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Review Article

THE CHARACTERISTICS OF SUPPORTED COBALT CATALYSTS ON CO HYDROGENATION USING ALUMINA, SILICA, AND ZIRCONIA AS SUPPORTS

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ABSTRACT

The catalytic details of cobalt catalysts supported on alumina, silica, and zirconia for CO hydrogenation and Fischer-Tropsch reaction were specifically addressed. The details were mentioned in terms of qualitative advantage and disadvantage points of the catalysts. High surface area synthesized zirconia seems to be a practical catalyst support for hydrocarbon synthesis owing to their significant modification of coverage cobalt oxide particles. The support interaction suggests lowering the standard reduction temperature, increasing active cobalt atom dispersions, and selecting towards long chain hydrocarbon products compared to silica and alumina supports. However, the application as industrial supported cobalt catalysts should be considered in corresponding to long lasting operation and highly expensive investment. The images of TEM, SEM, and the x-ray diffraction patterns were used as examples of the materials morphology and crystal characteristics. The comparison of advantages and disadvantages among different supports for the Co catalyst were discussed in details.

Keywords: Cobalt catalyst, support, CO hydrogenation, and catalytic activity.

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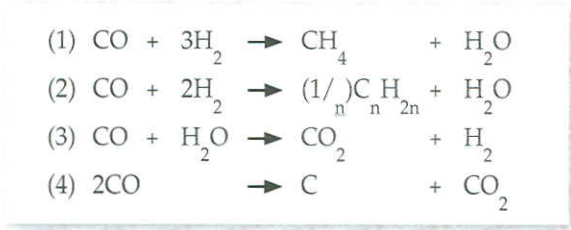
INTRODUCTION

Long chain hydrocarbon catalyticallysynthesized via the Fischer-Tropsch reaction, which can beascribed by the following set of reactions 1-4 (Farrauto and Bartholomew, 1997), has been raised most attention from many scientists and researchers in order to compensate crude oil deficiency causing to worldwide energy crisis.



This alternative fuel is available from variable sources, i.e., coal and biomass, converted by active catalysts as Co or Fe selectively towards hydrocarbon. The Fe catalysts focus on olefin production, whereas cobalt catalysts produce long chain hydrocarbons or petroleum wax to be sequentially cracked into synthetic fuels, such as gasoline and diesel fuel. The rarely available cobalt element is more expensive, but it has been the most remarkable one with high catalytic efficiency, appreciable selectivity to C_4-C_5, and decrease in side reaction such as water gas shift. The number of designated cobalt catalysts based on various types of support materials has been widely researched to find the promising one suitable for hydrocarbon synthesis; however, there has been none of any comparative article collecting these available catalytic results. This article aims to categorize the existing catalysts with their details, which have been researched on FT reaction or CO hydrogenation, by various types of general support, i.e., alumina, and silica in comparison with the novel one such as zirconia.

1. Catalytic characteristics of cobalt catalyst supported by alumina

1.1. Study of CH_4 formation from pre-adsorbed CO on alumina supported cobalt catalysts

The mechanisms of CO hydrogenation over cobalt catalysts supported by alumina have been of interest for many scientists since the mechanism pathways could selectively predict the hydrogenation products. Dai and Yu (2008) proposed two carbonaceous species over the cobalt catalysts supported by alumina in accordance with hydrogen temperature programed surface reaction (H_2-TPSR) results. The experimental conditions were varied with temperature of CO preadsortion and catalyst calcination temperature. They reported that the preadsorbed CO was slightly lost their activity according to increases of adsorption temperature and catalyst calcination temperature. The carbonaceous active states were defined as α-carbon and β-carbon, which were different in reactive temperature. Lee and Bartholomew (1989) found the point corresponding to the results of Dai and Yu. They proposed that the three-dimensional structure of cobalt crystallites possibly adsorb the more active state carbon, whereas the other less active state may exist on the catalyst supports, namely, as methoxy or formate species originally derived from spillover hydrogen and carbon monoxide.

