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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 [8].

Vehicles equipped with three-way catalysts have been shown to meet emission standards with minimal loss of fuel economy and driveability (Seiter and Clark, 1978; Engh and Wallman, 1977; Oster, 1979). Because of their wide-spread application, improvements in three-way catalysts would be desirable. A large study of three-way catalyst system has been made and has been summarized below.

Stephens, et at [9] invented the oxidation catalysts. The oxidation catalysts relates to novel lead promoted platinum. This method provides for preparing the novel catalyst composition.

Miyazaki, et al [10] presented the invention of catalyst for use in purification of exhaust gas containing carbon monoxide. This inventor consists

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of manganese oxide and lead oxides or one consists of manganese oxides and bismuth oxides. They are suitable for the oxidation and purification of exhaust gas containing carbon monoxides.

The various catalysts are examined for the simultaneous removal of CO and NO in an exhaust-like feed by Taylor [11]. He observed that rhodium supported on alumina possesses exceptionally high activity for reducing NO but forms mostly NH_3 below 600 °C. At higher temperature NH_3 is an intermediate in the reduction of NO to N_2. Rh shows high temperature selectivity for N_2 rather than NH_3 formation.

Ohara [12] studied the catalytic reduction of nitric oxide over supported rhodium and copper nickel catalysts. He reported that the comparative reactivity of CO and H_2 over the base metal catalysts and noble metal catalyst showed the same trends. Rh/Al_2O_3 has greater NO reduction efficiency than $Cu/Ni\text{-}Al_2O_3$. NO conversion efficiency over Rh/Al_2O_3 was inhibited at high CO concentration, presumably due to strong CO chemisorption. In general, catalysts treated at high temperature in an oxidative atmosphere tends to regain activity to some extent by further treatment in a reductive atmosphere without O_2.

Mc Arthur [13] studied dealing with contaminant poisoning of autoexhaust catalysts. He reported the development of catalysts with superior tolerance to contaminant poisons. He summarized that the ratio of Pb/P for poisoned NO_X catalyst is usually much smaller than the stoichiometric Pb/P ratio calculated for known lead phosphate compounds. This result indicates that much of the phosphorus retained on the catalyst is in the form of compounds resulting from the interaction of phosphorus with the catalyst support material. Catalyst degradation due to contaminant poisoning can be minimized by maintaining the catalyst operating temperature in the range 730-870 °C.

Schlatter and Taylor [14] discovered a supported rhodium catalyst with low loading (0.002 wt% Rh) was found to have good activity for convert nitric oxide to nitrogen in a laboratory feedstream, but its oxidation activity was inadequate. Addition of platinum or palladium improved the oxidation activity. However, it was found that compared to rhodium alone, these two-metal combinations (Pt-Rh or Pd-Rh) form more ammonia under reducing conditions and decrease nitric oxide conversion under oxidizing conditons.

The metal-support interaction in automotive exhaust catalysts : Rh washcoat interaction was investigated by Yao, Stepien, and Gandhi [15]. They reported that in γ-alumina supported Rh catalyst, dispersibility, adsorption capacity, and thermal stability of Rh are greatly affected by the γ-alumina support. High dispersion was easily obtained on samples of low Rh loading {2.5 μmol Rh/m^2 /BET}, but dispersed Rh was unstable to heat treatment in air at 600 °C or higher because of a strong Rh-γ-Al_2O_3 interaction resulting in diffusion of Rh oxide into the support. Rh-washcoat interactions of ZnO_2 and α-Al_2O_3 are resistant to thermal deactivation.

Kim [16] invented the method of preparing supported platinum group metal catalysts. He used refractory inorganic oxide support impregnated with a mixture containing a platinum sulfite complex solution, a palladium salfite complex solution, and a rhodium nitrate solution.

Eskinazi et al [17] exhibited the process for preparing a platinum/ rhodium catalyst using a single impregnation step. The process is particularly effective in preparing such a catalyst for use as an automotive emissions

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control catalyst. A substantial alumina support is impregnated in a platinum/rhodium controlled acidic solution of a strong acid and an ammonium salt or equivalent thereof.

The phenomenon of strong metal support interactions (SMSI) was investigated by Cairns, et al [18]. They explained this phenomenon in terms of a chemical bonding between dispersed metal atoms and cations of certain supports. The catalysts (Pt/Al_2O_3 , Rh/Al_2O_3, Pt/TiO_2 , and Rh/TiO_2) were heated in hydrogen or oxygen and observed by the technique of Nuclear Backscattering Spectrometry. This technique is confirmed for SMSI phenomenon.

The role of cerium oxide in automotive exhaust catalysts was studied by Yao and Yao [19]. They reported that cerium oxide is oxygen storage components of automotive catalysts. They measure the capacity of cerium oxide as an oxygen storage in an alumina-supported precious metal catalyst. Platinum or palladium can promote the reduction of cerium oxide by H_2 or CO and also its reoxidation by O_2.

