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Cobalt hybrid catalysts in Fischer-Tropsch synthesis

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Abstract: Currently, cobalt and zeolites are used in Fischer-Tropsch synthesis (FTS) to produce gasoline-range hydrocarbons (GRHs) that constitute clean and environmentally friendly fuels. This technology has earned a great deal of attention from researchers across the world, as it provides a substitute for fuel derived from fossil crudes, which have hitherto been the sole source of the petrol and diesel required by the industry. However, owing to the depletion of the earth's oil and coal reserves and the unfavourable environmental impact of conventional fuel production, an alternative source of fuel is needed. This article provides a critical review of the technological challenges involved in producing middle isoparaffins and olefins (gasoline hydrocarbons) by FTS. These involve combining cobalt-based catalysts and zeolites to form hybrid catalysts. In this review, we address most of these by setting out each method of creating cobalt and zeolite hybrid catalysts in turn, so that researchers can identify which applications are most effective for producing GRHs.

Keywords: cobalt-based catalysts; cobalt hybrid catalysts; Fischer-Tropsch synthesis; gasoline-range hydrocarbons; isoparaffins and olefins in FTS; zeolites.

1 Introduction

1.1 Fischer-Tropsch synthesis

The gas-to-liquid process is a modern technology that uses Fischer-Tropsch synthesis (FTS) for producing chemicals

and transportation fuels from natural or flare gas-derived synthesis gas or syngas (H_2/CO) via a reforming process. Biomass-to-liquid and coal-to-liquid processes involve the partial oxidation (in other words, the gasification) of biomass and coal, respectively, to generate synthesis gas or syngas (H_2/CO) for the production of FTS liquid transportation fuels, waxes and chemicals (Martínez et al. 2008, De Klerk and Furimsky 2011, Sousa-Aguiar et al. 2011, Beaumont 2014). The Fischer-Tropsch (FT) process forms the backbone of natural gas-, biomass- and coal-to-liquid technology.

High-quality liquid hydrocarbons and chemicals free of sulphur and nitrogen can be produced from natural gas, biomass, coal and any other hydrocarbon-containing wastes (for example plastics and papers), which are alternative sources to crude oil. These sources can also be used to generate syngas, which is used in FTS, a reaction that can be described as a catalytic step growth polymerisation process, or the synthesis of hydrocarbons through syngas (H_2/CO) over transition metal catalysts (Chadeesingh 2011). There is a wide range of active iron (Fe)-, cobalt (Co)-, nickel (Ni)- or ruthenium (Ru)-based catalysts (Martínez et al. 2008, De Klerk and Furimsky 2011, Beaumont 2014). The type of catalysts and the reaction conditions determine the product distribution, which comprises hydrocarbon complex mixtures – mainly oxygenates of alcohol, linear and branched olefins and paraffins, C_{2+} and methane (Blekkann et al. 2007). Of the four catalysts mentioned above, Fe and Co are the most commonly used for industrial FTS.

The FT reaction polymerisation mechanism perspective can be described as a carbon chain building reaction involving CH_2 groups, which are attached in sequence to the carbon chain, and the overall reaction can be explained as follows (Jacobs and Davis 2010, Chadeesingh 2011):

For example: $CO + 2H_2 \rightarrow -CH_2 - + H_2O \quad \Delta H = -165 \text{ KJ/mol.}$ (2)

Apart from the equations given above, several other reactions occur during FTS. The different explanations of these phenomena as reported by many other researchers are still fiercely debated because the mechanisms involved

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have not yet been sufficiently explained. At present, none of the mechanisms suggested by researchers fully explain all the FTS products produced (De Klerk and Furimsky 2011, Chadeesingh 2011, Förtsch et al. 2015). Some of the other reactions they report include using the exothermic nature of FTS as a general rule of thumb due to the production of H_2O or CO_2 in the reaction. The relevant equations are as follows (Chadeesingh 2011).

And, the water-gas shift (WGS) reaction equation is

The average value for the heat of these exothermic reactions is around 10 KJ/g (Sousa-Aguiar et al. 2011). The most important parameter for the researcher to follow, therefore, is the need for cooling the reaction and, thus, preventing an uncontrolled increase in temperature. This is crucial to prevent the production of lighter hydrocarbons, stabilise the reaction conditions and improve catalyst sintering and reduction activity (Chadeesingh 2011).

The stoichiometric reactions required to produce hydrocarbons and oxygenates as primary products during the FT process are as expressed below (Jacobs and Davis 2010, De Klerk and Furimsky 2011).

Eqs. (7) and (8) indicate the reactions that generate alkanes and alkenes, respectively, while Eqs. (9), (10) and (11) represent the reactions for the production of alcohols/ethers, aldehydes/ketones and carboxylic acids/esters, respectively. The primary products in FTS represent the compounds with functional groups on the terminal carbon (De Klerk and Furimsky 2011).

The predictions of the primary composition of products of FTS are based on the condensation-polymerisation hypothesis of Anderson-Schulz-Flory (ASF) (De Klerk and Furimsky 2011, Förtsch et al. 2015). This requires only a single parameter, which is the probability of chain growth, denoted as α , which can be defined in respect of the rate of termination, r_t , and the rate of chain propagation or polymerisation, r_p , of the growing hydrocarbon chain, as follows (De Klerk and Furimsky 2011, Förtsch et al. 2015):

$$\alpha_n = r_{p,n} / (r_{p,n} + r_{t,n}). \quad (12)$$

The rate of termination and propagation can depend on the chain length, n , and the conditions of the FT reaction (in other words, the relevant concentration, pressure and temperature) (Förtsch et al. 2015).

The distribution of FTS products can then be defined with respect to y_n , which is the mole fraction of all FTS components having the chain length or carbon number n , as follows:

$$y_n = (1 - \alpha)\alpha^{n-1}. \quad (13)$$

Eq. (13) assumes that the chain growth probability, α , is independent of the carbon number or chain length. This is referred to as the ASF distribution of carbon number (Förtsch et al. 2015).

Eq. (13) can also be solved to

$$\log y_n = \log[(1 - \alpha) / \alpha] + n \log \alpha. \quad (14)$$

ASF distribution is an idealised function that has limited uses due to its assumption of a constant chain growth probability (Kuipers et al. 1996, Liu et al. 2011, Förtsch et al. 2015). For example, some experimental results show deviations for C_1 and C_2 in FTS products. But ASF carbon number distribution has the advantage of simplicity since it contains only one parameter, which, as already noted, is the chain growth probability α . The ASF distribution can be checked experimentally by plotting a logarithm of mole fraction, y_n , against the chain length or carbon number from Eqs. (13) and (14) to give a straight-line plot. The resulting slope can be generated from Eq. (15) below (Förtsch et al. 2015):

$$\alpha = \exp [d(\ln y_n) / dn]. \quad (15)$$

If a straight line is not obtained and the deviations of the plot cannot be ignored, another, more complex model needs to be used, such as applying the ASF carbon number distribution to only $n \geq 3$ carbon numbers.

However, some reactions such as hydrocracking and branching on acidic zeolites sites and readsorption during

cobalt-zeolite FTS can improvably influence the product distribution and result in improved activity and selectivity of desired range of FT hydrocarbon products [for example gasoline-range hydrocarbons GRHs)] (Kuipers et al. 1996, Liu et al. 2011). These can lead to deviations from ideal ASF carbon number distributions. Some of the other reactions of FT primary hydrocarbons that can cause deviations from ASF are the reinsertion of the FT chain growth reaction, isomerisation, hydrogenolysis, oligomerisation and hydrogenation (Kuipers et al. 1996, Liu et al. 2011, Vo et al. 2013). The rates of reinsertion and hydrogenation have been previously shown to increase exponentially with the carbon number or chain length, which is caused by the diffusion, physisorption and solubility limitations of the longer hydrocarbons with the catalyst (Liu et al. 2011, Vo et al. 2013). Significant deviations from the ASF norm have been reported in most of the published literature. Also, the product distribution of iron and cobalt-based catalysts can be represented by double ASF distribution superposition functionalised by two growth probabilities (Nakhaei-Pour et al. 2013). Nakhaei-Pour et al. (2013) reported on the use of a modified ideal ASF distribution with two chain growth probabilities, which was developed by Langmuir-Hinshelwood-Hougen-Watson, modelling for FT carbon number distribution over an iron-based catalyst.

