Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts by noble metals—a review

by M. de Beer*, A. Kunene*, D. Nabaho*†, M. Claeys*†, and E. van Steen*†

Synopsis

The conversion of carbon-containing feedstock into liquid fuels can proceed via the Fischer-Tropsch synthesis, which is catalysed using supported cobalt catalysts. These catalysts contain noble metals to facilitate the reduction of oxidic cobalt species in the catalyst precursor to metallic cobalt, which is the catalytically active species for the Fischer-Tropsch synthesis. This is thought to occur via hydrogen spillover, i.e. the diffusion of atomic hydrogen over the support from the noble metal to the oxidic cobalt moieties. Noble metals may also affect the dispersion of cobalt in the active Fischer-Tropsch catalyst. The economic aspect of the addition of noble metals to the Fischer-Tropsch catalyst is discussed.

Keywords
catalysis, supported cobalt catalyst, noble metals, Fischer-Tropsch synthesis.

Background

The world depends on transportation fuels, which are classically obtained from oil refining. The dwindling resources of oil in conjunction with the increased costs of crude oil over the last decade yielded an opportunity for the synthesis of transportation fuels from other carbon-containing resources, such as natural gas, biomass, coal, or oil residue. The conversion of these materials into transportation fuels may proceed via the synthesis gas route, in which the carbon-containing feedstock is converted into synthesis gas, a mixture of H_2 and CO. Following a cleaning step and possibly the water-gas shift reaction, synthesis gas can be converted into long-chain hydrocarbons via the Fischer-Tropsch synthesis (Claeys and Van Steen, 2004). The long-chain hydrocarbons can subsequently be hydrocracked to yield high-quality diesel. The resulting product is low in aromatics (and has therefore a high cetane number (Knottenbelt, 2002; Lamprecht, Dancuart, and Harrilall, 2007; Leckel, 2011), and has a low nitrogen and sulphur content. These characteristics make this diesel a low-emission fuel (Knottenbelt, 2002; Huang, Wang, and Zhou, 2008; Hewu et al., 2009) and an ideal blending agent.

Figure 1 shows a generic overview of the Fischer-Tropsch process for fuel production. The carbon source is gasified (in the case of biomass/coal/or oil residue as a feedstock) or reformed (using natural gas as a feedstock), yielding a mixture of synthesis gas, CO_2, and H_2O. In addition, this mixture contains compounds that are poisons for downstream processes, such as H_2S, N-containing compounds, tars, and even alkali compounds (if biomass is used as a feedstock). These compounds have to be removed in the gas cleaning stage. Furthermore, the H_2/CO ratio of the synthesis gas can be adjusted using the water-gas shift reaction, after which CO_2 removal and water removal is required. The clean synthesis gas (with poison levels down to ppm or even ppb levels (Van Steen and Claeys, 2008)) is fed to the Fischer-Tropsch reactor. Some hydrogen is separated from this feed stream for downstream processing. The synthesis gas is partially converted in the Fischer-Tropsch reactor, with some of the unconverted gas being recycled to the Fischer-Tropsch reactor and some being recycled to the gasifier/reformer to ensure a high overall conversion. The liquid products of the Fischer-Tropsch synthesis are separated and the heavy fraction is hydrocracked back into the diesel range.

The Fischer-Tropsch synthesis, which is the heart of the Fischer-Tropsch process, is the hydrogenation of carbon monoxide yielding long-chain hydrocarbons (Schulz, 1985), which is catalysed using transition metals, although carbides (Anderson, 1956; Ranhotra,

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts
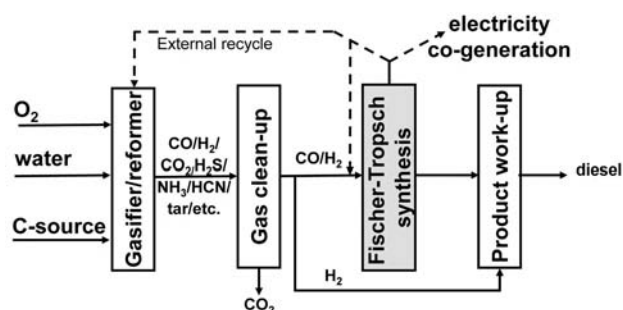

Figure 1—Schematic overview of a generic Fischer-Tropsch process for the production of diesel

Bell, and Reimer, 1987; Patterson, Das, and Davis, 2003) and nitrides (Ranhotra, Bell, and Reimer, 1987) may also catalyse this reaction. A common feature of these materials is their strong interaction with CO and the ability to dissociate adsorbed carbon monoxide. It should be noted that the CO adsorption should be neither too strong nor too weak, since this will lead to methanation rather than chain growth (Van Santen et al., 2012). Coupling of partially hydrogenated surface intermediates leads to the formation of long-chain surface species, which upon desorption form a mixture of organic product compounds.

Vannice (1975) explored the intrinsic activity and selectivity of transition metals supported on γ-Al_2O_3 in different H_2/CO mixtures at temperatures between 240–280°C and at 1 bar. It was concluded that activity for methane formation follows the order of Ru>Fe>Ni>Co>Rh>Pd>Pt>Ir, whereas the average molecular weight of the product follows the order of Ru>Fe>Co>Rh>Ni>Ir>Pt>Pd. On silica as a support, the order of activity was mainly retained, but cobalt was now the most active material (Vannice, 1997).

The comparative studies by Vannice (1995, 1997) show that for the production of long-chain hydrocarbons ruthenium, cobalt, iron, and to a lesser extent nickel are the metals of choice. From an industrial point of view, the cost of the catalytic active material must be taken into account as well (Van Steen and Claeys, 2008). Hence, iron and cobalt-based catalysts are the industrially used Fischer-Tropsch catalysts. Van Berge and Everson (1997) compared the performance of iron and cobalt-based catalysts in a slurry reactor under realistic Fischer-Tropsch conditions and defined regimes in which the cobalt-based catalyst was more active than a precipitated iron catalyst. The cobalt-based catalyst showed a higher productivity at lower relative space velocity and lower reactor pressures. This was ascribed to the higher resistance of cobalt-based catalysts to higher water partial pressures. This means that a higher conversion per pass can be achieved with the cobalt-based catalyst, thereby improving the economics of the overall Fischer-Tropsch process (see also Botes, Niemantsverdriet, and Van de Loosdrecht, 2013). Cobalt catalyst also shows a low activity for the formation of CO_2 under Fischer-Tropsch conditions up to moderate levels of conversion (Ma et al., 2011), making it ideal for the conversion of synthesis gas with a feed ratio of H_2/CO of 2. Furthermore, cobalt catalysts are preferred when a product with a low degree of branching is desired (Van Steen et al., 1996).

Supported cobalt catalysts for the Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis is a surface reaction (Claeys and Van Steen, 2004) and the cobalt-based Fischer-Tropsch synthesis is catalysed by the surface of metallic cobalt (Iglesia, 1997). Hence, smaller metallic crystallites should display a higher activity per unit mass of catalytically active material.