A process for improving the lead tolerance of a motor venicle exhaust purification catalyst system was invented by Harrison et al. [20] It comprises a platinum group metal carried on alumina. The improvement derives from impregnating the alumina with barium moiety and firing at least 400 °C before subsequent impregnation with the metal catalyst moiety.

Yao and Kummer [21] studied low-concentration supported precious metal catalysts prepared by thermal transport. They reported that the described results clearly show that in air the precious metals can be thermally transported from the bulk metallic phase to the Al_2O_3 surface at the

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temperatures studied. The presence of CeO_2 greatly enhances transfer from the bulk Pt and Rh to the support surface, but has much less effect in the case of Pd.

OH and Eickel [22] studied the effect of cerium addition on CO oxidation kinetics over alumina supported rhodium catalysts. They suggested that the addition of cerium to a low-loaded Rh/Al_2O_3 catalyst results in modifications of the kinetics of CO oxidation under moderately oxidizing or net reducing conditions. The observed changes in the kinetics include a suppression of the CO inhibition effect, decreased sensitivity of the rate to O_2 concentration, and decreased apparent activation energy.

Automotive exhaust gas catalysts : surface structure and activity was characterized by Engler, Koberstein, and Schubert [23]. They reported that the main part of ceria and alumina in the support is present in the form the separate particles, well mixed and up to calcination temperatures of about 700 °C with comparable particle size distributions. After aging (950 °C), ceria shows pronounced surface losses with corresponding particle size increases and separations. During aging, rhodium is deeply oxidized, whereas the platinum crystallites are only covered with a thin layer of oxygen. This difference in the oxidation behaviour is probably the reason for the stronger crystallization of platinum (particle size increases), especially on γ-alumina supports, whereas rhodium remains more dispersed. In addition, rhodium is kept in high dispersion by oxidations and reductions. Actually, under real operating conditions there must be a frequent restructuring of the rhodium component by this mechanism. The stability of the different oxides influences the precious metal dispersion by support oxide interaction. They have been no indications of a Pt-Rh alloy formation, but of clear metal-metal oxide support interactions.

The effect of sulphur on noble metal automotive catalysts was investigated by Gandi and Shelef [24]. They found that the small amount of sulphur, ca.300 ppm, in gasoline which is equivalent to ca.20 ppm SO_2 in exhaust, has multiple effects on the operation of automotive catalysts. The storage of the sulphur on the support under oxidizing condition may lead to the formation of objectionable emissions of H_2S when the catalyst is momentarily exposed to reducing condition. The presence of suphur species in the exhaust influences the partitioning of the products of nitric oxide reduction between dinitrogen and ammonia.

Kubsh et al [25] discovered operation of three-way catalysts at these high temperatures can result in significant activity losses. Surface area loss of cerium in high temperature, oxygen-rich atmospheres can be retarded by the use of stabilizers such as La, Nd, or Y. But in high temperature oxygen-rich atmosphere, the performance of three-way catalyst is poor with lanthanum or neodymia.

Leclercq et al [26] studied the influence of Rh and CeO_2 addition on the activity and selectivity of a Pt/Al_2O_3 catalyst in the CO+NO and $CO+NO+O_2$ reactions. They suggested that in the reaction between CO and NO, at low temperature, NO gives mainly N_2O the percentage of which in the products decreases when the reaction and conversion increase. On the contrary for reactions of $CO+NO+O_2$, at low temperature and low conversion, the selectivity of NO transformation into N_2O is low when oxygen is present in the gas phase because of a better adsorption of O_2 than that of NO. Rhodium and cerium oxide have a promoting effect on both CO+NO and CO+NO+O_2 reactions, but the promoting effect of cerium manifests itself mainly in the presence of oxygen. During the reaction between CO+NO, besides its oxidation by NO, CO is oxidized in another process which is likely to involve the supports (alumina or cerium oxide).

The behavior of catalysts in closed-loop emission fluctuates about the stoichiometric point was investigated by Weibel et al [27]. They found that the water-gas shift reaction is enhanced when cerium is added to Rh/Al_2O_3 catalyst. This reaction occurs following the formation of Rh oxide. The Rh-Ce/Al_2O_3 catalyst shows higher water-gas shift activity than the Rh/Al_2O_3 but the stability of Rh oxide decreases more rapidly when cerium oxide is added.

In order to advance the design of automotive catalysts for maximum durability performance, Silver, Summers, and Willamson [28] investigate the relative individual contributions of Pt, Pd, and Rh in current high performance cerium oxide-alumina catalyst formulations. They examine the noble metal durability performance over a variety of Ce-alumina supported. They conclude that the increasing Ce content in an alumina washcoat greatly improves the activity and thermal durability of Pt-only catalysts. The high temperature durability of Rh-only catalysts is improved via the addition of Zr to the washcoat, which has been attributed to decreasing Rh interaction with the alumina component. Rh-only catalysts provide the earliest light-off under stoichiometric and rich conditions.