1.2. Influence of the presence of promoters

Alumina has been mentioned as a remarkable support in comparison with TiO_2 and SiO_2 owning to the significant interaction of cobalt catalyst (Jacobs et al., 2002; Frøseth et al., 2005). Moreover, it has been reported that the cobalt catalyst supported by alumina enhance their catalytic activity with additional promoters. The reduction temperature of cobalt oxide species and cobalt oxide species interacting with support decreased with addition of Ru and Pt, while Re reduced only the reaction temperature of the supported cobalt species.

Generally, it was reported that noble metal promoters gave a smaller size of Co species after reduction proven by H_2 chemisorption/pulse reoxidation results, and it was reduced at the same temperature as the catalyst without promoter indicating that these promoters aided in reduction of smaller size clusters (Jacobs et al., 2002; Frøseth et al., 2005). Recently, the non-reducible oxide has been introduced as promoters, such as Mg, B, La, Zr, and K. The reduction temperature of Co species shifted to higher temperature causing decrease of reducibility. Magnesia is one of the interesting non-reducible promoters. Addition of small amount magnesia content can

prevent the formation of cobalt alumina compound and increase cobalt metal atom dispersion leading to enhance the catalytic activity (Zhang et al., 2005). However, the activity can decrease with more than 2 wt % additional content of magnesia according to the formation of MgO-CoO solid solution. Besides magnesia promoter, the experiment of Jongsomjit et al. (2003) focused on Zr-modified supports and they showed that increase of cobalt metal atom dispersion can occur with Zr-modified alumina support owing to decrease in reduction temperature leading to increase of cobalt oxide reducibility. Coverage of Zr modification over alumina was found to stabilize support surface and prevent or block the formation of cobalt aluminate. The major impact of Zr modification mainly on increase of active Co surface sites was confirmed by the results from steady-state isotopic transient kinetic analysis (SSIKA) demonstrating that intrinsic pseudo- first order activity ($1/T_M$) remained constant in accordance with the SSIKA results confirmed by Rohr et al. (2000). Jongsomjit et al. (2001) revealed the effect of water occurring from the standard reduction on increase of cobalt aluminate compound and existence of Ru promoter can minimize impact of water. The effect of Ru on Co species formation during the standard reduction, on which the in-situ atomic resolution images and electron energy-loss nanoanalyses were proven, was also investigated by Li et al. (2006). The Ru promoter was found to facilitate the formation of individual CoRu bimetallic nano-particles, small size Ru, and small CoO particles, which were easily reduced to be cobalt metallic sites and gave high reductive performance. Chu et al. (2007) exhibited that the promotion of Pt had no significant effect on the particle sizes of alumina supported Co_3O_4 crystallites, which seems to be varied primarily by the pore diameter of support. The conclusion of Chu and co-workers is in agreement with Jacobs et al. (2002) that the Pt promotion leads to the reduction of smaller cobalt oxide particles, which could not be reduced at the same condition in the cobalt monometallic catalysts confirmed by analysis of magnetization data.

