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Fischer-Tropsch synthesis: Relations between structure of cobalt catalysts and their catalytic performance

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ABSTRACT

Fischer-Tropsch synthesis has been experiencing a strong revival in recent years, due to the resource utilization considerations and environmental concerns. Cobalt supported catalysts represent the optimal choice for the synthesis of long-chained hydrocarbons from syngas with high H_2/CO ratio. This paper reviews the state of the art related to the influence of cobalt particle size and cobalt phase composition, catalyst support and support texture, and promotion with noble metals on Fischer-Tropsch reaction rates, hydrocarbon selectivity and catalyst stability. Possible mechanisms of catalyst deactivation and modification of cobalt active sites during the reaction are also discussed. Several requirements to the design of cobalt Fischer-Tropsch catalysts have been specified.

1. Introduction

Fischer-Tropsch (FT) synthesis produces hydrocarbons from syngas, which is a mixture of carbon monoxide and hydrogen. The reaction proceeds at 473–623 K and involves monometallic or bimetallic catalysts. Depending on catalyst, reactor and conditions, FT synthesis could produce a wide range of hydrocarbons: light hydrocarbons, gasoline, diesel fuel and wax [1–3]. As it is often the case, the objectives of FT technology evolve with time because of economic transformations, legislation and market requirements [2,4]. In the first half of the 20th century, the interest to FT synthesis has been primarily due to efficient use of coal, economical security and military constrains. After the Second World War, the interest to FT synthesis was mostly driven by energy independence concerns while the world economy was mostly orientated on oil consumption. At that time, several FT processes had been realized in South Africa. Oil crisis in the 1970s and gasoline shortage had led to some momentary recovery of worldwide interest in FT synthesis. In the eighties, the global resurgence of the interest in FT synthesis has been primarily motivated by the problems of utilization of stranded gas, by diversification of sources of fossil fuels, environmental concerns and possible utilization of biomass. Synthetic liquid fuels generally have very low content of sulfur and aromatic compounds compared to gasoline or diesel fuel from crude oil.

FT synthesis has been considered as a part of gas-to-liquids (GTL) technology, which converts natural and associated gases to more valuable middle distillates and lubricants. In this technology, natural gas is first converted to syngas (carbon monoxide/hydrogen mixtures) via vapor reforming, partial oxidation or autothermal reforming. Then the syngas reacts on cobalt or iron catalyst to yield a wide range of hydrocarbons. The hydrocarbons then undergo separation and further pretreatments such as hydrocracking and hydroisomerization. The GTL projects which were realized in last decades are summarized in Table 1. They involve Petro SA plant in Mossel Bay, Shell plant in Malaysia, and Oryx Sasol plant in Qatar. Several other GTL projects are currently in progress in Qatar and Nigeria. The world consumption of crude oil in 2015 has been estimated as 20 million barrels per day. If all projected GTL projects have been realized by that time, the total GTL capacity would be about 600,000 bpd that counts only 3% of total crude oil consumption.

Catalyst is a vital part of any industrial FT process. Catalysts containing iron are employed in the production of lighter

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Table 1
Recent GTL projects.

Localization	Company	Productivity, barrel per day	Current status
Mossel Bay, South Africa	Petro SA (SASOL technology)	30,000	In operation since 1991
Bintulu, Malaysia	Shell	12,500	In operation since 1993
Oryx, Qatar	Sasol	34,000	Inaugurated in 2006, start up
Pearl, Qatar	Shell	140,000	Under construction
Escravos, Nigeria	SasolChevron	34,000	Under construction

Table 2
Chemical composition of the state of the art cobalt FT catalysts.

Ingredient	Content (wt.%)
Cobalt	15–30
Oxide support (alumina, silica and titania)	Balance
Optionally	
Noble metal promoter	0.05–0.1
Oxide promoter	1–10

hydrocarbons and olefins (FT process at high temperature) [5]. They are essential for the conversion of syngas with low H_2/CO ratio ($\ll$2). A more recent generation of FT processes involves syngas with high H_2/CO ratio, which is produced from natural gas. In these processes, FT synthesis proceeds at 493–513 K (low temperature FT synthesis) and focuses on the production of middle distillate fractions and waxes [6,7]. These new processes mostly use cobalt supported catalysts. Cobalt catalysts represent the optimal choice for low temperature FT processes, because of higher stability, higher per single pass conversion (up to 60–70%), higher productivity, relatively smaller negative effect of water on conversion, and higher resistance to attrition especially in slurry bubble column reactors.

Table 2 displays chemical composition [1,8] of the state of the art cobalt catalysts. These catalysts usually contain between 15 and 30% of cobalt. Often these catalysts also contain small amounts of the second metal promoter (typically noble metals) and oxide promoter (zirconia, lantania, cerium oxide). The active phase is usually supported by an oxide with high surface area (silica, alumina, titania). The catalysts are almost exclusively prepared by incipient wetness or slurry impregnation.

This paper reviews recent data about the effect of cobalt particle size and cobalt phase composition, influence of the catalyst support and support texture, and promotion with noble metals on the structure and catalytic performance of cobalt supported FT catalysts.

2. Cobalt particle size and cobalt phase composition effects in FT synthesis

Iglesia et al. [9–11] showed that for relatively larger cobalt particles supported on alumina, silica and titania, FT reaction rate is usually proportional to the number of available cobalt surface atoms. This suggests that the cobalt site time yield does not depend on the sizes of cobalt particles. The invariance of cobalt site activity on particle size over different catalysts was also confirmed by steady-state isotopic transient kinetic analysis (SSTIKA) [12–14]. Thus, FT synthesis is a structure insensitive catalytic reaction. Hydrocarbon selectivity also only very slightly depends on cobalt dispersion for larger cobalt particles [15]. Variation in hydrocarbon selectivity on larger cobalt particles can be attributed to the rate of secondary reactions such as olefin readsorption.

