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Research Trends in Fischer–Tropsch Catalysis for Coal to Liquids Technology

Abstract Fischer–Tropsch Synthesis (FTS) constitutes catalytic technology that converts synthesis gas to synthetic liquid fuels and chemicals. While synthesis gas can be obtained from any carbonaceous feedstock, current industrial FTS operations are almost exclusively based on natural gas. Due to the energy structure of China where cheap coal is abundant, coal to liquids (CTL) technology involving coal gasification, FTS and syncrude upgrading is increasingly being considered as a viable option to convert coal to clean transportation fuels. In this brief paper, we review some pertinent issues about Fe- and Co-based FTS catalysts. Fe is better suited to convert synthesis gas derived from coal gasification into fuels. The authors limit themselves to noting some important trends in the research on Fe-based catalysts. They focus on the preparation of phase-pure carbides and innovative cheap synthesis methods for obtaining active and stable catalysts. These approaches should be augmented by (1) computational investigations that are increasingly able to predict not only mechanism, reaction rates and selectivity but also optimum catalyst composition, as well as (2) characterization of the catalytic materials under conditions close to the operation in real reactors.

Keywords: Fischer–Tropsch, FTS, CTL, Fe catalyst, iron carbide, computational modeling

Manuscript received July 10, 2016; accepted November 12, 2016

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1 Introduction

Coal oil and coal gas were important fuel sources for heating and lighting in the last two centuries. Coal became less important with the start of the oil era and the widespread availability of natural gas. One of the major incentives for this transition was the decrease of the pollution by coal combustion. Coal remains one of the cheapest fossil resources and it is abundantly available in many places in the world. Accordingly, there is widespread attention to develop cleaner technologies to convert solid coal into liquids or gases for use as fuels and chemicals. Transportation of solids is less efficient than liquids or gases and the conversion process will usually remove most of the impurities from coal, e.g., sulfur, which pose environmental threats (Martin, Larsen, & Wende, 1982).

China has substantially invested in coal-to-olefins (CTO) plants in the last decade. The CTO process involves the conversion of coal to synthesis gas (a mixture of CO and H₂, usually referred to as synthesis gas). The synthesis gas is then converted to methanol. Methanol is finally converted to ethylene and propylene, which are the chemical building blocks for polymers. The latter process is known as methanol-to-olefins (MTO) and remains at the center of the attention of academic and industrial research, as it is one of the few examples of successful commercialization of a catalytic process in the last decades. The main economic incentive for the CTO/MTO technology is to decrease the dependence on oil imports to satisfy the need for building blocks for the chemical industry, yet economic development of rural regions in China may also be put forward as an argument for the large investments made.

Another development is the conversion of coal to liquid fuels. The demand for fuels is much greater than the demand for chemicals. A way to decrease China's dependence on oil import for transportation fuel production is to convert coal, gas or biomass to transportation fuels in what is referred to as XTL, that is anything that contains carbon (natural gas, coal, biomass) to liquids (*Figure 1*). Another option would be coal hydrogenation, which will not be further discussed here. Considering that coal is