Therefore, due to ASF polymerisation kinetics, the FTS reaction can be characterised by a wide range of hydrocarbon products and a lack of selectivity towards any length of carbon chain in favour of selective production of a particular product range (such as GRHs). The addition of a second catalytic function or a bi-functional catalyst (such as acidic zeolite) to a conventional FTS catalyst, which might be cobalt based, creates a hybrid catalyst (Liu et al. 2007, Kibby et al. 2013, Cheng et al. 2015, Lu et al. 2015). For example, the maximum selectivity towards GRHs on conventional FTS catalysts is around 45–48% (Cheng et al. 2012, 2015, Kang et al. 2014). Cobalt-based catalysts produce mostly longer- and heavier-chain hydrocarbons from natural gas-derived syngas. When cobalt and zeolite are combined in the form of a hybrid catalyst, secondary reactions can occur on the acidic zeolites to generate GRHs (Li et al. 2009a,b, Lu et al. 2015).

1.2 Cobalt-based catalysts

Cobalt-based catalysts have been found to perform different functions in several processes and reactions, such as methane reforming and FTS (Rangel et al. 2010). Parameters like particle size, the nature of the reaction conditions, support type, pretreatment and preparation

method, the promoter, the metal-support dispersion and interaction and catalyst structure are important considerations when the researcher is ascertaining the optimally performing FT catalyst for each of a number of different processes. Iglesia (1997) reported on the structural effects of some of these parameters on cobalt-based catalysts during FTS. Cobalt-based catalysts are commercially promoted for use in FTS, owing to their high selectivity to olefins and long-chain hydrocarbons and their activity towards lower WGS reaction performance. These characteristics can be compared with those of iron-based and ruthenium-based catalysts. The former have the advantage of reacting under low- to medium-temperature operating conditions and cost less than ruthenium-based catalysts (Hills et al. 1997, Hilmen et al. 1997, Das et al. 2007, Rangel et al. 2010). Iron-based FT catalysts are also reported to reoxidise during the FT reaction. The probability of reoxidation of FT metal oxides in a water-containing reaction medium increases in the order $\text{Ru} < \text{Ni} < \text{Co} < \text{Fe}$ (Hilmen et al. 1997, Mothebe et al. 1997, Das et al. 2007).

Rhenium (Re) metal is said to promote both the reducibility of cobalt oxide in cobalt-based catalysts and that of metal oxides. During FTS, this decreases in the order $\text{Ru} > \text{Ni} > \text{Co} > \text{Fe}$ (Das et al. 2007).

It is widely accepted in FTS that the support of a catalyst promotes the synthesis of a well-dispersed and high-catalytic-reaction surface area phase (Keyser and Prinsloo 2007). This stabilises the active reaction phase against surface area loss and significantly influences the adsorption, reaction, morphology, selectivity and activity properties of the catalyst active phase (Keyser and Prinsloo 2007). FTS activity and selectivity are influenced by the composition and structure of cobalt (Co) crystallites and the support, which suggests an unexpected FTS chain growth reaction structure sensitivity on Co (Iglesia 1997). Cobalt-based catalyst designs with high specific rates have focused on the preparation methods to decrease the size of Co crystallites and on the supports used to increase the rate per surface Co atom.

Supported Co-based catalysts are considered to be the most favourable catalytic material for the production of long-chain and high-molecular-weight hydrocarbons from natural gas or methane-based syngas, due to their high selectivity to linear paraffins, high FT activity, low metal-carbide formation, low price compared to other supported metal-based catalysts and low WGS reaction activity (Borg et al. 2007, Marion and Hugues 2007).

The most common FT catalyst supports are silica (SiO_2), alumina (Al_2O_3), carbon material (C) and titania (TiO_2), and a strong interaction of these supports can affect the efficient generation of the active metallic cobalt, Co [see Eqs. (16) and (17)], phase during catalyst reduction (Roe et al. 1988, Borg et al. 2007, Hong et al. 2010). Other catalyst supports such as gallia, molecular sieves, magnesia, zirconia, silica-alumina, zeolites and ceria are also used in FTS (Jager and Espinoza 1995). Supported catalysts are synthesised using impregnation of metal precursor (metal nitrate or oxide) on the support (metal oxide and carbon materials), drying, calcination and catalyst reduction methods.

As it is well known that the catalytic selectivity and activity depend on the number of metal sites present on a catalyst surface for FT reaction, so is the use of stable metal oxides (for example Al_2O_3 and SiO_2) as supports for increasing the stability and dispersion of metal particles or crystallites on the support well established (Iglesia 1997, Iqbal et al. 2016). The undesirable strong interaction between metal and the support can lead to the formation of mixed metal oxides (such as CoAl_2O_4 when Al_2O_3 is used as support), which causes rapid deactivation of the FT catalysts. Therefore, the use of chemically inert materials such as carbon materials as supports is sometimes advisable to reduce the risk of generation of inactive and undesirable mixed metal oxides (Iqbal et al. 2016). Carbon materials serve as stable supports and enable supported metal oxides to reduce efficiently during FTS. Roe et al. (1988) have reported that the dispersion of the cobalt catalyst active phase on various supports varies with the nature and surface area of the kind of support used. However, a decrease in the FT activity of supported cobalt catalysts was observed by Reuel and Bartholomew in the order $\text{Co/TiO}_2 > \text{CoAl}_2\text{O}_3 > \text{Co/SiO}_2 > \text{Co/C} > \text{Co/MgO}$ when the FT reactions were performed using $\text{H}_2/\text{CO}=2$, pressure (P)=1 bar and temperature (T)=225°C (Ernst et al. 1999).

Catalyst supports and modifiers, which can also be classified as textural promoters, are usually used to improve attrition resistance and reducibility, increase cluster dispersion, modify the active metal site and enhance sulphur tolerance for efficient and effective FTS (Kapoor et al. 1992, Jacobs et al. 2002, Karaca et al. 2011).

In order to improve the reducibility of cobalt metal, bimetallic particle and support cobalt mixed-compound formation, cobalt dispersion, cobalt precursor decomposition, activation of hydrogen, deactivation and stability properties, desired product selectivity, FTS activity and active phase of cobalt-based catalysts, an appropriate amount of promoters are often added as well as to their

hybrid forms. Noble metal promoters such as Ru, Re and Pt reduce at lower temperature when compared with cobalt oxides and can be used in cobalt-based catalysis to catalyse and improve the reduction of the active cobalt oxide phase by lowering the reduction temperature through the advantage of hydrogen spillover effect from the promoter's surface (Kapoor et al. 1992, Jacobs et al. 2002, Karaca et al. 2011, Zhao et al. 2015, Kungurova et al. 2017, Vosoughi et al. 2017). These noble metal promoters can also improve the interaction between the active cobalt oxide phase and the support and enhance cobalt-based hybrid catalyst performance in achieving high catalytic selectivity and activity during FTS reactions due to the reduction ease (Kapoor et al. 1992, Jacobs et al. 2002, Bae et al. 2009, Karaca et al. 2011). Parnian et al. (2014) promoted $\gamma\text{-Al}_2\text{O}_3$ -supported cobalt-based catalysts with Ru, which resulted in lower reduction temperature of the active cobalt oxide phase, a reduction in the interaction of support and cobalt oxide phase and better overall FTS activity.

Rare earth metal oxides have been reported to modify cobalt-based catalysis reactions structurally or electronically by improving the performance to better activity and selectivity (Vada et al. 1994, Zeng et al. 2011, He et al. 2015, Brabant et al. 2017). He et al. (2015) developed composite lanthanum (La)- and cerium (Ce)-promoted cobalt-based catalysts for selectivity towards the maximal yield of diesel (that is, long-chain hydrocarbons) and efficient CO conversion in FTS. The use of La was also reported by Brabant et al. (2017), who stated that it improved the reduction and catalytic properties of an alumina-supported cobalt-based catalyst. Recently, the effect of CeO_2 on the surface of Al_2O_3 support in $\text{Co/Al}_2\text{O}_3$ catalysts was evaluated by Pardo-Tarifa et al. (2017). This promotion favoured the reducibility of the cobalt-based catalyst with an about 70°C decrease in the reduction temperature. And the presence of Ce (Al/Ce molar ratio=8) in the cobalt-based catalyst system resulted in activity and C_{5+} selectivity increase.