1.3 Impact of cobalt starting precursors, loading, support pretreatments and phases of alumina on catalytic activities

Besides the promoters, effect of intrinsic nature of alumina surface on cobalt metallic site dispersion and catalytic activity was reported by Pansanga et al. (2008). The CO hydrogenation was observed over cobalt catalysts supported by various mixed phases of χ- and γ- alumina, and these catalysts exhibited the significant increase of cobalt dispersion. The role of alumina phase, i.e., γ- and α- alumina on Fischer-Tropsch reaction, was also observed by Brog et al. (2008). Various cobalt particle sizes on α - and γ- alumina supports were prepared by the application of different starting cobalt precursor solvents, such as water, ethylene glycol, diethylene glycol at various cobalt loadings. The optimum cobalt particle size at 7-8 nm on γ- alumina based catalysts gave the highest value of C_5 selectivity among the other sizes, ranging from 3 to 18 nm, unlike α - alumina based catalysts giving a larger optimum cobalt particle size for C_5 selectivity. The various sizes of metallic cobalt particles on alumina supports synthesized via different chain length of cobalt carboxylate (C_2, C_5 and C_9) precursors were reported by Jalama et al. (2007). The cobalt catalysts derived from cobalt acetate was found to present the highest metal support-interaction and showed the poorest catalytic performance according to small metal particle sizes (7 nm), while loss of metal-support interaction owing to larger metal patches (60 nm) on alumina support arising from increase of acetate precursor content, and the cobalt particle size had the influence on catalytic activity significantly.

The impact of cobalt precursor and amount of loading on the ultimate metal particle size and catalytic performance of alumina-support cobalt catalysts was exhibited in 1997 by Van de Loosdrecht et al. (1997). The various cobalt oxide particle sizes obtained by different cobalt precursors, i.e., cobalt EDTA, ammonia cobalt citrate, and cobalt nitrate, gave a significant role on catalytic activity. The small oxide particle sizes derived from cobalt EDTA and ammonia cobalt citrate were inactive after standard reduction possibly due to the formation of cobalt aluminate, whereas the larger oxide particles derived from cobalt nitrate was easily

reduced and more active for Fischer-Tropsch reaction. They noticed the high loading cobalt oxide possessed high dispersion of cobalt metal atoms while comparing to the lower loading. Zhang et al. (2003) found that the cobalt oxide crystallite sizes of oxidic catalyst precursors were almost unaffected by different support pretreatment. However, it apparently influenced on the catalyst reducibility, adsorption and catalytic properties of these Co catalysts since the surface electronic charge of alumina treated by different chemicals, such as water, ethanol, acetic acid, ammonium nitrate, and ammonia significantly altered the interaction between support and surface cobalt oxide species. The TEM and SEM images and X-ray diffraction patterns of χ- alumina and γ- alumina are shown in Figure 1.

