

CHAPTER II

LITERATURE REVIEW

Although automotive exhaust catalysts are widely used for the reduction of emission levels, there is still a great deal of room for further improvement [7]. The elimination of hydrocarbons which represent in the automotive exhaust gases is raised up to be researched several times. They are eliminated by metal catalysts containing Pt, Pd, and Rh as active component. Some of these studies in this subject are summarized below.

Obuchi et al. [8] investigated the performances of platinum-group metals, platinum (Pt), palladium (Pd), rhodium (Rh) and ruthenium (Ru) supported on γ -alumina as catalyst for the selective reduction of nitrogen oxides by hydrocarbons. They reported that platinum and rhodium had high nitric oxide conversion activities both in model mixtures and in real diesel exhaust gases, especially at relatively low temperature between 200 and 350 °C. It was confirmed that the Pt-Rh and Pt catalysts had higher activity than the others catalyst. The Pt containing catalysts, however, produced more nitrous oxide than nitrogen.

Bart et al. [5] studied the reactions of saturated alkanes, olefins, acetylenes, aromatics, alcohols or various other oxygenated compounds in steady state condition with synthetic exhaust gases near stoichiometry by Pt-Rh and Pt catalysts. In a series of measurements, conversion rates were

determined as a function of temperature at stoichiometry. NO and mainly O₂ were shown to have a negative effect on the first terms of saturated alkane (C₁ to C₃) conversion under lean conditions. Water vapor had a positive effect in rich conditions (without SO₂), but was more pronounced for Pt-Rh than for a Pt catalyst. The role played by SO₂ in hydrocarbon conversion was evaluated. Its action was sometimes positive, i.e. for saturated alkanes with up to 3 carbon atoms, but more often negative, i.e. in stoichiometric and lean conditions for acetylene and for hydrocarbons which oxidation started below 200 °C (olefins, aromatics and alkanes with more than 3 carbon atoms), and in rich conditions for all kind of hydrocarbons.

Skoglundh et al. [3] had investigated the effects of hydrothermal treatment, compared with thermal treatment, of alumina substrate for Pt-Pd catalysts. Metals deposition on hydrothermally treated alumina yield a higher activity for the complete oxidation of xylene, propene and CO than those (of same concentration) deposited on thermally treated alumina.

Zhang et al. [9] studied the selective reduction of nitric oxide over platinum catalysts supported on different type of supports such as aluminium phosphate (AlPO₄), and BSA (B₂O₃-SiO₂-Al₂O₃) in the presence of sulfur dioxide and excess oxygen. The reaction results at steady-state conditions showed that the only by-product was N₂O which was formed for all the metal catalysts employed. While the effect of oxygen on the NO_x conversion and N₂O selectivity of these catalysts were shown that oxygen concentration less than 2% facilitated the reaction to a great extent but a large excess oxygen gradually inhibited the reaction.

Marecot et al. [1] investigated the oxidation of propane and propene on palladium and platinum supported catalyst. Catalyst intrinsic activities, evaluated by light-off temperatures in slightly oxidizing reactant mixture (5% excess oxygen), showed an optimum particle size which maximized the catalytic activity for a given metal loading. On catalyst prepared from chloride containing precursor salts, chloride poisoned the metallic activity at any particle size. Moreover, reaction isotherms under varying oxygen levels pointed out that the effect of chloride was more detrimental under oxidizing conditions.

Volter et al. [10] studied the catalytic combustion of n-heptane over Pt/Al₂O₃ and demonstrated that the catalytic activity was not effected by a large decrease in the dispersion. As a result, calcination of the sample between 500 and 900 °C did not decrease the activity, although dispersion was dramatically diminished. Addition of chloride mainly deactivated dispersed samples. The catalyst was more active in air than in oxygen. Under certain conditions a pronounced oscillatory behavior of the oxidation was observed. The results could be explained that the state of Pt alternated between less active oxidized Pt and highly active metallic Pt.

Barbier et al. [11] studied the reduced Pt/Al₂O₃ catalyst with different chloride contents and treated at different temperature under oxygen flow and showed that at low Cl/Pt atomic ratio (≤ 1) PtO₂ was formed at low temperature (400-500 K) and was totally decomposed (900 K) yielding reduced metallic Pt and inducing metal sintering. At high Cl/Pt atomic ratio (≥ 6) formation of stable (up to 1000 K) platinum oxichloride avoided metal sintering.

Briot et al. [12] studied reaction of Pt/Al₂O₃ catalyst in methane-oxygen-nitrogen mixture at 873 K with an oxygen to methane ratio of 4. The metal particle size increased from 2 to 12 nm. The catalytic activity for methane oxidation was slightly increased for reaction temperature below 700 K and not modified at higher temperature. As a consequence, the turnover number (i.e. the activity per surface platinum atom) was much higher on the large platinum particles.

