CHAPTER II

LITERATURE REVIEWS

The oxidation of carbon monoxide is an important reaction for air pollution treatment. The most efficient and commercial employed combustion catalysts are noble metals such as Pt and Pd. Because noble metals are scarce and expensive, therefore base-metal catalysts, especially copper catalyst, have been attempted to be used for these applications. Some of the more prominent studies and the evolution of copper catalyst are summarized below.

Hofman [9] indicated that the previously prepared surface of CuO would oxidize a mixture of CO and air, but the rate could be increased by a factor of 3 if the copper was moistened with small amount of alkali. The catalytic activity was further increased if small amount of iridium was incorporated in the oxide.

Bessalow and Kobosez [10] studied the activity of CuO powder and precipitated CuO aerosol in the oxidation of CO at temperature between 200-400 $^\circ$C. The aerosol form was 765 times more active than the corresponding powder at 250 $^\circ$C. The temperature for rapid catalytic action was approximately 200 $^\circ$C lower for the aerosol than for the powder. Although x-ray diffraction showed the same structure for both catalysts, the copper aerosol contained smaller crystals than the powder. According to Pieters [11], the oxidation of CO in air mixture with CuO alone does not commence until a temperature of 200 $^\circ$C is reached.

Garner and his associates [12,13] have been responsible for the principal studies of the oxidation of carbon monoxide on copper oxides and cuprous oxide in particular. They measured the chemisorption of O_2 and CO on the same Cu_2O crystal. By use of electrical conductivity measurements, it was found that the chemisorption of O_2 was faster than the oxidation of Cu_2O to CuO. This indicated that the O_2 was adsorbed as a boundary layer and not throughout the lattice. It was also concluded from the kinetic results that the chemisorbed O_2 was more reactive for CO oxidation than O_2 incorporated in the Cu_2O lattice.

Winter [14] studied the CO oxidation on cuprous oxide. He confirmed the presence of CO_2 in the gas desorbed after oxidation experiment by mass spectrometer analysis, yet also found no poisoning of the reaction by CO_2. He proposed a mechanism in which CO first reacted to form the carbonate ion and an anion vacancy. The filling of the anion vacancy by oxygen was then considered to promote decomposition of the carbonate ion to carbon dioxide.

Kobayashi et al.[15] found that the activity in the methanol steam reforming reaction over Cu/Al_2O_3 catalysts was strongly decreased when the particle size of metallic copper was below 10 nm. They described this behavior to a crystal size effect.

Evan et al. [16] studied the determination of copper surface area by reaction with nitrous oxide. The reaction of nitrous oxide has been used to measure metal surfaces for both pure and supported copper catalysts. The methods are based on the decomposition of a nitrous oxide molecule on a copper surface which is accompanied by the liberation of one nitrogen molecule according to:

$$N_2O \ (g) \ + \ 2 \ Cu_s \ \longrightarrow \ N_2 \ (g) \ + \ (Cu\text{-}O\text{-}Cu)_s$$
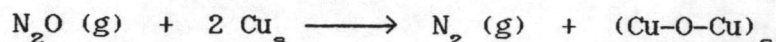
The temperature employed was 90 °C because irreproducible results were obtained at lower temperature and bulk oxidation was significant above 120 °C.

Miro et al. [17] studied the CuY zeolite to catalyzing CO oxidation in continuous-stirred tank reactor (CSTR), Bennett-type unit, operated both in the transient and steady-state regimes. The CSTR was used to determine the rate constant, the adsorption equilibrium constant, and the effective diffusivity under reaction conditions.

Strohmier et al. [18] reported that the surface characteristics of the catalysts were affected by both metal loading and calcination temperature.

Ta-Jen Huang et al. [19] found that calcination at 1273 K in air enhanced activity, for CO oxidation, for a catalyst with 3.7 wt% copper metal, whereas the same calcination greatly reduced the activity for catalysts with copper contents over 6 wt%. These results showed the importance of metal loading and calcination conditions on the activity and surface properties of catalysts.

Pepe et al. [20] observed a linear relationship between the kinetic constant and the surface area of copper metal for isopropanol dehydrogenation. They concluded that the activity is not size dependent, indicating a structure-insensitive reaction. For methanol synthesis, Robinson and Mol [21] found that a high copper dispersion has a negative effect on the catalytic activity of copper

site, denoting a structure-sensitive reaction.

Ta-Jen Huang et al. [5] reported that a sintered copper surface with high-temperature calcination in a reducing atmosphere enhance the carbon monoxide oxidation activity. It was concluded that the CO oxidation is a structure-sensitive reaction over copper catalyst.

G.A. El-Shobaky et al. [22] studied the effect of Na_2O-treatment on surface and catalytic properties of CuO/Al_2O_3 solids. They reported that the doping process resulted in a significant increase (44%) in the specific surface area of the investigated solids and significant decrease (about 66%) in their catalytic activity towards carbon monoxide oxidation by oxygen at 433-503 K. It was proposed that the decrease in the catalytic activity of CuO/Al_2O_3 solids by doping with Na_2O was attributed mainly to the decrease in the concentration of the catalytically active sites (surface Cu^{2+} ions) as a consequence of an enhanced crystallization of the CuO phase.

J. Barbier et al. [23] studied the role of copper deposition on Rh/Al_2O_3 catalysts. They suggested that copper can act like a sacrificial deposit (well-known in corrosion studies) and is able to avoid a partial oxidation of noble metals. On the other hand, a "sacrificial deposit" of a second metal can avoid such partial oxidation and can change to a large extent activity and selectivity.

Recently, calcination condition on copper/alumina catalysts for carbon monoxide oxidation and nitric oxide reduction were studied by Ta-Jen Huang and Tai-Chiang Yu [23]. It was found that

high temperature treatment in a reducing atmosphere was beneficial to carbon monoxide oxidation while an oxidizing atmosphere was usually prefered for nitric oxide reduction. In addition, copper species at higher oxidation states may lead to a higher activity of nitric oxide reduction, but an optimum state may exist. It can be concluded that nitric oxide reduction is a structure-sensitive reaction over copper catalysts.

Fabio B. Noronha and Martin Schmal [25] studied the metal-metal interaction of palladium-copper bimetallic catalysts supported on silica and niobia. They reported that the addition of copper to palladium supported on silica and niobia carriers changed the adsorptive and physicochemical properties of palladium. Palladium has a promoting effect, whereas copper has an inhibitory effect on the overall reduction. When the carrier of the bimetallic system is niobia, the presence of copper inhibits the possibility of SMSI formation between palladium and partially reduced niobia.