Funabiki, Yamada, and Kayano [29] summarized basic characteristics of the present auto exhaust catalysts used in the market. The $Pt/Rh/CeO_2$ catalyst is the main three-way conversion catalyst. The main catalyst support is a monolithic substrate composed of cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$). The basic precious metals used in catalysts are Pt, Pd, and Rh. Pt is used more in TWC catalysts. Pd is used less than Pt because (1) Pd susceptibility to lead (Pb) and sulfur (S) poisoning. (2) sintering in reducing atmosphere. (3) decrease in Rh activity. The effects fo thermal exposure on the catalyst are 1) precious metal sintering and Rh deterioration caused by interaction with the Al_2O_3 2) decreased BET surface area of Al_2O_3 due to shrinkage of the micropores.

OH, Eickel, and Carolyn [30] studied the effects of metal particle size and support material on the kinetics of the $CO\text{-}O_2$ and CO-NO reactions over Rh. They suggested that metal particle size and support material are the factors which repsonsible for the structure sensitivity. The turnover number and the apparent activiation energy for $CO\text{-}O_2$ reaction over Rh in the CO-inhibition regime are virtually independent of the metal particle size but are moderately sensitive to the nature of the support material. The apparent activation energy for CO oxidation was found to decrease in the order $Rh/SiO_2 > Rh/\theta\text{-}Al_2O_3 > Rh/\alpha\text{-}Al_2O_3$ and the activity ranking for low temperatures (< 190 °C) is given by $Rh/\alpha\text{-}Al_2O_3 > Rh/SiO_2 > Rh/\theta\text{-}Al_2O_3$.

Ansell et al [31] studied the effects of SO_2 on the alkane activity of three-way catalysts. They suggested that the conversion of alkanes occurs by two principal mechanisms : direct oxidation ($HC+O_2$) and steam reforming ($HC+H_2O$). Sulphur dioxide can influence both these mechanisms. Direct

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oxidation is enhanced by the transfer of electrons from the precious metal to the support, steam reforming occurs at interfacial sites, which can be blocked by adsorbed SO_X species.

Nunan et al [32] found that cerium oxide is the best promoter largely because interaction between Pt and Ce from using TPR and STEM on variety of catalysts was studied. The degree of Pt/Ce interaction was increased by decreasing CeO_2 crystallite size, and to lesser extent by increasing CeO_2 loading. Direct Pt/Ce interaction leads to a synergistic reduction of both Pt and surface Ce. This reduction qualitatively correlates with catalyst performance after activation in a reducing gas. It is proposed that this synergistic reduction of Pt and Ce is associated with observed improvements in catalyst performance using a non-oscillating exhaust gas.

Barbier and Duprez [33] studied the hydrogen formation in propane oxidation on Pt-Rh/CeO_2/Al_2O_3 catalysts. They found that in oxygen-deficient atmosphere, propane can be partially oxidized into carbon monoxides and hydrogen on PtRh/CeO_2/Al_2O_3 catalysts at 330-550 °C. H_2 is formed by steam-reforming and water-gas shift. Rhodium is the key component of the catalyst for the formation of H_2.

Taha and Duprez [34] studied the sintering of PtRh/Al_2O_3 in an oxygen periodic pulse flow. They found that coimpregnated PtRh catalysts were sintered at 973 K under a continuous flow of O_2 and Ar.

Aray and Berrios [35] studied the activity and infrared during carbon monoxide oxidation over bimetallic palladium-rhodium/silica catalysts. They suggested that the catalysts were prepared by three different methods (1) palladium and rhodium were coimpregnated on the support, (2) rhodium was impregnated first and, after calcining, the sample was impregnated with palladium, (3) the monometallic palladium and rhodium catalysts were physically mixed. The results showed that the acitvity of the catalysts prepared by coimprenation was much lower that of the other two catalysts. The low activity of coimpregnated catalyst can be explained by the formation of alloys which affect the surface concentration of each metal and the dispersion of rhodium. The most active catalyst was the one prepared by physical mixture, which also shows the highest concentration of linearly adsorbed carbon monoxide detected by FT-IR.

Marecot, et al [36] 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 coimpregnated catalysts are far less active than sequencial impregnated catalysts for propane oxidation. On the other hand, they show comparable activities for propene oxidation and reaction CO + NO. The characterization of bimetallic catalysts by TPR and FT-IR experiments suggests that the coimpregnation 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 of Pt/Rh alloy.

Marecot et al [37] suggested that ceria plays a decisive role within the preparation of bimetallic Pt-Rh/Al_2O_3 catalysts by sequencial impregnation when reduced capping cerium atoms (Ce^{3+}) are present on the parent Pt/Al_2O_3-CeO_2 catalyst before introduction of the rhodium salt. The preparation

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procedure of Pt-Rh/Al_2O_3-CeO_2 catalysts by SI method increases 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.

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