The situation is however different with smaller cobalt particles. In the eighties, Kuznetsov and co-workers [16,17] and Reuel and Bartholomew [18] discovered that FT turnover frequency is much lower with smaller cobalt particles than with larger ones. This finding has been further confirmed by more recent publications [19–21]. Fig. 1 displays the catalytic data [21] for a series of cobalt silica supported catalysts. The FT reaction rates are plotted as a function of the number of cobalt surface sites which was evaluated by propene chemisorption [22]. With larger cobalt particles, FT reaction rates were proportional to the number of cobalt surface sites. When the particles are getting superparamagnetic and their diameter is smaller than 70 Å, the specific catalytic activity of these sites was much lower than it could be predicted from the measurements of the number of cobalt surface sites.

These results about smaller specific activity of cobalt surface sites on small cobalt particles are consistent with the data by de Jong and co-workers [19]. De Jong and his group used carbon nanofibres as catalytic supports. It is known that carbon nanofibres do not react with cobalt and do not yield cobalt support mixed compounds (cobalt aluminate, cobalt silicate, etc.). Note that cobalt support mixed compounds usually form during FT reaction and different pretreatments of cobalt catalysts supported on oxides. Thus, carbon nanofibres can be considered as model systems [19,23] which are well-suited for evaluation of the cobalt particle size effects on FT catalytic performance. The catalytic experiments revealed that Fischer-Tropsch turnover frequencies on cobalt catalysts supported by nanofibres at 1 and 20 bar were much lower for cobalt metal particles smaller than 60–80 Å. In addition, it was found that cobalt particle size had a strong impact on cobalt selectivity. Decrease in cobalt particle size to 60–80 Å resulted in higher methane selectivity and higher yields of olefinic products. C5+ selectivity was also smaller with cobalt metal particles smaller than 60–80 Å.

Thus, the analysis of the literature suggests that the catalytic properties of small cobalt particles in FT synthesis could be different from larger ones. There might be two possible reasons responsible for this phenomenon. The first reason is catalyst deactivation. At the conditions of FT synthesis, the catalyst productivity can decrease because of several phenomena: cobalt oxidation, formation of cobalt support mixed compounds, coke

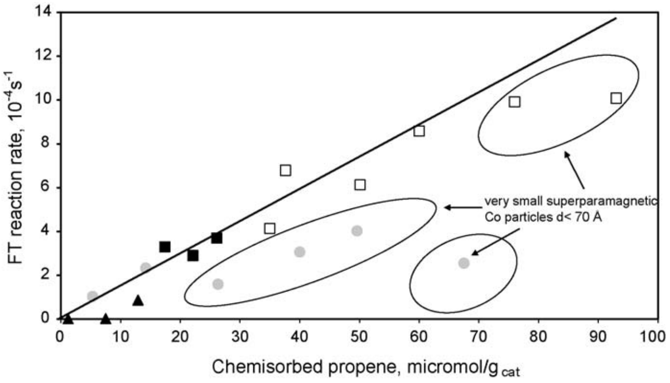

Fig. 1. Relation between FT reaction rate and number of cobalt metal sites measured by propene chemisorption (H_2/CO = 2, T = 463 K, P = 1 atm).

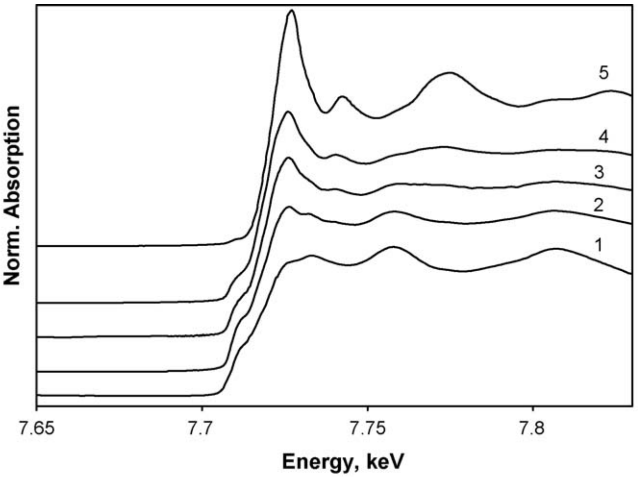

Fig. 2. In situ XANES spectra of CoPt/Al_2O_3 (20% Co, 0.1% Pt) catalyst and cobalt reference compounds: (1) Co foil, (2) CoPt/Al_2O_3 reduced in hydrogen at 673 K, cooled down to 493 K and purged with Ar, (3) CoPt/Al_2O_3 prepared as in (2) measured immediately after addition of water (H_2O/Ar = 5) at 493 K, (4) CoPt/Al_2O_3 prepared as in (2) after exposure for 1 h 50 min to humid Ar (H_2O/Ar = 5) at 493 K and (5) CoO reference compound.

deposition, cobalt particle sintering, and catalyst attrition [24,25]. One of the most probable reasons of catalyst deactivation at the conditions of FT synthesis seems to be cobalt oxidation by water. Water is a major product of FT synthesis. Holmen and co-workers [26–29] showed that cobalt catalyst deactivated rather rapidly on addition of significant amounts of water to the reaction feed. The effect was more pronounced with smaller cobalt particles. Thermodynamic calculations [30] show; however, that at FT reaction conditions, cobalt bulk metallic phase cannot be oxidized by water. The situation is different with smaller cobalt particles which might have different thermodynamic properties.

In situ and operando characterization techniques seem to be essential to obtain reliable information about the mechanism of catalyst deactivation and influence of water. Fig. 2 presents in situ X-ray absorption data about effect of water on the oxidation state of cobalt alumina supported catalysts which were reduced in hydrogen at 673 K. Addition of water to argon flow at 493 K results in reoxidation of cobalt metal particles of 70 Å diameter in cobalt alumina supported catalysts promoted with Pt. The XANES spectrum shifts from that characteristic of metallic cobalt to that characteristic of CoO. This result is consistent with previous in situ XANES data obtained by Saib et al. [31] for cobalt silica supported catalysts with cobalt particle sizes of 130 Å and numerous ex situ data of the group of Davis [32–38] for cobalt alumina supported catalysts. In addition, it has been shown [24,37,38] that oxidation of cobalt by water can be reversible and irreversible. Irreversible cobalt oxidation could lead to the formation of hardly reducible Co-support compounds (aluminate and silicate). Reversible oxidation of cobalt particles probably leads to the formation of thin layer of cobalt oxide on the surface of metal particles; the active sites can be regenerated in reductive atmosphere at relatively mild conditions.

