



## CHAPTER II

### LITERATURE REVIEWS

There are several studies of silica and zirconia-supported catalysts. Many researchers have found better knowledge about silica especially supported cobalt catalyst in Fischer-Tropsch synthesis. These reports are very useful and will use to develop works for the future.

#### 2.1 Silica supported cobalt catalysts

R.C. Reuel and C.H. Bartholomew (1984) studied the effect of support and dispersion on the CO hydrogenation activity/selectivity properties of cobalt. They found that the specific activity and selectivity of cobalt in CO hydrogenation is a function of support, dispersion, metal loading and preparation. The order of decreasing CO hydrogenation activity at 1 atm and 225°C for catalysts containing 3wt% cobalt is  $\text{Co/TiO}_2 > \text{Co/SiO}_2 > \text{Co/Al}_2\text{O}_3 > \text{Co/C} > \text{Co/MgO}$ . The specific activity of cobalt best correlated with dispersion and extent of reduction. In the  $\text{Co/Al}_2\text{O}_3$  system, activity and selectivity for high molecular weight hydrocarbons increase very significantly with increasing cobalt loading.

A. Feller *et al.* (1995) studied the addition of zirconium oxide chloride to the catalyst formulation of  $\text{Co/SiO}_2$ . It leads to a higher reducibility of cobalt, due to the formation of a cobalt zirconium species, which can be reduced at lower temperatures than cobalt silicate. Furthermore, the metal particle size of cobalt is increased, but the size of cobalt clusters is reduced. The  $\text{Co-Zr/SiO}_2$  catalysts were tested for their activity in the Fischer-Tropsch synthesis. The steady-state activity increased with increasing zirconium loading, which was attributed to the resistance against reoxidation of the larger cobalt particles and thus to the larger amount of surface cobalt metal present at steady-state in the zirconium promote catalysts. Based on the assumption that the intrinsic activity of cobalt in these catalysts remains unchanged, the observed changes in selectivity could be explained on the basis of secondary reactions in the Fischer-Tropsch system. With increasing zirconium content the number of surface

metal atoms at steady-state conditions increases, leading to a higher extent of secondary reactions, but the size of the cobalt clusters decreases, leading to a decrease in the extent of secondary reactions. With increasing zirconium content the extent of secondary hydrogenation of olefins (e.g., ethene) passes a minimum, and the C<sub>5+</sub>-selectivity passes a maximum due to readsorption of small, reactive organic product compounds, which can be incorporated in larger product compounds. Double bond isomerization increases with increasing zirconium content. This might be attributed to the catalytic activity of zirconia.

A. Kogelbauer *et al.* (1995) studied the formation of cobalt silicates on Co/SiO<sub>2</sub> under hydrothermal conditions. Hydrothermal treatment at 220°C led to a catalyst with lower reducibility due to the formation of both reducible and nonreducible (at temperatures < 900°C) Co silicates. They also showed that silicate was formed in catalysts which had been used for FT synthesis. No significant change occurred upon hydrothermal treatment of calcined catalyst. The presence of air during the hydrothermal treatment inhibited the formation of silicate and they proposed that the formation of silicate was linked to the presence of metallic cobalt.

J. Choi *et al.* (1995) investigated the reduction of cobalt catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> and the effect of metal loading on the reduction. He reported that the activation energy of reduction increased in the following order: Co/SiO<sub>2</sub> > Co/Al<sub>2</sub>O<sub>3</sub> > Co/TiO<sub>2</sub>. For different metal loading, the catalyst with the higher loading is more readily reducible than with the lower metal loading.

S. Ali *et al.* (1995) investigated the influence of Zr promotion of 20 wt% Co/SiO<sub>2</sub> on Fischer-Tropsch synthesis using catalysts prepared in different ways and having different loadings of Zr (up to 8.5 wt%). The catalysts were investigated using FTS (H<sub>2</sub>/CO=2), H<sub>2</sub>-D<sub>2</sub> exchange, and CO dissociation to provide insight into how Zr modifies the Co properties. The Zr-promoted exhibited higher overall rates of FTS compared to unpromoted Co/SiO<sub>2</sub>. The sequentially impregnated Co/Zr/SiO<sub>2</sub> catalysts appeared to be the most active. However, the co-impregnation method of preparation appeared to result in higher cobalt dispersion. While Zr promotion did not appear to promote or inhibit H<sub>2</sub> activation, hydrogen spillover may have been partly responsible

for enhancing the activity of the sequentially impregnated Zr/Co/SiO<sub>2</sub> catalysts. Zr also possibly created an active interface with Co that increased catalyst activity by facilitating Co dissociation. Although high levels of promotion tended to increase the selectivity for higher hydrocarbon, Zr appears to be primarily an excellent rate promoter for Co/SiO<sub>2</sub>.

