

CHAPTER II

LITERATURE REVIEW

Autocatalyst technology for control of pollutants from motor vehicles has been platinum group metal. Although they are active, there are some obvious disadvantages in the use of noble metal catalysts. Because they are scarce and expensive, and have many constraints in operation. Consequently, it is desirable to compensate noble metal by using a base metal catalyst. Some of the prominent studies are summarized below.

Shelef, Otto and Gandhi (1968) studied automobile exhaust treatment that removed NO from the exhaust. Using a catalysts showed that there was an excess of reducing reagents in the gas stream. These are CO and HC and for their removal an oxidizing atmosphere is required. Their research looked for a catalyst selective toward the CO-NO reaction with respect to the CO - O₂ reaction among the metal oxides of the first transition selection of the first row transition metal oxides following the oxides of Co, Cu, Mn, and Ni. On the other hand the sequence for the CO-NO reaction was :

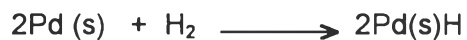
$\text{Fe}_2\text{O}_3 > \text{CuCr}_2\text{O}_4 > \text{Cu}_2\text{O} > \text{Cr}_2\text{O}_3 > \text{NiO} > \text{Pt} > \text{Co}_3\text{O}_4 > \text{Al}_2\text{O}_3 (5\%\text{SiO}_2) > \text{MnO} > \text{V}_2\text{O}_5$

Wise (1968) reported that palladium differs from other noble metals in interaction with hydrogen because, in addition to chemisorption, it absorbs hydrogen into the bulk.

Reduction :



Chemisorption :



Absorption :



Yao and Shelef (1974) studied the NO chemisorption on supported transition metal surface ions at room temperature. The solid-state interaction of Co_3O_4 with alumina has been very thoroughly investigated. It has been stated that the onset of surface CoAl_2O_4 formation might occur as low as 200°C . Cobalt ions which enter into cobalt aluminate do not chemisorb the change in the amount of active ions on the surface of the catalyst. The Co_3O_4 supported on pre-formed cobalt aluminate represents an intermediate case. The pre-forming of the spinel slows down the penetration of Co_3O_4 into support but does not prevent it entirely.

Ohara (1974) presented Cu and/ or Ni- Al_2O_3 catalysts as typical base metal catalysts and a Rh- Al_2O_3 catalyst as a representation of noble metal catalysts. Catalytic reduction of NO by H_2 and CO act as reductants. The reductive and oxidative heat treatment was studied for its effect on catalytic activity as they relate to the possible conditions in exhaust gas purification. It was found that CO showed higher reducing reactivity than H_2 over both base metal catalysts and noble metal catalysts. Rh- Al_2O_3 catalyst has greater NO reduction efficiency than Cu/Ni- Al_2O_3 which formed less NH_3 than the Rh- Al_2O_3 catalyst in NO reduction. In oxidative high temperature treatment the Cu/Ni- Al_2O_3 catalyst formed CuAl_2O_4 with obvious changes in physical properties.

Kummer (1975) investigated the oxidation of CO and C₂H₄ by base metal catalysts prepared on honeycomb supports. The oxidation activities of various oxides on propane oxidation are shown as follows :



In addition to the prevention of sintering on unsupported metal oxide that occurred occasionally in auto exhaust, a high surface area washcoat ($\gamma\text{-Al}_2\text{O}_3$ or ZrO_2) was used for more stable to sintering at high temperatures.

Harrison and Diwell (1978) invented a catalyst suitable for the purification of exhaust gases. The invented catalyst comprises a compound from the group represented by the general formula $\text{A}_x\text{M}_y\text{O}_z$ in which A is one or more metals selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Al, Sc, Y the lathanides, Ti, Zr, Cr, Mn, Fe, Co, Ni, Cu, Zn and M is a metal selected from a group consisting of Ir, Rh, Pt, Pd and Ru. Examples of compounds are LaRhO_3 , BaRhO_3 , MgRh_2O_4 , Ba_4PtO_6 , CoAlRhO_4 , CaPd_3O_4 and $\text{LaNa}_{0.5}\text{Ir}_{0.5}\text{O}_3$. Their structures are perovskite. They also need inert material for deposit when applied to honeycomb structures. They found that the invented catalysts can purify an exhaust gas which includes the simultaneous reduction of nitrogen oxide and oxidation CO and unreacted HC.

