

## CHAPTER II

### LITERATURE REVIEWS

In the total oxidation or combustion of organic compounds, diesel soot,  $N_2O$ , and CO, supported cobalt catalysts show the high catalytic activity when compare with other transition metal oxide. For many studies, supported cobalt catalysts have been known for many decades as active in many reactions such as Fischer-Tropsch synthesis, combustion, hydrogenation, hydrodesulfurization, and synthesis gas conversion reactions. However, there are a few studies about selective oxidation over supported cobalt catalysts.

This chapter reviews the works about catalytic activities and characterization of supported cobalt catalysts in various reactions. In addition, the effect of support, metal concentration, and catalyst preparation on the property of catalysts is demonstrated in this section.

#### 2.1 Literature reviews

Busca *et al.* (1990) explored the surface property of cobalt oxide by means of Fourier-transform infrared (FT-IR) spectroscopy. The IR spectrum of  $Co_3O_4$  is observed at 667, 580, and 385  $cm^{-1}$ . Their pretreatment data showed that the surface of  $Co_3O_4$ , even after the slight reduction arising from evacuation at 517°C, is highly oxidized, showing only  $Co^{3+}$  centers. The surface of evaluated  $Co_3O_4$  exposed  $Co^{3+}$  cations reacted rapidly with CO, producing  $Co^{2+}$  and probably  $Co^+$ . The surface of  $Co_3O_4$  was very active, even with respect to stable molecules such as ammonia and methanol, which were rapidly decomposed at room temperature. This agreed with the very high catalytic activity of cobalt oxide towards methanol, ammonia, and hydrocarbon combustion, and was probably related to the instability of  $Co^{3+}$  ions that tended to be reduced to  $Co^{2+}$ , or even lower oxidation states.

Garbowski *et al.* (1990) has reported that cobalt oxide ( $\text{Co}_3\text{O}_4$ ) deposited on alumina-based supports active for the oxidation of methane to  $\text{CO}_2$  and water within  $500^\circ\text{C}$ . Alumina was found not to be a good support because at reaction temperature higher than  $500^\circ\text{C}$ , reaction between  $\text{Co}_3\text{O}_4$  and alumina support occurring which resulted in the formation of  $\text{CoAl}_2\text{O}_4$ , which was an inactive compound, then deactivation of the catalyst took place. This is because alumina support has a spinel structure with octahedral and tetrahedral vacancies and  $\text{Co(II)}$  ions have a strong affinity, therefore leading to  $\text{CoAl}_2\text{O}_4$  formation. In addition, for a good catalytic oxidation,  $\text{Co(II)}$  and  $\text{Co(III)}$  ions must be presented at the catalyst surface is possible. At low temperature the kinetics of this reaction are slow. At high temperature and in the presence of water, the formation of the cobalt aluminate phase is thermodynamically and kinetically favored. During the catalytic activity measurement deactivation is often observed. The main causes have been suggested to be (i) sintering of the active phase and (ii) reaction of the support with an active phase leading to an inactive phase.

Okamoto and co-workers (1991) have investigated the effects of the starting cobalt salt on the cobalt-alumina interaction modes and cobalt dispersion in  $\text{Co/Al}_2\text{O}_3$  catalysts. The catalysts were characterized by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) techniques. It was found that the cobalt-alumina interaction modes depended strongly on the starting salt of cobalt. It was demonstrated that  $\text{CoO/Al}_2\text{O}_3$  catalysts prepared from cobalt acetate showed higher cobalt dispersion than the catalysts prepared from conventional cobalt nitrate. From the intensity of TPR profiles, the total TPR areas were measured between room temperature and  $650^\circ\text{C}$  as function of  $\text{CoO}$  content. They found that the TPR areas steadily increased with increasing cobalt oxide content. Accordingly, the easily reducible cobalt species abruptly raised.

Sinha and Shankar (1993) explored cobalt oxide catalysts supported on silica gel for the catalytic combustion process for removal of organic pollutants from effluents streams, total oxidation of n-hexane, present in lean mixtures. Catalyst prepared by decomposition of cobalt oxalate was more effective than that catalyst

prepared by decomposition of cobalt nitrate. Catalyst prepared from cobalt oxalate proved more superior dispersion than prepared by cobalt nitrate. The activity and deactivation patterns of several catalysts were differed depending on their method of preparation. The activity of catalysts prepared by the decomposition of cobalt oxalate depended on the decomposition temperature and the surrounding gases. At low temperature of decomposition (250°C), there was no effect of the surrounding gas on the activity, but it was substantially affected when high decomposition temperature was used. While catalysts prepared by the decomposition of cobalt nitrate did not respect the decomposition temperature and the surrounding gases. Results of studies were obtained from using nitrogen adsorption, XRD, and XPS techniques.