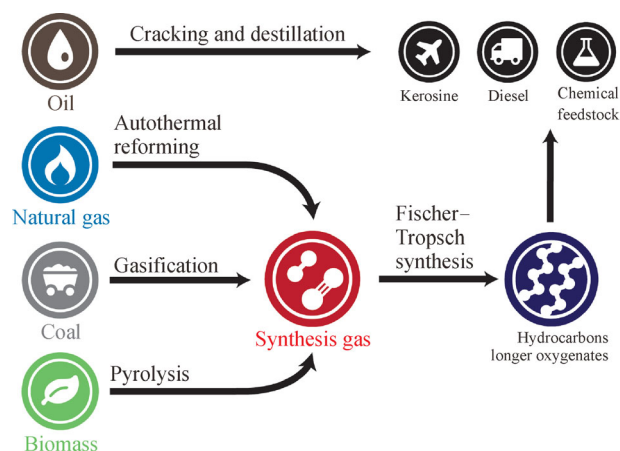


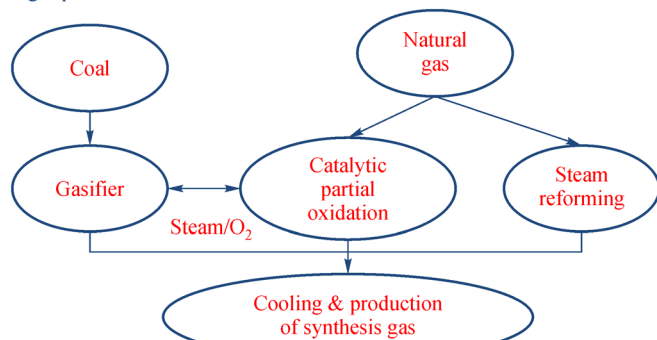
Figure 1. Main conversion pathways from fossil and renewable feedstock to transportation fuels and chemical intermediates, highlighting the direct route from crude oil and the indirect route from other carbonaceous resources involving synthesis gas as a platform. Fischer-Tropsch synthesis is an essential technology to convert synthesis gas to clean transportation fuels (used with permission of Dr. Ivo Filot, Eindhoven University of Technology).

to syncrude—a mixture of hydrocarbons which is usually rich in heavy paraffin's, and syncrude upgrading to liquid fuels and other products. Compared with synthesis gas manufacture from natural gas, CAPEX and OPEX for coal gasification are much higher. One important issue is water consumption, which poses also environmental concern. The conversion of synthesis gas to syncrude is known as Fischer Tropsch synthesis (FTS) (Mousavi, Zamaniyan, Irani, & Rashidzadeh, 2015). In the FTS process, synthesis gas is converted into long-chain hydrocarbons. Research into this subject has been intensified over the last decade as the conversion into liquid energy carriers adds value to cheap natural gas resources in particular settings (Santos et al., 2015). Besides conversion of the carbonaceous feedstock to synthesis gas and synthesis gas conversion itself, syncrude processing is also important to optimize the yield of valuable transportation fuels (Dry, 2004; Dalai & Davis, 2008; Fahim, Alsahhaf, & Elkilani, 2010; Jahangiri, Bennett, Mahjoubi, Wilson, & Gu, 2014) (Figure 2).

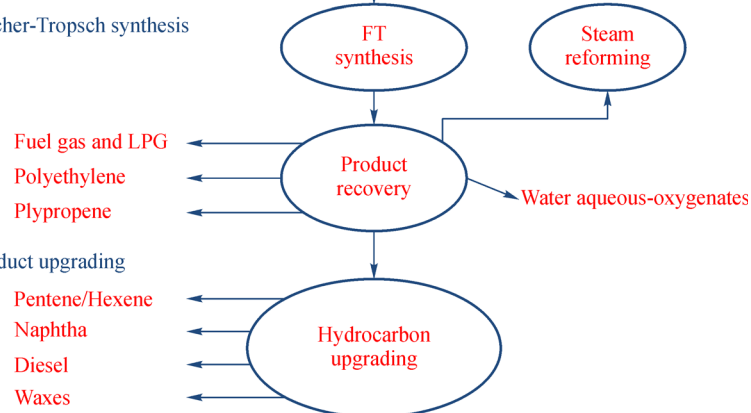
Further advantages of Fischer-Tropsch fuels are the low sulfur content and the lower propensity of transportation fuels to yield NO_x and soot emissions during combustion, which pose environmental and health threats (Davis & Occelli, 2016). As a result of these economic and environmental drivers, Fischer-Tropsch technology has

abundantly available in China and at low cost, coal-to-liquids (CTL) is a logical next step after CTO. It entails coal gasification to obtain synthesis gas which is converted

1. Synthesis gas production



2. Fischer-Tropsch synthesis



3. Product upgrading

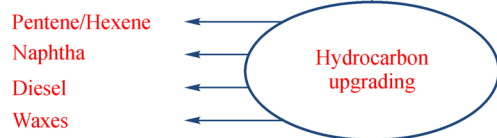


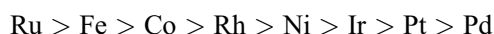
Figure 2. Three basic steps of CTL technology (Jahangiri, Bennett, Mahjoubi, Wilson, & Gua, 2014).

gained increasing academic and industrial interest over the last few decades (Calderone, Shiju, Ferre, & Rothenberg, 2011; Kang et al., 2011; Khodakov, Chu, & Fongarland, 2007; Liu, Ersen, Meny, Luck & Pham-Huu, 2014; Saib et al., 2010; Rytter & Holmen, 2015; de Smit & Weckhuysen, 2008; Tsakoumis, Ronning, Borg, Rytter, & Holmen, 2010; Zhang, Kang, & Wang, 2010). Although the impact of the Fischer–Tropsch synthesis technology on fulfilling global energy demand remains small at this moment, considerable efforts are made around the globe to develop this technology from different feedstock in various socio-economic settings (Liu, Ersen, Meny, Luck, & Pham-Huu, 2014).