It has been observed that the intrinsic catalytic activity decreases with decreasing average crystallite size of the cobalt crystallite for metallic cobalt crystallites less than 6–10 nm) (Barbier et al., 2001; Bezemer et al., 2006; Martínez and Prieto, 2007; Fischer, Van Steen, and Claeys, 2013). Hence, the mass-specific activity of cobalt-based Fischer-Tropsch catalysts passes a maximum as a function of the crystallite size (Den Breejen et al., 2010), since with increasing crystallite size of the active phase the intrinsic activity of surface atoms increases, but the dispersion (i.e. the fraction of metal atoms at the surface) decreases (see Figure 2). Thus, ideally, the most active catalyst contains all cobalt in crystallites of a defined crystallite size, although the exact position of this optimum crystallite size depends on the nature of the dependency of the surface atom specific activity on the crystallite size, which has not yet been established beyond doubt.

The synthesis of supported cobalt-based catalysts has been reviewed by Khodakov, Chu, and Fongarland (2007). These catalysts are typically synthesized by impregnation (most commonly using cobalt nitrate as the cobalt source). The resulting metallic crystallites are somehow related to the average pore diameter of the support material (Khodakov et al., 2001; Saib, Claeys, and Van Steen, 2002; Borg et al., 2001), although cobalt supported on materials with a small average pore diameter might be located on the outer surface or in the larger pores of the materials (Saib, Claeys, and Van Steen, 2002). The impregnation of γ-Al_2O_3 or SiO_2 with cobalt nitrate yields clusters of cobalt crystallites (Feller, Claeys, and Van Steen, 1999; Storsæter et al., 2005), i.e. regions with a typical diameter of approximately 100-400 nm with cobalt crystallites and regions without cobalt crystallites. This phenomenon is not observed with supports with a large average pore diameter, such as α-Al_2O_3 and TiO_2 (Storsæter et al., 2005). Drying of the catalyst precursor will lead to the formation of cobalt nitrate droplets, which are typically of the
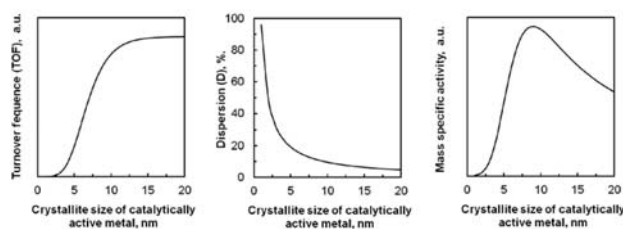

Figure 2—Schematic dependence of observed catalytic activity per surface atom in working cobalt-based Fischer-Tropsch synthesis (Barbier et al., 2001; Bezemer et al., 2006; Martínez and Prieto, 2007; Fischer, Van Steen, and Claeys, 2013) (left), the dispersion, i.e. the number of surface atom relative to the total number of atoms in a metallic cobalt crystallite (centre), and the corresponding activity per unit cobalt mass (right) as a function of the cobalt metal crystallite size

size of the resulting clusters. Calcination of the droplets results in the formation of multiple Co_3O_4 crystallites, which will be trapped within the constraint of a narrow pore system, but will spread over a larger support area in systems with a large average pore diameter.

Reduction of cobalt oxide on materials with a large average pore diameter may result in break-up, leading to smaller crystallites (Borg *et al.*, 2001; Hauman *et al.*, 2012). The preparation of relatively large cobalt crystallites with a size of approximately 8–10 nm therefore requires support materials with an average pore diameter between 10–15 nm.

The use of supported catalysts results in a change in the ease of the transformation of the oxidic catalyst precursor into the catalytically active, metallic, phase. This is typically evidenced using temperature programmed reduction (TPR), in which the catalyst sample is reduced in a hydrogen-containing gas, while the temperature is linearly increased (see Figure 3). The TPR profile is characterized by multiple peaks, which represent different processes taking place with different reaction kinetics. The TPR profile of pure Co_3O_4 is characteristic of the two-stage reduction process $Co_3O_4 \rightarrow CoO \rightarrow Co$ (Van Steen *et al.*, 1996; Li *et al.*, 2009; Rane *et al.*, 2010). The oxide-supported Co_3O_4 shows a number of additional peaks. The additional low-temperature peak might be attributed to either reductive nitrate decomposition of residual nitrates in a catalyst synthesized from cobalt nitrate (see Figure 4 and Van Steen *et al*, 1996; Rane *et al.*, 2010) or the reduction of CoOOH (Li *et al.*, 2009). The two peaks in the TPR profile in the range between approximately 220°C and 500°C are typically attributed to the reduction of Co_3O_4 unperturbed by the support. The reduction peaks of Co_3O_4 are followed by H_2 consumption due to the interaction of cobalt with the support. A higher reduction temperature implies a stronger interaction between cobalt and support, with the reduction of cobalt aluminate (Rane *et al.*, 2010), cobalt silicate (Van Steen *et al.*, 1996), or cobalt titanate (Jongsomjit *et al.*, 2004) typically taking place at temperatures of approximately 800-1000°C.

The interaction of cobalt with the support results in a material that is more difficult to reduce. Hence, a higher reduction temperature is required to ensure a reasonable extent of reduction. However, a higher reduction temperature typically results in larger cobalt crystallites due to sintering (thus representing a loss in the catalytically active metal surface area). It is thus desired to keep the reduction temperature as low as possible, while obtaining a high degree of reduction.

Promotion of cobalt Fischer-Tropsch catalysts with noble metals

Noble metals such as Pt, Ru, or Au (but also Re) are added to the catalyst in small amounts, mainly to enhance the transformation of the cobalt oxide in the supported catalyst precursor to the catalytically active metallic phase (Schanke *et al.*, 1995). Figure 4 shows the effect of the addition of 0.5 wt% Pt to a 20 wt% Co/Al_2O_3 catalyst. All reduction processes are more facile, allowing a lower reduction temperature while obtaining a high degree of reduction.

Promotion with small amounts of Pt, typically around 0.1 wt%, has a significant effect on the extent of this reduction

when the reduction takes place isothermally. However, the effects observed depend on the applied reduction conditions and the catalyst used. Schanke *et al.* (1995) noted an increase in the extent of reduction from 48% to 77% with the addition of 0.4 wt% Pt to 9.0 wt% Co/Al_2O_3, but a much smaller increase (from 90% to 92%) with the addition of 0.4 wt% Pt to 8.9 wt% Co/SiO_2. Tsubaki, Sun, and Fujimoto (2001) noted a larger increase in the degree of reduction from 50% to 56% upon promotion of a 10 wt% Co/SiO_2 catalyst with 0.2 wt% Pt. A similar increase for cobalt supported on silica was reported by Jacobs *et al.* (2002), with an increase in the degree of reduction from 64% to 72% when promoting a 15 wt% Co/SiO_2 catalyst with 3.8 wt% Pt (and an increase from 51% to 53% when promoting a 20 wt% Co/ZrO_2-SiO_2 catalyst with 0.5 wt% Pt).
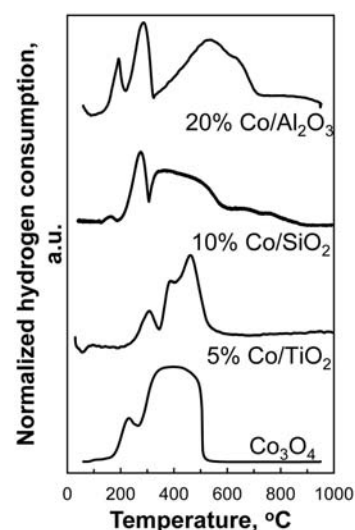