Chang *et al.* (1993) studied the partial oxidation of methane to synthesis gas over Co/MgO catalysts with high Co-loading (28wt%). They were able to initiate the reaction of methane with oxygen at temperature around 500°C. High conversions of methane (~70%) and very high selectivity for hydrogen and carbon monoxide (~90%) were obtained at very high reactant gas space velocities ( $10^5$ - $10^6$  h<sup>-1</sup>).

Murthy *et al.* (1994) investigated catalytic activity of the  $\text{Co}_{1+x}\text{Al}_{2-x}\text{O}_4$  ( $0 < x < 1$ ) solid solution system on 2-propanol decomposition reaction. Selectivity for dehydrogenation increased with increase in x. Dehydration activity was found to occur due to the presence of acid centers as determined by n-butyl amine titration and pyridine poisoning experiments. Dehydrogenation activity was found to be causing by  $\text{Co}^{3+}$  ions.

Santos *et al.* (1996) have studied the oxidation of methane to synthesis gas on Co(12%Co)/MgO catalysts. The XRD patterns showed that the fresh catalysts were made up of MgO and  $\text{MgCoO}_2$ . No cobalt oxide crystalline was detected in these patterns. Besides, the TPR thermograms did not show any well-defme reduction peak up to 900°C due to the low reducibility of catalyst. This was expected that  $\text{MgCoO}_2$  was more difficult to reduce than the single cobalt oxide. The oxidation of methane to synthesis gas was performed on Co/MgO catalyst. Between 400°C and 800°C, the products detected were almost exclusively  $\text{CO}_2$  and  $\text{H}_2\text{O}$  but when the temperature

was increased to 800-900°C the reaction rate increased strongly, and the product distribution shifted. At 900°C, the measured methane conversion was approximately 98% and the selectivity to CO and H<sub>2</sub> reached values close to thermodynamic equilibrium. The Co/MgO catalyst reached the reaction at about 800-850°C, they become partially reduced, and metallic centers were generated on their surface, with a sharp increase in the overall activity and in the selectivity for both CO and H<sub>2</sub> that reached values very close to equilibrium.

Finocchio *et al.* (1997) have studied the oxidation of the C<sub>3</sub> organic compounds propane, propene, acrolein, propan-2-ol, and acetone over three transition-metal oxide catalysts, Co<sub>3</sub>O<sub>4</sub>, MgCr<sub>2</sub>O<sub>4</sub>, and CuO in a flow reactor and using FT-IR spectroscopy to study the adsorbed species. They found that Co<sub>3</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> were very active in propane and propene catalytic combustion. FT-IR study suggested that adsorbed isopropoxide species and adsorbed acetone and acetates were intermediates in propane oxidation while adsorbed acrolein and acrylates were intermediates in propene oxidation. Their flow reactor studied supported these hypotheses. It was suggested that the reaction rates in the propane and propene total oxidation could be influenced, at low temperature, by the rate of oxidation of adsorbed acetate and acrylate intermediates, respectively. Co<sub>3</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> was also active and quite selective catalyst for the oxydehydrogenation of propan-2-ol to acetone at low conversion, suggesting that the same oxygen species were involved in total and partial oxidation of organic compounds. CuO, as such, was not active in the adsorption and oxidation of C<sub>3</sub> hydrocarbons and oxygenates, at low temperature. At higher temperature the reactants reduced the catalyst and catalytic activity started. The data presented here gave three different scales for the catalytic activity in the oxidation of the three compounds: for propane oxidation the scale was Co<sub>3</sub>O<sub>4</sub> > MgCr<sub>2</sub>O<sub>4</sub> > CuO; for propene oxidation the scale was Co<sub>3</sub>O<sub>4</sub> ≈ MgCr<sub>2</sub>O<sub>4</sub> > CuO; for propan-2-ol oxidation the conversion scale was Co<sub>3</sub>O<sub>4</sub> ≥ CuO > MgCr<sub>2</sub>O<sub>4</sub>.

Novochinsky *et al.* (1998) studied the selective catalytic reduction of NO by methane over impregnated cobalt-containing catalysts. The active component of all the impregnated cobalt-containing catalysts was Co<sub>3</sub>O<sub>4</sub>. The role of O<sub>2</sub> seemed to

maintain the surface stoichiometry of  $\text{Co}_3\text{O}_4$ . The main reason of decrease of catalytic activity of samples based on  $\text{MgO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  in selective catalytic reduction of  $\text{NO}$  is due to oxide-oxide interaction promoted by water. All the carriers can be placed by the capability for oxide-oxide interaction in the following order:  $\text{SiO}_2 \gg \text{MgO} > \text{Al}_2\text{O}_3$ .