The thermodynamic analysis that takes into account surface energy of small cobalt metal and cobalt oxide particles suggests [30] that spherical cobalt crystallites with a diameter less than 44 Å are likely to be oxidized under realistic conditions of FT synthesis. Detailed analysis of the literature on oxidation of cobalt particles at FT reaction conditions has been recently conducted by van de Loosdrecht et al. [24]. The authors conclude that larger cobalt metal particles should be stable at FT reaction conditions, while a number of reports are indicative of oxidation of smaller cobalt metal particles in FT reactors. It was also shown that for an industrial Co/Al_2O_3 catalyst the oxidation of cobalt particles of 60 Å diameter could be prevented by efficient control of partial pressures of hydrogen and water in FT reactor. Cobalt particle size seems to be an essential parameter that influences oxidation of cobalt particles.

The second reason responsible for different catalytic performance of large and smaller cobalt particles relates to the kinetics of elementary steps on small and larger cobalt particles. The elementary steps of FT synthesis were studied on cobalt catalysts supported by nanofibres which had cobalt particle size between 30 and 170 Å. The SSITKA experiments conducted by Radstake et al. [39] showed that the surface of coverage of cobalt catalysts by reaction intermediates varied as a function of cobalt particle size. Different reactivity of small and large cobalt particles could be probably related to different electronic structure. This suggests that quantum size effect could affect the kinetics of several elementary steps of FT synthesis over cobalt metal particles smaller than 60–80 Å.

Besides different specific activity of cobalt surface sites in smaller and larger cobalt particles, cobalt phase composition could also affect FT catalytic performance. Three crystalline phases of metallic cobalt (face centered cubic (fcc), hexagonal close packed (hcp) and novel phase discovered [40] in 1999) have been described in the literature. Cobalt cubic phase is usually the dominant phase in alumina, silica and titania supported cobalt catalysts reduced at relatively high temperatures (>723 K).

The proportion of cobalt fcc and hcp phases in cobalt supported catalysts can be controlled by the technique proposed by Lynch and co-workers [41]. The cobalt fcc phase can be selectively obtained by pretreatment of cobalt catalysts in nitrogen and then reduction in H_2 at 823 K. The catalysts containing high concentration of cobalt hcp phase could be obtained by the reduction of cobalt catalysts in hydrogen at lower temperatures (600 K). The catalysts with similar dispersion and similar number of cobalt surface sites measured by carbon monoxide chemisorption but with higher fractions of hcp phase exhibited higher conversion [42] in carbon monoxide hydrogenation than those which contain cobalt fcc metallic phase. This evokes that cobalt sites situated on cobalt hcp phase might have higher specific activity in FT synthesis.

3. Effect of support and support texture on the structure and catalytic performance of cobalt catalysts

Catalytic support has significant and multiple roles in the design and catalytic performance of cobalt FT catalysts. The principal function of catalyst support is to disperse cobalt and to produce stable cobalt metal particles after catalyst reduction and activation. Efficient control of metal dispersion is often a challenge in the design of efficient metal supported catalysts. Porous structure of the support could control the sizes of supported cobalt particles. A "negative" effect of support could be related to the formation of cobalt support mixed compounds (aluminate and silicate). These mixed cobalt support compounds should be avoided since they do not produce active sites for FT synthesis. In addition, the catalytic support could modify diffusion of reagents and products inside the catalyst grains, capillary condensation of the reaction products in the catalyst pores, heat dissipation and mechanical strength. The paragraphs below principally address the chemical effects of catalyst support and effects of support texture on FT catalytic performance.

Periodic mesoporous silicas (MCM-41, SBA-15, MCM-22 [43]) appear to be model systems to study the effect of support texture of FT catalytic performance. These materials were discovered [44,45]

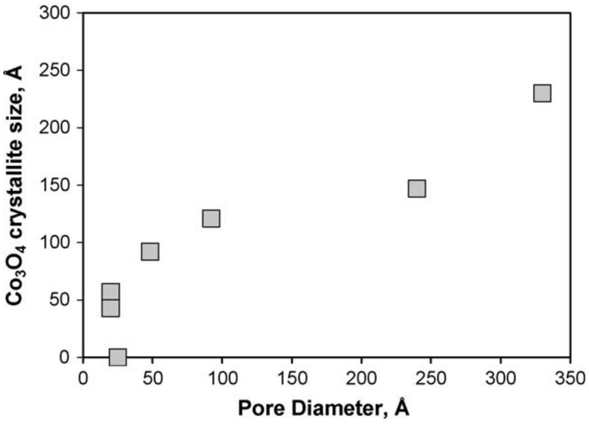

Fig. 3. Correlation between support pore diameter and Co_3O_4 crystallite size in Co/SiO_2 supported catalysts prepared via aqueous impregnation from cobalt nitrate and calcination.

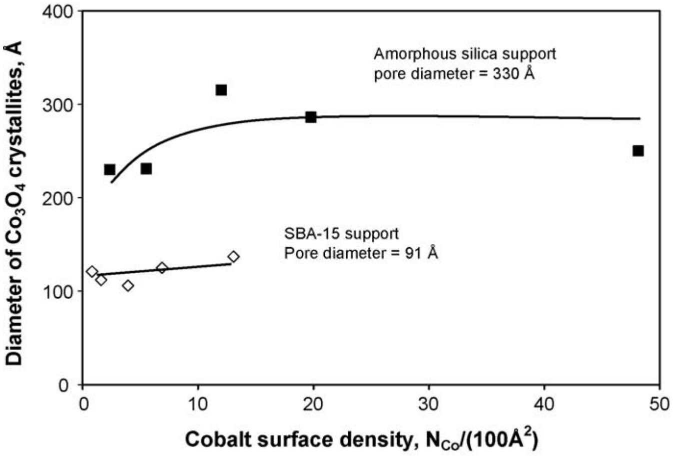

Fig. 4. Co_3O_4 crystallite size as a function of cobalt surface density in cobalt catalysts supported by SBA-15 and amorphous silica. Reprinted from [53] with permission from Elsevier.

in the nineties. They have ordered structure which can be observed by XRD, narrow pore size distribution, high surface area and pore volume.

