

## CHAPTER II

### LITERATURE REVIEW

Catalyst technology, which has played a key role in significantly reducing emission from motor vehicles over the past 15 years, will continue to advance and will help meet the emission clean-up challenges of the 1990s and beyond. Two types of catalyst have been used. Oxidation catalysts convert unburnt hydrocarbons and carbon monoxide to carbon dioxide and water, while three-way catalysts, in addition, convert oxides of nitrogen to nitrogen and oxygen [5].

Vehicles equipped with three-way catalysts have been shown to meet emission standards with minimal loss of fuel economy and driveability. Because of their widespread application, improvements in three-way catalysts would be desirable. A large number of studies on three-way catalyst system has been made and summarized below.

US. Patent 3,881,696 [6] Lepeyre *et al.* studied decreasing the pollutants in automobile exhaust gases. There was provided a catalyst containing a ceramic carrier such as alumina combined with manganese oxide and/or chromium oxide, and impregnated thereon a mixture of platinum and a metal oxide such as nickel, cobalt or iron oxides. An aluminum salt was preferably impregnated into the ceramic carrier, and then calcined to form an aluminum oxide layer, this step being conducted prior to the introduction of platinum. They found that the efficiency of the oxides of the metals of group Ni, Fe, Co in the catalyst, more particularly for eliminating nitrogen oxides increases in the following order: Co>Fe>Ni, consequently. Furthermore, they suggested that the catalytic efficiency of Mn is higher than that of Cr.

US. Patent 4,048,098 [7] Edgar and Eduard claimed a carrier catalyst comprising the catalytically active component of at least three metals, wherein at least one of three metals was selected from the group consisting of (a) ruthenium, rhodium, palladium and

platinum, and wherein at least one of three metals was a base metal selected from the group consisting of (b) aluminum, titanium, chromium, manganese, cobalt and nickel, and further wherein group (a) metals and group (b) metals are in an atomic ratio of about 1:4 to 1:1, provided that, when system contains platinum, rhodium and at least one of base metals, the atomic ratio is 1:4 to 1:2.4. They found that these catalysts could eliminated CO and C<sub>3</sub>H<sub>6</sub> under air/fuel ratio greater than 14.6 and eliminated NO under air/fuel ratio less than 14.6. Furthermore, they reported that the activity of catalysis aged for 24 hours at an 800°C gas temperature in an exhaust gas stream decreases about 10 percent.

US. Patent 4,440,874 [8] Charies and Thomson claimed a catalyst composition well suited for oxidation, reduction and oxidation reactions comprises a platinum group metal component, an oxide composite, and a refractory metal oxide support. The oxide composite comprises at least one member selected from a first group consisting of iron, cobalt and nickel plus at least one member selected from a second group consisting of alkaline earth metals, aluminum and titanium, with the metals of oxide composite present in proportions such that the atomic ratio of the total of the member or members of said first group to the member or members of said second group is from 1:1 to 10:1. The catalysts were used for the purification of gases, including internal combustion engine exhaust gas at 400°C under stoichiometric condition. They found that additional of iron to catalysts showed highest activity for elimination CO, HC and NO.

US. Patent 4,808,394 [9] Kolt and Kukes claimed a catalyst comprising alumina and Pt and/or Pd. The catalyst was prepared by a process comprising the steps of impregnating an alumina-containing support material with a solution of a thiocyanate compound (preferably NH<sub>4</sub>SCN), drying the thus impregnated material, contacting the dried material with solution of at least one compound of Pt and/or Pd, drying and calcining the Pt and/or Pd impregnated material, and heating it in a reducing gas, preferably free hydrogen at a temperature of about 550-700°C. They founded that the

addition of Co and Mn to Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was detrimental to the CO oxidation activity of this catalyst, whereas the addition of Fe improved the CO oxidation activity of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

US. Patent 5,179,059 [10] Rainer *et al.* improved light-off behavior and durability of a catalyst for purifying the exhaust gases of internal combustion engines by using reduced specific noble-metal content. This was carried by using active aluminum oxide provided with customary promoters as carrier and platinum and/or palladium and rhodium in customary amounts as noble metals. Furthermore, the catalysts were contained at least one base metal selected from the series of lithium, potassium, rubidium, magnesium, calcium, barium, lanthanum, cerium, praseodymium, neodymium, samarium, iron, cobalt and nickel in an amount of up to 5 times the total mass of the noble metal. They claimed that additional of base metal K, Ba and Fe into Pt, Pd, Rh three way catalysts showed the lowest light-off temperature for CO and HC were 168°C, respectively.

Volter *et al.* [11] studied the catalytic combustion of n-heptane over Pt/Al<sub>2</sub>O<sub>3</sub> and demonstrated that the catalytic activity was not affected 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.