The effect of a manganese (MnO) promoter on a magnesium-oxide-supported cobalt-based catalyst was tested by Warayanon et al. (2015) to improve the metal dispersion, surface area, catalyst reducibility and catalytic performance of the catalyst. They also noted that adding manganese, which acts as an electronic and structural promoter, can also result in the production of higher long-chain hydrocarbons in the diesel product range and a lower amount of methane (Thiessen et al. 2012, Warayanon et al. 2015). Recently, Johnson and Bell (2016) investigated the impact of metal oxides such as Zr, Mn, Ce, Gd and La on a porous silica-supported cobalt-based catalyst and found that these promoters increase the selectivity towards C_{5+} hydrocarbons and decrease methane selectivity, owing to

interactions of the Lewis acid-base between the promoter metal cations and reaction intermediates.

In Table 1, there is an indication that conventional supports gave good promoted catalyst surface area and Co cluster size, while in Table 2, the C_2 - C_4 selectivity increased when HZSM-5 and montmorillonite (MMT) were used as cobalt supports due to a hydrocracking reaction (that is, the acid properties) of the zeolite and MMT supports on the produced long-chain hydrocarbons (C_{5+}) to short-chain hydrocarbons. Therefore, it can be deduced from Tables 1 and 2 that when the cobalt-based catalysts are promoted, the CO conversion increased, C_{5+} (long chain hydrocarbons) selectivity increased and mostly CO_2 and methane selectivity decreased. It can also be noted from Table 2 that the CO_2 selectivity increased when MMT was used as a support instead of other conventional supports because this was not the case for the HZSM-5-supported cobalt-based catalyst when the same promoter, Ru, was used. The Co/HZSM-5 catalyst has a $208.6 \text{ m}^2/\text{g}$ BET surface area with a reaction temperature of 573 K , which are higher than the $144.7 \text{ m}^2/\text{g}$ BET surface area and 508 K reaction temperature of Co/MMT. The increase in CO_2 selectivity for MMT support can also be connected to the different acidity behaviours of MMT and HZSM-5 supports, where HZSM-5 zeolite as a support has hydrogenation property to convert CO_2 to CO and H_2O , thereby decreasing the production of CO_2 . Also, the methane selectivity increased for HZSM-5-supported cobalt catalyst when a Ni promoter was used, but this was not the case when a Ru promoter was used for the same catalyst. This is due to the known production of methane for Ni metal in the FT reaction, because both catalysts have almost the same catalytic properties of pore volume and diameter, BET surface area and other reaction conditions from Table 1.

Relatively little attention has been paid by researchers to the effects of using alkali and alkaline earth metals, such as Na, Li, K and Ca, for cobalt-based catalysts for FTS. This can be attributed to the distinct reduction they cause in catalytic activity, although they improve selectivity towards heavier- and long-chain hydrocarbons, olefin-to-paraffin (O/P) ratios and CO_2 (Lillebø et al. 2013).

1.3 Zeolite catalysts

In recent studies (Ribeiro et al. 1995, O'Connor et al. 1996, Romanovsky 2001, Botes and Böhringer 2004, Stöcker 2005, Maesen 2007), researchers have proposed an ideal matrix to host nano-sized particles and produce hybrid forms of FT catalysts by means of zeolites and zeolite-like materials. These have well-organised shape selectivity, high chemical resistance and thermal stability and

Table 1: Summary of properties of some promoted and supported cobalt-based catalysts.

Catalyst	Pore volume (cm^3/g)	BET surface area (m^2/g)	Average pore diameter (nm)	Cluster size (nm)	Reactor	H_2/CO	Process condition		Promoter(s)
							Pressure (MPa)	Temperature (K)	
Co/MMT (Zhao et al. 2015)	0.220	144.700	6.100	12.50	Fixed-bed	2	1.00	508	Ru ($RuCl_3 \cdot 3H_2O$)
Co/SBA-15 (Rodrigues et al. 2012)	0.710	385.000	6.600	16.10	Slurry-phase	1	2.03	513	Ru ($Ru(NO)(NO_3)_3$)
Co/HZSM-5 (Wang et al. 2013)	0.231	208.600	4.400	12.00	Fixed-bed	2	2.00	508–573	Ru ($RuCl_3$)
Co/HZSM-5 (Wang et al. 2013)	0.199	198.500	4.000	9.00	Fixed-bed	2	2.00	508–573	Ni ($Ni(NO_3)_2$)
Co/ SiO_2 (Zhao et al. 2015)	0.438	272.451	5.130	9.48	Fixed-bed	2	2.00	493 and 513	La (La_2O_3) and/or Ce (CeO_2)
Co/ SiO_2 (Zhao et al. 2015)	0.360	280.296	4.920	9.55	Fixed-bed	2	2.00	493 and 513	La (La_2O_3)

Table 2: Summary of effects of promoters in some promoted and supported cobalt-based catalysts.

Catalyst	Promoter(s)	CO conversion (%)	CO ₂ selectivity (%)	Methane selectivity	C ₂ -C ₄ selectivity	C ₅ + selectivity	Effect of promoter(s) addition
Co/MMT (Zhao et al. 2015)	Ru	Increased	Increased	Decreased	Increased	Increased	Improved FTS activity and structural and compositional changes, which gave significant decrease in reduction temperature
Co/SBA-15 (Rodrigues et al. 2012)	Ru	Increased	–	Decreased	Decreased	Increased	Increased Fischer-Tropsch activity, C ₅ + hydrocarbons and catalyst reducibility
Co/HZSM-5 (Wang et al. 2013)	Ru	Increased	Decreased	Decreased	Increased	Increased	Increased the reduction degree of the cobalt-based catalysts, amount of weaker acid sites and selectivity towards GRHs
Co/HZSM-5 (Wang et al. 2013)	Ni	Increased	Decreased	Increased	Increased	Increased	Increased the CO conversion and selectivity of GRHs
Co/SiO ₂ (Zhao et al. 2015)	La and/or Ce	Increased	Decreased	Decreased	Decreased	Increased	2:1, 1:1 and 1:2 of La:Ce maintained high diesel (C ₁₂ -C ₁₈) yield and better FTS activity at both temperatures
Co/SiO ₂ (Zhao et al. 2015)	La	Increased	Decreased	Decreased	Decreased	Increased	Improved reducibility of the cobalt-based catalyst and enhancement of the dispersion degree

regular systems of pores and cavities. Zeolite cavities can be referred to as the channelled reaction nano-vessels in which chemical reactions take place and the reaction products are affected by reaction confinements (Ribeiro et al. 1995, Romanovsky 2001). Zeolites are crystalline aluminosilicates with three-dimensional framework patterns that form uniformly sized ranging pores of molecular dimensions. These pores serve as molecular sieves on the molecular scale by preferentially fitting and adsorbing molecules while leaving out molecules that are too big (Stöcker 2005, Maesen 2007). Zeolites and other related materials are useful components of adsorption processes, can be used in bifunctional catalysts (such as cobalt-based hybrid catalysts) to upgrade FT hydrocarbons and can be separated from the products and educts easily.

Zeolite catalysts are usually used in acid catalysed reactions such as isomerisation, oligomerisation, aromatisation, hydrogenation and hydrocracking. The strength of their acid sites can be controlled by de- or re-alumination, the ion exchange mechanism and the tetrahedral atom isomorphous substitution (O'Connor et al. 1996, Botes and Böhringer 2004). The design of various forms of cobalt hybrid catalysts, combining FT catalysts and zeolite catalysts such as H-ZSM-5, H-Y zeolite, ZSM-11, ZSM-12, mordenite and β -, omega- and L-zeolite, has been investigated for selectivity towards a desired range of hydrocarbons, especially diesel-range hydrocarbons (DRHs) and GRHs (O'Connor et al. 1996, Botes and Böhringer 2004, Chalupka et al. 2015, Plana-Pallejà et al. 2016). Hierarchical zeolites having both micropores and mesopores can also be developed and combined with FT catalysts for better diffusion of FT hydrocarbons and improvement in the performance of cobalt hybrid catalysts (Xing et al. 2015a,b, 2016, Hao et al. 2016). Although FTS active metals (Fe, Ru, Ni or Co) can be placed directly on zeolite supports to generate metal-zeolite catalyst systems for a one-step synthesis of GRHs from syngas, they are considerably less active because FTS active metals cannot be effectively reduced on zeolite supports. This is owing to the strong interaction between the FTS active metals and zeolite supports, which leads to a very low FTS activity (Li et al. 2009a,b). However, a separate supported cobalt catalyst can be prepared that is FTS-active and can be used with zeolites to achieve the desired product range.

