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, cobalt oxide and acidic 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. Nevertheless, there are a few studies about basic supported cobalt oxide catalyst.

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

2.1 Reviewed literature

This section presents studies about cobalt oxide and oxidation reactions:

Garbowski *et al.* (1990) have reported that cobalt oxide (Co_3O_4) deposited on alumina-based supports active for the oxidation of methane to carbon dioxide and water within 500°C. Alumina was found not to be a good support because at reaction temperature higher than 500°C, reaction between Co_3O_4 and alumina support occurred 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 present 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

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

Chan and Smith (1990) investigated a series of Co-Mg-oxide catalysts for the oxidative coupling of methane. The performance of the mixed oxides was found to be depended on the preparation procedure and their cobalt oxide content. The catalysts prepared by coprecipitation were amorphous according to X-ray Diffraction (XRD) analysis and inactive toward the oxidative coupling of methane whereas the catalysts prepared by mixing procedure retained their crystallinity and were active toward the oxidative coupling reaction. From these results it was concluded that the crystallinity of the MgO was important in producing selective catalysts. Preparation by physically mixing the oxide led to crystalline MgO that gave active and selective cobalt-magnesium oxide catalyst, whereas, the materials prepared by coprecipitation, were amorphous and nonselective to higher hydrocarbon production.

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°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/Al_2O_3, a broad peak appeared above 900°C. As cobalt loading was increased, a H_2 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 the cobalt loading. In addition, both peaks shifted to a lower temperature as cobalt loading was increased. 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 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/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.

Halawy and Mohamed (1993) have studied the thermal decomposition of ammonium heptamolybdate and $Co(NO_3)_2.6H_2O$ 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 were 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.

Pepe and Occhiuzzi (1994) studied the spinel solid solutions of $Co_xMg_{1-x}Al_2O_4$ 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°C temperature range on the solid solution. The catalytic activity increased with increasing cobalt content. 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).

Kang and Wan (1994) investigated the role of acid and basic additive to the cobalt oxide catalyst. They found that 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.

Yoon and co-workers (1995a) have investigated catalytic activities of magnesium molybdates actived for the oxidative dehydrogenation of propane with and without molecular oxygen under atmospheric pressure. They found that catalytic activity properties of many molybdates drastically changed with the catalyst composition, and it turned out that $Mg_{0.95}MoO_x$ catalysts having slight excess molybdenum showed the highest activity in the oxidative dehydrogenation of propane, which gave 61% selectivity to propene at 22% conversion of propane at 515°C. The reaction of propane took place at about 360°C and the conversion of propane increased with increasing reaction temperature. On the other hand, the selectivity to propene decreased with increasing reaction temperature. 2-Propanol dehydration/dehydrogenation reaction was used to investigate the acidity and basicity of the catalysts. This reaction indicated that the oxidation activities of the catalysts linearly increased with increasing acidic properties of the magnesium molybdate catalysts. In addition, the lattice oxide ions of the catalyst surface acted as active species for the oxidative dehydrogenation of propane to propene.

Yoon *et al.* (1995b) have studied catalytic activities of various metal molybdates for the gas-phase partial oxidation of propane with molecular oxygen under an atmospheric pressure in the temperature range 325-500°C. Metal molybdate catalysts were found to mostly promote the oxidative dehydrogenation of propane to propene. Of the catalysts, cobalt molybdate showed the highest catalytic performance for the oxidative dehydrogenation and the catalytic property strongly depended on the catalyst composition. $Co_{0.95}MoO$ catalyst gave 60% selectivity to propene at 20% conversion at 450°C. The catalytic activity strongly depended on the kind of metal cations. $CoMoO_4$ catalyst was found to be the most active and selective for the oxidative dehydrogenation of propane while $NiMoO_4$ was found to show the highest activity for the propane oxidation but was nonselective. $MnMoO_4$ catalyst revealed a

very poor activity. All molybdates of metal oxides having solid-base properties such as MgO, CaO, SrO, BaO, La_2O_3, Sm_2O_3, and ZnO showed quite high selective to propene formation but the catalytic activities were lower than $CoMnO_4$. More than 80% selectivity to propene was attained on each catalyst but their catalytic activities differed greatly. Temperature-programmed desorption (TPD) measurement and pulse reduction experiments suggested that the weak surface acidic molybdate catalysts may effective by promote the oxidative dehydrogenation of propane and reduced surface catalyst was more selective for the formation of propene

Grabowski *et al.* (1996) studied the oxidative dehydrogenation of isobutane on chromia supported on SiO_2, Al_2O_3, TiO_2, ZrO_2 and MgO. The supported chromia has been found to be active in the ODH of isobutane at relatively low temperatures 200-400°C. The total selectivity and selectivity to isobutene depending on the nature of the support.

Hilmen and co-workers (1996) have investigated the effect of small amount of Re on the reduction properties of γ-alumina supported cobalt catalyst by TPR technique. An intimate mixture of Co/Al_2O_3 and Re/Al_2O_3 catalysts showed a promoting effect of Re on the reduction of cobalt. It was suggested that Re promotes the reduction of cobalt oxide by hydrogen spillover. It was also shown that the presence of high temperature TPR peak at 900°C assigned to cobalt aluminate.