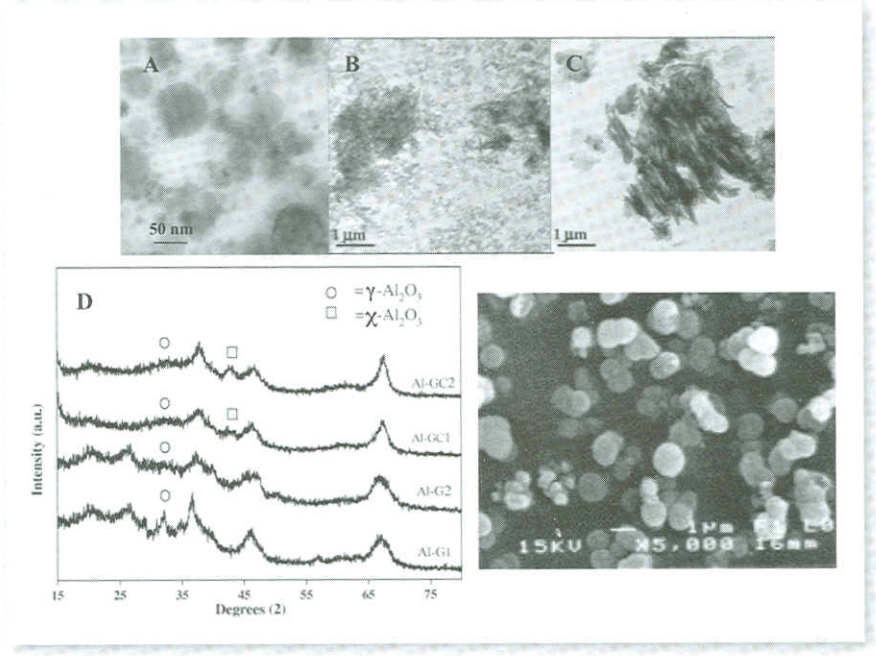


Figure 1. (A) TEM image of nano-alumina (Burakorn et al., 2008), (B) and (C) TEM images of cobalt catalyst supported (B) γ-alumina (Pansanga et al., 2008), (C) mixed phases of γ- and χ-alumina (Pansanga et al., 2008), (D) X-ray diffraction patterns of γ- and χ- alumina (Pansanga et al., 2008), (E) SEM image of as-synthesis alumina prepared by solvolthermal method (Mekasuwandamrong et al, 2003).

2. Catalytic characteristics of cobalt catalyst supported by silica

2.1 The catalytic activity of silica supported cobalt catalysts prepared by controlling pH

The silica or silica gel has been regarded as catalyst support owing to high surface area for dispersion of active component. Many studies reported that silica surface could react strongly with cobalt species at high temperature to form cobalt silicate, although it is chemically inert. However, it has been introduced as a cobalt catalyst support for Fischer-Tropsch reaction since it was found that the surface electronics charge and ion exchange behavior in an aqueous solution might significantly affect the cobalt-support interaction and catalyst reducibility. Ming and Baker (1995) studied on the role of surface electronics charge and ion exchange behavior on Fischer-Tropsch reaction at various pH impregnations, which were controlled by nitric acid, urea, and ethylene diamine. At pH condition around the point of zero charge (at pH~ 4.6 approximately), the silica gel surface is slightly negative charged and the attraction forces favor adsorption of the positive cobalt ions consequently resulting in high metallic cobalt dispersion and good catalytic activity. Ernts et al. (1999) suggested that structure of silica supports

was controllable by the pH of preparation. They prepared two structurally different catalysts from a pseudo sol-gel method combining the hydrolysis of cobalt nitrate precursor chelated by oxalic acid and condensation of tetra-ethoxysilane (TEOS). The resulting silica consisted of a polymeric network with few branches bringing about the microporous structure in acid medium, whereas the mesoporous structure composed of more branched polymers was obtained by basic medium. The resulting silica was employed as support for cobalt catalysts by one-step synthesis to obtain high cobalt content (≥ 25 wt %) and they exhibited high surface reduction degree. However, the catalytic activity was not as high as that of the catalyst prepared by impregnation method with lower cobalt content.

2.2 Influence of the presence of promoters

Matsuzaki and colleagues studied the role of silica that supported cobalt catalyst with promoters in 1996 (Matsuzaki et al., 1996). The cobalt (II) acetate was introduced as a cobalt precursor and it was promoted with transition metals, i.e., Ir, Ru, Rh, Re, Pt, or Os and basic additives, such as alkali and alkaline earth. The particle size of cobalt oxide synthesized by acetate precursor was less than 1 nm observed by TEM, but it was inactive in comparison with cobalt species derived from cobalt nitrate, cobalt chloride, and dicobalt-octracarbonyl precursors. This is owing to a formation of strongly connected Co^{2+} with Si through oxygen as same as Co (II) acetate adsorbed on silica. During standard reduction, the spillover hydrogen activated on the noble metal sites was proposed to promote the reduction of the Co^{2+} oxide species derived from Co (II) acetate to cobalt metals, while the best silica-supported cobalt catalyst was the catalyst derived from dicobalt-octracarbonyl dissolving in hexane without any promoter and the catalyst was active for oxygenated compound formation especially C_2-oxygenates.