Sasaki and Hamada [12] studied the role of coexisting oxygen in the selective reduction of nitrogen monoxide by propane on H-zeolites, alumina, Cu-ZSM-5 zeolite and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. In the case of H-zeolites and alumina, oxidation of NO to NO<sub>2</sub> played an important role for the overall selective reduction of NO. On the other hand,

the initial reaction step was considered to be partial oxidation of propane over Cu-ZSM-5 and Pt/Al<sub>2</sub>O<sub>3</sub>.

Thawatchai Majitnapanul [13] studied the development of supported copper catalysts for carbon monoxide removal. It was found that development of copper catalyst could be made by using platinum as a promoter. It appeared that separative impregnation of 0.3 wt.% platinum prior to 8 wt.% copper on alumina support and subsequent calcination at 500°C for 7 hours under a reducing atmosphere gave the highest catalyst activity. The synergistic effect of the catalyst was due to the formation of alloy between platinum and copper. In this way, phenomena that are similar to the SMSI phenomena and the augmentation of copper active sites were induced. Additionally, it was found that the strength of carbon dioxide adsorption played an important role on the catalytic activity of the catalyst.

Obuchi [14] investigated the performances of platinum-group metals, platinum, iridium, rhodium and ruthenium supported on  $\gamma$ -alumina, as catalysts for the selective reduction of nitrogen oxides by hydrocarbons. Platinum and rhodium had high nitric oxide conversion activities both in model mixtures and in real diesel exhaust gases, especially at relatively low temperatures between 200 and 350°C. It was confirmed that the platinum-rhodium and platinum catalysts have higher activity and durability than a catalyst composed of copper supported on ZSM-5 under real diesel exhaust conditions. The platinum containing catalysts, however, produced more nitrous oxide than nitrogen. It is expected that platinum group metal catalysts will be able to be used for practical purposes if once their selectivity toward nitrogen is improved.

Marecot *et al.* [15] investigated the oxidation of propane and propene on palladium and platinum supported catalysts. Catalyst intrinsic activities, evaluated by light-off temperatures in slightly oxidizing reactant mixture (5% excess oxygen), show an optimum particle size which maximizes the catalytic activity for a given metal loading.

For catalysts prepared from chloride containing precursor salts, chloride poisoned the metallic activity whatever the particle size. Moreover, reaction isotherms under varying oxygen levels pointed out that the effect of chloride was more detrimental under oxidizing conditions. After successive oxidation cycles, this poisoning effect disappeared as a consequence of the removal of chloride from the catalyst surface by water produced during propane and propene combustion. On the other hand, addition of relatively large quantities of water (equivalent to the content of the exhaust gas) inhibits the oxidation of hydrocarbon. Poisoning effects of chloride and water are explained by a decreasing active surface for the reactions under consideration.

Marecot *et al.* [16] studied the effect of the preparation procedure on the properties of three-way automotive platinum-rhodium/alumina-ceria catalysts. They found that after high-temperature aging, bimetallic co-impregnated catalysts were far less active than sequential impregnated catalysts for propane oxidation. On the other hand, they showed comparable activities for propene oxidation and reaction CO+NO. The characterization of bimetallic catalysts by TPR and FT-IR experiments suggested that the co-impregnation leads to an intimate interaction between platinum and rhodium while rhodium added by successive impregnations with a reduction step after platinum impregnation would be selectively deposited onto cerium oxide surface in the vicinity platinum particles, avoiding the formation for Pt/Rh alloy.

Marecot *et al.* [17] suggested that ceria played a decisive role within the preparation of bimetallic Pt-Rh/Al<sub>2</sub>O<sub>3</sub> catalysts by sequential impregnation when reduced capping cerium atoms (Ce<sup>3+</sup>) were present on the parent Pt-Rh/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>3</sub> catalysts before introduction of the rhodium salt. The preparation procedure of Pt-Rh/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalysis by successive impregnation (SI) method increased the thermal stability of the metallic species under oxidizing conditions. This improvement would be the consequence of a higher resistance to the formation Pt-Rh alloys with surface enrichment in rhodium.

Ishikawa *et al.* [18] studied the effect of the acidic property of support materials, using a series of single metal oxide, mixed oxides and  $\text{SO}_4^{2-}$  - 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.  $\text{SO}_4^{2-}$ - doped oxides, known as solid superacids, were superior support material giving high activity at low temperature.

Svoronos *et al.* [19] characterized a series of platinum catalyst supported on  $\gamma$ -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 impregnate 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.