Figure 3—Normalized hydrogen consumption during temperature programmed reduction (TPR) of Co_3O_4 and supported cobalt catalysts (heating rate 10°C/min)
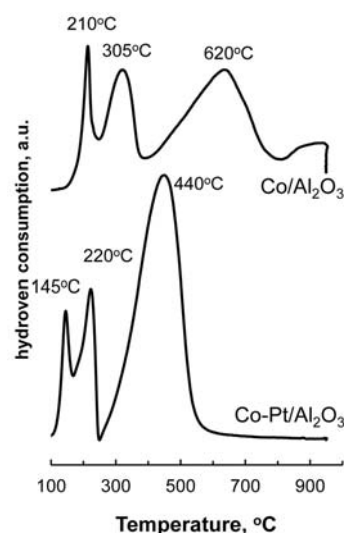

Figure 4—Normalized hydrogen consumption during temperature programmed reduction (TPR) of Co_3O_4 supported on alumina (20 wt% Co) and the catalyst co-impregnated with 0.5 wt% Pt

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts

A similar increase in the degree of reduction has been observed upon the addition of other noble metals to supported cobalt catalysts (Morales and Weckhuysen, 2006; Diehl and Khodakov, 2009; Hilmen, Schanke, and Holmen, 1996; Xu, et al., 2008, 2005, Kogelbauer, Goodwin, and Oukaci, 1996; Jacobs et al., 2009; Jalama et al., 2007; McCue et al., 2013). For instance, Jacobs et al. (2009) showed that promoting a 15 wt% Co/Al₂O₃ catalyst with Au resulted in a significant enhancement in the degree of reduction (see Table I). However, a Au loading of larger than 1.51 wt%, resulted in a decrease in the degree of reduction. A similar result was obtained by McCue et al. (2013).

Mechanism for enhanced reduction by noble metal promotion

It is commonly postulated that improved reducibility upon addition of noble metal promoters such as platinum occurs via hydrogen spillover from the promoter to the cobalt oxides (Diehl and Khodakov, 2009; Hilmen, Schanke, and Holmen, 1996; Jacobs et al., 2004) (it should be noted that unequivocal evidence for this phenomenon is available only for Re-promoted cobalt catalysts (Hilmen, Schanke, and Holmen, 1996). Hydrogen spillover is defined as: the chemisorption of hydrogen molecules on metal surfaces to form adsorbed hydrogen species followed by their migration to another surface such as the support, (Roland, Braunschweig, and Roessner, 1997; Conradie, Gracia, and Niemantsverdriet, 2012). The driving force for hydrogen spillover is the difference in the energetic stability between adsorbed hydrogen on the metal and the adsorbed hydrogen on the support (Conradie, Gracia, and Niemantsverdriet, 2012). The energy levels associated with steps in the hydrogen spillover assisted reduction may be represented schematically by the dissociative adsorption of H_2 on the noble metal promoter, followed by the diffusion of atomic hydrogen on to the support and subsequently on to the reducible cobalt oxide (see Figure 5). The surface diffusion of adsorbed hydrogen species requires continually breaking and re-forming equivalent bonds with similar neighbouring atoms (Conner and Falconer, 1995) on the noble metal surface as well as the support surface. It has been observed that adsorbed species may travel over distances of up to several millimetres away from the dissociating metal surface (Conradie, Gracia, and Niemantsverdriet, 2012; Conner, and Falconer, 1995; Baeza et al., 2006). The supply of dissociated (activated) hydrogen due to the presence of the noble metal in the catalyst by surface diffusion may facilitate the reduction of cobalt oxide, if the activation of hydrogen on cobalt oxide is kinetically the slow step in the reduction process.

The extent of surface diffusion depends not only on the noble metal present, but also on the support used. Baeza et

al. (2006) studied the extent of hydrogen spillover during hydrodesulphfurization and observed that the extent of hydrogen spillover was: γ-Al_2O_3 < C < SiO_2 < $MgSiO_3$. This trend mimics the extent of surface 'acidity' or presence of OH groups. On oxidic surfaces such as Al_2O_3, spillover of hydrogen is commonly thought to occur via formation of 'hydroxyls' (Conradie, Gracia, and Niemantsverdriet, 2012). According to Luo and Epling (2010), the energetics of hydrogen transportation via continual formation and breakage of adjacent hydroxyl groups on an Al_2O_3 surface are quite high and slow because the spillover hydrogen first has to bond to a surface oxygen atom to form a hydroxyl group. The surface hydroxyls formed then act as a 'bucket brigade' with which subsequent spillover H species interact weakly as they are transported over the Al_2O_3 surface (see Figure 6). The bucket-brigade phenomenon can also be used to explain why the range of hydrogen spillover is reduced when catalysts are exposed to high temperature, because surface hydroxyls start to desorb, making spillover energetically less favourable.

It should, however, be realized that the reduction process of supported cobalt catalysts may be more complex than outlined above. The strong increase in the degree of reduction typically reported upon addition of the noble metal as a reduction promoter cannot be explained only by the enhanced rate of reduction of cobalt oxide crystallites present in the catalyst precursor. Cobalt in the supported cobalt catalyst prepared via impregnation may also contain highly dispersed cobalt (e.g. cobalt atomically dispersed over the support) in addition to cobalt-containing crystallites. This cobalt will be

Figure 5—Schematic representation of the energy levels required to facilitate the reduction of cobalt oxide due to the presence of a noble metal promoter

Figure 6—Illustration of hydrogen spillover transport assisted by OH group formation on Al_2O_3 giving rise to a 'bucket brigade' (Luo and Epling, 2010)

Table I				
Effect of promotion with Au on the cobalt reducibility in 15 wt-% Co/Al₂O₃ (Jacobs et al. 2009)				
Au-loading, wt.-%	0	0.1	1.51	5.05
Reduction of Cobalt (%)	49.8	58.9	94.1	81.5

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts

difficult to reduce. The supply of hydrogen to the support may result in the formation of mobile cobalt species, which may diffuse to larger cobalt crystallites. The slow reduction of this type of cobalt species on the support may account for the observed increase in the degree of reduction of the industrial cobalt Fischer-Tropsch catalysts during Fischer-Tropsch synthesis (Van de Loosdrecht et al., 2007).