Recently, Sun et al. (2002) exhibited the Co^{2+} in cobalt acetate can be easily reduced by the promotion of readily reduced metallic crystalline from cobalt nitrate via H_2 spillover mechanism during the catalyst reduction process and the catalyst promoted with Ru possessed high catalytic activity and high reducibility, whereas Pt and Pd promoters gave high CH_4 selective catalysts, but they was unable to improve the cobalt reduction degree. There was a difference in contact between Co and Ru, Pt or Pd. The cobalt metallic surface particle was enriched with Ru. On the other hand, Pt and Pd dispersed well in the form of Pt-Co or Pd-Co alloy. The impact of Zr promoter was introduced for silica supported cobalt catalyst in order to reduce the strong interaction between cobalt and silica with Zr covered silica surface (Feller et al., 1999). The promotion of Zr seemed to be the most powerful for CO hydrogenation in C_{5+} selectivity when compared to other promoters, and it was confirmed by the results of zirconia-modified-alumina supported cobalt catalyst of Jongsomjit et al. (2003).

2.3. Impact of cobalt starting precursors, catalyst pretreatments and various types of silica supports on catalytic activities

The effect of cobalt precursor on active metallic cobalt particles was also reported by Panpranot et al. (2003). In this experiment, the cobalt nitrate was reported to be the best precursor for preparing high-activity MCM-41-supported cobalt Fischer-Tropsch synthesis catalyst when compared to cobalt chloride, cobalt acetate, and cobalt acetylacetonate. The organic precursors, i.e., cobalt acetate, and acetylacetonate, gave very small cobalt oxide particles that could not be detected by XRD even for cobalt loading as high as 8 wt%. Furthermore, Girardon et al. (2005) noticed the effect of catalyst pretreatment conditions on the structure and catalytic performance over cobalt silica-supported Fischer-Tropsch catalysts when the octahedral coordinated cobalt complex occurred the impregnating and drying processes of the catalysts with cobalt nitrate and cobalt acetate precursors, and after the complex decomposition it apparently became Co_3O_4 crystallites. The cobalt silicate species appeared to be dependent on the oxidizing condition,i.e., the exothermic decomposition of different salls in air, and the temperature of oxidative pretreatment.

The well ordered-mesoporous silica (MCM-41) supported CoRu catalysts having average pore

size diameters of 3 and 7 nm were studied for Fischer-Tropach reaction in comparison with the conventional amorphous silica-support CoRu catalyst by Panpranot et al. (2002a). The CoRu/MCM41 had comparable percent Co dispersion to CoRu/SiO_2 for similar Co loading, although the surface areas of CoRu/MCM41 catalysts were much higher than that of CoRu/SiO_2. The CoRu/MCM41 was proven to be poor catalyst with lower reducibility since the water diffusion out of the pore during reduction may be impeded by the restricted mesoporous structure. The effect of pore size on reaction rate or selectivity would be absence probably due to the pores being sufficiently large for the reaction to easily proceed at 1 atmospheric pressure and 220 °C.

The deactivation of mesoporous-silica supported cobalt catalyst was proposed as the results of hydrothermal condition created by high conversion in Fischer-Tropsch hydrocarbon synthesis. Kiss et al. (2003) suggested that the produced water vapor seems to be an important cause of catalyst deactivation since the occurrence of cobalt-silica mixed oxide displaying as a distinctive needle-like morphology found after steamed catalyst samples was likely the same as its morphology appeared after the high FT conversion reaction. A comparative study of two series of Fischer-Tropsch mesoporous silica supported cobalt catalysts, i.e., SBA-15 periodic mesoporous silica with narrow pore size distribution (9.1 nm), and the commercial mesoporous silica with broader pore size distribution (33 nm) was reported by Khodakov et al. (2003). The Co_3O_4 particle sizes, rate of reaction, and product selectivity were clearly dependent on silica pore diameter since the support with large surface area usually contains small pore sizes. These factors could affect various results, i.e., poor and intra-pellet diffusion efficiency of reactants, products bringing about the low transportation of reactant to, and product from catalytic sites. This is in agreement with the results of Panpranot et al. (2002b).

