behavior during the sol-to-gel transition. However only a few dynamic rheological measurement performed on transition metal oxo-polymer-based gels have been reported.

Knowledge of the evolution in rheological properties during sol-gel processing is a useful guide to the manufacturer when formulating dispersion to optimize the physical properties required in the final product. Thus, in this work, the objectives are to synthesize high surface area cubic form of cerium dioxide and to study the rheological properties of cerium glycolate complex synthesized directly from inexpensive and widely available cerium hydroxide and ethylene glycol via the Oxide One Pot Synthesis (OOPS) method. The influence of the acid concentration used in acid-catalyzed hydrolysis, the effect of calcination temperature on morphology, surface area and the mechanism of gelation process are also investigated.