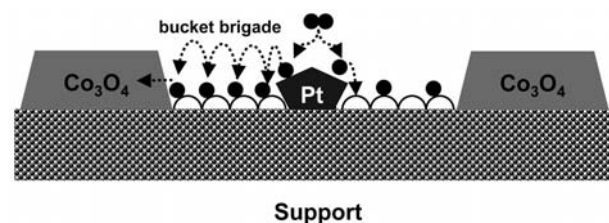It is currently unclear where the noble metal promoter is positioned after the reduction process. Platinum and ruthenium seem to be incorporated into the oxidic cobalt in the catalyst precursor and in the cobalt metal after reduction (Weststrate, Saib, and Niemantsverdriet, 2013). Promotion with group 11 metals seems to lead to segregation between metallic cobalt particles and metallic group 11 particles (Ma et al., 2012).

Change in cobalt dispersion due to noble metal addition

The preparation method may also result in a close proximity of the cobalt oxide phase and the noble metal (salt). It has been noted that the promotion of cobalt-based catalysts does affect the dispersion of cobalt particles in cobalt Fischer-Tropsch catalysts (Schanke, et al., 1995; Tsubaki, Sun, and Fujimoto, 2001; Jacobs et al., 2002) (see Table II). The increase in dispersion upon addition of noble metal promoter has been attributed to a higher concentration of cobalt oxide nucleation and crystallization sites (Khodakov, 2009). A higher number of sites will result in a larger number of crystallites and hence a smaller average particle size and larger percentage dispersion.

The enhanced cobalt dispersion may be beneficial for cobalt-based Fischer-Tropsch catalysts, since the number of exposed metal atoms will increase more rapidly than by an increase in the degree of reduction. However, an enhanced dispersion in addition to an enhanced degree of reduction will not necessarily lead to an increase in the catalytic activity, since the turnover frequency depends on the dispersion as well (see Figure 2).

Change in catalytic behaviour due to noble metal addition

An increase in the degree of reduction (in conjunction with an increase in the cobalt dispersion) may, but does not necessarily, result in an increase in the catalytic activity.

Table III summarizes some of the obtained activities and selectivities upon promoting a Co/γ-Al$_2$O$_3$ Fischer-Tropsch catalyst with various noble metals as reported by Jacobs et al. (2009); Ma et al. (2012). The activity is given as the rate of CO conversion per surface atom as determined by H$_2$ desorption on the freshly reduced catalyst (reduction in hydrogen at atmospheric pressure and 350°C for 10 h) in order to assess whether the promoter elements affect the intrinsic activity of the catalyst (i.e. enhance the catalyst activity beyond the change in dispersion and the change in the degree of reduction). This comparison is non-trivial since the catalyst undergoes further changes during the Fischer-Tropsch synthesis (viz. further reduction and deactivation (Van de Loosdrecht et al., 2007). The further reduction may have a significant effect on the turnover frequency of, in particular, the unpromoted cobalt catalysts, and these turnover frequencies are much higher than those typically obtained for impregnated catalysts (Van Steen and Claeys, 2008). Nevertheless, a tentative comparison of the intrinsic activity of the various promoter elements can be made, which starts mostly at a degree of reduction of approximately 70%.

Copper, the typical reduction promoter for iron-based Fischer-Tropsch catalysts, which would be the cheapest reduction promoter, yields an increase in the degree of reduction, but a decrease in the catalytic activity (Jacobs et al., 2009; Baker, Burch, and Yuqin, 1991), despite the observed increase in the cobalt dispersion. This can be ascribed to blockage of the active metallic cobalt surface with copper. Surface enrichment or blockage with copper can be expected if copper is associated with metallic cobalt, since the surface energy of copper is much lower than that of cobalt (Swart, Van Helden, and Van Steen, 2007). A similar surface blockage effect could have been expected for silver, gold, and to a lesser extent palladium, if these metals are associated with metallic cobalt in the reduced catalyst.

Other noble metals have a higher surface energy than metallic cobalt (Vitos et al., 1998), and surface enrichment with these metals is therefore not expected. The addition of platinum was originally thought to increase the intrinsic activity as well as the degree of reduction (Schanke et al., 1995), but tests under more realistic Fischer-Tropsch conditions (Vada et al., 1995; Jacobs et al., 2002) do not seem to show an enhancement of the intrinsic activity. However, Xu et al. (2005) reported an enhancement of the catalytic activity due to a catalytic synergistic effect between

Table II

Effect of noble metal addition on cobalt dispersion

Catalyst	$D_{Co, unpromoted}$, %	Promoter	$D_{Co, promoted}$, %	Ref.
9 wt% Co/SiO$_2$	7.5	0.4 wt.-% Pt	9.6	Schanke et al., 1995
10 wt% Co/SiO$_2$	8.6	0.2 wt.-% Pt	22.7	Tsubaki, Sun, and Fujimoto, 2001
15 wt% Co/SiO$_2$	2.1	3.8 wt.-% Pt	2.7	Jacobs et al., 2002
15 wt% Co/Al$_2$O$_3$	17.5	0.5 wt.-% Pt	18.4	Jacobs et al., 2002
25 wt% Co/Al$_2$O$_3$	8.7	0.5 wt.-% Pt	9.4	Jacobs et al., 2002
15 wt% Co/Al$_2$O$_3$	11.4	0.1 wt.-% Au 1.5 wt.-% Au 5.1 wt.-% Au	12.6 15.3 16.0	Jacobs et al., 2009

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts

Table III

Physical characteristics (DOR: degree of reduction of cobalt; D_{Co}: corrected dispersion of cobalt), activity (expressed as turnover frequency for CO conversion as determined from the space velocity to obtain X_{CO} = 50% after approximately 100 h on line relative to the amount of H_2 desorbed on the freshly reduced catalyst) and selectivity for the formation of methane (S_{CH4}) and for the formation of liquid hydrocarbons (S_{C5+}) of some noble metal promoted cobalt catalysts

Mn	**25**	**Fe**	**26**	**Co**		**27**	**Ni**	**28**	**Cu**	**29**
					[a]	[b]			wt.-% [b]	0.49
				DOR, %	54.5	49.8			DOR, %	69.4
				D_{Co}, %	5.5	11.4			D_{Co}, %	15.2
				TOF, min⁻¹	4.0	1.6			TOF, min⁻¹	0.8
				S_{CH4}, C-%	7.9	8.9			S_{CH4}, C-%	9.9
				S_{C5+}, C-%	83.4	80.6			S_{C5+}, C-%	76.6
Tc	**43**	**Ru**	**44**	**Rh**		**45**	**Pd**	**46**	**Ag**	**47**
		wt.-% [a]	0.26				wt.-% [a]	0.27	wt.-% [b]	0.49
		DOR, %	70.7				DOR, %	72.1	DOR, %	69.4
		D_{Co}, %	9.3				D_{Co}, %	8.1	D_{Co}, %	15.2
		TOF, min⁻¹	2.4				TOF, min⁻¹	1.4	TOF, min⁻¹	1.3
		S_{CH4}, C-%	7.7				S_{CH4}, C-%	12.6	S_{CH4}, C-%	8.5
		S_{C5+}, C-%	85.2				S_{C5+}, C-%	73.8	S_{C5+}, C-%	81.5
Re	**75**	**Os**	**76**	**Ir**		**77**	**Pt**	**78**	**Au**	**79**
wt.-% [a]	0.48						wt.-% [a]	0.5	wt.-% [b]	1.51
DOR, %	67.2						DOR, %	68.4	DOR, %	94.1
D_{Co}, %	10.1						D_{Co}, %	8.3	D_{Co}, %	15.3
TOF, min⁻¹	2.94						TOF, min⁻¹	1.5	TOF, min⁻¹	1.0
S_{CH4}, C-%	7.0						S_{CH4}, C-%	8.3	S_{CH4}, C-%	8.7
S_{C5+}, C-%	86.2						S_{C5+}, C-%	83.2	S_{C5+}, C-%	82.0