Tabata *et al.* [20] investigated deactivation by poisoning of a Pt-Rh three way catalyst used in natural gas-fueled engine systems. They reported that P, Ca, Zn, Fe and trace amounts of Pb were detected as elements which increased in the used catalyst, and Zn, Fe and Pb were observed in the washcoat layer of the catalyst, while P and Ca existed on the surface of the washcoat. From these results, they concluded that the selectivity of nitric oxide reduction was decreased by chemical poisoning due to trace amounts of Pb on the used catalyst and that the absolute rates of nitric oxide reduction as well as the other reactions were additionally reduced by an decreased in the effective surface area of the catalyst due to the covering the surface of the washcoat layer by accumulated compounds consisting of P, Ca, Zn and Fe.

Panee Asavapitchyont [21] prepared the modified three-way catalyst composed with Pt-Rh as the active components and cerium as the promoter for the removal CO, NO and propane. It was found that the catalyst contained 9 wt%Ce at constant ratio of Pt/Rh of 3/1 in the catalyst showed the highest activity of CO, propane and NO conversion. The light-off temperature of this catalyst is 240°C for CO conversion, 424°C for propane conversion and 470°C for NO 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.

Janjira Wongpaitoonpiya [22] studied the conventional three-way catalyst modified for NO reduction, CO and propane oxidation. It was found that the modified three-way catalyst which contained 9 wt.% of Ce (as promoter), palladium metal and cobalt metal seemed to behave similarly to conventional three-way catalyst. The light-off temperature range of NO is 400-500°C, that of CO is 150-300°C and that of propane is 400-500°C. The highest activity of modified three-way catalyst is obtained at Pd/Co ratio of 1. The calcination of catalyst under reducing atmosphere at high temperature (700°C) for 7 hours could induce the strong metal support interaction (SMSI) phenomenon. This effect only enhanced the oxidation of carbon monoxide.

Chalermchai Sringagam [23] studied the development of alumina supported platinum catalyst for carbon monoxide and hydrocarbon oxidation. His objective was to enhance the performance of platinum supported on gamma-alumina catalysts for CO and propane abatement by replacing calcination step with catalyst pretreatment in exhaust gas technique. The experiments were carried out in a quartz tube reactor with inside diameter of 0.6 cm in the temperature range of 150-700°C. The feed gas composition comprised 0.05 vol.% NO, 0.3 vol.% CO, 0.215 vol.% propane and 0.05-5 vol.% oxygen at gas hourly space velocity of 15,000 h<sup>-1</sup>. He found that the light off temperatures of CO and propane were reduced by 15% and 20%, respectively. The platinum supported on alumina and washcoat monolithic catalyst reached the maximum NO conversion of 80%

at 500-700°C. When the pretreated catalyst was adopted, the light-off temperature for NO conversion was reduced by 15%.

Tillaart *et al.* [24] investigated of noble metal precursor and support oxide of their catalytic activity for the conversion of diesel exhaust gas components. The noble metal precursors used in this investigation were hexachloroplatinic acid, platinum nitrate, and tetraammine platinum (II) hydroxide. As support metal oxides zirconia, a base metal doped alumina, alumina, and titania were used. Catalysts were prepared from all combinations of precursors and supports and were tested in an integral model gas test reactor both in the fresh and in the aged state, The catalysts were also characterized by various techniques including BET surface area, CO chemisorption, XRD, and TEM. The results indicate that the catalyst prepared from the tetraammine platinum(II)hydroxide precursor on the base metal doped alumina support shows the highest activity for the conversion of the gaseous exhaust components.

Burch and Watling [25] studied the activities of Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> samples with comparable Pt dispersions for the reduction of NO<sub>x</sub> under lean-burn condition using C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> as the reductant. C<sub>3</sub>H<sub>6</sub> is more effective than C<sub>3</sub>H<sub>8</sub> at reducing NO<sub>x</sub> with both catalysts. With C<sub>3</sub>H<sub>6</sub>, Pt/SiO<sub>2</sub> exhibits greater deNO<sub>x</sub> activity than Pt/Al<sub>2</sub>O<sub>3</sub>, while with C<sub>3</sub>H<sub>8</sub> the opposite was observed. Kinetics measurements show that at steady state during the C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> reaction the surface is dominated by carbonaceous species, while during the C<sub>3</sub>H<sub>8</sub>-NO-O<sub>2</sub> reaction adsorbed oxygen is the main surface species. As a consequence, the surface of the catalyst is quite different for the two reactions (reduced versus oxidized) and this provides a rational for apparent discrepancies in the reaction mechanisms which have been proposed.