China is at the center of the coal world. It is not only responsible for 80% of the rise in coal use since 2000 and now responsible for half of the global use of coal but also the world's top coal producer and- until recently- the largest coal importer. As shown in *Figure 3*, there is also strong growth in coal use in other rapidly developing economies such as India and South-east Asia, which compensate for the decline of coal use in the Western world. The Chinese National Energy Strategy and Policy 2020 refers to the reality that it will be difficult to change the country's coal based energy consumption structure in the short-term. Most of this consumption is based on combustion of raw coal. Therefore, it is important to find cleaner ways to convert coal into liquid fuels in which CTL processes may play an increasingly important role.

2 Fischer–Tropsch catalysts

Catalysts are at the heart of the Fischer–Tropsch synthesis technology. The dependence of FTS activity on the transition metal choice has been widely studied and continues to be of interest. Vannice (1975) found that the average molecular weight of produced hydrocarbons decreased in the order



Usually, Ru, Fe, Co, Rh, and Ni can be considered as FTS-active metals. Pd, Pt, and Ir are mainly selective for methanol and also produce methane, while Rh exhibits a reasonable selectivity to C₂-oxygenates (Brady & Pettit, 1980; Mousavi, Zamaniyan, Irani, & Rashidzadeh et al., 2015). Ru is one of the most active catalysts for FTS operating at low reaction temperature producing long chain hydrocarbons without the need for any promoters. However, this metal is too expensive for the production of liquid fuels and is therefore not considered a sustainable option for use in industrial processes. Ni is not useful as its methane selectivity is too high (Biloen & Sachtler, 1981; Mousavi, Zamaniyan, Irani, & Rashidzadeh et al., 2015). In brief, Co and Fe are deemed to be the best metals for application in industrial scale FTS processes (Jahangiri, Bennett, Mahjoubi, Wilson, & Gu, 2014; Khodakov, Chu, & Fongarland, 2007), as shown in *Figure 4*.

To make a more informed selection between Fe and Co, one needs to take into account the nature of the carbon feed stock (Khodakov, Chu, & Fongarland, 2007). Co is especially suitable for gas-to-liquid (GTL) plants that make use of the high H₂/CO ratio obtained from reforming or gasification of natural gas into synthesis gas as it obviates the need for shifting CO with steam to yield more hydrogen (and CO₂) for the FT reaction step. Although Co is more expensive than Fe, its lower water-gas shift (WGS) activity is important. Co is also more active than Fe, produces a simpler product slate of mainly paraffins and some α -olefins. It requires however the use of precious metal promoters and advanced catalyst preparation technology, making Co catalysts more expensive than Fe catalysts. Co catalysts typically lose about half their activity within a few months. Assuming an economically acceptable catalyst lifetime of 2–3 years, this means that catalyst cost will add several USD to the price per bbl of produced synthetic crude (Brady & Pettit, 1980). On the other hand, Fe-based catalysts exhibit higher selectivity to olefins and C₅₊ hydrocarbons, they produce less methane and are more tolerant to sulfur compounds. Moreover, Fe-based catalysts can be operated in a broader temperature

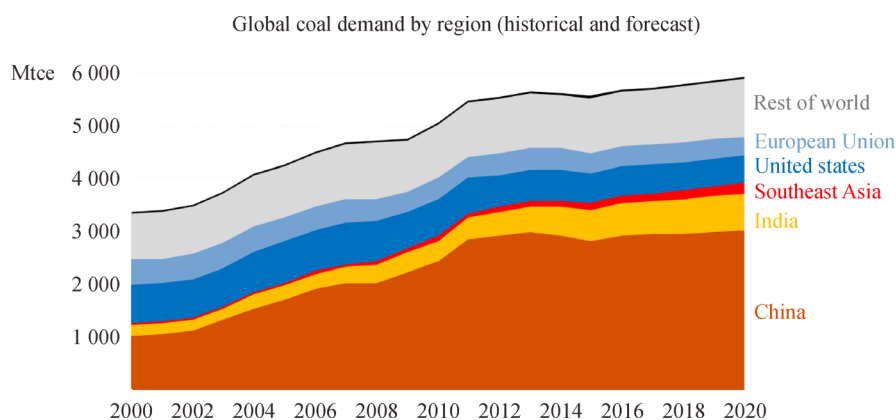


Figure 3. Global coal demand by region (historical and forecast) from IEA, 2015.

