

CHAPTER II

LITERATURE REVIEW

Oxidation of organic vapor in the presence of solid catalysts has gained importance as one of the promising methods for organic synthesis and air pollution control. Among the transition metal oxide Co_3O_4 exhibits the highest catalytic activity for the total oxidation of organic compounds, ammonia, and CO. For many researches, supported cobalt oxide catalysts have been known for many decades as active in many reactions such as oxidation, Fischer-Tropsch synthesis, hydrogenation, synthesis gas conversion, and hydrodesulfurization reactions. However, only a few papers have reported the combustion reaction of organic acid over supported cobalt catalysts.

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

2.1 Literature reviews

Busca *et al.* (1990) explored the surface property of cobalt oxide by mean 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 evacuated 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.

Okamoto and co-workers (1991) have investigated the effects of the starting cobalt salt on the cobalt-alumina interaction modes and cobalt dispersion in Co/Al₂O₃ 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 CoO/Al₂O₃ 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°C as function of CoO content. They found that the TPR areas steadily increased with increasing cobalt oxide content. Accordingly, the easily reducible cobalt species abruptly raised.

Wang and Chen (1991) investigated a series of cobalt oxide/alumina with various metal loadings prepared by incipient-wetness impregnation. The reducibility of cobalt oxide in these samples was investigated by TPR technique. TPR result indicated that the nature of cobalt species varied with the cobalt loading. For 1.5 wt.%Co/Al₂O₃, a broad peak appeared above 900°C. As cobalt loading was increased, a H₂ consumption peak started to appear at around 500°C and the relative proportions of this peak increased as the cobalt loading increased. This result clearly indicated that the nature of cobalt species varied with cobalt loading. In addition, both peaks shifted to a lower temperature as cobalt loading was increased. For low cobalt loading the cobalt phase was present primarily as CoAl₂O₄. For catalysts having high cobalt contents, bulk Co₃O₄ was observed. CO hydrogenation activity measurement was carried on these catalysts. The catalytic activity was increased with increasing cobalt loading when expressed in moles of carbon dioxide converted per second and per gram of catalyst. Nevertheless, if the comparison was based on cobalt metal, there was an optimum activity at 12 wt.% Co/Al₂O₃. They suggested that might be due to different causes. First, the introduction of cobalt onto alumina led to a decrease in the pores of alumina during the preparation process. Second, the dispersion of the active phase was changed with the cobalt content. Higher cobalt loading favored large particles gave a low activity when expressed per gram of cobalt introduced.

Halawy and Mohamed (1993) have studied the thermal decomposition of ammonium heptamolybdate and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ mixture by TGA and DTA. Their results showed that a small amount of cobalt (up to 5% expressed as Co_3O_4) did not alter the way in which ammonium heptamolybdate decomposed. Larger amounts of cobalt (10-90% as Co_3O_4) reduced the number of steps from three to one. XRD patterns of samples containing high content of cobalt (>50 mol%) gave the typical XRD pattern of Co_3O_4 .

Sinha and Shankar (1993) explored cobalt oxide catalysts supported on silica gel for the catalytic combustion process for removal of organic pollutants from effluent 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 deactivations 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 gas. Results of studies were obtained from using nitrogen adsorption, XRD, and XPS techniques.

Kang and Wan (1994) investigated the role of acid and basic additive enhanced the carbon monoxide oxidation, but acid additives decreased oxidation. On the other hand, the addition of a base additive to the catalyst could reduce the ethane conversion.

Pepe and Occhiuzzi (1994) studied the spinel solid solutions of $\text{Co}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ with $x = 0-1$ as catalysts for CO oxidation by molecular O_2 . The catalytic activity for carbon monoxide oxidation was investigated in the $170-470^\circ\text{C}$ temperature range on the solid solution. The catalytic activity increased with increasing cobalt contents. The activity per ion (turnover frequency) was fairly

constant over the whole range of cobalt contents. It was inferred that each Co^{2+} ion was active irrespective of its concentration and configuration (isolated, in clusters).

Sewell *et al.* (1996) studied a combined TPR/TPO technique for characterization of supported cobalt catalysts. The results showed that the extent of metal reduction following hydrogen reduction at 500°C is affected considerably by the type of metal carrier. In particular, the extent of metal reduction decreased with increasing aluminium content of the support material. Decreasing extents of metal reduction could be correlated with an increase in the temperature required for reduction of the nitrate ion during TPR. Increasing the time and temperature of hydrogen reduction results in increased extents of metal reduction.

Drago and co-workers (1997) studied the catalytic decomposition of N_2O using metal oxides supported on silica magnesium oxide, and calcium oxide. CoO was more active than CuO and Fe_3O_3 when supported on silica. A conversion of 95% was achieved using CoO on silica at $1500\text{ h}^{-1}\text{GHSV}$, 1500°C , and 50,000 ppm feed N_2O . They found that when supporting CoO on MgO , a much more active catalyst was attained. A conversion of 95% was achieved using this catalyst at $40,000\text{ h}^{-1}\text{GHSV}$, 500°C and 100,000 ppm N_2O feed. This was a significant improvement over any catalyst currently in the literature. The activity of this catalyst was decreased by calcination at $1,000^\circ\text{C}$. XPS and XRD studies revealed that higher calcination temperature led to an inactive crystalline phase. The active catalyst displayed a less crystalline phase involving the support and metal oxide. Other oxide combination catalysts were found to be less active than the CoO/MgO catalyst.