R. Oukaci *et al.* (1999) studied the catalyst support in both promoted and non-promoted cobalt catalysts was found to play a major role in influencing the overall hydrocarbon production rate with little or no effect on catalyst selectivity (except for titania) in both the fixed-bed and the slurry bubble column reactor. Zr oxide had a similar effect on the activity of Co/silica. Addition of ZrO<sub>2</sub> to the support prior to the impregnation of cobalt probably serves somewhat to hinder the formation of cobalt silicates. ZrO<sub>2</sub> was found, thus, to be an excellent F-T synthesis rate promoter for SiO<sub>2</sub>-supported Co catalysts without any effect, negative or positive, on catalyst selectivity. However, the long-term protecting effect of the zirconia remains to be determined. It is also important to note the differences observed in the two reaction systems, i.e. fixed-bed versus slurry bubble column reactors.

V. Curtis *et al.* (1999) synthesized TiO<sub>2</sub>- and SiO<sub>2</sub>-supported cobalt Fischer-Tropsch catalysts load with low concentration of sulfur (100-2000 ppm) from different sources ((NH<sub>4</sub>)<sub>2</sub>S, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>) and characterized using diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and TPR. They reported that, for the IR data, sulfur inhibits CO adsorption onto the surface of Co catalysts for a sulfur concentration studied possibly due to (i) site blockage and (ii) inhibited reduction of the catalysts. They also found that sulfur also affects the TiO<sub>2</sub>- and SiO<sub>2</sub>-supported cobalt catalysts during the Fischer-Tropsch reaction. The *in situ* F-T reactions, monitored by DRIFTS, further suggest that lower concentrations of sulfur (100 ppm) on TiO<sub>2</sub>-supported cobalt catalysts improves catalysts activity. Besides, the surface of the silica supported catalysts decreased the intensity of the TPR peak related to reducible silicate.

R. Riva *et al.* (2000) studied the interaction of cobalt with two different kinds of support: silics and titania and their effect on the dispersion and reducibility by XPS, TPR, TPO, XRD and TEM. They also showed that the interaction is much stronger in the case of titania. The different reactivity of cobalt with silics and titania explains why reducing and reoxidizing treatments have opposite effects on the dispersion of cobalt depending on whether it is supported on SiO<sub>2</sub> or TiO<sub>2</sub>. The low reactivity of cobalt with silica favours sintering effects. Conversely, due to the high reactivity of cobalt with titania, the coverage of TiO<sub>2</sub> by cobalt tends to increase after the same treatments.

S.L. Sun *et al.* (2000) prepared by mixed impregnation of cobalt(II) nitrate and cobalt(II) acetate displayed higher activity than the catalysts prepared from either mono-precursor at mild reaction conditions (1MPa total pressure, H<sub>2</sub>/CO=2, TD513 K) of Fischer–Tropsch synthesis (FTS). X-ray diffraction (XRD) indicated that highly dispersed cobalt metal provided the main active sites on the catalyst prepared by mixed impregnation method. Through the mixed impregnation, different cobalt species were formed and their reduction performances were detected by the temperature-programmed reduction (TPR) and thermal gravimetric analysis. Transmission electronic microscopy (TEM) and FT-IR spectroscopy of adsorbed CO as probe molecule revealed that the presence of different sites associated with cobalt after the reduction of the catalysts with hydrogen at 673 K. It was assumed that the metal readily reduced from cobalt nitrate promoted the reduction of Co<sup>2+</sup> to metallic state in cobalt acetate by H<sub>2</sub> spillover mechanism during catalyst reduction process. The reduced cobalt from cobalt acetate was highly dispersed and remarkably enhanced the catalytic activity.