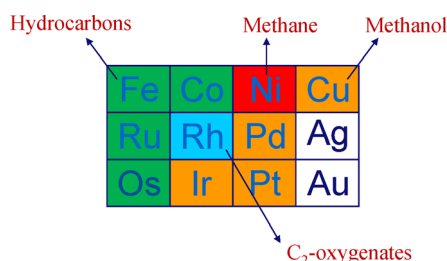


Figure 4. Selectivity of transition metals in syngas conversion (colors refer to main reaction products; green: long-chain hydrocarbons; red: methane; blue: methane and ethanol; orange: methanol; white: no activity in syngas conversion).

and H_2/CO ratios range (including low H_2/CO ratios), which is especially important to synthesis gas derived from coal gasification. Here, the high WGS activity under typical FTS conditions of Fe-based catalysts is useful as in this way the H_2/CO molar can be increased in the FTS reactor. This also holds for high temperature FTS which delivers a product slate of short-chain (unsaturated) hydrocarbons and short-chain oxygenates, which are important chemical building blocks (Santos et al., 2015). Based on the above, it is clear that Fe is the more suitable catalyst for CTL processes.

3 Research on Fe-based catalysts

3.1 Conventional research

Iron-based FTS catalyst formulations are usually based on large amounts of Fe with alumina and silica as structural promoters to increase stability and mechanical properties (Cheon et al., 2010; Jin & Datye, 2000; Li, S., Krishnamoorthy, Li, A., Meitzner, & Iglesia, 2002). Other promoters are used to enhance the reducibility of iron species, to increase chain growth probability, to increase the content of catalytically active phases such as iron carbide and to improve catalyst stability during FTS reaction (Cheon et al., 2010). Cu, Zn, Mn and K are the most used promoters in this class. Typical compounds in

Fe-based FTS catalysts, their content and their function are summarized in Table 1.

Early research on alkali or alkaline earth metal promoters presented that the promoter effect on FT activity was correlated to the alkaline of the alkali metal. Dry and coworkers found that alkaline promoter addition to Fe led to increased activity in the order $K > Na > Ca > Li > Ba$ (Dry & Oosthuizen, 1968). A more recent study by Davis and coworkers (Ngantsoue-Hoc, Zhang, O'Brien, Luo, & Davis, 2002) showed that the FT reaction stability is also related with alkali promoters. Catalysts promoted with K, Na, Li display more stable performance compared with Rb and Cs promoters. K, Rb and Cs promoted samples exhibit the lowest CH_4 selectivity.

Iglesias and coworkers showed that optimum FTS rate without affecting chain-growth probability can be obtained at intermediate Zn/Fe ratios in the Fe-Zn-Cu-K system. Cu increases the rate of Fe_2O_3 reduction to Fe_3O_4 in H_2 , while K promotes the activation of CO and the rate of carburization of Fe_3O_4 . The combined result is that Cu and K increase the overall FTS rates of catalysts from Fe-Zn oxide precursors (Li, S., Li, A., Krishnamoorthy, & Iglesia, 2001).

The Goodwin group (Lohitharn, Goodwin, & Lotero, 2008) focused on adding third transition metal (Cr, Mo, Mn, Ta, V, Zr, W) to Fe Cu-based FTS catalysts. The addition of Cr, Mo, Mn, Ta, V and Zr enhanced catalyst activity for both CO hydrogenation and the WGS reaction, while W suppressed performance. One dominant effect of these promoters appears to be on the dispersion of the Fe phase. Among these promoters, Cr, Mn and Zr showed the highest promoter effect. The selectivity for hydrocarbons and the chain growth probability (α) were not significantly affected (Lohitharn, Goodwin, & Lotero, 2008).