Querini *et al.* (1998) investigated the catalytic combustion of diesel soot particles on Co/MgO (12wt%Co) and potassium-promoted Co/MgO (1.5wt%K) catalysts that were calcined at different temperatures in the 300 to 700°C range. The results of characterization and catalytic activity show a correlation between the structure of the catalyst and the calcination temperature. While the samples calcined at temperature of 300 and 400°C show catalytic activity for soot combustion, those calcined at 500°C or higher are practically inactive. The TPR, ESR and XRD results indicated that this is due to the formation of Mg-Co mixed oxide. The promotion of

these solids with potassium not only increases the sample activity, probably due to the important in surface mobility, but also enhanced stability at high temperatures.

Szalowski *et al.* (1998) studied a cobalt oxide catalyst for ammonia oxidation. Its active compound was Co_3O_4 . It has been found that much less nitrous oxide was produced in ammonia oxidation on this catalyst than on platinum. The microstructure of the cobalt catalysts, and especially the presence of mesopores of diameter $<0.1 \mu\text{m}$ have an essential effect on their activity and selectivity and on the stability of these properties. In the macrostructure of selective and stable catalysts the share of the mesopores $<0.1 \mu\text{m}$ is extremely low, while the total pore volume amounts from some tens to a hundred and some ten of mm^3/g .

Youngwanishate (1998) studied the oxidation property of the Co-Mg-O catalyst in the oxidation reaction of propane, propene, 1-propanol, and CO. It was found that the oxidation property of Co-Mg-O catalysts depends upon the type of reactants. For 1-propanol oxidation, at low reaction temperature and low 1-propanol conversion Co-Mg-O catalyst behaves as a selective catalyst. While at high reaction temperature it plays role as a combustion catalyst. 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.

Kittikerdkulchai (1999) investigated the oxidation property of the Co/MgO (8wt%Co) and Co/Al₂O₃ (8%wtCo) catalysts by using the oxidation reaction of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol as test reactions. The nature of support affected the catalytic activity and selectivity of the catalyst for ethanol, 1-propanol, and 2-propanol oxidation. The basic support, MgO, promoted aldehyde formation for the oxidation of the ethanol and 1-propanol while the acidic supports promoted the formation of alkene instead.

Miro *et al.* (1999) studied the catalytic combustion of diesel soot over 12%Co and 4.5%K, supported on MgO and CeO₂ 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, CoO_x species were responsible for the supply of oxygen by a redox reaction. In this catalyst, K plays different roles, one of them being the stabilization of the CoO_x particles. XPS analysis indicated that the oxygen availability on the surface is much higher on CeO_2 than on MgO.

Ruckenstein and Wang (2000) investigated the effect of calcination conditions on the species formed and the reduction behavior of the Co/MgO catalysts. As observed by TPR and XRD results, many factors affect the structural and chemical properties of the MgO-supported Co catalysts. The structural changes are mainly induced by the tendency to form a solid solution between CoO and MgO. The extent of solid solution formation increased as the calcination temperature and calcination time increased. A much lower calcination temperature was needed to form a solid solution in the impregnated catalysts than in the physically mixed ones. The formation of a solid solution rendered the catalyst less reducible.

Ji *et al.* (2001) studied the catalytic combustion of methane over cobalt-magnesium oxide solid solution catalysts. A series of cobalt-magnesium oxide solid solution catalysts (CoMgO) have been prepared using urea combustion methods, and characterized by X-ray diffraction (XRD) and laser Raman (LR). The catalytic activities for methane combustion have been tested in a continuous flow microreactor. The Co content has a significant effect on the activity of the cobalt-magnesium oxide solid solution catalysts. The catalysts containing 5 and 10% Co have the lowest light-off temperature in methane combustion. In the preparation of cobalt-magnesium oxide solid solution catalysts, higher urea to metal ratio favors the formation of the catalysts with smaller crystal particles and leads to a better catalytic performance for methane combustion. Addition of lanthanum nitrate to the solution of Co and Mg nitrate depressed the formation of the cobalt-magnesium oxide solid solution and decreased the activity of the catalysts for methane combustion. The cobalt magnesium oxide solid solution catalysts are very stable when the calcination or reaction temperature is no more than 900°C . However, the catalytic activity decreases rapidly after high temperature ($>1000^\circ\text{C}$) calcination, possibly due to sintering of the catalyst and thus decrease of the surface area.

Ruckenstein and Wang (2001) studied the combined catalytic partial oxidation and CO₂ reforming of methane over the reduced Co/MgO, Co/CaO, and Co/SiO₂ catalysts. Only Co/MgO has proved to be a highly efficient and stable catalyst. It provided about 94-95% yields to H₂ and CO at the high space velocity of 105 000 ml g⁻¹h⁻¹ and for feed ratios CH₄/CO₂/O₂ = 4/2/1, without any deactivation for a period of study of 110 h. In contrast, the reduced Co/CaO and Co/SiO₂ provided no activity for the formation of H₂ and CO.

2.2 Comments on previous works

In the previous researches there are many works about cobalt oxide for the combustion of methane, ammonia and diesel soot. However, there are a few studies about supported cobalt catalysts on the combustion of organic acids. Since MgO is not a too strong basic metal oxide to adsorb carbon dioxide to form carbonate compound and it is strong enough to adsorb organic acid, it is used as basic metal oxide for cobalt oxide, acidic metal oxide, to attain organic acids combustion catalyst.

In this study, the oxidation properties of Co-Mg-O/Al₂O₃ catalyst on phthalic anhydride and maleic anhydride are studied. Moreover, the effects of cobalt and magnesium loading on the oxidation property of Co-Mg-O/Al₂O₃ catalyst are also investigated.

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