[a] Catalyst contains 25% Co on γ-Al₂O₃ and the Fischer-Tropsch synthesis was performed at 493 K, 2.2 MPa, $(H_2/CO)_{inlet}$ = 2.1 (Ma *et al*. 2012)

[b] Catalyst contains 15% Co on γ-Al₂O₃ and the Fischer-Tropsch synthesis was performed at 493 K, 2.0MPa, $(H_2/CO)_{inlet}$ = 2.1 (Jacobs *et al*. 2009)

cobalt and noble metals, which resulted in an increased reactivity of the adsorbed carbon monoxide. Induced electronic effects by the promoter may result in electronic donation or withdrawal, which may lead to an increased intrinsic turnover frequency or a change in product selectivity (Morales and Weckhuysen, 2006). This may be attributed to the high promoter loading, when the noble metal and metallic cobalt form a single particle. At relative low loadings of industrial interest (*vide verde*), the synergistic effect is expected to diminish. Addition of low amounts of ruthenium increase the site time yield, which is ascribed to a reduced deactivation of the catalyst (Jacobs *et al.*, 2002) (this could not be confirmed with Co/Al₂O₃ (Kogelbauer, Goodwin, and Oukaci, 1996; Vada *et al.*, 1995; Hosseini et al., 2004)). Rhenium shows a high turnover frequency (Ma *et al.*, 2012), although it was previously thought not to affect the intrinsic activity of the resulting metallic cobalt crystallites (Vada *et al.*, 1995; Barkhuizen *et al.*, 2006).

The selectivity towards the desired products, typically expressed as the conversion of CO to C_{5+} hydrocarbons, is of prime importance in the conversion of CO to liquid hydrocarbons. It can be seen from Table III that, in particular, the addition of Pd and Cu at the tested levels results in a decrease in the selectivity for the desired products (and concomitantly an increase in the selectivity for the undesired methane).

Economic outlook for noble metal additions to cobalt Fischer-Tropsch catalysts

The Fischer-Tropsch synthesis is nowadays still a relative small process with a total world-wide capacity on the industrial scale of approximately 363 000 bbl per day. The total amount of liquid fuels produced using cobalt-based catalyst will be approximately 193 000 bbl per day in 2014. The required amount of cobalt can thus be estimated using the typically quoted turnover frequency of 0.01 s⁻¹ (Van Steen and Claeys, 2008) (see Figure 7). A Fischer-Tropsch plant producing 100 000 bbl per day of liquid products (amounting to the capacity of a single small oil refinery) would then require 646 t of cobalt (taking into account a dispersion of 12%, average crystallite size of the cobalt metal of 8 nm, and a degree of reduction of 80% (Luo and Epling, 2010) or approximately 1% of annual cobalt production (Diehl, and Khodakov, 2009).
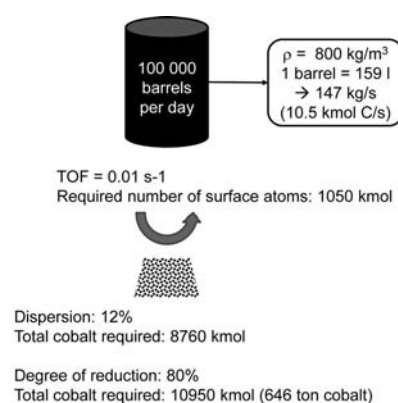

Figure 7—Amount of cobalt required to produce 100 000 bbl per day of liquid hydrocarbons using the Fischer-Tropsch process

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts

The choice of metal utilized as the noble metal promoter in cobalt-based Fischer-Tropsch catalysts depends on the amount of noble metal required, its effect, its current price, and the effect of the newly added market on the price of the metal. The latter is difficult to establish, but might be anticipated comparing the required amount of the noble metal to its annual production (see Table IV).

The effectiveness of the noble metal promoters depends on the level of the promotion (Jacobs et al., 2009). However, it should be realized that most academic studies are performed to show the effect of the noble metal promoter, and the amount of promoter may be higher than required. For instance, the comparison of the effect of different noble metals by the group of Davis (Jacobs et al., 2009; Ma et al., 2012) utilized 0.5 wt% Pt for a catalyst containing 25 wt% cobalt. The commercial catalyst seems to have a lower platinum loading of approximately 0.05 wt% Pt with a cobalt loading of 20 wt% (Ma et al., 2012). This affects the required amount of the noble metal significantly.

The reported levels for the use of rhenium are high (0.02–0.04 g Re per gram Co), implying a high demand on rhenium if this promoter is to be used on a large scale. Furthermore, the large amount of rhenium used in the catalyst implies that a large amount of capital will be locked up in the reactor (assuming that rhenium itself does not contribute to the Fischer-Tropsch synthesis – *vide supra*). Worldwide rhenium production is low, and the amount of rhenium required corresponds to 33–57% of annual production. Hence, the introduction of rhenium on a large scale in Fischer-Tropsch catalysts may result in large fluctuations in the rhenium price.

Ruthenium as a promoter is quite attractive (Xu et al., 2008; Kogelbauer, Goodwin, and Oukaci, 1996; Ma et al., 2012; Iglesia et al., 1993; Hosseini et al., 2004), certainly at the anticipated level of 0.1 g Ru per gram Co (this value may even be further reduced). The evaluation of ruthenium as a promoter is somewhat complicated, since ruthenium itself shows activity for Fischer-Tropsch synthesis (Bertole, Mims, and Kiss 2004). The low price of ruthenium will result in a relative low amount of capital being locked up in the reactor. However, the low annual worldwide production of ruthenium will result in a volatile price if this metal is used on a large scale in Fischer-Tropsch catalysts.

Platinum is currently used as a noble metal promoter in an industrial cobalt-based Fischer-Tropsch catalyst. The typical platinum content seems to be 0.003 g Pt per gram Co (Van de Loosdrecht et al., 2007) (significantly lower than used by Ma et al., (2012). The amount of platinum to be used in a 100 000 barrel per day Fischer-Tropsch plant is expected to be in the range of 1% of the annual worldwide production. A concern from an economic viewpoint is the large amount of capital that is locked up in the reactor.

Gold as a noble metal promoter can enhance the degree of reduction (Jacobs et al., 2009), but the typically tested levels are too high to be of economic use. The high price of gold in conjunction with the required level of promotion results in a large amount of capital being locked up in the process, making the conversion of carbon-containing feedstock into liquid hydrocarbons economically not feasible.