Yao and Yu Yao (1984) studied the oxygen storage capable of CeO_2 , $\text{CeO}_2/\text{Al}_2\text{O}_3$, $\text{PM/CeO}_2/\gamma\text{-Al}_2\text{O}_3$. Higher thermal pretreatment lowers the oxygen storage capacities. But the presence of precious metal increases the oxygen storage capacity of CeO_2 , and showed that TPR was used to measure the

oxygen removal at various temperatures. The TPR traces of various catalysts could show the oxygen species on the surface of catalysts.

Chang and et.al (1985) investigated the reduction and hydrogen sorption for palladium catalysts on various supports by combination of temperature-program reduction and temperature-resolved sorption techniques. It was found that palladium was reduced at temperatures lower than 200°C and spillover of hydrogen from Pd to supports occurred at higher temperatures. Hydrogen treatment at high temperature also induced SMSI and sintering. The extent of spillover, sintering and SMSI are support - dependent. Under the same reduction conditions, the sintering of supported palladium catalysts follows the trend :



Ogata and et al. (1990) studied direct decomposition of nitric oxide to nitrogen on supported palladium catalysts at 550°C-750°C. It found that nitric oxide decomposition activities of Pd/MgAl₂O₄, Pd/MgO, Pd/Mg₂Si₃O₈, and Pd/MgZrO₃ were higher than those of Pd/γ-Al₂O₃, Pt/γ-Al₂O₃ and Cu-ZSM-5 in this temperature range.

Hamada (1990) reported an excellent additive effect of silver on the catalyst performance of silica and alumina for the direct decomposition of nitrogen monoxide with propane in the presence of a high concentration of oxygen. The metal alumina catalysts containing metal aluminate showed excellent activity at low temperatures and under high space velocity conditions.

Stegenga and et.al (1991) showed that 10% wt Cu-Cr/Al₂O₃ catalysts are very effective for NO reduction, CO and HC oxidation. Monolith type catalysts exhibit a three-way catalyst behavior, comparable to noble metal catalysts under the same condition mixture, and the original activity returned in an overall oxidizing atmosphere at 623 K. The CO oxidation activity level of a freshly prepared catalyst under reducing gas condition is higher than under oxidizing condition after thermal treatment in a stoichiometric mixture. This is the reverse case. From the above review, this research may examine the preparation of catalyst under reducing conditions (both H₂ as reducing agent and feed mixture as reducing condition).

Ukisu et al. (1992) have investigated adsorbed species on Cu-containing alumina supported catalysts in a NO/O₂/propylene system and reported that a surface isocyanate species (-NCO) is a reaction intermediate for the NO_x reduction. They have found that NO is adsorbed on Cu/Al₂O₃ and Cu-Cs/Al₂O₃ but not on Al₂O₃. Therefore the high catalytic activity of Cu-Cs/Al₂O₃ as compared to Cu-Al₂O₃ is ascribable to the activation of isocyanate species by the electron donation of Cs to Cu.

Nunan (1992) proposed that the direct Pt/Ce interaction led to a synergistic reduction of both Pt and surface Ce. This reduction qualitatively correlates with catalyst performance after activation in a reducing gas. The catalysts were activated in the rich feed gases or pretreated during the hold between the testing profiles.

Halasz and Brenner (1993) studied the reduction of nitric oxide by carbon monoxide, by hydrogen and by a mixture of CO+H₂ in presence of different amounts of oxygen at reaction temperatures from 25 to 550°C over PdO-MoO₃ / Al₂O₃ catalysts. They reported that the catalytic activity and

selectivity of Pd-MoO₃/Al₂O₃ is active. Furthermore they suggested that the activity of base metals on the amount of contaminants in fuel is decreasing, so the use of a mixed noble metal and base metal catalyst is becoming more plausible.

Panee Asavapitchyont (1995) prepared the conventional three-way catalyst with cerium as promoter and enhancer activity of the catalyst. It is found that when the cerium content reached 9wt% the highest activity of CO, propane and NO conversion was shown. 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 modified three-way catalyst use the effect of the high calcination temperature under reducing atmosphere and pretreated in simulated exhaust gases (rich condition). This effect can enhance activity for control of the three pollutants.