Baldi and co-workers (1998) investigated the catalytic oxidation of propane, propene, 1-propanol, 2-propanol, prop-2-en-1-ol (allyl alcohol), propanal, propanone (acetone), and propenal (acrolein) over  $\text{Mn}_3\text{O}_4$  in the presence of excess oxygen. Total combustion to  $\text{CO}_2$  occurred at temperature  $> 350^\circ\text{C}$  ( $400^\circ\text{C}$  for propane). For propane oxidation, the main product observed was always  $\text{CO}_2$ , but significant amounts of propene were observed when propane conversion was still definitely incomplete. While propene oxidation,  $\text{CO}_2$  selectivity was always near 100% with only traces of  $\text{CO}$  and ethene as by products. For 1-propanol oxidation, at low propanol conversions yielded propanal as main product while at high conversion propanal selectivity progressively decreased with increasing the formation of  $\text{CO}_2$  and acetaldehyde. Comparison with the previous study, in the case of propane and 2-propanol oxidation,  $\text{Mn}_3\text{O}_4$  was lower active than  $\text{Co}_3\text{O}_4$  catalyst.

Youngwanishsate (1998) studied the oxidation property of the Co-Mg-O catalyst in the oxidation reaction of propane, propene, 1-propanol, and  $\text{CO}$ . It was found that the cobalt composition in Co-Mg-O catalyst affected the catalytic activity and selectivity for propane oxidation. Co-Mg-O (8wt%Co) catalyst was the suitable catalyst for propane oxidation because it was active and selective for olefin production. It provided the maximum olefin selectivity about 40% and the maximum olefin yield 30% at  $500^\circ\text{C}$ .

Querini *et al.* (1998) studied the catalytic combustion of diesel soot particles over Co/MgO (12wt%Co) and potassium-promoted Co/MgO (1.5wt%K) catalysts that were calcined at different temperatures in the  $300$  to  $700^\circ\text{C}$  range. As observed by TPO experiments, the catalyst activity depended strongly on the calcination temperature: calcination at  $300$  and  $400^\circ\text{C}$  produced samples that were much more

active than those calcined at higher temperatures, on which an inactive Mg-Co mixed oxide is formed, as suggested by TPR, ESR, and XRD results.

Szalowski *et al.* (1999) studied a cobalt oxide catalyst for ammonia oxidation. Its active compound was  $\text{Co}_3\text{O}_4$ . It has been found that much less nitrous oxide was produced in ammonia oxidation on this catalyst than on platinum.

Xanthopoulou (1999) has investigated modified Mg-Al spinel catalysts for the pyrolysis of diesel fuel for the production of industrial gases and liquids. The substitution of Mg by Co in the  $\text{MgAl}_2\text{O}_4$  spinel and the use of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and MgO, increased significantly the catalytic conversion efficiency of the spinel while at the same time it suppressed substantially the formation of coke. The addition of up to 50%Co in the structure did not change the catalytic activity appreciably, possibly due to the existence of an optimum number of active centers in the surface and an optimum concentration of lattice defects in the Mg-Al spinel structure at a very low concentration of  $\text{CoAl}_2\text{O}_4$  in the catalyst.

Querini *et al.* (1999) have studied the catalytic combustion of diesel soot over 12%Co and 4.5%K, supported on MgO and  $\text{CeO}_2$  catalysts. It has been found that this reaction occurred by a redox mechanism when Co and K were deposited on any of the above-mentioned supports. On MgO-supported catalysts,  $\text{CoO}_x$  species were responsible for the supply of oxygen by a redox reaction.

Cimino *et al.* (1999) investigated high and low surface area NiO-MgO and CoO-MgO solid solutions by XPS surface composition and CO oxidation activity. The surface  $\text{Ni}^{2+}$  concentration was found to be equal to the bulk concentration. It was analogous to that found previously for the low surface area NiO-MgO system and for both the high and low surface area systems of CoO-MgO. Turnover frequency data ( $\text{CO}_2$  molecules produced per second per surface atom) showed that the activity was due primarily to the transition metal ions and was not subjected to the ions being in special configurations (dimers or trimers) or in special positions (edges, corners). The activity of CoO-MgO was higher than that of NiO-MgO solid solution.

## 2.2 Comment on previous works

From the previous studies there are many researches about cobalt oxide on various supports such as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  but most of reactions are total oxidation. The studies about supported cobalt catalysts on the selective oxidation are still scarcely. Since MgO support can reduce the strong oxidation capability of catalyst, it is used as support for cobalt oxide catalyst to attain selective oxidation catalyst. From literature, Co/MgO catalyst (8wt%Co) can give selective product such as propene and ethene from propane oxidation reaction [Youngwanishsate (1998)]. Therefore, there is an idea to apply the Co/MgO catalyst for other selective oxidation reaction.

In this study, the oxidation property of Co/MgO catalyst on methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol are studied. Moreover, the effect of support to the oxidation property of catalyst is also investigated.