CHAPTER II
LITERATURE REVIEWS

Partial oxidation processes using air or oxygen are used to manufacture a variety of chemicals, and complete catalytic oxidation is a widely used method for elimination of organic pollutants in gaseous streams. Effective catalysts for oxidation reactions fall into two categories, transition metal oxides and metals. Supported cobalt catalysts show high catalytic activity when compare with other transition metal oxides. 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 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 means of Fourier-transform infrared (FT-IR) spectroscopy. The IR absorption bands of Co_3O_4 were 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 $517^{\circ}C$, 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) reported that cobalt oxide (Co_3O_4) deposited on alumina-based supports active for the oxidation of methane to CO_2 and water within $500^{\circ}C$. Alumina was found not to be a good support because at reaction temperature higher than $500^{\circ}C$, reaction between Co_3O_4 and alumina support occurring which resulted in the formation of $CoAl_2O_4$, 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 Co(II) ions have a strong affinity, therefore leading to $CoAl_2O_4$ formation. In addition, for a good catalytic oxidation, Co(II) and Co(III) ions must be presented at the catalyst surface is possible. At low temperature the kinetics of this reaction were slow. At high temperature and in the presence of water, the formation of the cobalt aluminate phase was thermodynamically and kinetically favored. During the catalytic activity measurement deactivation is often observed. The main causes were suggested to be (i) sintering of the active phase and (ii) reaction of the support with an active phase leading to an inactive phase.

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 low cobalt loadings the cobalt phase was present primarily as $CoAl_2O_4$. For catalysts having high cobalt contents, bulk Co_3O_4 was observed. CO hydrogenation activity measurement was carried on these catalysts. The catalytic activity was increased with increasing cobalt loading. Nevertheless, if the comparison was based on cobalt metal, there was an optimum activity at $12wt\%Co/Al_2O_3$. 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. A higher cobalt loading favored large particles gave a low activity when expressed per gram of cobalt introduced.

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/Al_2O_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 CoO/Al_2O_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 $650^\circ C$ 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.

Sewell *et al.* (1996) characterized supported cobalt catalysts by TPR/TPO techniques. They found that the extent of metal reduction decreased with increasing aluminum content of the support material. Decreasing extents of metal reduction correlated with an increase in the temperature required for reduction of the nitrate ion during TPR. Increasing time and temperature of hydrogen reduction resulted in increased extents of metal reduction. The temperature at which oxidation of the supported metal occurred was generally lower than that for unsupported cobalt metal. These differences may be due either to a particle size effect or to an electronic interaction between the reduced metal and the cobalt support.

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_3O_4. The role of O_2 seemed to maintain the surface stoichiometry of Co_3O_4. The main reason of decrease of catalytic activity of samples based on MgO, SiO_2, and Al_2O_3 in selective catalytic reduction of NO was due to oxide-oxide interaction promoted by water. All the carriers could be placed by the capability for oxide-oxide interaction in the following order: $SiO_2 \gg MgO > Al_2O_3$.

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 $700^\circ C$ range. Catalyst samples were characterized by various techniques then they observed by TPO experiments that the catalyst activity depended strongly on the calcination temperature: calcination at 300 and 400 $^\circ C$ produced samples that were much more

active than those calcined at higher temperatures, on which an inactive Mg-Co mixed oxide was formed. The activity of unpromoted samples correlated with the amount of reducible Co species present. Potassium not only increased the sample activity but also enhanced stability at high temperatures.

Szalowski et al. (1998) studied the properties of cobalt oxide catalyst for ammonia oxidation. The catalyst active component was Co_3O_4. It was found that much less nitrous oxide was produced in ammonia oxidation on this catalyst than on platinum. The macrostructure of the catalysts had an essential effect on their activity, selectivity and stability.

Youngwanishsate (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 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°C. 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 played role as a combustion catalyst.

Kittikerdkulchai (1999) studied oxidation property of the Co-Mg-O (8wt%Co) catalyst by using the oxidation reaction of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol as test reactions. The oxidation property of 8Co/MgO catalyst depends upon the type of reactant. For the oxidation of methanol and 1-butanol, 8Co/MgO catalyst played a role as a combustion catalyst at all the reaction temperature range. In case of ethanol, 1-propanol, and 2-propanol oxidation reaction, it was found that 8Co/MgO catalyst was an active and selective catalyst. It provided the maximum acetaldehyde and propionaldehyde yield ca. 58% and 53%, respectively, at 400°C. In addition, it was also shown that the type of support affected the catalytic activity and selectivity of supported cobalt oxide catalyst.