Burch et al. [13] investigated the catalyst activity of Pt/Al₂O₃ and Pd/Al₂O₃ prepared from chlorine-free precursors for the combustion of methane under lean, stoichiometric and rich condition using dilute mixtures. It had been found that, under lean conditions and at low conversions under stoichiometric or rich conditions, Pd/Al₂O₃ was a more effective catalyst. However, at higher conversions with stoichiometric or rich mixtures, Pt/Al₂O₃ was a more active catalyst. This change over between Pd/Al₂O₃ and Pt/Al₂O₃ was associated with a "light-off" effect observed with Pt/Al₂O₃ catalysts. The possible inhibition of activity by chlorine used in many catalyst preparations might also be the cause of the above observation. It was concluded that platinum could be a more effective catalyst than palladium for methane combustion under real conditions and that Pt might play an important role in multimetallic catalyst for emission control for natural gas vehicles.

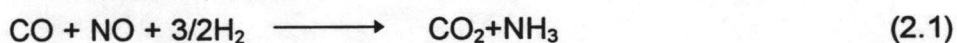
Svoronos et al. [14] had characterized a series of platinum catalyst supported on γ -alumina, prepared by using a wet impregnation procedure, by steady-state CO-NO reaction test. The impregnation pH was the crucial variable in the generation of five catalysts of 0.75-0.87% Pt load. The

impregnant pH showed a clear impact on catalytic performance. The catalyst prepared under acidic conditions demonstrated a higher catalytic activity than those prepared under basic conditions.

Ishikawa et al. [7] studied the effect of the acidic property of support materials, using a series of single metal oxide, mixed oxides and SO_4^{2-} -doped oxides as the support materials, on the activity of Pt catalyst in the low-temperature catalytic combustion of propane. It was revealed that the catalytic activity strongly depended on the acidic property of the support materials: the activity was higher on the support having strong acidity. SO_4^{2-} -doped oxides, known as solid superacids, were superior support material giving high activity at low temperature.

Dumpelmann et al. [4] investigated the effect of adding hydrogen to a reaction mixture of NO and CO over platinum and palladium catalyst on the conversion of NO and CO. Hydrogen caused large increase in the conversion of NO and, surprisingly, also of CO. Oxygen atoms from the additional NO conversion were eventually combined with CO to give CO_2 rather than reacted with hydrogen to form water.

This reaction was described by equation



and accounts for 50-100% of the CO_2 formed with $\text{Pt}/\text{Al}_2\text{O}_3$ and 20-50% with $\text{Pd}/\text{Al}_2\text{O}_3$.

Wu et al. [15] investigated a new three-way catalyst (TWC) system consisting of a palladium (Pd) catalyst as the inlet half and a standard platinum (Pt) and rhodium (Rh) TWC as the outlet half. This Pd/TWC system offered the improvement of thermal resistance, light-off performance,

and reduction in precious metal cost compared to an equal volume standard TWC. However, several open issues, such as the cost of manufacturing a two-part catalyst system, the poison resistance, and vehicle durability, remained to be resolved. The study of the Pd/TWC system was based on the concept that activity of the outlet portion of a catalyst could be protected from thermal damage by the inlet portion as long as the inlet remains active. To prove this, a series of catalyst systems with different formulations for the inlet and outlet halves were studied using engine dynamometers. The performances of these catalyst systems were evaluated and compared during and after an emission durability cycle, with and without the imposition of 601-min long, 2000 °F episodes with excess air to simulate severe thermal environments experienced in some vehicles.

Yu-Yao et al. [16] studied the thermal transport from bulk phase to the dispersed phase by using a simple model system. The described result clearly showed that in air the precious metals could be thermally transported from the bulk metallic phase to the Al_2O_3 surface at the temperatures studied. The presence of CeO_2 greatly enhanced the transfer from the bulk Pt and Rh to the support surface, but had much less effect in the case of Pd. The Pt catalysts prepared by this method were comparable in activity to those of similar concentration prepared by the impregnation method. It was also shown that thermal transport took place between different supports which might cause dynamic redistribution of the noble metals between these supports when used as catalyst in oxidizing conditions at high temperature.