The catalysts supported by periodic mesoporous silicas have exhibited good performance in FT synthesis. Silicate crystalline mesoporous materials synthesized by hydrothermal treatment of Si, Mg and Al hydroxides with quaternary ammonium salts were used as catalytic supports for preparation of cobalt FT catalysts [46]. Carbon monoxide conversion was higher on crystalline matrix relative to silica gel. Higher FT catalytic activity and C5+ selectivities were also observed on hexagonal mesoporous silicas (HMS) rather than on MCM-41 cobalt supported catalysts [47]. The stability of cobalt catalysts supported by mesoporous silica could be enhanced by promotion with aluminum and titanium [48].

The effect of silica pore sizes on the diameter of supported cobalt oxide particles has been studied in a number of publications. Fig. 3 shows that the sizes of supported Co_3O_4 crystallites supported by mesoporous silicas and prepared by impregnation with cobalt nitrate and calcination depend on their pore diameter [49–52]. The diameter of Co_3O_4 particles increases as a pore diameter increases. It should be noted that the Co_3O_4 particles always have the sizes comparable with silica pore diameters. This suggests that Co_3O_4 particles are probably located in the pores of mesoporous silicas. Similar results about effect of pore sizes on cobalt dispersion were also obtained recently by Holmen and co-workers [15] for alumina supported cobalt catalysts.

Both support pore sizes and overall cobalt content could affect cobalt dispersion in the supported catalysts. It was shown [53,54], however, that in silica supported catalysts overall cobalt content could have a much smaller effect on cobalt dispersion than support pore diameter. To minimize the effects on cobalt dispersion which might be due to different BET surface areas of the catalysts, cobalt surface densities were used instead of overall cobalt weight contents. The cobalt surface density was defined as the number of cobalt atoms in the catalyst divided by its BET surface area. Fig. 4 shows that a more than ten times increase in cobalt surface density does not have any noticeable effect on Co_3O_4 particle sizes in periodic mesoporous silica with narrow pore size distribution. In amorphous silicas, the Co_3O_4 particle sizes only slightly increase with increase in cobalt loading. This observation is consistent with preferential localization of cobalt particles within the pores of silicas. Narrow pore size distribution in periodic mesoporous silicas seems to prevent cobalt particles from sintering. In amorphous silicas with broader pore size distribution, cobalt dispersion decreases to some extent with an increase in cobalt surface density.

Catalyst support via its texture could also affect cobalt reducibility. XANES spectra of the reduced Co catalysts supported by silica with pore sizes that varied from 20 to 330 Å are presented in Fig. 5. The XANES spectra of the reference compounds: metallic cobalt and CoO are shown for comparison. As silica pore sizes increase, the XANES spectra shift from CoO to metallic cobalt. This suggests [50] an increase in the extent of cobalt reduction with an increase in silica pore sizes and diameters of cobalt particles. It is known that smaller cobalt particles are much more difficult to reduce than larger ones. The fraction of metallic cobalt was much lower for smaller cobalt particles. Fig. 6 showed the relations between pore diameters of the support and cobalt-time yields on cobalt silica supported catalysts. The cobalt-time yields are defined as FT reaction rates normalized by the number of cobalt atoms loaded into the reactor. The catalysts with narrow pore sizes have much lower activity than their counterparts with larger pores. Lower reducibility of small cobalt particles in narrow pore supports appears [49] to be the principal cause of their poor catalytic performance. Note however that in addition to support

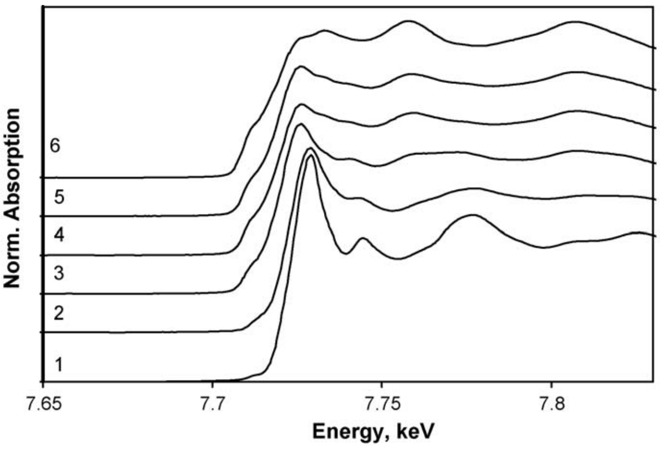

Fig. 5. XANES spectra of cobalt catalysts supported on mesoporous silicas reduced in situ at 773 K and reference compounds: (1) reference CoO, (2) MCM-41 silica with pore diameter 20 Å, (3) SBA-15 silica with pore diameter 42 Å, (4) SBA-15 silica with pore diameter 91 Å, (5) Cab-osil M5 amorphous silicas with pore diameter 330 Å and (6) Co foil. The spectra were measured in hydrogen at room temperature. Reproduced from [50] Copyright 2001 with permission from the American Chemical Society.

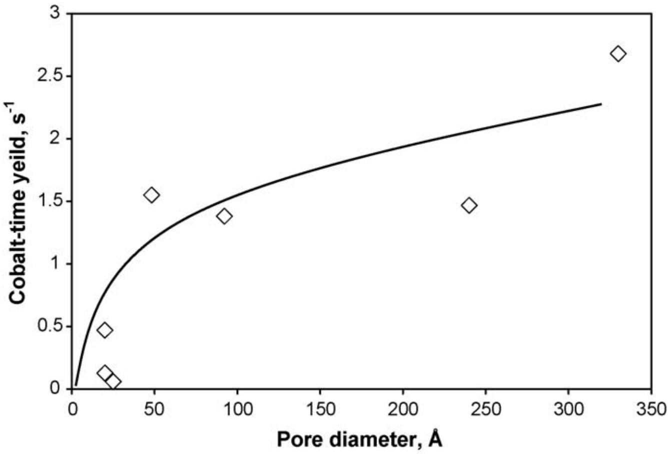

Fig. 6. Cobalt-time yield as a function of pore sizes of mesoporous silicas used as catalytic supports. Reprinted from [49] with permission from Elsevier.

texture, use of different precursors could also result in different sizes of Co_3O_4 particles and could affect the crystallinity of the supported cobalt species [55]. For example, Ohtsuka et al. [56,57] showed that impregnation of mesoporous silicas with cobalt acetate led to inactive FT catalysts, while the catalysts from the nitrate or equimolar mixture of both nitrate and acetate have shown higher activity in FT reaction.