In this critical review, most of the lapses in the challenges facing cobalt-zeolite hybrid catalyst engineering and reactions are figured out for better applications in synthesising GRHs, because despite the different engineered cobalt-zeolite hybrid catalysts, including the addition of promoters to produce GRHs that have surfaced over the last decade, there are still considerable challenges that are

yet to be addressed, such as best reaction conditions and preparation methods suited for the hybrid catalyst, the size and structure type of the hybrid catalyst and zeolite deactivation rate in the hybrid catalyst (Li et al. 2009a,b, Kibby et al. 2013). Other challenges reported are difficulties in moulding the zeolites physically mixed cobalt-based catalysts, zeolites changes to amorphous phase due to a strong acid metal precursor solution and limited concentration of cobalt in zeolite-supported cobalt-based catalysts, and large quantity synthesis difficulties in zeolites encapsulated cobalt-based catalysts (Kang et al. 2014).

2 Cobalt-zeolite hybrid concepts

Following the ASF carbon number distribution model (function of the chain growth probability, α) of FTS hydrocarbons for cobalt-based catalysts, the polymerisation type kinetics for direct selective synthesis of a desired range of hydrocarbon cuts is not feasible except for an infinite chain growth probability, where $\alpha = 1$, and methane, where $\alpha = 0$. Therefore, the current strategies in catalysis engineering for selective synthesis of a desired range of hydrocarbons involve breaking the ASF distribution product selectivity with specific carbon number distributions. These include the use of LTFT processes (that is, cobalt-based catalysis) and downstream conversion for hydrocracking and isomerisation at conditions where α is around unity (Sartipi et al. 2013a,b). This downstream conversion involves the use of a formulated or structured hybrid catalyst system that contains a zeolite catalyst coupled with the customary FTS catalyst, which is cobalt based. This structured hybrid catalyst system can be combined in one reactor, using different patterns or multistage catalysis processes such as a dual-bed configuration, a homogeneous mixed bed and/or a hybrid catalyst pellet bed configuration to prevent the FTS product distribution from following a normal ASF distribution (Sartipi et al. 2013a,b, Wijayapala et al. 2014). At FT reaction conditions, the zeolite catalyst system has the potential to oligomerise, hydrocrack, isomerise, aromatise and hydrogenate in some instances, by upgrading the hydrocarbon products of the FTS cobalt-based catalyst system to produce GRHs, desired selectively in the reactor.

2.1 Zeolite physically mixed cobalt-based catalysts

The FT process can be modified by the use of hybrid catalysts containing a physical mixture of a conventional

FT catalyst of cobalt for the production of long-chain paraffins and waxes, with a bifunctional or acidic zeolite containing acid-metal sites for hydrocracking, oligomerisation and isomerisation of these products. The advantage of this modification is that it would enable selective production of the desired products (such as GRHs).

Most of the other reportedly tackled factors in cobalt hybrid catalysis are coke formation, deactivation properties, selectivity towards DRHs and decrease in methane selectivity (Martínez et al. 2007, 2008, Huang et al. 2011, Sartipi et al. 2013a,b). The physical form of cobalt hybrid catalysts using zeolite as the acid catalyst can be combined by different patterns in one reactor as homogeneous mixed bed or dual bed or hybrid catalyst pellet bed (Sartipi et al. 2013a,b). Martínez et al. (2007, 2008) reported on the use of a physical mixture of different industrial zeolites with different acidities and pore topologies and Co/SiO₂ FT catalyst for their coke formations and deactivation factors in a down-flow fixed-bed FT reactor. The coke formation and deactivation rate of each acidic zeolite part correlated well with each zeolite pore dimension (that is, its topology), but not its acidity, and with respect to this, the stability decreased in the order H-ZSM-5 > HMOR > H- β > USY (Martínez et al. 2007) but was hardly affected by zeolite acidity. The surface acidity determined the zeolite activity, where ITQ-2, with a larger surface area than ZSM-5, MCM-22 and IM-5, showed the highest initial yield of GRHs rather than by the total amount of Bronsted acid sites and lack of diffusion of long-chain hydrocarbons through the 10-membered ring channel of the zeolites (Martínez et al. 2008). The physically mixed hybrid catalyst containing protonated ZSM-5 exhibited the highest amount of medium isoparaffin production (for example GRHs) (Martínez et al. 2007, 2008).

There is an indication in Table 3 that H- β zeolite gave high BET surface area and total pore volume, but the effects of these properties on hydrocarbon selectivity could not be ascertained. Tables 3 and 4 also show that when zeolite was physically added to a cobalt-based catalyst, the methane and C₁₃₊ selectivity decreased, while that of the short-chain hydrocarbons, including the isoparaffins, increased. This can be explained by the migration of the long- and heavier-chain hydrocarbons generated by cobalt-based catalysts to the acidic zeolite sites and channels for hydrocracking and isomerisation, including oligomerisation of the methane molecules. It is also evident that the CO₂ selectivity reduced and that O/P selectivity rose.

The addition of a small amount of noble metal such as palladium (Pd), controlling the SiO₂/Al₂O₃ ratio and decreasing the crystallite size when ZSM-5 or its protonated

Table 3: Summary of properties of the zeolites in zeolites physically mixed cobalt-based catalysts.

Zeolite	Total pore volume (cm ³ /g)	BET surface area (m ² /g)	Pore diameter (nm)	Co particle size (nm)	Si/Al ratio	Bronsted acidity at 350°C (μmol/g)	Lewis acidity at 350°C (μmol/g)	Reactor	Total catalyst weight (g)	H ₂ /CO catalyst(s)	Process condition			Cobalt-based catalyst
											Pressure (MPa)	Temperature (K)	Space velocity (ml/g _{cat} /h)	
H-ZSM-5 (Martínez et al. 2008)	0.160	379.0	–	–	15.0	204.0	78	Fixed-bed	2.00	2.0	2.0	523	13,510	Co/SiO ₂
H-ZSM-5 (Martínez et al. 2007)	0.390	388.0	3.60	13.90	15.0	205.0	78.0	Fixed-bed	2.00	2.0	2.0	523	13,510	Co/SiO ₂
H-ZSM-5 (Yang et al. 2015)	–	–	–	–	–	–	–	Fixed-bed	–	2.0	1.0	553	–	Co/SiO ₂
ZSM-5 (Tsubaki et al. 2003)	–	–	–	–	24.0	–	–	Fixed-bed	1.00	3.0	1.0	513	–	Co/SiO ₂
H-ITQ-2 (Martínez et al. 2008)	0.120	560.0	–	–	14.0	126.0	99	Fixed-bed	2.00	2.0	2.0	523	13,510	Co/SiO ₂
H-β (Li et al. 2009a,b)	0.590	719.2	–	13.80	17.6	–	–	Fixed-bed	0.65	2.2	1.0	538	–	Co/Al ₂ O ₃
H-β (Martínez et al. 2007)	1.020	598.0	–	13.90	12.5	148.0	162.0	Fixed-bed	2.00	2.0	2.0	523	13,510	Co/SiO ₂

Table 4: Summary of effects of the physical mixture of zeolites with cobalt-based catalysts.