A study by Tao et al. (2007) showed that Mn promoter can decrease the formation of methane and increase the selectivity to light olefins, yet the C_{5+} selectivity was not increased. Another study by Yang, Xiang, Xu, Bai, and Li (2004) concerns the promoting effect of K on Fe-Mn catalysts. When K addition is in the range 0–3.0 wt%, it increases the crystallite size of the catalyst and decreases the reduction degree. The catalyst reaches the highest

Table 1

Typical Composition of Fe-based FTS Catalysts

Component	Relative content	Function
Fe (Fe^{3+}/Fe^{2+})	100	Active metal
$SiO_2/Al_2O_3/TiO_2/ZrO_2$	5–30	Improve anti-abrasion
Cu	1–6	Improve reduction
K	1–6	Improve activity, α -value
Mn/Zn/Cr/La/Ti/Zr/V/Ce/Mg/Ca	0.05–40	Adjust dispersion, improve activity
Alkaline earth metal	1–6	Improve activity, α -value
Alkaline metal (except K)	1–6	Improve activity, α -value
Co/Ru	1–10	Improve activity, increase light olefin selectivity with K promoters

activities (FTS and WGS) for 0.7 wt% K and limits methane and oxygenates formation leading to enhanced selectivity to light olefins.

Gallegos et al. (1996) studied addition of Mg to SiO_2 as a support to Fe catalyst with the aim to improve the olefins selectivity. Mg addition increased the total hydrocarbon productivity. An optimal amount of MgO around 4% is suggested to result in the highest selectivity to olefins and lower the CH_4 yield.

Bedela, Rogera, Rehspringerb, Zimmermann, and Kiennemann (2005) focused on La as a promoter and prepared $\text{La}_{(1-y)}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ materials by thermal decomposition of mixed La-Co-Fe propionates. The activity is related to the La amount and for $y=0.4$ the catalyst shows high $\text{C}_2\text{--C}_4$ olefins selectivity.

The use of noble metal promoters was also studied. Coville's (Bahome et al., 2007) work dealt with Fe-Ru bimetallic catalysts supported on carbon nanotubes. Small Fe-Ru particles (<4 nm) were dispersed on carbon and were found to be stable against sintering during the FTS reaction. A Fe-Ru-K catalyst shows high C_2 olefin yield up to 47% and low methane selectivity.

Marvast's group (Nakhaei Pour et al., 2008) modified precipitated Fe/Cu/ SiO_2 catalyst with Ca, Mg or La promoters and showed that the addition of these promoters enhances the catalysts surface in the order $\text{Ca} > \text{Mg} > \text{La} > \text{unpromoted}$, and enhanced the reduction and carburization in CO, while decreasing catalyst reducibility by H_2 . The promoters also increase carbon deposition on the catalyst during the FTS reaction, and thus accelerate deactivation rates. It is also claimed that FTS and WGS activities are increased together with olefins, while the methane selectivity decrease.

Despite the many insights gained from such studies, more detailed investigations are desired to understand the underlying principles that govern activity, selectivity and stability of FTS catalysts. Major efforts are needed to derive catalyst design rules, which are in essence structure-performance relations.

3.2 Active phase and performance investigations

To understand in detail the relation between structure and catalytic performance of Fe-based FTS catalysis, it is essential to resolve the active phase structure. When iron is used as a catalyst, several forms of iron oxide and iron carbides (FeC_x) may be simultaneously present during the FTS reaction. These forms include magnetite and various iron carbides such as $\epsilon\text{-Fe}_2\text{C}$, $\epsilon'\text{-Fe}_{2.2}\text{C}$, $\chi\text{-Fe}_5\text{C}_2$, $\theta\text{-Fe}_3\text{C}$ and Fe_7C_3 . It is essential to determine the active phase composition under operating conditions and also to follow phase changes during the lifetime of the catalyst. Such insights guide the design of better or step-out catalysts.

An exemplary work in this respect is from the groups of de Smit et al. (2010) who used a combination of in situ XRD and quantum-chemical density-functional theory

studies to predict the stability of different carbides under operating conditions (Figure 5). The latter is in essence a thermodynamic stability analysis which allows identifying the most likely present phases and surface terminations. This allows predicting the introversion of Fe phases under different conditions. In situ XRD shows that a catalyst pretreated in 1% CO/H_2 at 350°C will contain $\theta\text{-Fe}_3\text{C}$, $\chi\text{-Fe}_5\text{C}_2$ as well as amorphous Fe_xC . This catalyst is much more susceptible to the buildup of surface graphitic carbonaceous deposits during FTS. The lower porosity of the catalyst, induced by the carburization at higher temperatures ($\sim 350^\circ\text{C}$), leads to a lower susceptibility to oxidation, while the more metallic nature of the $\theta\text{-Fe}_3\text{C}$ and Fe_xC phases is likely to contribute to formation of deactivating carbonaceous surface adsorbents. A slow transformation of $\theta\text{-Fe}_3\text{C}$ to $\chi\text{-Fe}_5\text{C}_2$ was observed under high pressure FTS conditions. A generic result is that simple descriptors can be used to predict stable phases of the catalyst (Table 2). Nevertheless, experiment shows the limitations of this computational approach as amorphous, low crystalline Fe-carbides may play a more significant role in Fe-based FTS than considered hitherto.