Interaction of cobalt oxide with catalysts supports can result in the formation of Co-support compounds (cobalt aluminate and cobalt silicate), which are hardly reducible cobalt phases. In addition to the formation of bulk stoichiometric cobalt support oxide compounds, non-stoichiometric amount of support ions such as Al^{3+} can incorporate cobalt oxide spinel matrix. Note that the ion radii of Co^{3+} and Al^{3+} ions are rather similar ($r_{Co^{3+}} = 0.63\,\text{Å}$, $r_{Al^{3+}} = 0.54\,\text{Å}$). Incorporation of Al^{3+} ions in Co_3O_4 spinel structure would result in lower cobalt reducibility without affecting the apparent cobalt dispersion. This suggestion is illustrated by the data obtained for cobalt alumina supported catalysts. It was found that calcination did not affect the size of cobalt oxide crystallites in the cobalt alumina supported catalysts (Fig. 7). If cobalt reducibility were dependent only on the sizes of cobalt oxide particles, Co/Al_2O_3 catalysts calcined at different temperatures should have similar reducibility and behave in the same manner during TPR experiments. TPR data shown in Fig. 7 indicate however more difficult cobalt reduction in Co/Al_2O_3 catalysts calcined at higher temperatures. More difficult reduction of cobalt species in Co/Al_2O_3 particles calcined at higher temperatures cannot be assigned to smaller sizes of cobalt oxide crystallites. A partial substitution of Co^{3+} ions by Al^{3+} in spinel matrix could be a reason of more difficult reducibility of cobalt oxide particles on alumina supported catalysts which were pretreated at higher temperatures.

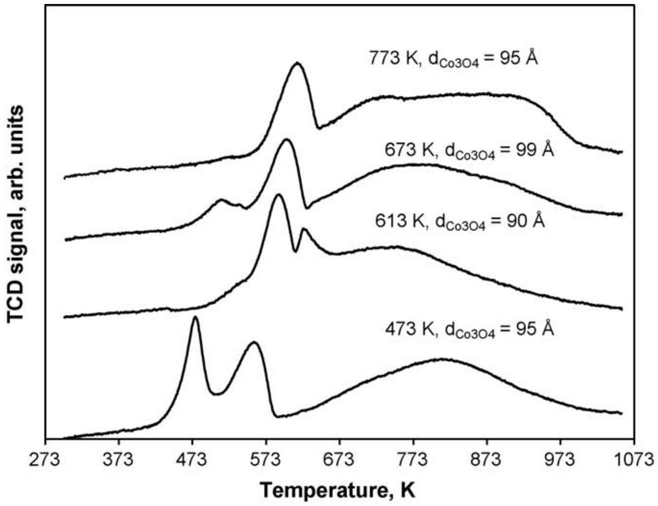

Fig. 7. TPR profiles of cobalt monometallic catalysts supported on alumina which have Co_3O_4 crystallite sizes between 90 and 100 Å and which were calcined at temperatures ranging from 473 to 773 K (5% H_2/Ar mixture, ramping rate 3 K/min). Reprinted from [66] with permission from Elsevier.

4. Promotion of cobalt catalysts

The goal of promotion is to enhance cobalt FT catalysts by the addition of small amounts of noble metals and metal oxides. Numerous studies have shown that introduction of a noble metal (Ru, Rh, Pt and Pd) has strong impact on the structure and dispersion of cobalt species, FT reaction rates and selectivities. The promoting metal is typically introduced via co-impregnation or subsequent impregnation. Analysis of the literature data [1] suggests that introduction of noble metals could result in the following phenomena:

(1) easing cobalt reduction;
(2) enhancement of cobalt dispersion;
(3) better resistance to deactivation;
(4) formation of metallic alloys;
(5) high concentration of hydrogen activation site;
(6) modification of intrinsic activity of surface sites.

Promotion with oxides has also been one of the methods to improve activity and hydrocarbon selectivity of FT catalysts. Among the oxide promoters, ZrO_2, La_2O_3, MnO and CeO_2 have been most often employed. Addition of oxide promoters could [1]:

(1) modify the catalyst texture and porosity;
(2) reduce formation of hardly reducible cobalt mixed oxides;
(3) increase cobalt dispersion, reducibility and fraction of different cobalt metal crystalline phases;
(4) enhance mechanical and chemical attrition resistance of cobalt FT catalysts;
(5) improve chemical stability of the support.

More information about the effect of promotion on cobalt based catalysts is available in recent reviews [1,58].

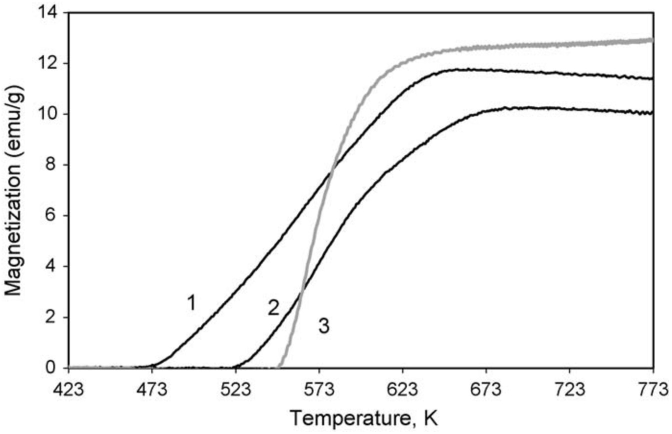

Fig. 8. In situ magnetization curves of cobalt catalysts measured during temperature-programmed reduction in pure hydrogen. $CoRu/SiO_2$ (1), $CoRe/SiO_2$ and Co/SiO_2 catalysts were prepared via decomposition of cobalt nitrate and calcination at 673 K.