Santos *et al.* (1996) have studied the oxidation of methane to synthesis gas on Co(12%)/MgO catalysts. The XRD patterns showed that the fresh catalysts were made up of MgO and $MgCoO_2$. No cobalt oxide crystalline was detected in these patterns. Besides, the TPR thermograms did not show any well-define reduction peak up to 900°C due to the low reducibility of catalyst. This was expected that $MgCoO_2$ 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 CO_2 and H_2O 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 selectivities to CO and H_2 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 selectivities for both CO and H_2 which reached a value very close to equilibrium

Finocchio et $al.$ (1997) have studied the oxidation of the C_3 organic compounds propane, propene, acrolein, propan-2-ol, and acetone over three transition-metal oxide catalysts, Co_3O_4, $MgCr_2O_4$, and CuO in a flow reactor and using FTIR spectroscopy to study the adsorbed species. They found that Co_3O_4 and $MgCr_2O_4$ 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_3O_4 and $MgCr_2O_4$ were 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_3 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 $Co_3O_4 >$ $MgCr_2O_4 > CuO$; for propene oxidation the scale was $Co_3O_4 \approx MgCr_2O_4 > CuO$; for propan-2-ol oxidation the conversion scale was $Co_3O_4 \geq CuO > MgCr_2O_4$.

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 h^{-1} 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 h^{-1} 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°C. XPS and XRD studied revealed that higher temperature calicination 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.

Baldi and co-worker (1998) investigated the catalytic oxidation of propane, propene, 1-propanol, 2-propanol, prop-2-en-1-ol (allyl alcohol), propanal, propanone (acetone), and propenal (acolein) over Mn_3O_4 in the presence of excess oxygen. Total combustion to CO_2 occurred at temperature > 350°C (400°C for propane). For propane oxidation, the main product observed was always CO_2, but significant amounts of propene were observed when propane conversion was still definitely incomplete. While propene oxidation, CO_2 selectivity was always near 100% with only traces of 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 CO_2 and acetaldehyde. Comparison with the previous study, in the case of propane and 2-propanol oxidation, Mn_3O_4 was lower active than Co_3O_4 catalyst.

Luo et al. (1998) studied silver-cobalt oxide supported on Al_2O_3 catalyst for carbon monoxide oxidation reaction. The catalyst was characterized by means of XRD, H_2-TPR, and O_2-TPD. They reported that the silver promoted the reduction of cobalt oxide. The activity of silver-cobalt oxide catalysts was higher than that of cobalt oxide catalyst for carbon monoxide, acetone, and pyridine oxidation.

Grzybowska et al. (1998) have investigated the oxidative dehy- drogenation of isobutane on the chromium oxide-alumina catalyst of Cr loading varied between 1 and 50 Cr nm^{-2}. The initial activity increased sharply with the increase in the Cr loading up to about 10 Cr nm^{-2}. A small increase in the activity with the further increase in the Cr loading showed that the chromia phase detected at higher Cr content was only

a little active. In accordance to the general rules for partial oxidation reaction, the higher bond energy of the labile oxygen species during the catalytic reaction might account for the higher selectivity to isobutene in the chromium oxide-alumina catalyst, compare with unsupported chromia. The difference in the oxygen bond energy in CrO_x species on alumina support and on the unsupported chromia could be due to the interaction of the active phase with the support and the formation of the Cr-O-Al bonds, which were stronger than those in the Cr-O-Cr chain on chromia. The marked difference in the reoxidation rate, on the other hand, suggested that the dissociation of the oxygen molecule and the electron transfer accompanying the passage from O_2 to O^{2-}. Comparison of the catalytic properties of the chromium-oxide alumina catalyst with those of unsupported chromia showed that unsupported chromia was more active but less selective to isobutene than the chromium-oxide alumina catalyst at the optimum range of the Cr loading.

2.2 Comment on previous works

In the previous researches there are many works about cobalt oxide and acidic supported cobalt oxide, such as Co_3O_4/Al_2O_3 catalysts, for total oxidation of organic compounds and CO. However, there are a few studies about basic supported cobalt oxide catalyst for the oxidation of organic compounds and CO [*e.g.* Chan and Smith (1990), Santos *et al.* (1996)]. Many studies find that the basic support that usually be used for partial oxidation reaction is MgO [*e.g.* Chaar *et al.* (1987), Yoon *et al.* (1995a)]. Due to the fact that MgO support can reduce strong oxidation capability of catalyst to attain partial oxidation catalyst. For that reason, in this research MgO is used as support for cobalt oxide catalyst. In order to investigate the characteristic of this catalyst, the oxidation reaction of Co-Mg-O catalyst was performed on organic compounds and CO.

In this study, the oxidation property of Co-Mg-O catalyst on propane, 1-propanol, propene, and CO are explored and the effect of cobalt loading on the oxidation property on Co-Mg-O catalyst is investigated.