G. Jacobs *et al.* (2002) investigated the effect of support, loading and promoter on the reducibility of cobalt catalysts. They have reported that significant support interactions on the reduction of cobalt oxide species were observed in the order Al<sub>2</sub>O<sub>3</sub> > TiO<sub>2</sub> > SiO<sub>2</sub>. Addition of Ru and Pt exhibited a similar catalytic effect by decreasing the reduction temperature of cobalt oxide species, and for Co species where a significant surface interaction with the support was present, while Re impacted mainly the reduction of Co species interaction with the support. They also suggested that, for catalysts prepared with a noble metal promoter and reduced at the same temperature,

the increase in the number of active sites was due mainly to improvements in the percentage reduction rather than the actual dispersion (cluster size). Increasing the cobalt loading, and therefore the average Co cluster size, was found to exhibit improved reducibility by decreasing interactions with the support.

M. Voß *et al.* (2002) investigated the structural, chemical and electronic properties of Co and Co/Mn catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> by a combination of different methods such as TEM, XRD, XPS, TPR and TPO. They reported that temperature-programmed reduction and oxidation reveal the formation of various oxides in dependence on temperature. In case of the alumina- and titania-supported cobalt catalysts, the formation of high-temperature compounds CoAl<sub>2</sub>O<sub>4</sub> and CoTiO<sub>3</sub>, respectively. Moreover, these compounds are not reducible under the applied conditions, the degrees of reduction are only 18-20% (Co/Al<sub>2</sub>O<sub>3</sub>) and 77% (Co/TiO<sub>2</sub>).

G.R. Moradi *et al.* (2003) studied the effect of zirconia addition at various loading ratios on the performance of 10 wt% Co/SiO<sub>2</sub> catalysts for the so-called reaction of Fischer–Tropsch synthesis. The catalysts were prepared through a new pseudo sol–gel method which permits a uniform distribution of the incorporated components and a low deviation from theoretical composition. By increasing zirconia, Co–SiO<sub>2</sub> interaction decreases and is replaced by Co–Zr interaction which favours reduction of the catalysts at lower temperatures. The activity and selectivity toward higher hydrocarbons of the promoted catalysts increase with increasing zirconium loading ratios. No appreciable decrease in activity was observed when all catalysts were employed under H<sub>2</sub>/CO at 230 °C and 8 bar for 240 h.

L.S. Sales *et al.* (2003) prepared silica embedded with transition metals exhibits adequate properties for applications in catalysis, sensors and optics. Cobalt–silica (Co–SiO<sub>2</sub>) nanocomposites were prepared by the sol–gel method and thermally treated at 700, 900, 1100 and 1250 °C. Characterization of the samples was performed by XRD and BET nitrogen adsorption. The performance of the nanocomposites was investigated by catalysis reactions of oxidation. These catalysts were found to be recyclable showing a catalytic activity even after a third recovering. The results indicate that thermal

treatment of sol–gel nanocomposites at temperatures higher than 900 °C is essential for the preparation of active heterogeneous catalysts.

M.S. Rana *et al.* (2003) prepared high specific surface area and better textural properties  $\text{TiO}_2\text{-SiO}_2$  mixed oxide supports by urea hydrolysis precipitation and characterized by BET, XRD, pore volume, zero point charge (ZPC) and low temperature oxygen chemisorptions (LTOC). They reported that mixing of  $\text{TiO}_2$  with  $\text{SiO}_2$  alters the nature of weak interaction of active phases with the  $\text{SiO}_2$  support, and overcome the poor dispersion on  $\text{SiO}_2$  supported catalysts.  $\text{TiO}_2$  counterpart in  $\text{SiO}_2$  plays a role to provide high intrinsic activity and generate favorable morphology for  $\text{MoS}_2$  phases and promote metal support interaction. HDS and HYD activities comparison on various supports for both functionalities relishes possible role of support, not only by increasing the number of sites but also changing the active sites through subtle modifications of metal support interactions. The different loading of molybdenum does not change the nature of active sites for HDS and HYD functionalities, however at different concentration, the dispersion of active site is different and as a result the relative number of active site varies as a function of Mo loadings.