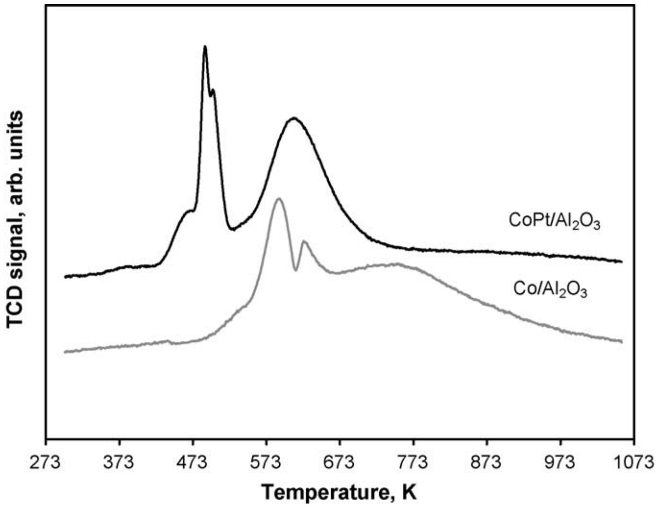

Fig. 9. TPR profiles of monometallic cobalt alumina and Pt-promoted supported catalysts (5% H_2/Ar mixture, ramping rate 3 K/min).

The paragraphs below address our recent data about the effect of promotion with noble metals on cobalt reducibility and dispersion in silica and alumina supported catalysts. The catalysts were characterized by in situ magnetic method [59,60] which is selectively sensitive to the presence of cobalt ferromagnetic metallic phases. Fig. 8 shows the effect of promotion with Ru and Re on cobalt reduction in the silica supported catalysts prepared via impregnation and calcination from cobalt nitrate. Re and especially Ru reduce [61] the temperature of cobalt reduction, which is observed by an increase in sample magnetization. Similar effect on the reducibility of cobalt catalysts supported on alumina is observed in the presence of Pt. The TPR hydrogen consumption peaks shift to lower temperature in the presence of 0.1% of platinum (Fig. 9).

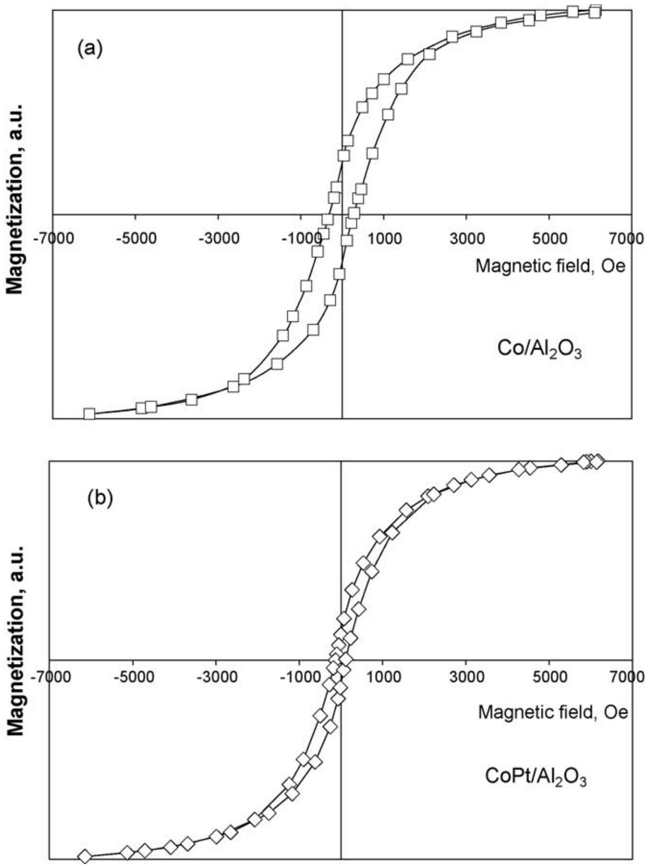

Fig. 10. Field dependence curves for Co/Al_2O_3 (a) and $CoPt/Al_2O_3$ (b) catalysts reduced at 673 K. The size of parent Co_3O_4 crystallites in both calcined catalysts was the same (96 Å). Reprinted from [66] with permission from Elsevier.

Previous reports [20,62] also suggest that the presence of noble metals can result in the increase in cobalt dispersion. The presence of noble metals seems to result in higher concentration of cobalt oxide nucleation sites [20] and thus in smaller size of cobalt oxide crystallite. Smaller cobalt oxide particles in the presence of Pt and Ru were observed in silica supported catalysts.

The second effect involves influence of the promoters on cobalt dispersion in the reduced catalysts. It appears that reduced catalysts have cobalt dispersion increase in different order compared to the oxidized catalyst precursors. The effect has been uncovered with alumina supported catalysts. First, the size of cobalt oxide particles in the calcined catalysts was characterized by XRD. XRD patterns for monometallic and Pt-promoted cobalt catalysts were identical. This suggests the same sizes of cobalt oxide crystallites in both series of catalysts. Then, both promoted with platinum and monometallic cobalt catalysts were reduced by hydrogen. Note that higher proportion of cobalt can be reduced in the presence of Pt in alumina supported catalysts. The field dependence curves obtained for the reduced catalysts are shown in Fig. 10. Preliminary analysis [60] indicated the presence of cobalt metal particles smaller than 20 nm in both promoted and monometallic catalysts. Smaller coercive force indicates [60] smaller sizes of cobalt metal particles in $CoPt/Al_2O_3$. Thus, the average size of cobalt metallic particles was different in monometallic and catalysts promoted with Pt, while both catalysts had the same particle sizes of Co_3O_4 precursors. This observation was interpreted in terms of different reducibility of small and large cobalt oxide particles. The presence of Pt probably leads to the reduction of much smaller cobalt oxide particles, while only relatively large cobalt oxide particles are reduced in the monometallic catalysts.