The primary role of the noble metals added to cobalt-based Fischer-Tropsch catalysts is to increase the degree of reduction of cobalt in supported catalysts, while at the same time yielding high cobalt dispersion. Noble metals were introduced in the catalyst at a time when the price of cobalt was relatively high (approximately 200 times the price of iron, whereas it is nowadays approximately 70 times the price of iron). Hence, it might be argued that the need for noble metal promoters has diminished. However, the drive nowadays is to increase reactor yields, which must be achieved by having catalysts containing a high level of metallic cobalt per unit mass of catalyst. This can be achieved by addition of (low levels of) noble metal promoters or changing the catalyst preparation route (Fischer et al., 2012).

Concluding remarks

Noble metals are added to the cobalt-based Fischer-Tropsch catalyst primarily to facilitate the reduction of oxidic cobalt in the impregnated, supported catalyst precursor. The enhancement in reduction is attributed mainly to H_2 spillover due to the presence of reduced metal facilitating the production of dissociated hydrogen, which may diffuse over the support to oxidic cobalt moieties. The increased degree of reduction (with the often observed change in dispersion) results in an improved catalyst activity. The catalyst activity may be further enhanced through a synergistic effect between the noble metal and the catalytically active metallic cobalt.

Table IV

Market aspects of the utilization of noble metals as a promoters in cobalt-based Fischer-Tropsch catalysts to produce 100 000 barrels of liquid per day (assuming TOF = 0.01 s^{-1}, D_{Co} = 12%, DOR = 80%)

Promoter	Promoter level, g per gram Co	Required[1], t	Price[2], 10^6 US$	Relative usage[3], %
Re	0.042 [30]	26.9	94.1	57
0.019 [58]	15.5	54.2	33	
Ru	0.010 [58]	6.7	16.2	56
Pt	0.020 [58]	12.9	590.5	7
0.003 [53]	1.6	73.8	1	
Au	0.100 [44]	65.0	2798	3

[1]Required tonnage of the noble metal to add to 646 t of cobalt
[2]Cost of the noble metal adding to 646 t of cobalt in 2013 (Re: US$ 3500/kg; Ru: US$ 2410/kg; Pt: US$ 45730/kg; Au: US$ 43050/kg)
[3]The amount of noble metal to be added to 646 t of cobalt relative to the annual production of the noble metal in 2012 (Re: 47.2 t; Ru: 75 t; Pt: 192 t; Au: 2350 t)

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts

The levels of promotion of most metals as currently reported in the open literature seem too high for commercial operation, and a decrease in the level of the noble metal promoter is desired, for which a more detailed understanding on the effect of the loading of the noble metal promoter is required.

References

ANDERSON, R.B. 1956. Hydrocarbon synthesis, hydrogenation and cyclization. *Catalysis*. Emmet, P.H. (ed.). vol. IV, Reinhold, New York.

BAEZA, P., VILLARROEL, M., AVILA, P., AGUDO, L.A., DELMON, B., and GIL-LLAMBIAS, F.J. 2006. Spillover hydrogen mobility during Co–Mo catalyzed HDS in industrial-like conditions. *Applied Catalysis A: General*, vol. 304. pp. 109–115.

BAKER, J.E., BURCH, R., and YUQIN, N. 1991. Investigation of $CoAl_2O_4$, $Cu/CoAl_2O_4$ and $Co/CoAl_2O_4$ catalysts for the formation of oxygenates from carbon monoxide – carbon dioxide – hydrogen mixture. *Applied Catalysis*, vol. 73. pp. 135–152.

BARBIER, A., TUEL, A., ARCON, I., KODRE, A., and MARTIN, G.A. 2001. Characterization and catalytic behaviour of Co/SiO_2 catalysts: Influence of dispersion in the Fischer-Tropsch reaction. *Journal of Catalysis*, vol. 200. pp. 106–116.

BARKHUIZEN, D., MABASO, I., VILJOEN, E., WELKER, C., CLAEYS, M., NAN STEEN, E., and FLETCHER, J.C.Q. 2006. Experimental approaches to the preparation of supported metal nanoparticles. *Pure and Applied Chemistry*, vol. 78. pp. 1759–1769.

VAN BERGE, P.J. and EVERSON, R.C. 1997. Cobalt as an alternative Fischer-Tropsch catalyst to iron for the production of middle distillates. *Studies in Surface Science and Catalysis*, vol. 107. pp. 207–212.

BERTOLE, C.J., MIMS, C.A., and KISS, G. 2004. Support and rhenium effects on the intrinsic site activity and methane selectivity of cobalt Fischer-Tropsch catalysts. *Journal of Catalysis*, vol. 221. pp. 191–203.

BEZEMER, G.L., BITTER, J.H., KUIJPERS, H.P.C.E., OOSTERBEEK, H., HOLEWIJN, J.E., XU, Z., KAPTEIJN, F., VAN DILLEN, A.J., and DE JONG, K.P. 2006. Cobalt particle size effects in the Fischer-Tropsch reaction studied with carbon nanofiber supported catalysts. *Journal of the American Chemical Society*, vol. 128. pp. 3956–3964.

BORG, Ø., ERI, S., BLEKKAN, E.A., STORSÆTER, S., WIGUM, H., RYTTER, E., and HOLMEN, A. 2007. Fischer-Tropsch synthesis over γ-alumina-supported cobalt catalysts: effect of support variables. *Journal of Catalysis*, vol. 248. pp. 89–100.

BOTES, F.G., NIEMANTSVERDRIET, J.W., and VAN DE LOOSDRECHT, J. 2013 A comparison of cobalt and iron based slurry phase Fischer–Tropsch synthesis. *Catalysis Today*, vol. 215. pp.112–120. http://dx.doi.org/10.1016/j.cattod.2013.01.013

CLAEYS, M. and VAN STEEN, E. 2004. Fischer-Tropsch synthesis: basic studies. *Studies in Surface Science and Catalysis*, vol. 152. pp. 601–680.

CONNER, W.C. JR. and FALCONER, J.L. 1995. Spillover in heterogeneous catalysis. *Chemical Reviews*, vol. 95. pp. 759–788.

CONRADIE, J., GRACIA, J., and NIEMANTSVERDRIET, J.W. 2012. Energetic driving force of H spillover between rhodium and titania surfaces: a DFT view. *Journal of Physical Chemistry C*, vol. 116. pp. 25362–25367.

DEN BREEJEN, J.P., SIETSMA, J.R.A., FRIEDRICH, H., BITTER, J.H., and DE JONG, K.P. 2010. Design of supported cobalt catalysts with maximum activity for the Fischer–Tropsch synthesis. *Journal of Catalysis*, vol. 270. pp. 146–152.

DIEHL, F. and KHODAKOV, A.Y. 2009. Promotion of cobalt Fischer-Tropsch catalysts with noble metals: a review. *Oil and Gas Science and Technology – Review IFP*, vol. 64. pp. 11–24.