Shinoda et al. (2004) developed a simple preparation method of bimodal pore support by application of SiO_2 or ZrO_2 sols into large pores of silica gel pellet directly. The developed bimodal pore structure was composed of large pores and small pores enlarging surface areas and facilitating high dispersion of supported cobalt crystalline, meanwhile the larger pore would encourage the diffusion of reactants to and product from active sites. The obtained bimodal support was applied in liquid-phase Fischer-Tropsch synthesis for cobalt catalyst, and it presented the best reaction performance as higher reaction rate and lower methane selectivity in comparison with silica gel-supported cobalt catalyst.

Elbashir et al. (2005) proposed an interesting way to overcome the drawback of mass transfer limitation inside the restricted pore structure. The conventional gas-phase Fischer-Tropsch reaction was carried out in comparison with supercritical-phase reaction for silica supported cobalt catalysts. The comparative study revealed the mass transfer limitations typically controlled by inter-particle characteristic of the catalyst was alleviated by the supercritical hexane Fischer-Tropsch synthesis. The TEM and SEM images and x-ray diffraction patterns of amorphous silica are shown in Figure 2.

3. Catalytic characteristics of cobalt catalyst supported by zirconia

The application of zirconia as the cobalt catalyst support has begun a couple decades on CO hydrogenation since zirconia support was found to be selective towards higher hydrocarbon for nickel catalyst of the methanation in 1982 (Bruce and Mathew, 1982). The extended study in Fischer-Tropsch reaction was focused on the combination of nickel and cobalt with zirconia prepared in various ways in 1983 (Bruce et al., 1983). The cobalt-nickel-zirconia catalyst exhibited the comparable activity and selectivity with traditional formulation of cobalt-kieselguhr-additive (Co/SiO_2), but the products was over 60 wt % C_5+ and rich in unsaturated olefin (1-ene) at C_4, C_5, and C_6 levels.

3.1. Effect of zirconia mixed oxide on CO hydrogenation

The available zirconia usually possesses low BET surface area. Thus, they may have limited their

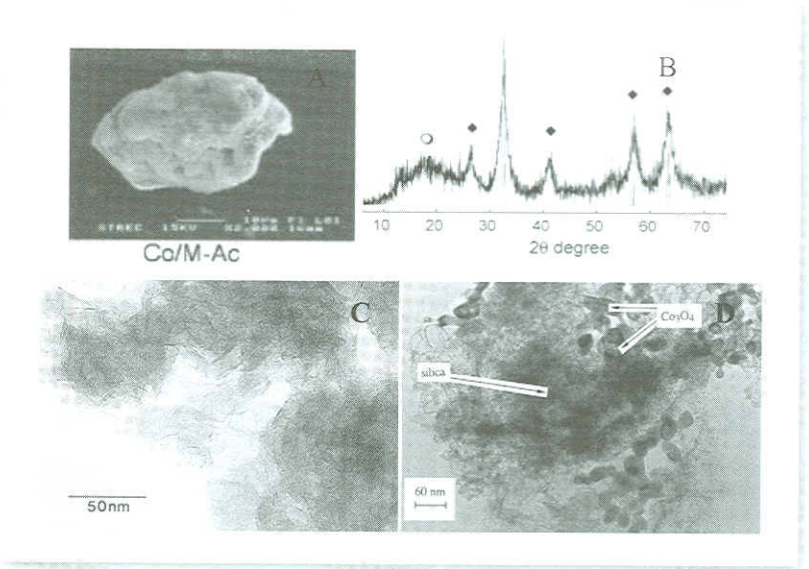


Figure 2. (A) SEM image of MCM41 supported cobalt catalyst (Panpranot et. al., 2003), (B) X-ray diffraction pattern of Co/SiO_2; O: Amorphous silica, and ◆: Co_3O_4 (González et al., 2009), (C) TEM image of a silicate crystalline mesoporous materials (Iwasaki et al., 1998), (D) TEM image of $25\%Co/SiO_2$ (Ernst et al., 1999).