5. Conclusion

Cobalt particle size and cobalt phase composition, catalyst support and support texture as well as promotion are essential parameters that control catalyst structure and catalytic performance in FT synthesis. All these parameters should be competently controlled in the design of efficient cobalt FT catalysts. It is known that FT synthesis proceeds on cobalt surface sites. The primary goal of any catalyst preparation for FT synthesis is to produce a significant concentration of stable cobalt metal surface sites. Cobalt dispersion and number of cobalt metal sites in FT catalysts could be enhanced for example by using catalyst support with narrower pores or via decomposition of cobalt nitrate in 1–5% NO/He mixtures [63] or in glow discharge plasma [64].

In addition, it has been demonstrated that apparent activity of cobalt surface sites in smaller particles is lower than in larger ones. This implies that cobalt metal particles in the activated catalysts should not be smaller than an optimum size (60–80 Å). Though several methods of deposition of active phase could generate very small cobalt particles (<40–60 Å), the catalysts containing these very small particles do not normally exhibit acceptable catalytic performance. Repartition of cobalt surface sites in a catalyst grain could be essential in attaining high yield of hydrocarbons. No intraparticle diffusion limitations have been generally reported for slurry phase catalytic reactors operating with catalyst grains of about 50–80 μm. In fixed bed tubular reactors, which involve catalyst particles of 1–3 mm, diffusion of reagents, intermediates and final products can affect FT reaction rate and selectivity.

The goal of catalyst preparation is also to avoid loss of cobalt atoms in the support matrix during catalyst preparation, pretreatments and FT reaction. Cobalt oxide could react with most of the oxide supports yielding cobalt support mixed compounds. These compounds are not reducible at moderate reduction temperatures and they do not produce any active sites for FT synthesis. Catalyst deactivation and production of undesired mixed compounds could be minimized by adjusting parameters of catalyst synthesis, pretreatments and FT reaction.

It has been largely shown that performance of FT catalysts evolves with time-on-stream. Significant modifications of catalyst structure could occur during the reactor start up and during FT synthesis. These modifications could be related to different phenomena: exothermicity of the reaction, temperature control, and impurities in the feed, cobalt sintering, presence of water, carbon dioxide, heavier hydrocarbons and organic compounds in the reaction products. Catalyst attrition could be also one of the reasons responsible for the drop in catalytic performance in slurry reactor, especially at higher conversions and high operating rates [65]. Understanding and controlling the transient behavior of FT catalysts represent a significant challenge.

FT synthesis is an industrial process. Cobalt is an expensive metal. Significant amount of catalyst is required for both slurry bubble column and fixed bed multi-tubular reactor. Promotion with even small amounts of noble metals could dramatically affect the cost of overall FT and GTL technologies.