Zeolite	CO conversion (%)	CO ₂ selectivity (%)	C ₁ selectivity	C ₂ -C ₄ selectivity	C ₅ -C ₁₂ selectivity	Iso-C ₅ -C ₁₂ selectivity	C ₁₃ -C ₂₂ selectivity	C ₂₃ + selectivity	Olefins-to-paraffins ratio	Effect(s) of zeolite addition
H-ZSM-5 (Martínez et al. 2008)	–	–	Decreased	Increased	Increased	Increased	Decreased	Decreased	–	Improved and increased the formation amount of high-octane GRHs and branched products
H-ZSM-5 (Martínez et al. 2007)	–	–	Decreased	Increased	Increased	Increased	Decreased	Decreased	–	Cracking of the long-chain hydrocarbons to mainly GRHs and branched products
H-ZSM-5 (Yang et al. 2015)	Decreased	Decreased	Decreased	–	–	Increased	Decreased	Decreased	Increased	Improved and increased the catalytic reaction of light gasoline-range isoparaffin production from syngas
ZSM-5 (Tsubaki et al. 2003)	Unchanged	Decreased	Increased	–	–	Increased	Decreased	Decreased	Increased	Resulted in direct synthesis of middle isoparaffins from syngas
H-ITQ-2 (Martínez et al. 2008)	–	–	Unchanged	Increased	Increased	Increased	Decreased	Decreased	–	Improved and increased the formation amount of high-octane GRHs and branched products
H-β (Li et al. 2009a,b)	Decreased	Decreased	Decreased	–	–	Increased	–	–	Increased	Improved and increased the direct synthesised gasoline-range isoparaffins
H-β (Martínez et al. 2007)	–	–	Decreased	Increased	Increased	Increased	Decreased	Decreased	–	Cracking of the long-chain hydrocarbons to mainly GRHs and branched products

form is used as the co-catalyst or bifunctional catalyst in cobalt-based hybrid catalysis, can significantly improve the stability of the zeolite part against coke formation and deactivations and has a strong effect on the catalyst activity and selectivity towards the desired product (Martínez et al. 2007, Wu et al. 2015). Li et al. (2004) prepared some hybrid catalysts containing physical mixtures of Co/SiO₂ with β or H-ZSM-5 or USY or H-mordenite zeolite and Pd/SiO₂ with USY or mordenite or H-ZSM-5 used in upper and lower fixed-bed reactor systems for middle isoparaffin production. The carbon number distribution within C₃-C₆ and isoparaffin-rich hydrocarbons was observed in the two-reactor systems. The hydrocracking of long-chain hydrocarbons over physically mixed catalysts containing various compositions of Pd/SiO₂ and H-ZSM-5 in the presence of hydrogen resulted in high and stable catalyst activity and generated selectivity towards isoparaffin-rich hydrocarbons. The isomerisation of the primary hydrocarbons produced was most favourable for physical mixtures rich in Pd/SiO₂, as seen in Figure 1. The role of palladium (Pd) in this catalyst system was attributed to the inlet spilling of hydrogen onto the zeolite surface. Li et al. (2005) used almost the same approach for the synthesis of middle isoparaffins, emphasising deactivation patterns and coke formation on Pd/ β by feeding more hydrogen to the lower reactor system.

2.2 Zeolite-supported cobalt-based catalysts

The use of zeolites as supports in FTS provides several advantages, such as high metal dispersion,

better metal-zeolite interaction, shape selectivity and bifunctionality, compared to the traditional supports of silica, alumina, titania and carbon materials (Chen et al. 1983). The cobalt crystallites may be supported within the pores or the surface of the zeolites. Many of the published works on the subject have reported the benefits of using a bifunctional catalyst system to produce high octane and carbon number GRHs from syngas (Tsubaki et al. 2003, Li et al. 2004, Martínez et al. 2007, Huang et al. 2011, Yang et al. 2015). Mixed metal-ZSM-5 catalyst FT systems have been found to promote selectivity towards gasoline-range products through improved synthesis of high-octane branched and aromatic hydrocarbons by enhancing cracking, isomerisation, oligomerisation and aromatisation reactions on the zeolite catalyst system (Wijayapala et al. 2014). Most conventional FT catalysts can also generate branched and aromatic hydrocarbons by chain propagation network reactions of initially produced low-molecular-weight straight hydrocarbons or oxygenates, followed by dehydration, cyclisation and dehydrogenation.

The use of alkaline metals to promote catalyst activity in FTS has been practised for the last half-century. For example, several research publications have reported the advantages of copper and potassium for this purpose (Pendyala et al. 2015, Xiong et al. 2015, Visconti et al. 2016). Copper-based WGS reactions, which exhibit high selectivity and activity toward decreasing water (H₂O) and increasing effective H₂/CO ratio in FTS, have been employed since early 1960 (Wijayapala et al. 2014). This type of copper-based promotion can be exhibited at temperatures between 170 and 500°C, which also allows for LTFT and HTFT processes (such as 170–240°C and 250–350°C)

Figure 1: CO conversion and hydrocarbons selectivity for physically mixed zeolites and cobalt-based catalyst in a one-step FT reaction: H₂/CO ratio = 2; W/F = 5.1 g h/mol; 1.0 MPa; 513 K; reaction time, 4 h; (Co/SiO₂)/zeolite ratio, 4:1 by weight (Li et al. 2004). Reproduced with permission from Elsevier.

(Kuipers et al. 1995, Visconti et al. 2016). Wijayapala et al. (2014) synthesised a potassium (K)-, molybdenum (Mo)- and copper (Cu)-promoted cobalt-based catalyst supported over a ZSM-5 zeolite to produce branched hydrocarbons of alkyl-substituted benzenes in FTS. The Cu metal in the synthesised catalyst helped the WGS reaction by raising the H_2/CO ratio and reducing the water (H_2O) components during an FTS catalytic test to produce branched hydrocarbon products, whereas the ZSM-5 zeolite helped to form aromatic and branched hydrocarbon products.

Zeolites such as ZSM-5/H-ZSM-5, ZSM-11, ITQ-6, ITQ-2, mordenite and β - and Y-zeolite supported cobalt-based catalysts have been reported for the production of middle isoparaffin, olefin and aromatic products, which contrasts with the normal synthesis of a wide range of hydrocarbon cuts using conventional supports such as alumina, silica and carbon materials in FTS (Concepción et al. 2004, Espinosa et al. 2011). Meanwhile, the mean crystallite size of these zeolites appears to be one of the most critical and important parameters for cobalt-zeolite catalyst engineering because smaller catalyst crystallites (that is, nano-sized particles) should provide a better proportion of surface active sites and shorter diffusion channel for the reacting hydrocarbon molecules. These lead to minimum coke formation and short contact times at the zeolite surface active sites and pores (Concepción et al. 2004, Espinosa et al. 2011). Espinosa et al. (2011) prepared a nano-sized β -zeolite that supported different cobalt metal concentrations for the production of isoparaffins and branched hydrocarbon products at a temperature of 220°C, which differs from the normal production of conventional zeolite-cobalt catalysts at this temperature.

As already noted, cobalt-based catalyst engineering is preferred to iron-based systems for the synthesis of long-chain and heavier hydrocarbons (for example DRHs) since it favours more production of long-chain normal paraffins, is less involved in WGS reaction, is more stable in the presence of water molecules and generates less oxygenates (Concepción et al. 2004). Therefore, it allows the involvement of zeolites and, sometimes, their derivatives in cobalt catalyst engineering for the production of DRHs or GRHs during FTS reactions, due to their hydrocracking, isomerisation, hydrogenation, oligomerisation and aromatisation properties. But dispersion and reducibility factors are some of the challenges that affect the synthesis of the hybridised form of cobalt-zeolite catalysts. Concepción et al. (2004) reported on delaminated ITQ-6- and ITQ-2-zeolite-supported cobalt catalysts compared with mesoporous MCM-41- and SiO_2 -supported cobalt catalysts for the synthesis of C_{5+} hydrocarbon products. These delaminated ITQ-6- and ITQ-2-zeolite-supported cobalt

catalysts presented relatively better dispersion and reducibility to overcome the challenge of poor reducibility due to strong cobalt-zeolite interaction in cobalt-zeolite catalyst engineering and hybridising.