uses as catalyst supports where a high dispersion of metal is required in order to have high catalytic activity (Panpranot et al., 2005). Synthesis of high surface area zirconia has been developed in particular with the use of zirconia mixed oxide which could be recognized as one of the promising way to obtain excellent support (Jongsomjit et al., 2007). It is not only surface area improvement, but also alters metal-support interactions owing to the synergetic properties arising from mixing process. Moreover, the metal-modified zirconia was employed as rhodium catalyst support for selective syngas conversion towards ethanol in 1990 (Benedetti et al., 1990). Tentatively, as a general consideration, support acidic sites were likely to promote the formation of hydrocarbon, whereas basic sites preferably promoted the formation of methanol, and amphoteric sites presumably promoted higher alcohol.

Benedettie et al. (1990) revealed the minor effect of basic (K_2O), acidic (P_2O_5), and oxophillic (Y_2O_3) properties on catalytic activity and selectivity for zirconia supported rhodium catalysts. In the case of B-modified zirconia supports reported by Chitpong et al. (2009), the B-modified supports resulted in preventing the agglomeration of cobalt oxide species, which leads to highly dispersed active cobalt particles, whereas C_2-C_4 selectivity only slightly decreased for methanation (Chitpong et al., 2009). Silica-zirconia mixed oxides were employed as cobalt catalyst supports for CO hydrogenation, and the presence of zirconia in mixed support resulted in larger number of active cobalt metal atoms due to the less metal-support interaction subsequently leading to high catalytic activity (Jongsomjit et al., 2007). Moreover, Enache et al. (2002) discovered zirconia support promoted the formation of amorphous or poorly crystalline hexagonal metallic cobalt, which assumed to be active phase in Fischer-Tropsch synthesis according to the more crystallographic defects on active cobalt metal phase after standard reduction. The direct reduction of nitrate precursor led to increase of their quantities and lower metal support interaction in comparison with the calcined catalysts composed of crystallized Co_3O_4. The reduction of perfectly crystalline cobalt oxide was found to promote formation of cubic cobalt that was less active than hexagonal cobalt.

These activities are relevant to those structures found in the images of TEM, SEM, and the X-ray diffraction patterns, as shown in Figure 3.

It was shown that the zirconia-supported cobalt catalyst gave the cobalt catalytic activity more active than alumina-supported cobalt catalysts since the spillover hydrogens were supposed to cover on zirconia surface, and it probably enhanced turn over frequency (TOF) and the chain growth probability (Enache et al., 2004). However, cobalt catalyst supported on alumina prepared from the modified-Pechini method possessed the catalytic performance and TOF as high as the one on zirconia support despite consisting of higher surface area. The small amount of alumina in zirconia supports gave the catalyst higher in performance rather than pure zirconia support according to lower metal-support interaction (Soisuwan et al., 2006). On the contrary, it should notify that alumina-zirconia supported cobalt catalysts synthesized via flame spray pyrolysis was less active than cobalt catalyst supported on nano alumina synthesized in the same way, but it apparently produced higher long chain hydrocarbons (Burakorn et al., 2008). It was noticed that the crystalline