S. Hu *et al.* (2003) studied Binary  $\text{TiO}_2\text{-SiO}_2$  mixed oxides display interesting catalytic properties which have not been attributed to the pure  $\text{TiO}_2$  and  $\text{SiO}_2$ . Many authors have proposed that Brønsted acidity is generated upon interaction of the two oxides. They have demonstrated that high-purity crystalline and amorphous  $\text{TiO}_2\text{-SiO}_2$  mixed oxides do not possess Brønsted acidity, only Lewis acidity. The similarity in the composition of reaction products obtained with  $\text{TiO}_2$  and  $\text{TiO}_2\text{-SiO}_2$  and the difference with reaction products obtained with Brønsted acids suggest that the reaction takes place on  $\text{TiO}_2$  in both cases. The activity of  $\text{TiO}_2\text{-SiO}_2$  mixed oxides in the double bond isomerization of 1-butene could be accounted for simply by a high degree of dispersion of the  $\text{TiO}_2$  nanoparticles. In this hypothesis, the role of  $\text{SiO}_2$  could be that of enhancing the degree of dispersion of  $\text{TiO}_2$  during the preparation process, and stabilizing the nanoparticles of  $\text{TiO}_2$  against thermal sintering. They suggested that the pure  $\text{TiO}_2$  sintering takes place at temperatures lower than those at which sintering of  $\text{TiO}_2\text{-SiO}_2$  mixed oxides takes place. This reduction in surface area of  $\text{TiO}_2$  could be the cause of the low catalytic activity reported in previous studies.

K. Okabe *et al.* (2004) investigated Fischer–Tropsch synthesis was carried out in slurry phase over uniformly dispersed Co–SiO<sub>2</sub> catalysts prepared by the sol–gel method. When 0.01–1 wt.% of noble metals were added to the Co–SiO<sub>2</sub> catalysts, a high and stable catalytic activity was obtained over 60 h of the reaction at 503K and 1MPa. The addition of noble metals increased the reducibility of surface Co on the catalysts, without changing the particle size of Co metal significantly. High dispersion of metallic Co species stabilized on SiO<sub>2</sub> was responsible for stable activity. The uniform pore size of the catalysts was enlarged by varying the preparation conditions and by adding organic compounds such as *N,N*-dimethylformamide and formamide. Increased pore size resulted in decrease in CO conversion and selectivity for CO<sub>2</sub>, a byproduct, and an increase in the olefin/paraffin ratio of the products. By modifying the surface of wide pore silica with Co–SiO<sub>2</sub> prepared by the sol–gel method, a bimodal pore structured catalyst was prepared. The bimodal catalyst showed high catalytic performance with reducing the amount of the expensive

A. K. Dalai *et al.* (2005) studied The effect of water on the performance of narrow and wide-pore silica-supported cobalt catalysts was investigated during Fischer–Tropsch synthesis in a continuously stirred tank reactor (CSTR). In these studies the added water replaced an equivalent amount of inert gas so that all other reaction conditions remained the same before, during and after water addition. A low cobalt loading of 12.4 wt.% on wide-pore silica exhibited a beneficial effect on CO conversion with the addition of water up to 25 vol.% of the total feed. In contrast, the addition of up to 20 vol.% water to a 20 wt.% Co on narrow- or wide-pore silica did not significantly alter the CO conversion. It appears that the CO conversion mainly increases when cobalt clusters are small enough to fit inside the silica pores.

B. Jongsomjit *et al.* (2005) studied the catalytic behaviors of mixed TiO<sub>2</sub>-SiO<sub>2</sub>-supported cobalt (Co) Fischer–Tropsch (FT) catalysts via carbon monoxide (CO) hydrogenation were investigated. The various weight ratios of TiO<sub>2</sub>/SiO<sub>2</sub> were prepared, then consequently impregnated with the cobalt precursor. After calcination, the various samples were characterized using XRD, Raman spectroscopy, scanning electron microscopy/energy dispersive X-ray (SEM/EDX), transmission electron microscopy (TEM), temperature-programmed reduction (TPR), and H<sub>2</sub> chemisorption. The characteristics of various samples were further discussed in more details. Based on

the reaction study, it revealed that the presence of titania in the mixed supports resulted in decreased activities dramatically. However, longer chain hydrocarbons such as C<sub>2</sub>–C<sub>5</sub> can be obtained substantially with increasing the amounts of titania in the mixed supports.

## **2.2 Zirconia support and zirconia modified other supports for cobalt catalysts**

K. Maruya *et al.* (2000) investigated the selective formation of isobutene from CO and H<sub>2</sub> over ZrO<sub>2</sub>. ZrO<sub>2</sub> catalysts having different fraction of monoclinic phase were prepared by changing pH value in the mother solution at the precipitation of zirconium hydroxide. The rate of isobutene formation increased with an increase in the volumetric fraction of monoclinic phase in ZrO<sub>2</sub>, while those of C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>5</sub>+ were independent of the fraction. The amounts of adsorbed methoxy and formate species during the reaction and also of the surface sites with strong basicity increased with an increase in the fraction of monoclinic phase. Chemical trapping experiment showed that the amount of surface methoxy species is comparable to that of site with the strong basicity. These findings were explained by both coordinate unsaturation and stronger basicity based on the configuration of ZrO<sub>2</sub> group in the monoclinic structure.