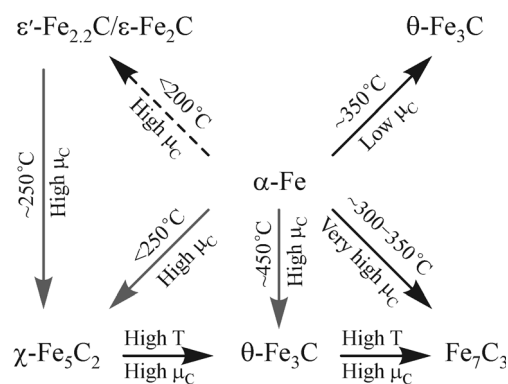


Figure 5. Qualitative interpretation of the ab initio atomistic thermodynamics study of the iron carbide structures (de Smit et al., 2010).

There is also considerable scope for novel synthetic approaches. While preparation of Fe-based FTS catalyst is cheap, it is still difficult to make highly dispersed systems in this way. Gascon and coworkers used a MOF-mediated synthesis (MOF = metal organic frameworks) strategy to prepare highly dispersed Fe nano-particles on a porous carbon matrix. Compared with reference samples, the performance of such catalyst was very good as was its stability. The approach to prepare such samples is simple as a Fe (BTC) (BTC = 1,3,5-benzenetricarboxylate) MOF is obtained under very mild conditions, followed by direct pyrolysis with furfural being used as a way to adjust the Fe/C ratio (Santos et al., 2015). The resulting systems are very active and remarkably stable (Table 3).

In other works (Yang, Zhao, Hou & Ma, 2012) it has been shown that pure metal carbide phase could be

Table 2*Overview of the Physicochemical and Catalytic Properties of the Catalyst Materials before and after 6 h FTS at 10 bar, 250°C (de Smit et al., 2010)*

Catalyst pretreatment		XAFS ^a (mol %)	XRD ^b (vol %, crystallite size)	Raman	Fischer–Tropsch performance
High μ_C	Before FTS	χ -Fe ₅ C ₂ (76%), Fe _x C (24%)	χ -Fe ₅ C ₂ (90%, 16 nm) ϵ -carbides (10%, 20 nm)	Some graphitic C	
	After FTS	χ -Fe ₅ C ₂ (74%), Fe _x C (12%) Fe ₃ O ₄ (14%)	χ -Fe ₅ C ₂ (57%, 15 nm) ϵ -carbides (5%, 24 nm) Fe ₃ O ₄ (38%, 15 nm)	No significant increase of graphitic C	Conversion relatively high and increasing with time-on-stream, C ₄₊ selectivity high, WGS active
Low μ_C	Before FTS	χ -Fe ₅ C ₂ + θ -Fe ₃ C (51%), Fe _x C (49%)	χ -Fe ₅ C ₂ (56%, 18 nm) θ -Fe ₃ C (44%, 15 nm)	Some graphitic C	
	After FTS	χ -Fe ₅ C ₂ (76%) + θ -Fe ₃ C (50%), Fe _x C (50%)	χ -Fe ₅ C ₂ (61%, 11 nm) θ -Fe ₃ C (39%, 13 nm)	Incremental formation of graphitic C	Conversion relatively low, C ₄₊ Selectivity, decreasing with time-on-stream, pCO ₂ low

Note: ^a Errors: ± 5 mol %; ^b Errors: ± 5 vol %, crystallite sizes $\pm 10\%$.**Table 3***Productivities of Promoted Fe@C and Commercial Catalysts*

Catalyst	FTY* (mol/gFe/s)	Catalyst productivity (L/kg/s)	Reference
0.6K38-Fe@C	4.38×10^{-4}	6.9 ^a	This work
Ruhrchemie	4.90×10^{-6}	0.1 ^a	38
Fused HTFT (slurry reactor) ^b	–	0.7 ^c	39
Fused HTFT (fluidized reactor) ^b	–	0.2 ^c	39