FELLER, A., CLAEYS, M., and VAN STEEN, E. 1999. Cobalt cluster effects in zirconium promoted Co/SiO_2 Fischer-Tropsch catalysts. *Journal of Catalysis*, vol. 185. pp. 120–130.

FISCHER, N., VAN STEEN, E., and CLAEYS, M. 2013. Structure sensitivity of the Fischer-Tropsch activity and selectivity on alumina supported catalysts. *Journal of Catalysis*, vol. 299. pp. 67–80.

FISCHER, N., MINNERMANN, M., BAEUMER, M., VAN STEEN, E., and CLAEYS, M. 2012. Metal support interactions in Co_3O_4/Al_2O_3 catalysts prepared from w/o microemulsions. *Catalysis Letters*, vol. 142. pp. 830–837.

HAUMAN, M.M., SAIB, A., MOODLEY, D.J., DU PLESSIS, E., CLAEYS, M., and VAN STEEN, E. 2012. Re-dispersion of cobalt on a model Fischer-Tropsch catalyst during reduction-oxidation-reduction cycles. *ChemCatChem*, no. 4. pp. 1411–1419.

HEWU, W., HAN, H., XIHAO, L., KE, Z., and MINGGAO, Q. 2009. Performance of Euro III common rail heavy duty diesel engine fuelled with Gas to Liquid. *Applied Energy*, vol. 86. pp. 2257–2261.

HILMEN, A.M., SCHANKE, D., and HOLMEN, A. 1996. TPR study of the mechanism of rhenium promotion of alumina supported cobalt Fischer-Tropsch catalysts. *Catalysis Letters*, vol. 38. pp. 143–147.

HOSSEINI, S.A., TAEB, A., FEYZI, F., and YARIPOUR, F. 2004. Fischer-Tropsch synthesis over Ru-promoted $Co/\gamma-Al_2O_3$ catalysts in a CSTR. *Catalysis Communications*, vol. 5. pp. 137–143.

HUANG, Y., WANG, S., and ZHOU, L. 2008. Effects of Fischer-Tropsch diesel fuel on combustion and emissions of direct injection diesel engine. *Frontiers of Energy and Power Engineering in China*, vol. 2. pp. 261–267.

IGLESIA, E. 1997. Design, synthesis and use of cobalt-based Fischer-Tropsch synthesis catalysts. *Applied Catalysis A: General*, vol. 161. pp. 59–78.

IGLESIA, E., SOLED, S.L., FIATO, R.A., and VIA, G.H. 1993. Bimetallic synergy in cobalt ruthenium Fischer-Tropsch catalysts. *Journal of Catalysis*, vol. 143. pp. 345–368.

JACOBS, G., RIBEIRO, M.C., MA, W., JI, Y., KHALID, S., SUMODJO, P.T.A., and DAVIS, B.H. 2009. Group 11 (Cu, Ag, Au) promotion of 15%Co/Al_2O_3 Fischer–Tropsch synthesis catalysts. *Applied Catalysis A: General*, vol. 361. pp. 137–151.

JACOBS, G., CHANEY, J.A., PATTERSON, P.M., DAS, T.K., MAILLOT, J.C., and DAVIS, B.H. 2004. Fischer-Tropsch synthesis: study of the promotion of Pt on the reduction property of Co/Al_2O_3 catalysts by in situ EXAFS of Co K and Pt L_{III} edges and XPS. *Journal of Synchrotron Radiation*, vol. 11. pp. 414–422.

JACOBS, G., PATTERSON, P.M., ZHANG, Y., DAS, T., LI, J., and DAVIS, B.H. 2002. Fischer-Tropsch synthesis: deactivation of noble metal-promoted Co/Al_2O_3 catalysts. *Applied Catalysis A: General*, vol. 233. pp. 215–226.

JACOBS, G., DAS, T.K., ZHANG, Y., LI, J., RACOILLET, G., and DAVIS, B.H. 2002. Fischer–Tropsch synthesis: support, loading, and promoter effects on the reducibility of cobalt catalysts. *Applied Catalysis A: General*, vol. 233, pp. 263–281.

JALAMA, K., COVILLE, N.J., HILDEBRANDT, D., GLASSER, D., JEWELL, L.L., ANDERSON, J.A., TAYLOR, S., ENACHE, D., and HUTCHINGS, G.J. 2007. Effect of the addition of Au on Co/TiO_2 catalyst for the Fischer–Tropsch reaction. *Topics in Catalysis*, vol. 44. pp. 129–136.

JONGSOMJIT, B., SAKDAMNUSON, C., GOODWIN, J.G., and PRASERTHDAM, R. 2004. Co-support compound formation in titania-supported cobalt catalysts. *Catalysis Letters*, vol. 94. pp. 209–215.

Technical and economic aspects of promotion of cobalt-based Fischer-Tropsch catalysts

KHODAKOV, A.Y. 2009. Fischer-Tropsch synthesis: relations between structure of cobalt catalysts and their catalytic performance. *Catalysis Today*, vol. 144. pp. 251–257.

KHODAKOV, A.Y., GRIBOVAL-CONSTANT, A., BECHARA, R., and VILLAIN, F. 2001. Pore size control of cobalt dispersion and reducibility in mesoporous silicas. *Journal of Physical Chemistry B*, vol. 105. pp. 9805–9811.

KHODAKOV, A.Y., CHU, W., and FONGARLAND, P. 2007. Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long chain hydrocarbons and clean fuels. *Chemical Reviews*, vol. 107. pp. 1692–1744.

KNOTTENBELT, C. 2002. Mossgas 'gas-to-liquid' diesel fuels—an environmentally friendly option. *Catalysis Today*, vol. 71. pp. 437–445.

KOGELBAUER, A., GOODWIN, J.G., and OUKACI, R. 1996. Ruthenium promotion of Co/Al_2O_3 Fischer-Tropsch catalysts. *Journal of Catalysis*, vol. 160. pp. 125–133.

LAMPRECHT, D., DANCUART, L.P., and HARRILALL, K. 2007. Performance synergies between low-temperature and high-temperature Fischer-Tropsch diesel blends. *Energy & Fuels*, vol. 21. pp. 2846–2852.

LECKEL, D. 2011. Diesel production in coal-based high-temperature Fischer–Tropsch plants using fixed bed dry bottom gasification technology. *Fuel Processing Technology*, vol. 92. pp. 959–969.

LI, Y., ZHAO, Z., DUAN, A., JIANG, G., and LIU, J. 2009. Comparative study on the formation and reduction of bulk and Al_2O_3-supported cobalt oxides by H_2-TPR technique. *Journal of Physical Chemistry C*, vol. 113. pp. 7186–7199.

LUO, J.-Y. AND EPLING, W.S. 2010. New insights into the promoting effect of H_2O on a model $Pt/Ba/Al_2O_3$ NSR catalyst, vol. 97. pp. 236–247.

MA, W., JACOBS, G., KEOGH, R.A., BUKUR, D.B., and DAVIS, B.H. 2012. Fischer–Tropsch synthesis: effect of Pd, Pt, Re, and Ru noble metal promoters on the activity and selectivity of a $25\%Co/Al_2O_3$ catalyst. *Applied Catalysis A: General*, vol. 437–438. pp. 1–9.