Burch and Watling [26] studied the effect of temperature, contact time, and reactant concentration on the kinetics of NO reduction by C<sub>3</sub>H<sub>8</sub> under lean burn conditions over Pt/Al<sub>2</sub>O<sub>3</sub> and a kinetic model, which satisfactorily fits the data. Under



reaction conditions adsorbed atomic oxygen is the dominant species on the metal surface, resulting in  $C_3H_8$  oxidation being inhibited by  $O_2$  and in the facile oxidation of NO to  $NO_2$ . The rate determining step in  $C_3H_8$  oxidation by  $O_2$  is believed to be dissociative chemisorption of  $C_3H_8$  involving the breaking of a C-H bond. Possible mechanisms for the reduction of NO to  $N_2$  and  $N_2O$  are discussed and the kinetics predicted for each mechanism, compared with the empirical data. It is concluded that NO dissociation on the Pt surface is not a major route. Instead, the reduction of NO appears to occur by spillover of  $NO_2$  from the Pt metal onto the  $Al_2O_3$  support where it reacts with  $C_3H_8$ -derived species to form  $N_2$  and  $N_2O$ .

Castillo *et al.* [27] suggested that platinum and rhodium supported on alumina and titania were synthesized by the sol-gel method. Characterization and catalytic activity for the reduction of nitric oxide by carbon monoxide was performed. In sol-gel 'sintered/reduced catalysts' a redispersion of the metal phase and higher resistance to sintering was observed. On the other hand, in the impregnated 'sintered/reduced catalysts', an important sintering effect was observed. The sol-gel 'reduced catalysts' and 'sintered/reduced catalysts' showed higher activity than that of impregnated reference catalysts, mainly when the titania is the support. Moreover, sol-gel preparations are more selective to  $N_2$ , whereas impregnated reference catalysts are selective to  $N_2O$ . The increase in dispersion and high resistance to sintering on sol-gel 'sintered/reduced catalysts' was interpreted as a surface migration effect of the metal particles buried in alumina and titania gels.

Burch and Watling [28] investigated the effect of sulphur on the  $C_3H_6$ -NO- $O_2$  and  $C_3H_8$ -NO- $O_2$  reactions over Pt/ $Al_2O_3$  and the results interpreted in terms of previously proposed mechanisms. Ex-situ treatment of the catalyst with  $SO_2$  under oxidizing conditions, results in the formation of sulphate species on the  $Al_2O_3$  but not on the Pt. This results in strong poisoning of the  $NO_x$  reduction activity in the  $C_3H_8$ -NO- $O_2$  reaction, where  $NO_x$  reduction occurs on the  $Al_2O_3$ , but has no effect on the  $C_3H_6$ -NO- $O_2$

reaction, where the reaction occurs exclusively on the Pt surface. These sulphate species were characterised by IR and TPR. Introduction of SO<sub>2</sub> (0-100 ppm) into the reaction feed inhibits the C<sub>3</sub>H<sub>6</sub>-NO-O<sub>2</sub> reaction, but results in only modest shifts in the C<sub>3</sub>H<sub>6</sub> light-off curve and the temperature of maximum NO<sub>x</sub> conversion. The system responds slowly when the concentration of SO<sub>2</sub> is changed, but activity returns to its original level when SO<sub>2</sub> is removed from the feed.

Bahamonde *et al.* [29] suggested that monolithic catalyst supports were prepared with mixtures of titanium dioxide and a natural magnesium silicate. Some properties of relevance to their scale-up for industrial applications using monoliths manufactured with various commercial titanias and treated at different temperatures were compared. Thus, their textural properties, anatase phase stability and axial strength were evaluated. Taking into account these results, a support was selected for the preparation of platinum catalysts, which were prepared by varying the impregnation time and the platinum solution concentration. Equations were obtained describing the dependence of the catalyst platinum content on each of these parameters. Catalyst activities were tested in the catalytic reduction of nitrogen oxide with propylene in lean-burn conditions.

Lee and Kung [30] studied reduction of NO by propene under lean-burn exhaust conditions and oxidation of NO on two Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts of 4.4% and 82% dispersion of Pt. At 265°C, the turnover frequency for the oxidation of NO was over 100 times higher on the low dispersion than the high dispersion catalyst. The difference was much less pronounced for the reduction of NO. In the reduction of NO, the N<sub>2</sub>O/N<sub>2</sub> ratio in product was found to increase with the conversion of hydrocarbon, while depend much less on Pt dispersion, temperature, or NO conversion.

From the literature reviews, many catalysts for the removal of exhaust gases from internal combustion engines, e.g., Pt, Pd and Rh supported on  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  have been reported. The catalytic preparation has been demonstrated as a substantial influencing factor on the catalytic performance.

Hence, it is our thesis objective to study influences of the catalyst preparation, i.e., calcination temperature and atmosphere on the catalytic performance of Pt/ $\text{TiO}_2$  and Pt/ $\text{Al}_2\text{O}_3$  for the removal of exhaust gases from internal combustion engines.