Note: *HTFT, High Temperature Fischer–Tropsch; Iron time yield (FTY) = mol of CO converted to hydrocarbons (excluding CO₂) per time (s) per weight of iron (g).
^aVolume of CO converted per time per mass of catalyst (L/kg/s). In this calculation, we assume that the fused HTFT is only composed by iron, and therefore represents the maximum productivity that can be achieved with this material. ^bTemperature range (320–330°C). ^cVolume of syngas converted per time per mass of catalyst (L/kg/s).

obtained which is very instructive to understand their performance. The group of Ma at Peking University obtained phase-pure Fe₅C₂, for which a wet chemical route was used. Bromide plays a key role in inducing the conversion of Fe(CO)₅ to Fe₅C₂ (Figure 6). The as-synthesized Fe₅C₂ nanoparticles were applied in the Fischer–Tropsch synthesis (FTS) and exhibited intrinsic catalytic activity in FTS, demonstrating that Fe₅C₂ is an active phase for FTS. It provides a facile method for the synthesis of iron carbide NPs but also proposes a new approach for obtaining a better understanding of the FTS mechanism. It has also been found that the activity of these highly active particles decreased with time on stream and characterization showed that surface oxidation could be one of the reasons for it.

Similarly, the group of Zong (Xu et al., 2014) succeeded in preparing ϵ -Fe₂C by carburization of rapidly quenched skeletal iron (RQ Fe) during LTFTS. The structural peculiarities of such RQ Fe (low coordination number, nanoscale and expanded lattice) are essential to overcome the barriers to carburize metallic Fe to ϵ -Fe₂C at low enough temperatures where the ϵ -Fe₂C phase is stable. Interestingly, the ϵ -Fe₂C catalyst also shows high activity compared to a common Fe–Cu–K–Si catalyst (43 to 4.6, Table 4). Furthermore, the selectivity and the stability also show high performances.

3.3 Computational modeling

Theoretical modeling is increasingly able to explain not only the stability of active phases under reaction conditions but also to predict on the basis of mechanism the way molecules are converted from reactants to products. Instrumental in this respect are ab initio density functional theory calculations that are sufficiently developed to model with an accuracy of ca. 10 kJ/mol stability of surfaces, adsorbents configurations and transition state of the elementary reaction steps occurring at the surface. How the rate constants of the elementary reaction steps together with the composition of the adsorbed layer lead to macroscopic rates and selectivities can be appreciated by carrying out micro kinetics simulations (Filot, van Santen, & Hensen, 2014; van Santen, Ciobîcă, Steen & Ghouri, 2011; van Santen, Markvoort, Filot, Ghouri, & Hensen, 2013). An appealing example is found in the work of the group of Hensen, who studied the complete FTS reaction mechanism on terrace and stepped Ru surface including CO dissociation, C hydrogenation, coupling reactions as well as O removal. An example of the reaction network under FTS conditions is shown in Figure 7. These simulations show that steps are needed for sufficiently fast generation of growth monomers by CO bond dissociation, water is the main product next to hydro-

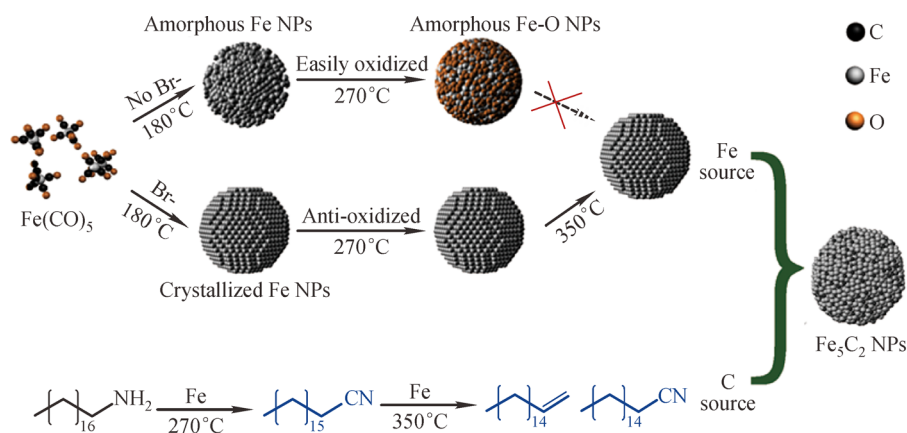


Figure 6. Schematic Illustration of the Formation Mechanism of $\text{Fe}_5\text{C}_2\text{NPs}$ (Yang, Zhao, Hou & Ma, 2012).