Querini et al. (1999) studied the diesel soot catalytic combustion over 12 wt.% of Co and 4.5 or 7.5 wt.% of K, supported on MgO and 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. Cobalt oxide species were responsible for the supply of oxygen during the redox reaction. It has been found that the thermal deactivation mechanism strongly depended on the support. In case of MgO, the formation of solid solution (Co,Mg) with low redox capacity is responsible for deactivation. The presence of 7.5% of K avoided the formation of the solid solution thus preserving the activity

Chaiyasit (2000) investigated the selective oxidation reaction of 1-propanol and 2-propanol over Co-Mg-O/TiO$_2$ (8wt%Co, 1wt%Mg) catalyst. It was found that the oxidation property of Co-Mg-O/TiO$_2$ catalyst depends on type of the reactants. Propionaldehyde was the main product for selective oxidation of 1-propanol. In case of 2-propanol oxidation reaction, it was found that Co-Mg-O/TiO$_2$ catalyst was an active catalyst for selective oxidation reaction. The main product at low reaction temperature was propylene while at high reaction temperature the main reaction products are propylene and propionaldehyde. From the result of propylene oxidation, it could be indicated that propionaldehyde was produced directly from propylene. In addition, the sequence of cobalt and magnesium loading has no effect on the structure and catalytic performance of this catalyst. While the type of support affected the selectivity of supported cobalt catalyst.

Ruckenstein and Wang (2000) investigated the structural characteristics and the reduction behavior of the Co/MgO catalysts by using temperature programmed reduction (TPR) and X-ray diffraction (XRD). The variables investigated include the preparation method and heat treatment conditions (calcination temperature and time). Depending on these factors, Co-containing species. Co$_3$O$_4$, MgCo$_2$O$_4$ and (Co,Mg)O (solid solution of CoO and MgO) were identified. 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. Finally, it was found that the amount of carbon deposited decreased with increasing extent of solid solution formation.

Zhenghong *et al.* (2001) studied the effect of different resin supports on activity and stability of Co catalyst for the oxidation of *p*-cresol to *p*-hydroxybenzadehyde by using four kinds of supported cobalt oxide catalysts. The catalysts were prepared by using different resins as support. It was found that three kinds of supported cobalt oxide catalysts using general macroporous resins as support were all of good catalytic activity and selectivity, but the stability of these catalysts was related to each resin's composition and polarity. As a result, the macroporous strongly acidic action exchange resin (D072) was selected as an ideal support of Co catalyst for this reaction, because D072-supported cobalt oxide catalyst exhibited both extremely high activity and good stability.

Brik *et al.* (2001) investigated ethane oxidative dehydrogenation (ODH) over TiO_2-supported cobalt and cobalt-phosphorous catalysts. It was found that at low cobalt loadings, the carrier is essentially covered by octahedral Co^{2+} ions, whereas at concentrations superior to 3.7 wt.% formation of the Co_3O_4 spinel was observed. The best performance in ethane ODH was achieved at 550 °C with the sample containing 7.6 wt.% Co. Addition of phosphorous to $Co(7.6)/TiO_2$ catalysts results in the reduction of Co^{3+} ions and growth of amorphous cobalt-phosphorous compounds which provoke a severe decrease of the catalyst performance.

Ji *et al.* (2001) studied catalytic combustion of methane over cobalt-magnesium oxide solid solution catalysts. The catalysts were prepared by urea combustion method, Co content has a significant effect on the activity of the cobalt-magnesium oxide solid solution catalysts. In the preparation of cobalt-magnesium oxide 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. The 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°C) calcination, possibly due to sintering of the catalyst.

Ruckenstein and Wang (2001a) investigated the partial oxidation of methane to synthesis gas over alkaline earth metal oxide supported Co catalysts. Only MgO has proved to be a suitable support. The reaction behavior of the MgO-supported Co

catalysts was significantly influenced by the calcination temperature and Co loading. The 24 wt.% Co/MgO catalyst precalcined at 800 °C provided a high and stable activity; those precalcined at higher temperatures provided a lower stable activity and those precalcined at lower temperatures provide a lower stability.

Ruckenstein and Wang (2001b) investigated the combined partial oxidation and CO_2 reforming of methane to synthesis gas over the reduced Co/MgO, Co/CaO and Co/SiO_2 catalysts. Only Co/MgO has proved to be a highly efficient and stable catalyst. It provided high yield to H_2 and CO, without any deactivation through the period of study.

Bechara *et al.* (2001) studied the carbon monoxide hydrogenation by using Co/Al_2O_3 catalysts, prepared from four commercial aluminas, with different loading. It was found that an increase in the reaction temperature improves the activity and the selectivity for light products. For the 15 wt.% Co on powder alumina catalyst, the activity and the paraffin/olefin ratio follow a logarithmic decrease with the time on stream. Characterization by XRD, XPS and SSA measurements have shown the presence of heavy hydrocarbon in the tested catalyst porosity. The cobalt loading and the porosity of supports modify the catalytic properties through their effects on the reducibility of the active phase. An increase in the extent of reduction improves the activity and the selectivity for high molecular hydrocarbons weight.

2.2 Comment on previous works

From the previous studies, there are many researches about cobalt oxide on various supports such as Al_2O_3, TiO_2, MgO and SiO_2. Most of these researches studied only activity and selectivity of their catalysts but they ignore to consider the stability, which is the important property of catalyst.

In this study, the stability of Co-Mg-O/TiO_2 and Co-Mg-O/Al_2O_3 catalysts on the selective oxidation of 1-propanol and 2-propanol are investigated. Moreover, the effects of sequence of metal loading to the stability of catalysts are also examined.