D. I. Enache *et al.* (2002) reported the thermal treatment, which leads to the best catalytic results, is the direct reduction of the nitrate precursor in the reactor. The effect of the pretreatment is higher in the case of zirconia supported catalyst. The direct reduction of nitrate precursors is even more effective when using a slow-temperature ramping protocol. This phenomenon is explained by the exothermicity of the nitrate reduction. The slower the temperature ramps, the better the heat evacuation, avoiding any increase in cobalt-support interactions or particle agglomeration. The reduction of Co<sub>3</sub>O<sub>4</sub> oxide is difficult and leads to an increase of the cubic crystallised cobalt at the expense of amorphous cobalt or hexagonal cobalt with stacking faults. The direct reduction of nitrate precursor increases the quantity of amorphous cobalt or hexagonal cobalt with crystallographic defects, which are active phases in this reaction. At the same time, the direct reduction leads to weaker metal-support interactions than does precalcination of catalysts.



The nitrogen-flow calcination conducts to an intermediate situation. The quantity of crystallised  $\text{Co}_3\text{O}_4$  is less important than in the case of airflow calcination and it is more reducible.

M. Kraum and M. Baerns (2002) studied the influence of various cobalt compounds applied in the preparation of supported cobalt catalysts on their performance. From the impregnation and calcination procedures, X-ray diffraction (XRD) showed the formation of  $\text{CoTiO}_3$  by the use of cobalt (III) acetyl acetonate (Co-ACAC3) as a precursor in  $\text{Co/TiO}_2$  catalysts. They reported that this effect can be attributed by the migration of cobalt ions into the lattice, with the consecutive formation of titanate. Furthermore, the addition of Ru to the Co-ACAC3 catalyst influenced the phase composition. For Co-ACAC3-Ru, only  $\text{Co}_3\text{O}_4$  was detected and no peaks corresponding to  $\text{CoTiO}_3$  phase were present.

For catalysts prepared by incipient wetness impregnation, titania, ceria and zirconia were additionally used as supports. The activity changed in the following order:  $\text{ZrO}_2 < \text{TiO}_2 < \text{CeO}_2$ .

B.Jongsomjit *et al.* (2003) investigated the impact of Zr modification of alumina used to support Co catalysts. Zr was first impregnated into alumina to produce Zr-modified alumina supports containing 2–11 wt% of  $\text{ZrO}_2$  in the final catalyst. Co catalysts having 20 wt% Co were then prepared from these supports by incipient wetness. It was found that Zr modification had a significant impact on the catalyst properties: FTS rate per gram of catalyst increased significantly (> 65% at steady state) with Zr modification and Co reducibility, especially during standard reduction, also increased.  $\text{H}_2$  chemisorption, however, was found to be essentially constant with Zr modification. The impact of Zr modification is likely due to stabilization of the alumina support, prevention or blockage of Co surface “aluminate” formation, and an increase in Co reducibility to the active catalytic metallic phase. SSITKA results for CO hydrogenation showed an increase in the number of active surface intermediates ( $NM$ ) with Zr modification while the intrinsic activity ( $1/\tau M$ ) remained constant, confirming that the major impact of Zr was in increasing the concentration of active Co surface sites. Because of the inconsistency of the turnover frequency calculated based on  $\text{H}_2$  chemisorption with the  $1/\tau M$  results, it is suggested that the standard adsorption

conditions usually used for Co may not be adequate for modified Co catalysts such as the ones studied here.

R. Mueller *et al.* (2004) investigated of flame spray synthesis of  $ZrO_2$  nanoparticles was conducted at high production rates up to 600 g/h using a commercially available external-mixing stainless-steel gas-assisted nozzle. The influence of  $ZrO_2$  powder production rate, precursor concentration, and oxidant dispersion gas flow rate was investigated on the product morphology, average primary particle diameter and size distribution, crystallinity, and purity using 0.5 M and 1 M zirconium n-propoxide in EtOH. The average particle diameter of pure  $ZrO_2$  was controlled from 6 to 35 nm by varying the production rate, precursor composition, and dispersion gas flow rates. The crystal structure consisted of mostly tetragonal phase (80-95 wt%) and the balance monoclinic phase at all used process conditions. XRD-determined tetragonal crystal sizes were close to the BET-determined primary particle sizes, which indicated that the primary particles were weakly agglomerated single crystals.