Barbier Jr. et al. [17] investigated the catalytic behavior of Pt (1%wt.), Rh (0.2 %wt.) and Pt (1 %) Rh (0.2 %) catalysts supported on Al_2O_3 and on 12

%wt. $\text{CeO}_2/\text{Al}_2\text{O}_3$ in steam and oxygen/steam conversion of carbon monoxide and of propane. The reactions were carried out in oxygen-deficient medium, under isothermal or temperature-programmed reaction (TPR) conditions. Light-off temperatures as well as turnover number frequency (N_t) deduced from the low-conversion branch of the TPR curves were used to evaluate the catalytic activities. In oxygen/steam conversion of carbon monoxide, the relative N_t values were:

$$\text{Pt-CeO}_2/\text{Al}_2\text{O}_3, 2500 > \text{Pt}/\text{Al}_2\text{O}_3, 240 > \text{Rh-CeO}_2/\text{Al}_2\text{O}_3, 75 > \text{Rh}/\text{Al}_2\text{O}_3, 1$$

for carbon monoxide oxidation at 100 °C and

$$\text{Pt-CeO}_2/\text{Al}_2\text{O}_3, 43500 > \text{Rh-CeO}_2/\text{Al}_2\text{O}_3, 100 > \text{Pt}/\text{Al}_2\text{O}_3, 75 > \text{Rh}/\text{Al}_2\text{O}_3, 1$$

for the water-gas shift at 200 °C. This reaction, on Al_2O_3 and to lesser extent on $\text{CeO}_2/\text{Al}_2\text{O}_3$, was inhibited by oxygen, the water-gas shift activities being one to three orders of magnitude higher in the $\text{CO}+\text{H}_2\text{O}$ mixture. In oxygen/steam conversion of propene, the relative N_t values were:

$$\text{Pt}/\text{Al}_2\text{O}_3, 76 > \text{Pt-Rh}/\text{Al}_2\text{O}_3, 5.4 > \text{Pt-CeO}_2/\text{Al}_2\text{O}_3, 3.6 > \text{Rh-CeO}_2/\text{Al}_2\text{O}_3, 1.8 > \\ \text{Rh}/\text{Al}_2\text{O}_3, 1 > \text{Pt-Rh-CeO}_2/\text{Al}_2\text{O}_3, 0.8$$

for propane oxidation at 300 °C while the activity order was:

$$\text{Pt-Rh-CeO}_2/\text{Al}_2\text{O}_3 > \text{Pt-Rh}/\text{Al}_2\text{O}_3 > \text{Rh-CeO}_2/\text{Al}_2\text{O}_3 > \text{Pt}/\text{Al}_2\text{O}_3 > \text{Rh}/\text{Al}_2\text{O}_3$$

for the propane steam reforming at 400 °C. This reaction started when oxygen was consumed and was inhibited by carbon monoxide, while explaining why there was a definite cooperation effect between $\text{Rh-CeO}_2/\text{Al}_2\text{O}_3$ intrinsically active in steam reforming and platinum active in oxidation and in the water-gas shift.

Byong K. Cho. [18] investigated the performance of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst for the removal of CO, NO, and hydrocarbons in engine exhaust using a fixed-

bed reactor connected to a dynamometer-mounted engine. The effect of air/fuel ratio oscillation on the catalyst performance was examined over a wide temperature range. Results showed good activity of fresh $\text{Pt/Al}_2\text{O}_3$ catalysts for the oxidation of CO and hydrocarbons as well as for the reduction of NO, when the feed composition oscillated symmetrically at 0.1 Hz around a time-average stoichiometric point which yielded higher conversions for all three pollutants than steady feed operation, whereas this trend reverse above the reaction light-off temperatures. The presence of excess O_2 above the stoichiometric amount in engine exhaust lowered considerably the reaction light-off temperatures for the oxidation of CO and hydrocarbons but severely suppressed the NO reduction activity of $\text{Pt/Al}_2\text{O}_3$.

Pannee A. [19] prepared the modified three-way catalyst composed with Pt-Rh as active component and cerium (Ce) as promoter for removal CO, NO and C_3H_8 . It was found that the catalyst contained 9 wt%Ce at constant ratio of Pt/Rh equal 3/1 in the catalyst showed the highest activity of CO, NO and C_3H_8 conversion. In addition, the pretreatment of modified three-way catalyst in simulated exhaust gases under rich gas composition enhanced activity for control of all three pollutants. '

The above studies show that $\text{Pt/Al}_2\text{O}_3$ has high activity in the oxidation of CO and hydrocarbons as well as for the reduction of NO. Furthermore, its activity for removal exhaust gas can be effected by several factors. Marecot et al.[1] showed the negative effect of chloride on the catalyst prepared from chloride containing precursor salts. Chloride poisoned the metallic activity whatever the catalyst particle size for the oxidation of propane and propene. Whereas, Barbier et al. [11] proposed the beneficial

effect of chloride on the prepared catalyst at high Cl/Pt atomic ratio (≥ 6). The formation of stable (up to 1000 K) platinum oxichloride avoided metal sintering. Besides, Pannee A. [19] proposed that the pretreatment of modified three-way catalyst in simulated exhaust gases under rich condition enhanced activity for removal CO, C₃H₈ and NO. As a result, the purpose of this study is involved with these effects on the catalytic performances of Pt/Al₂O₃ for the elimination of CO, C₃H₈ and NO.