CHAPTER II

LITERATURE REVIEW

Ceria, which is now used as a common additive in automotive exhaust control catalysts, has been studied, materially and continuously for its effectiveness in the last three decades. Many benefits of using ceria have been reported. In 1977, Gandhi et al. reported that base metal oxides were effective for *storing oxygen* and also enhanced the water-gas shift reaction for three-way catalysts(TWC). This was followed by several publications and patents on the beneficial effects of rare earth oxides during automotive catalytic processes.

Summers and Ausen (1979) showed an *increase in CO oxidation activity* by adding a small amount of ceria (0.6-1.3% Ce) to $Pt/CeO_2/Al_2O_3$ catalysts but the same trend could not be seen with higher ceria loading. Oh and Eickel (1988) also reported that an addition of ceria in sufficient amounts (not less than 2 %wt Ce) to the Rh/Al_2O_3 enhanced the CO oxidation activity by changing the reaction kinetics. This corresponds to the work of Nunan et al. (1992) who attributed the improvements in TWC performance to the Pt/Ce interaction.

Another function of ceria in the TWC is the *promotion of the water-gas shift reaction* which was studied by Harrison et al. (1988), Weibel et al. (1991) and Barbier and Duprez (1993).

In addition to the catalytic promoter to the CO oxidation and the WGS reaction, ceria is also believed to be the *structural promoter* for stabilization of precious metals and alumina against particle growth as reported by Harrison et al. (1988).

The other function of ceria is its ***ability to store and release oxygen*** during transients from rich(reducing) to lean(oxidizing) environments. Yao and Yu Yao (1984) published a classical paper on the oxygen storage capacities of catalysts. The catalyst containing ceria was found to give up as high as 25% of the oxygen atoms during temperature-programmed reduction (TPR) at 900 °C. They also performed chemisorption at 0 °C and 500 °C on the catalysts as a function of ceria loading. A phase change of CeO_2 as the loading increased was found. The catalyst OSC was estimated by a pulse injection method and it was found that the OSC was decreased with increasing pretreatment temperature, and increased with pulsing temperature. However, the dependence of the OSC on the ceria loading was not reported.

Metcalfe and Sundaresan (1986) confirmed the migration of the oxygen in the catalyst by electrochemical technique. The charge transfer reactions were studied at a three-phase interface between platinum, yttria-stabilized zirconia(YSZ) and the gas phase. From the study, the electron transfer at the interphase between platinum and support was present. The charge transfer reactions were proved as the cause of an enhancement in the CO oxidation rate under cyclic operation while the total rate of CO oxidation was almost negligible in the steady-state condition.

Cho (1991), who studied the transient catalytic activity of nitric oxide reduction by carbon monoxide, indicated that an increase in catalytic activity of gadolinia-modified ceria was attributable to the oxygen storage and transport characteristics.

Hepburn and Gandhi (1992) went further in identifying the source of oxygen. They related the catalyst hydrocarbon conversion efficiency to its oxygen storage capacity. After a short aging time, the catalyst lost greatly in its oxygen storage capacity but the hydrocarbon conversion efficiency was still high. It appeared as if most of the usable oxygen storage was derived from the precious metals and surface of ceria, therefore, the breaking of ceria-noble metal interaction by aging reduced the OSC but the metal was still active for hydrocarbon conversion. The TPR also showed that the usable oxygen storage was from surface ceria which was interacting with precious metals because the surface peak disappeared after catalyst aging.

The mixed oxides between ceria and other rare earth oxides were investigated by some authurs who believed that the oxygen atoms were from bulk, Logan and Shelef (1994) who studied mixed cerium/ praseodymium oxides. The uptake and release of the oxygen was studied by temperature-programmed desorption(TPD), TPR and temperature-programmed oxidation (TPO). Amount of oxygen given off by the mixed oxide was higher than that of the pure ceria. An addition of the second rare earth oxide was believed to induce the oxygen vacancies in bulk which accelerated the movement of oxygen atoms through the lattice. Fornasiero et al. (1995) incorporated the ZrO_2 into a solid solution with CeO_2. The TPR indicated that the OSC of Rh-loaded solid solution was higher than Rh/CeO_2 sample. This OSC enhancement was explained in light of bulk structural dependence.

It can be seen from the last two paragraphs that the mechanism of the migration of the oxygen atoms is still being debated although the benefits of ceria are reported unanimously for many years.