2.2.1 ZSM-5-/H-ZSM-5-supported cobalt-based catalysts

Zeolites supporting cobalt-based catalysts usually show high selectivity towards gasoline-range aromatic and isoparaffin hydrocarbons, but with low CO conversion, due to the strong interaction between the conventional FTS active metal cations and zeolitic framework negative charges (Bessell 1994, Ngamcharussrivichai et al. 2007). These strong interactions are also attributed to the lower reducibility factors of the FTS active Co-metal on zeolite supports (Ngamcharussrivichai et al. 2007). ZSM-5 and its protonated form (H-ZSM-5) are among the preferred acidic zeolite supports when it comes to good selective synthesis of GRHs (isoparaffins and aromatics) because of their pore structure shape selectivity (for example hierarchical zeolites), coking resistance and stability during FTS conditions (Bessell 1994, Khodakov et al. 2007, Ngamcharussrivichai et al. 2007, Li et al. 2010, Wang et al. 2013). This direct supported form of cobalt-based catalyst with ZSM-5 as the support can also result in lower activity and the formation of undesirable CO_2 and CH_4 due to its strong Co-ZSM-5 interaction, leading to lower catalyst reducibility efficiency when compared with the use of conventional SiO_2 as the support (Ngamcharussrivichai et al. 2007, Yao et al. 2014). Yao et al. (2014) addressed the reducibility factor in a ZSM-5-supported cobalt catalyst by proposing a polyethylene glycol (PEG) additive method to support the cobalt in the catalyst for the production of GRHs in FTS. The PEG additive protocol made it possible to deposit cobalt oxide particles on the outer surface of the ZSM-5 support. This method, with Ru as the promoter, provided higher reducibility factor and CO conversion than did the ZSM-5-supported cobalt-based catalyst prepared by the impregnation process (Yao et al. 2014). Tables 5 and 6 show that when ZSM-5 or its protonated form, H-ZSM-5, supported the cobalt-based catalyst directly, the C_1 selectivity increased, owing to the strong cobalt-ZSM-5/HZSM-5 interaction and lower reducibility factor. There was also a slightly higher cobalt particle or cluster size when compared with the use of conventional supports. Most of the other types of zeolites that were used did not produce these results.

To address the problem of lower CO conversion in conventional zeolite-supported cobalt catalysts, Kim et al. (2014) synthesised a mesoporous MFI zeolite nanosponge

Table 5: Summary of properties of zeolite-supported cobalt-based catalysts.

Zeolite	Total pore volume (cm ³ /g)	BET surface area (m ² /g)	Pore diameter (nm)	Co particle size (nm)	Si/Al ratio	Bronsted acidity at 350°C (μmol/g)	Lewis acidity at 350°C (μmol/g)	Reactor	Total catalyst weight (g)	H ₂ /CO	Process condition			Compared cobalt-based catalyst
											Pressure (MPa)	Temperature (K)	Space velocity (ml/g _{cat} /h)	
MesoH-ZSM-5 (Sartipi et al. 2013a,b)	0.350	448.0	–	11.00	26.0	–	–	Fixed-bed	0.197–0.556	2.0	1.5	513	2400	Co/SiO ₂
H-ZSM-5 (Sartipi et al. 2013a,b)	0.220	388.0	–	13.00	41	138	37	Fixed-bed	0.500	2.0	1.5	513	2400	Co/SiO ₂
SiO ₂ /HZSM-5 (Li et al. 2008)	0.630	356.0	6.80	15.80	–	–	–	Fixed-bed	1.000	2.0	2.0	523	–	Co/SiO ₂
ZSM-5 (Wang et al. 2016)	0.900	481.3	–	9.20	–	–	–	Fixed-bed	–	2.0	2.0	493	1200	Co/SBA-15
ZSM-5 (Kang et al. 2012)	0.070	306.0	–	23.2	–	–	–	Fixed-bed	0.300	2.0	2.0	513	4000	Co/SiO ₂
ITQ-2 (Concepción et al. 2004)	0.550	484.0	4.50	17.30	–	–	–	Fixed-bed	1.000	2.0	2.0	493	13,500	Co/SiO ₂
MCM-22 (Ngamcharussrivichai et al. 2007)	0.380	–	0.55	–	30	–	–	Slurry-phase	1.000	2.0	1.0	503	–	Co/Al ₂ O ₃
NS-MFI (Kim et al. 2014)	0.550	630.0	4.00	–	46	–	–	Fixed-bed	0.500	2.0	2.0	493	2400	Co/γ-Al ₂ O ₃

that supported cobalt nanoparticles for the production of GRHs in FTS. This catalyst provided high dispersion of cobalt on the MFI zeolite support due to the large surface area of the hierarchical zeolite walls and its spongy mesoporosity. It also presented high FT catalytic activity, with lower production of gaseous hydrocarbons. In Table 6, it can be noted that when an unimproved ZSM-5 support was used, the CO conversion of the catalysts dropped, while the CO conversion rose when other zeolites such as SiO₂/HZM-5 and MesoH-ZSM-5 were used as the support. Certain zeolites, such as ZSM-5 and its protonated form, have structures that limit the molecular size of the hydrocarbons produced during FTS on the metal and hence make better catalysts for combination with Co (Calleja et al. 1995). These limitations on the zeolite structures lead to the formation of non-ASF carbon number distribution for selectivity towards a desired range of products, but this can be improved by introducing hierarchical walls of mesoporosities in addition to the existing microporosities for better zeolite reactions and diffusion of the long- and short-chain hydrocarbon products.

The stability, hydrocarbon selectivity and activity of the ZSM-5-supported cobalt-based catalysts during FTS reactions can be significantly affected by both the methods of preparation and the properties of the ZSM-5 support (Shamsi et al. 1984). Olefins produced from the FT cobalt active metal sites can be oligomerised by the ZSM-5 support in ZSM-5-supported cobalt-based catalysts to produce heavier olefins, followed by cyclisation, isomerisation and aromatisation to generate GRHs (Shamsi et al. 1984, Li et al. 2010). These gasoline-range products contain isoparaffins, branched olefins and aromatics, which are high-octane gasoline main components (Shamsi et al. 1984, Khodakov et al. 2007, Ngamcharussrivichai et al. 2007). Tables 5 and 6 show that, in general, the CO conversion and GRHs increased while the CO₂ and C₁₃₊ selectivity declined when zeolites were used instead of conventional supports such as silica, alumina, titania and carbon materials.

2.2.2 Hierarchical zeolite-supported cobalt-based catalysts

A hierarchically porous structure in zeolites improves the diffusion and mass transport of larger viscous systems or hydrocarbon molecules when added to cobalt-based catalysts for FT reactions. This can improve the resistance to coke deposition in these combined microporous and macro/mesoporous catalyst structures, owing to their large pore volume and better mass transport (Chen et al.

Table 6: Summary of effects of the zeolite supports in cobalt-based catalysts.

Zeolite	CO conversion (%)	CO ₂ selectivity (%)	C ₁ selectivity	C ₂ -C ₄ selectivity	C ₅ -C ₁₂ selectivity	Iso-C ₅ -C ₁₂ selectivity	C ₁₃ -C ₂₂ selectivity	C ₂₃ + selectivity	C ₅ -C ₁₂ O/P ratio	Effect(s) of zeolite(s) support
MesoH-ZSM-5 (Sartipi et al. 2013a,b)	Increased	–	Increased	Increased	Decreased	Increased	Decreased	–	Increased	Improved the proximity of FTS and zeolite acid sites
H-ZSM-5 (Sartipi et al. 2013a,b)	Increased	Decreased	Increased	Increased	Increased	Increased	Decreased	Decreased	Increased	Increased the direct synthesis of GRHs
SiO ₂ /HZSM-5 (Li et al. 2008)	Increased	Decreased	Increased	Increased	Increased	Increased	Decreased	Decreased	Increased	Increase in selectivity of GRHs, including the olefins
ZSM-5 (Wang et al. 2016)	Decreased	–	Increased	Increased	Increased	Increased	Decreased	Decreased	–	High CO conversion and selectivity towards GRH products
ZSM-5 (Kang et al. 2012)	Decreased	Decreased	Increased	Increased	Decreased	Decreased	Decreased	Decreased	Decreased	Increase in light hydrocarbons and GRHs with a decrease in long-chain hydrocarbon products
ITQ-2 (Concepción et al. 2004)	Increased	–	Decreased	Decreased	Increased	Increased	–	–	–	Increase in C ₁ and other light hydrocarbons due to high hydrogenation and cracking activities at a temperature of 513 K
MCM-22 (Ngamcharussrivichai et al. 2007)	Increased	–	Increased	Increased	Decreased	Increased	Decreased	–	Decreased	Resulted in higher selectivity towards C ₃ ⁺ hydrocarbon products and increase in reaction rate and turnover frequency (TOF) of the FTS reactions
NS-MFI (Kim et al. 2014)	Unchanged	Decreased	Decreased	Increased	Decreased	Increased	Decreased	Decreased	Increased	Increased the CO conversion, FT activity and C ₄ ⁺ isoparaffin production
										High stability of the Co nanoparticles against particle growth and high FT activity with high selectivity towards GRHs

2012, Li et al. 2013, Xing et al. 2015a,b, Sartipi et al. 2013a, Sun et al. 2016a). Diffusion and mass transport limitations impair catalytic activity in terms of selectivity loss, coke deposition and earlier deactivation of the catalyst (Chen et al. 2012, Li et al. 2013).