D. I. Enache *et al.* (2004) studied the activity and the selectivity of cobalt catalysts supported on a crystallised and on an amorphous zirconia were compared with cobalt supported on a  $\gamma$ -alumina catalyst. The catalysts supported on zirconium dioxide were found to present a better reducibility of the active phase and also to be capable of hydrogen adsorption via a spillover mechanism. It is proposed that these properties could account for a better catalytic activity and an increase of the chain growth probability ( $\alpha$ ). At the same time, the estimated quantity of crystallised  $Co_3O_4$  obtained after airflow calcination (for the same total cobalt loading) is related with the surface area of the support.

Y. Zhang *et al.* (2004) developed a new and simple method for preparing multi-functional nano-sized silica-silica or zirconia-silica bimodal pore catalyst support was developed by direct introduction of silica or zirconia sols into silica gel. The pores of the obtained bimodal pore supports distributed distinctly as two kinds of main pores. On the other hand, the increased BET surface area and decreased pore volume, compared to those of original silica gel, indicated that the obtained bimodal pore supports formed according to the designed route, and it is found that the zirconia-silica

bimodal support improved catalyst activity significantly via not only spatial effect, the intrinsic property of the bimodal structure, but also chemically promotional effect of zirconia, when this kind of support was applied in the liquid-phase Fischer–Tropsch synthesis (FTS) as a cobalt-loading catalyst.

M. Shinoda *et al.* (2004) investigated the Co/SiO<sub>2</sub> catalysts derived from silica bimodal supports were tested in slurry phase FTS. It showed higher activity and favorable selectivities, due to its improved dispersion of supported cobalt crystalline by bimodal structure, as proved by XRD and TEM, and fastened diffusion efficiency inside catalyst pellet with bimodal structure. Furthermore, besides the spatial effect from bimodal structure as shown in silica–silica bimodal catalyst, significantly enhanced activity was realized using ZrO<sub>2</sub>-silica bimodal support, as ZrO<sub>2</sub> inside the large pores of SiO<sub>2</sub> not only formed small pores but also intrinsically promoted FTS.

J. Panpranot *et al.* (2005) prepared nanocrystalline zirconia by the glycothermal method with two different glycols (1,4-butanediol and 1,5-pentanediol) and employed as the support for cobalt catalysts. Commercial zirconia supported cobalt catalyst was also prepared and used as a reference material. The glycothermal-derived zirconia possesses large surface areas with crystallite sizes of 3–4 nm. The catalytic activities for CO hydrogenation of the glycothermal-derived zirconia supported cobalt catalysts were found to be much higher than that of the commercial zirconia supported one. However, the cobalt catalysts supported on zirconia prepared in 1,4-butanediol with lower amount of Zr content in the starting solution exhibited higher activities than the ones supported on zirconia prepared in 1,5-pentanediol. The results suggest that the different crystallization mechanism occurred in the two glycols may affect the amount of crystal defects produced in the corresponding zirconia. As shown by TPR profiles, lower metal-support interaction was observed for the catalysts supported on the zirconia formed via solid-state reaction in 1,4 butanediol (more defects). Consequently, higher active surface cobalt was available for H<sub>2</sub> chemisorption and CO hydrogenation reaction.

J.Panpranot *et al.* (2006) prepared nanocrystalline zirconia by decomposition of zirconium tetra n-propoxide in 1,4-butanediol and was employed as a support for cobalt catalysts. The activity and the selectivity of the catalysts in CO hydrogenation were compared with cobalt supported on commercial available micron- and nano sized zirconia. The catalytic activities were found to be in the order: Co/ZrO<sub>2</sub> nanoglycol >>Co/ZrO<sub>2</sub>-nano-com > Co/ZrO<sub>2</sub>-micron-com. Compared to the micron-sized zirconia supported one, the use of commercial nano-sized zirconia resulted in higher CO hydrogenation activity but lower selectivity for longer chain hydrocarbons (C<sub>4</sub>-C<sub>6</sub>), whereas the use of glycothermal-derived nanocrystalline zirconia exhibited both higher activity and selectivity for C<sub>4</sub>-C<sub>6</sub>. The better performance of the latter catalyst can be ascribed to not only the effect of the crystallite size but also the presence of pure tetragonal phase of zirconia.