MA, W., JACOBS, G., LI, Y., BHATELIA, T., BUKUR, D.B., KHALID, S., and DAVIS, B.H. 2011. Fischer-Tropsch synthesis: influence of CO-conversion on selectivities, H_2/CO usage ratios, and catalyst stability for a Ru promoted Co/Al_2O_3 catalyst using a slurry reactor. *Topics in Catalysis*, vol. 54. pp. 757–767.

MARTÍNEZ, A. and PRIETO, G. 2007. Breaking the dispersion-reducibility dependence in oxide supported cobalt nanoparticles. *Journal of Catalysis*, vol. 245. pp. 470–476.

MCCUE, A.J., APONAVICIUTE, J., WELLS, R.P.K., and ANDERSON, J.A. 2013. Gold modified cobalt-based Fischer-Tropsch catalysts for conversion of synthesis gas to liquid fuels. *Frontiers of Chemical Science and Engineering*, vol. 7, no. 3. pp. 1–8.

MORALES, F. and WECKHUYSEN, B.M. 2006. Promotion effects in Co-based Fischer-Tropsch catalysis. *Catalysis*, vol. 19. pp. 1–40.

PATTERSON, P.M., DAS, T.K., and DAVIS, B.H. 2003. Carbon monoxide hydrogenation over molybdenum and tungsten carbides. *Applied Catalysis A: General*, vol. 251. pp. 449–455.

RANE, S., BORG, Ø., YANG, J., RYTTER, E., and HOLMEN, A. 2010.Effect of alumina phases on hydrocarbon selectivity in Fischer–Tropsch synthesis. *Applied Catalysis A: General*, vol. 388. pp. 160.

RANHOTRA, G.S., BELL, A.T., and REIMER, J.A. 1987. Catalysis over molybdenum carbides and nitrides: II. Studies of CO hydrogenation and C_2H_6 hydrogenolysis. *Journal of Catalysis*, vol. 108. pp. 40–49.

ROLAND U., BRAUNSCHWEIG, T., and ROESSNER, F. 1997. On the nature of spilt-over hydrogen. *Journal of Molecular Catalysis A: Chemical*, vol. 127. pp. 61–84.

SAIB, A.M., CLAEYS, M., and VAN STEEN, E. 2002. Silica supported cobalt Fischer-

Tropsch catalysts: effect of pore diameter of support. *Catalysis Today*, vol. 71. pp. 395–402.

VAN SANTEN, R.A., CIOBICA, I.M., VAN STEEN, E., and GHOURI, M.M. 2011. Mechanistic issues in Fischer-Tropsch catalysis. *Advances in Catalysis*, no. 54. pp. 127–187.

SCHANKE, D., VADA, S., BLEKKAN, E.A., HILMEN, A.M., HOFF, A,. and HOLMEN, A. 1995. Study of Pt-promoted cobalt CO hydrogenation catalysts. *Journal of Catalysis*, vol. 156. pp. 85–95.

SCHULZ, H. 1985. Selectivity and mechanism of the Fischer-Tropsch CO-hydrogenation. *C1 Molecular Chemistry*, vol. 1. p. 231.

VAN STEEN, E. and CLAEYS, M. 2008. Fischer-Tropsch catalysts for the Biomass-to-Liquid (BTL)-process. *Chemical Engineering and Technology*, vol. 31, no. 5. pp. 655–666.

STORSÆTER, S., TØTDAL, B., WALMSLEY, J.C., TANEM, B.S., and HOLMEN, A. 2005. Characterization of alumina-, silica-, and titania-supported cobalt Fischer-Tropsch catalysts. *Journal of Catalysis*, vol. 236. pp. 139–152.

SWART, J.C.W., VAN HELDEN, P., and VAN STEEN, E. 2007. Surface energy estimation of catalytically relevant fcc transition metals using DFT-calculations on nano-rods. *Journal of Physical Chemistry C*, vol. 111. pp. 4998–5005.

TSUBAKI, N., SUN, S., and FUJIMOTO, K. 2001. Different functions of the noble metals added to cobalt catalysts for Fischer–Tropsch synthesis. *Journal of Catalysis*, vol. 199. pp. 236–246.

VADA, S., HOFF, A., ADNANES, E., SCHANKE, D., and HOLMEN, A. 1995. Fischer-Tropsch synthesis on supported cobalt catalysts promoted by platinum and rhenium. *Topics in Catalysis*, vol. 2. pp. 155–162.

VADA, S., HOFF, A., ADNANES, E., SCHANKE, D., and HOLMEN, A. 1995. Fischer-Tropsch synthesis on supported cobalt catalysts promoted by platinum and rhenium. *Topics in Catalysis*, vol. 2. pp. 155–162.

VAN DE LOOSDRECHT, J., BALZHINIMAEV, B., DALMON, J.-A., NIEMANTSVERDRIET, J.W., TSYBULYA, S.V., SAIB, A.M., VAN BERGE, P.J., and VISAGIE, J.L. 2007. Cobalt Fischer-Tropsch synthesis: deactivation by oxidation? *Catalysis Today*, vol. 123. pp. 293–302.

VAN STEEN, E., SEWELL, G.S., MAKHOTE, R.A., MICKLETHWAITE, C., MANSTEIN, H., DE LANGE, M., and O'CONNOR, C.T. 1996. TPR study on the preparation of impregnated Co/SiO_2 catalysts. *Journal of Catalysis*, vol. 162. pp. 220–230.

VANNICE, M.A. 1975. The catalytic synthesis of hydrocarbons from H_2/CO mixtures over the group VIII metals. I The specific activity and product distributions of supported metals. *Journal of Catalysis*, vol. 37. pp. 449-–461.

VANNICE, M.A. 1977. The catalytic synthesis of hydrocarbons from H_2/CO mixtures over the group VIII metals. V. The catalytic behaviour of silica-supported metals. *Journal of Catalysis*, vol. 50. pp. 228–236.

VITOS, L., RUBAN, A.V., SKRIVER, H.L., and KOLLAR, J. 1998. The surface energy of metals. *Surface Science*, vol. 411. pp. 186–202.

WESTSTRATE, C.J., SAIB, A., and NIEMANTSVERDRIET, J.W. 2013. Promoter segregation in Pt and Ru promoted cobalt model catalysts during oxidation–reduction treatments. *Catalysis Today*, vol. 215, no. 15. pp. 2–7. http://dx.doi.org/10.1016/j.cattod.2013.01.009

XU, D., DAI, P., GUO, Q., and LI, W. 2008. Promotional effects of noble metal addition to cobalt Fischer-Tropsch catalysts. *Reaction Kinetics and Catalysis Letters*, vol. 94. pp. 367–374.

XU, D., LI, W., DUAN, H., GE, Q., and XU, H. 2005. Reaction performance and characterization of Co/Al_2O_3 Fischer–Tropsch catalysts promoted with Pt, Pd and Ru. *Catalysis Letters*, vol. 102. pp. 229–235. ◆