Recently, the use of these hierarchically mesoporous structures for catalyst support has attracted much attention from FTS researchers due to their improved hydrocarbon mass transport and multi-functionalities (Chen et al. 2012, Li et al. 2013, Wang et al. 2016). The combination of zeolites with FTS active metal for non-ASF carbon number distributions can be dated back to the 1980s, but even four decades later, the methane selectivity for these hybrid catalysts is as high as 20% (Sun et al. 2016b). However, in recent studies, researchers have reported that the introduction of hierarchical walls of mesoporosities in cobalt-zeolite catalysts has effectively reduced methane selectivity and further increased the production of FT GRHs. These improvements in performance are attributable to zeolite mesoporous structures, which have a larger pore volume, higher specific surface area, better resistance to reactants and/or products, improved cobalt dispersion and accessibility, reduced diffusion path length, favourable chemical compositions, low density, appropriate cobalt-zeolite mean distance, high thermal stability and lower acidity (Chen et al. 2012, 2015, Sartipi et al. 2013a,b, Sineva et al. 2014, Sun et al. 2016b, Wang et al. 2016). Xing et al. (2015a) described a hierarchically synthesised HZSM-5-supported cobalt catalyst for FTS, which was synthesised by a one-step approach using dual templates, F127 and TPAOH, as represented in Figure 2. The effectiveness of their innovation was compared with the use of conventional

HZSM-5 supports in cobalt-based catalysis for selectivity towards GRHs. The hierarchical HZSM-5-supported cobalt catalyst they had prepared gave a very good CO conversion (79.0%), low methane (13.4%) and better selectivity to GRHs (C_5 - C_{11} = 65.4% and C_{5+} = 74.1%) in FTS than the more commonly used supported cobalt catalysts (Xing et al. 2015a). The hierarchical ZSM-5-supported cobalt catalyst recently reported by Xiong et al. (2017) also gave a good conversion (28.6%) and almost similar selectivity (C_5 - C_{20} = 68.9% and C_{5+} = 79.2%) like that of the catalyst reported by Xing et al. (2015a).

2.3 Zeolite encapsulated cobalt-based catalysts

The complete encapsulation of cobalt clusters inside the channels and shells of zeolites is another mode of engineering bifunctional cobalt-based catalysts, which are composed of the acidic zeolite as the coat or capsule/shell with a conventional FTS cobalt-based catalyst as the core. This type of core-shell bifunctional catalyst can completely suppress the production of heavy- and long-chain hydrocarbons (n-paraffins and α -olefins) to produce middle-range hydrocarbons, including GRHs. The FTS active metal (that is, the core cobalt catalyst) converts the syngas into normal aliphatic hydrocarbons, which then migrate to the acidic zeolite shell sites for further reactions (Bao and Tsubaki 2012). The zeolite shell subverts the conventional ASF distribution of FTS products by hydrocracking, oligomerising, aromatising and isomerising the normal aliphatic hydrocarbons, to selectively produce the desired range of middle-branched hydrocarbons (GRHs) (Bao and Tsubaki 2012, Xing et al. 2014, Farrusseng and Tuel 2016). The zeolites used as capsule or shell catalysts in combination with the active metal nanoparticles in FTS are usually ZSM-5, β - and Y-zeolites and their protonated forms (H-ZSM-5, H- β) (Li et al. 2008, 2009a,b). Recently, the synthesis of FTS branched hydrocarbons with a high octane value, which can be used as substitutes for gasoline, by using zeolite-encapsulated conventional FTS metals, is boosting the reputation of FTS processes in the scientific and industrial world (Yang et al. 2008a,b, Bao and Tsubaki 2012, Liu et al. 2013, Xing et al. 2014, Farrusseng and Tuel 2016).

In order to generate branched hydrocarbon products selectively, and without any form of upgrading in FTS, especially for gasoline blends, many effective efforts have been made by researchers to modify cobalt-based catalysts by coating them with acidic zeolite (He et al. 2005, Ryu et al. 2014). The advantage of a cobalt-based catalyst is the

Figure 2: Representation of the procedure for preparing hierarchical zeolite (Xing et al. 2015a). Reproduced with permission from Elsevier.

production of sulphur- and nitrogen-free n-paraffins with high cetane number as diesel fuel, which can be further processed to produce a desired range of hydrocarbons. Zeolites are special aluminosilicate materials with unique cavities and pores, varied molecular diffusion and mass transportation and useful acidic properties (He et al. 2005, Yang et al. 2008a,b, Farrusseng and Tuel 2016). These features assist them, via hydrocracking, hydrogenation, oligomerisation and isomerisation reactions, to synthesise the desired types of hydrocarbon products. The long- and heavier-chain hydrocarbons from the main FTS core catalyst, which diffuse through the zeolite membrane, react longer than the short-chain hydrocarbons for better cracking and isomerisation. This kind of zeolite-coated cobalt-based catalyst is of great importance in experimental applications to convert the long- and heavier-chain hydrocarbons to GRHs (He et al. 2005, Yang et al. 2007a,b, 2008a,b, Jin et al. 2013).

Core-shell configuration has properties such as composition, thermal stability and functionalities with significant potentials, which can be tuned during catalyst engineering. Potentially, each participating core in the core-shell catalyst is isolated by a permeable capsule with a homogenous environment, which effectively protects the participating core catalyst against sintering and damage (Yang et al. 2007b, 2008a,b, Bao et al. 2011, Sun et al. 2015). This core-shell catalyst can be extended to many simultaneous reaction systems as the capsule and inner core parts are independent catalysts for various reactions (He et al. 2006). Yang et al. (2007a) and He et al. (2006) prepared a core-capsule catalyst (Figure 3) containing Co/SiO₂ as the core and protonated ZSM-5 zeolite (H-ZSM-5) as the shell. These catalysts were used for direct synthesis of GRHs from syngas during FT reactions. The core catalyst, Co/SiO₂, was involved in the conventional production of long- and heavier-chain hydrocarbons, migrating to the capsule or shell catalyst, H-ZSM-5, for hydrocracking, oligomerisation and isomerisation reactions to depress the long- and heavier-chain and unwanted lighter hydrocarbons, and selectively produced

Figure 3: Schematic depiction of the reactions on zeolite (H-ZSM-5) encapsulated cobalt-based catalyst (Co/SiO₂) (He et al. 2006). Reproduced with permission from Wiley.

Table 7: Summary of properties of zeolites encapsulated cobalt-based catalysts.