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References

[1] A.Y. Khodakov, W. Chu, P. Fongarland, Chem. Rev. 107 (2007) 1692.
[2] Fischer-Tropsch Technology, in: A.P. Steynberg, M. Dry (Eds.), Stud. Surf. Sci. Catal. 152 (2004) 1–722.
[3] M.E. Dry, Catal. Today 71 (2002) 227.
[4] C.H. Bartholomew, AIChE Spring Meeting, New Orleans, 2003 (paper 83b).
[5] A.P. Steynberg, R.L. Espinoza, B. Jager, A.C. Vosloo, Appl. Catal. 186 (1999) 41.
[6] B. Jager, Stud. Surf. Sci. Catal. 119 (1998) 119.
[7] B. Jager, R. Espinoza, Catal. Today 23 (1995) 17.
[8] R. Oukaci, A.H. Sigleton, J.G. Goodwin Jr., Appl. Catal. A 186 (1999) 129.
[9] S.L. Soled, E. Iglesia, R.A. Fiato, J.E. Baumgartner, H. Vroman, S. Miseo, Top. Catal. 26 (2003) 101.
[10] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Adv. Catal. 39 (1993) 221.
[11] E. Iglesia, Appl. Catal. A 161 (1997) 59.
[12] G. Haddad, B. Chen, J.G. Goodwin, J. Catal. 161 (1996) 274.
[13] M. Rothaemel, K.F. Hanssen, E.A. Blekkan, D. Schanke, A. Holmen, Catal. Today 38 (1997) 79.
[14] F. Rohr, O.A. Lindvåg, A. Holmen, E.A. Blekkan, Catal. Today 58 (2000) 247.
[15] Ø. Borg, S. Eri, E.A. Blekkan, S. Storsæter, H. Wigum, E. Rytter, A. Holmen, J. Catal. 248 (2007) 89.
[16] A.S. Lisitsyn, A.V. Golovin, V.L. Kuznetsov, Y.I. Yermakov, C1 Mol. Chem. 1 (1984) 115.
[17] A.S. Lisitsyn, A.V. Golovin, V.L. Kuznetsov, Y.I. Yermakov, J. Catal. 95 (1985) 527.
[18] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 78.
[19] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, J. Am. Chem. Soc. 128 (2006) 3956.
[20] J.-S. Girardon, E. Quinet, A. Griboval-Constant, P.A. Chernavskii, L. Gengembre, A.Y. Khodakov, J. Catal. 248 (2007) 143.
[21] J.-S. Girardon, Ph.D. Thesis, University of Lille, 2005.
[22] A.S. Lermontov, J.-S. Girardon, A. Griboval-Constant, S. Pietrzyk, A.Y. Khodakov, Catal. Lett. 101 (2005) 117.
[23] G.L. Bezemer, U. Falke, A.J. Van Dillen, K.P. de Jong, Chem. Commun. (2005) 731.
[24] J. van de Loosdrecht, B. Balzhinimaev, J.-A. Dalmon, J.W. Niemantsverdriet, S.V. Tsybulya, A.M. Saib, P.J. van Berge, J.L. Visagie, Catal. Today 123 (2007) 293.
[25] M. Bremaud, P. Fongarland, J. Anfray, S. Jallais, D. Schweich, A.Y. Khodakov, Catal. Today 106 (2005) 137.
[26] O. Borg, S. Storsaeter, S. Eri, H. Wigum, E. Rytter, A. Holmen, Catal. Lett. 107 (2006) 95.
[27] S. Storsaeter, O. Borg, E.A. Blekkan, A. Holmen, J. Catal. 231 (2005) 405.
[28] S. Storsaeter, O. Borg, E.A. Blekkan, B. Totdal, A. Holmen, Catal. Today 100 (2005) 343.
[29] A.M. Hilmen, D. Schanke, K.F. Hanssen, A. Holmen, Appl. Catal. A 186 (1999) 169.
[30] E. van Steen, M. Clayes, M.E. Dry, J. van de Loosdrecht, E.L. Vilkoen, J.L. Visagie, J. Phys. Chem. B 109 (2005) 3575.
[31] A.M. Saib, A. Borgna, J. van de Loosdrecht, P.J. van Berge, J.W. Geus, J.W. Niemantsverdriet, J. Catal. 239 (2006) 326.
[32] T.K. Das, G. Jacobs, B.H. Davis, Catal. Lett. 101 (2005) 187.
[33] G. Jacobs, J.A. Chaney, P.M. Patterson, T.K. Das, J.C. Maillot, B.H. Davis, J. Synchrotron Radiat. 11 (2004) 414.
[34] G. Jacobs, P.M. Patterson, T.K. Das, M. Luo, B.H. Davis, Appl. Catal. A 270 (2004) 65.
[35] T.K. Das, W. Conner, G. Jacobs, J. Li, K. Chaudhari, B.H. Davis, Stud. Surf. Sci. Catal. 147 (2004) 331.
[36] G. Jacobs, T.K. Das, P.M. Patterson, J. Li, L. Sanchez, B.H. Davis, Appl. Catal. A 247 (2003) 335.
[37] J. Li, G. Jacobs, T. Das, B.H. Davis, Appl. Catal. A 233 (2002) 255.
[38] J. Li, X. Zhan, Y. Zhang, G. Jacobs, T. Das, B.H. Davis, Appl. Catal. A 228 (2002) 203.
[39] P.B. Radstake, J.P. den Breejen, G.L. Bezemer, J.H. Bitter, K.P. de Jong, V. Frøseth, A. Holmen, Stud. Surf. Sci. Catal. 167 (2007) 85.
[40] D.P. Dinega, M.G. Bawendi, Angew. Chem. Int. Ed. 38 (1999) 1788.
[41] (a) M.-C. Marion, O. Ducreux, J. Lynch, M. Roy, American Chemical Society, Division of Petroleum Chemistry, Preprints, vol. 45, 2000, p. 244;
(b) O. Ducreux, B. Rebours, J. Lynch, M. Roy-Auberger and D. Bazin, Oil &Gas Science and Technology-Revue de l'IFP, doi:10.2516/ogst:2008039.
[42] D.I. Enache, B. Rebours, M. Roy-Auberger, R. Revel, J. Catal. 205 (2002) 346.
[43] R. Ravishankar, M.M. Li, A. Borgna, Catal. Today 106 (2005) 149.
[44] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[45] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[46] T. Iwasaki, M. Reinikainen, Y. Onodera, H. Hayashi, T. Ebina, T. Nagase, K. Torii, K. Kataja, A. Chatterjee, Appl. Surf. Sci. 130–132 (1988) 845.
[47] D. Yin, W. Li, W. Yang, H. Xiang, Y. Sun, B. Zhong, S. Peng, Micropor. Mesopor. Mater. 47 (2001) 15.
[48] K. Okabe, M. Wei, H. Arakawa, Energy Fuels 17 (2003) 822.
[49] A.Y. Khodakov, A. Griboval-Constant, R. Bechara, V.L. Zholobenko, J. Catal. 206 (2002) 230.
[50] A.Y. Khodakov, A. Griboval-Constant, R. Bechara, F. Villain, J. Phys. Chem. B 105 (2001) 9805.
[51] A.Y. Khodakov, J.-S. Girardon, A. Griboval-Constant, A.S. Lermontov, P.A. Chernavskii, Stud. Surf. Sci. Catal. 147 (2004) 295.
[52] A.Y. Khodakov, R. Bechara, A. Griboval-Constant, Stud. Surf. Sci. Catal. 142 B (2002) 1133.
[53] A.Y. Khodakov, R. Bechara, A. Griboval-Constant, Appl. Catal. A 254 (2003) 273.
[54] A. Griboval-Constant, A.Y. Khodakov, R. Bechara, V.L. Zholobenko, Stud. Surf. Sci. Catal. 144 (2002) 609.
[55] Y. Wang, M. Noguchi, Y. Takahashi, Y. Ohtsuka, Catal. Today 68 (2001) 3.
[56] Y. Ohtsuka, T. Arai, S. Takasaki, N. Tsubouchi, Energy Fuels 17 (2003) 804.
[57] Y. Ohtsuka, Y. Takahashi, M. Noguchi, T. Arai, S. Takasaki, N. Tsubouchi, Y. Wang, Catal. Today 89 (2004) 419.
[58] F. Morales, B.M. Weckhuysen, Catalysis 19 (2006) 1 (Royal Society of Chemistry).
[59] V.V. Kiselev, P.A. Chernavskii, V.V. Lunin, Russ. J. Phys. Chem. 61 (1987) 151.
[60] P.A. Chernavskii, A.Y. Khodakov, G.V. Pankina, J.-S. Girardon, E. Quinet, Appl. Catal. A 306 (2006) 108.
[61] J.-S. Girardon, A. Constant-Griboval, L. Gengembre, P.A. Chernavskii, A.Y. Khodakov, Catal. Today 106 (2005) 161.
[62] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, J. Catal. 156 (1995) 85.
[63] J.R.A. Sietsma, J.D. Meeldijk, J.P. den Breejen, M. Versluijs-Helder, A.J. van Dillen, P.E. de Jongh, K.P. de Jong, Angew. Chem. Int. Ed. 46 (2007) 4547.
[64] W. Chu, L.-N. Wang, P.A. Chernavskii, A.Y. Khodakov, Angew. Chem. Int. Ed. 47 (2008) 5052.
[65] Project update: Oryx gas-to-liquids (GTL) Joint Venture, 22 May 2007, www.sasol.com/sasol_internet/frontend/navigation.jsp?articleTypeID=2&articleId=17800001&navid=4&rootid=4.
[66] W. Chu, P.A. Chernavskii, L. Gengembre, G.V. Pankina, P. Fongarland, A.Y. Khodakov, J. Catal 252 (2007) 215.