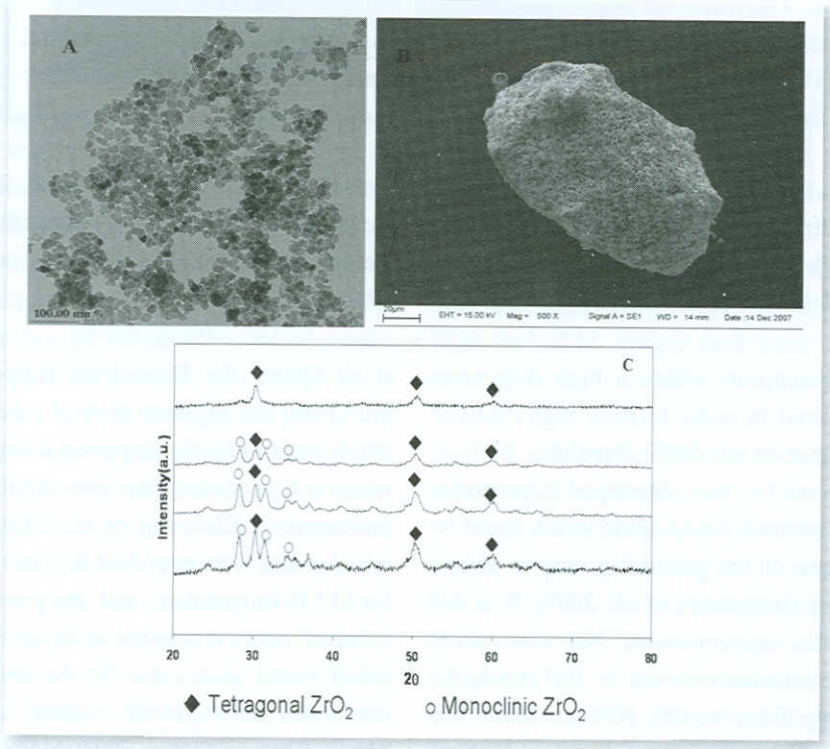


Figure 3. (A) Transmission Electron Microscopy of ZrO_2, (B) Scanning Electron Microscopy of cobalt catalyst supported by zirconia mixed oxide, (C) X-ray diffraction patterns of tetragonal-ZrO_2, and monoclinic-ZrO_2.

system of zirconia supports exhibited none of influence on cobalt catalytic performance (Enache et al., 2004). The influence of defective crystalline zirconia on cobalt catalytic activity was investigated by Panpranot et al. (2005), and it was found that the difference in crystallization mechanism derived from two glycols presumably affected the amount of crystalline zirconia defects. The crystalline zirconia supports with higher defects exhibited the lower metal-support interaction, higher active cobalt metal dispersion, and it consequently increased in catalytic activity.

The high surface area synthesized zirconia seems to be a practical catalyst support for hydrocarbon synthesis owing to their significant modification of coverage cobalt oxide particles. The support interaction was leading to lowering the standard reduction temperature, increasing active cobalt atom dispersions, and selecting towards long

chain hydrocarbon products compared to silica and alumina supports. Once the industrial application was considered, the application as industrial supported cobalt catalysts should be considered in corresponding to long lasting operation and highly expensive investment. An overview of the comparison and advantages and disadvantages among different supports for the Co catalyst are summarized in Table 1.

Table 1. The comparisons of advantage and disadvantage points of supported cobalt catalysts using alumina, silica, and zirconia as supports.

Points	Supports	Summaries
Advantages	Alumina	1. Increase of active cobalt metal dispersion owing to high surface area.
		2. Mixed phases of alumina had an influence on a good cobalt metal dispersion.
		3. Among the other precursors, cobalt nitrate gave an optimal size of CoO_x clusters on alumina for significant metal-support interaction of the standard reduction.
	Silica	1. Mesoporous materials with high surface area and narrow pore size distribution.
		2. Co_3O_4 particle sizes, rate of reaction and product selectivity were clearly dependent on silica pore diameter.
	Zirconia	1. Found to be selective for long chain hydrocarbon.
		2. The presence of zirconia resulted in larger number of active cobalt metal atoms due to the less metal-support interaction.
Disadvantages	Alumina	1. Formation of cobalt aluminate compounds resulted in decrease of catalytic activity.
		2. Water occurring during the standard reduction assisted a formation of cobalt aluminate compound.
	Silica	1. Formation of cobalt silicate at high temperature despite of chemically inert surface property.
		2. Deactivation of mesoporous silica structures was proposed as the results of hydrothermal condition occurred during Fischer-Tropsch reaction.
	Zirconia	Usually possess low BET surface area thus may have limited their uses for CoO_x clusters dispersion.

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