Zeolite	Pore volume (cm ³ /g)	BET surface area (m ² /g)	Total pore diameter (nm)	Particle size (nm)	Si/Al ratio	Bronsted acidity at 350°C (μmol/g)	Lewis acidity at 350°C (μmol/g)	Reactor	Total catalyst weight (g)	H ₂ /CO	Process condition			Compared cobalt-based catalyst
											Pressure (MPa)	Temperature (K)	Space velocity ml/g cat/h	
HZSM-5 (Huang et al. 2011)	0.300	174.9	—	9.30	—	—	—	Fixed-bed	—	2.0	2.0	483–533	—	Co-ZrO ₂
H-ZSM-5 (Sartipi et al. 2013a,b)	0.180	319.0	—	13.00	193.0	—	—	Fixed-bed	0.197–0.556	1.0	1.0	533	25,800	Co/SiO ₂
Meso H-ZSM-5 (Xing et al. 2014)	0.310	408.0	—	—	—	—	—	—	—	2.0	1.0	533	—	Co/SBA-15
HZSM-5 (Liu et al. 2013)	—	—	—	13.5	46.7	—	—	—	—	2.0	1.0	533	—	Co/HZSM-5
HZSM-5 (Yang et al. 2008a,b)	0.529	275.3	—	11.0	—	—	—	Fixed-bed	—	2.0	1.0	533	—	Co/SiO ₂
HZSM-5 (Jin et al. 2013)	—	—	—	—	43.6	—	—	Fixed-bed	—	2.0	1.0	533	—	Co/SiO ₂

Table 8: Summary of effects of zeolites capsule in the zeolites encapsulated cobalt-based catalysts.

Zeolite	CO conversion (%)	CO ₂ selectivity (%)	C ₁ selectivity	C ₂ -C ₄ selectivity	C ₅ -C ₁₂ selectivity	Iso-C ₅ -C ₁₂ selectivity	C ₁₃ -C ₂₂ selectivity	C ₂₃ + selectivity	C ₅ -C ₁₂ O/P ratio	Effect(s) of zeolite(s) shell
HZSM-5 (Huang et al. 2011)	Decreased	–	Decreased	–	–	Increased	Decreased	Decreased	–	Increase in the selectivity of C ₅ -C ₁₁ isoparaffin production
H-ZSM-5 (Sartipi et al. 2013a,b)	Decreased	Decreased	Increased	Increased	Increased	Increased	Decreased	Decreased	–	Improved GRH synthesis
Meso H-ZSM-5 (Xing et al. 2014)	Decreased	Decreased	Increased	Decreased	Decreased	Increased	Decreased	Decreased	Increased	Increased the direct isoparaffin production of the FT process
HZSM-5 (Liu et al. 2013)	Increased	Decreased	Decreased	Decreased	Increased	Increased	Increased	Unchanged	Increased	Good increase in GRH production
HZSM-5 (Yang et al. 2008a,b)	Decreased	Decreased	Increased	–	–	Increased	–	–	Increased	Improved synthesis of middle isoparaffins used in gasoline blending
HZSM-5 (Jin et al. 2013)	Decreased	Decreased	Increased	–	–	Increased	–	–	Increased	Increased the production of isoparaffins and olefins

branched products of GRHs, including a noticeable slight increment in methane selectivity when compared with only the core catalyst, Co/SiO₂.

It can be drawn from Tables 7 and 8 that, in general, the CO conversion, C₁₃₊ and CO₂ selectivity reduced, while GRHs, O/P ratio and methane selectivity were raised. The increase in methane selectivity and decrease in CO conversion can be related to the closeness of the zeolite shell and the core (cobalt-based catalyst), which lowers the reducibility factor of the cobalt-zeolite catalyst and increases its strong cobalt-zeolite interactions. But the increase in C₁ selectivity and decrease in CO conversion were not the case in the recently synthesised catalysts by Javed et al. (2018). A ZSM-5-zeolite-supported cobalt-based microcapsule catalyst was encapsulated using silicate-1 zeolite. In this research, the support of the core catalyst and the shell were zeolites, and the encapsulated catalyst gave a high selectivity (74.7%) to GRHs. with a decrease in C₁ selectivity and an increase in CO conversion when compared with only the core catalyst, Co/ZSM-5.

One of the drawbacks of zeolite-cobalt multifunctional catalysts is the deactivation of the acidic sites of the zeolite catalysts by water produced during FTS (Yoneyama et al. 2008, Zhang et al. 2014). This challenge was addressed by Yoneyama et al. (2008) through the use of helium and supercritical butane reaction medium. This medium helped in removing the reaction heat and water from the catalyst bed and selectively produced medium-range branched hydrocarbon products.

3 Conclusion

Although many researchers have reported on the advantages of using cobalt-zeolite hybrid catalysts for the production of GRHs, C₅-C₁₂ isoparaffins and olefins, many technological challenges continue to present themselves. A limitation of the physical mixture type of the hybrid catalysts that researchers have reported is that some of the long-chain hydrocarbons produced from the conventional FT cobalt catalyst fail to reach the surface, channels and pores of the acidic zeolites, which is necessary for effective hydrocracking and isomerisation. These long-chain hydrocarbons are said to have random reactions within the zeolites and raise the possibility that some of them may leave the reaction sites without undergoing zeolite reactions. This can limit selectivity towards GRHs and hinder overall FT activity. However, we can assert that when zeolite is physically added to a cobalt-based catalyst, the methane and C₁₃₊ selectivity reduces, while the

short-chain hydrocarbons, including the isoparaffins, are raised. These phenomena can be explained by migration of the long- and heavier-chain hydrocarbons generated from cobalt-based catalysts to the acidic zeolite sites, creating channels for hydrocracking and isomerisation, including oligomerisation, of the methane molecules. It can also be noted that the CO_2 selectivity falls and O/P ratio rises when zeolite is physically mixed with a cobalt-based catalyst.

The size of the zeolite crystallites in zeolite-supported cobalt catalyst systems has been reported to affect the amount of coke formation during the FT reaction. Smaller zeolite crystallites produce short diffusion channels, and less contact time is advised for the zeolite reactions in order to avoid secondary or tertiary cracking of the long- and heavier-chain hydrocarbons, which in turn can lead to the production of lighter hydrocarbons.

Another problem in using zeolite-supported cobalt catalyst systems is the formation of strong cobalt-zeolite interactions, which hinder the dispersion, CO conversion and reducibility factors of the hybrid catalysts. This can lead to a drop in both overall FT activity and selectivity to desired GRHs. But the PEG additive method to support the cobalt in the hybrid catalyst systems for production of GRHs in FTS can be used to address the problem of reducibility. The PEG additive protocol can make it possible to deposit cobalt oxide particles on the outer surface of the zeolite supports. This method can provide a higher reducibility factor and CO conversion. In addition, the use of hierarchical zeolites as supports for cobalt-based catalysts can also help to address the problem of low CO conversion and cobalt dispersion.

There are indications that conventional supports such as silica, alumina, titania and carbon materials are more effective supports for core unpromoted and promoted cobalt catalysts than cobalt-zeolite hybridisations during the synthesis of GRHs in FTS. However, when zeolites are used as direct supports, without any coatings or physical mixtures (instead of the conventional supports), in most cases, the CO conversion and production of GRHs increase while the CO_2 and C_{13+} selectivity decrease. Other types of supports such as acidic ZSM-5 and HZSM-5 zeolites for secondary reactions produce more of the lighter hydrocarbons during FT processes. This leads to the deduction that when ZSM-5 or its protonated form, H-ZSM-5, supported cobalt-based catalyst directly, the C_1 selectivity can increase due to the strong cobalt-ZSM-5/HZSM-5 interaction and the lower reducibility factor. This was not the case when most of the other types of zeolites were used in some of the research reported.

Core-shell cobalt-zeolite hybrid catalyst configurations have been shown to produce better FT activity and selectivity towards GRHs due to the ease with which FT long- and heavier-chain products transport to the zeolite shell and channels, for cracking and branching. On the other hand, deactivation of the zeolite shell by water from the inside and the production of more methane remain unsolved problems for researchers using this hybrid catalyst type.

The encapsulation of cobalt-based catalysts with zeolites can produce more C_1 hydrocarbon and middle-range isoparaffins and olefins of GRHs and less CO conversion, C_{13+} and CO_2 selectivity. This can be explained by the closeness of the zeolite shell and the core (cobalt-based catalyst), which lowers the reducibility factor of the cobalt-zeolite catalyst and increases its strong cobalt-zeolite interactions.

Promotions of cobalt-based catalysts normally result in better CO conversion and overall FT activity. When an unimproved ZSM-5 support is used, the CO conversion of the catalysts decreases. The physical addition of zeolites to cobalt-based catalysts can result in a drop in methane and C_{13+} selectivity and an increase in the short chain hydrocarbons, including the isoparaffins and olefins of GRHs.

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