Table 4

Catalytic Activities in LTFTS

Entry	Catalyst	d^a (nm)	T (K)	r_0 (mol _{CO} mol _M /h) ^b
1	RQ Fe	8.2	423	16
2	RQ Fe	8.1	443	43
3	RQ Fe	8.3	473	71
4	Crystalline Fe NPs	33.2	443	3.7
5	Fe-Cu-K-Si	8.6	443	4.6
6	RQ Fe- λ	8.3	443	10
7	RQ Co	7.3	443	9.8
8	Co-B	9.5	443	7.8

Note: ^aOther reaction conditions: $P = 30$ bar at RT, $\text{H}_2/\text{CO}/\text{N}_2 = 64/32/4$, 4.48 mmol Fe or Co, 20 ml PEG200 and stirring rate of 800 r.p.m. ^aParticle size, is determined by TEM for the amorphous Co–B catalyst and by XRD for other iron- and cobalt-based catalysts. ^bInitial activity, expressed as numbers of moles of converted CO per mole of iron or cobalt per hour, is determined from the initial reaction rate by extrapolating the slope of the CO conversion–time curves to zero reaction time; M = Fe or Co.

carbons and coupling of CH with CR (R = alkyl) is the dominant growth mechanism. By making use of scaling laws based on Brønsted-Evans-Polanyi relations, optimum composition for the highest catalytic performance was determined. They exemplify how the rates and selectivities depend on the metal-C and metal-O bond strengths as the main reactivity descriptors (Filot, Shetty, Hensen, & van Santen, 2011).

An important conclusion from these considerations, shown in Figure 8, is that typical FT catalysts such as Fe, Co and Ru operate below the optimum with respect to the metal-carbon and –oxygen bond energies (Filot, van Santen, & Hensen, 2014). Figure 8 is a volcano curve, which is the direct consequence of the Sabatier principle. In essence, three rate-controlling regimes are distinguished, i.e., where CO dissociation, chain-growth and water removal are controlling the overall rate. While Ru binds O relatively strongly so that O removal as water is rate-controlling, it is found that for Co both O removal and CO dissociation are relatively slow under reaction conditions. Fe as a metal binds C too strongly so that chain growth will be limited. A prediction is then that conversion of Fe metal

to Fe carbide will move it toward the top of the volcano-curve, as the average Fe-C bond strength will be lower for the carbide surfaces. In line with experimental observations, carburizing Co would lead to lowered activity and chain-growth probability. Obviously, these considerations help to understand what limits the current generation of catalysts and makes possible suggestions to improve catalysts. The volcano behavior in Figure 8 suggests that alloying can help to decrease the metal-oxygen bond energy.

4 Summary and outlook

This brief note demonstrates the importance of coal conversion into liquid fuels for China. Just like CTO technology offers a convenient way to obtain building blocks from coal for the chemical industry, CTL offers a way of producing liquid fuels from coal. The specific socio-economic setting of China may be one of the drivers to develop such technology. Coal is expected to stay the backbone of the energy structure in China for years to

choice for CTL operations, because Fe catalysts

(1) can be operated in wider range of temperatures and H_2/CO ratios, which is especially important to the low H_2/CO ratio of the synthesis gas derived from coal gasification,

(2) are more tolerant to sulfur compounds in the synthesis gas,

(3) display higher selectivity to olefins and C_{5+} hydrocarbons at lower CH_4 selectivity, and

(4) can be used to produce short-chain (unsaturated) hydrocarbons and short-chain oxygenates at elevated temperature (HTFTS).

A large number of papers deal with Fe-based FTS catalysts which provide a solid basis for more detailed investigations which should aim to understand the molecular-level detail of the operation of these catalysts. A challenge in this respect is the complexity of the catalyst composition under reaction conditions. Typically, different promoters are used and Fe can be present in various oxide and carbide phases. A strategy to move forward is to better understand catalyst activation and evolution under reaction conditions for which operands/in situ studies are essential. In this way, it may be possible to better understand the way the catalysts deactivate over time. Special synthesis approaches are important as they allow access to phase-pure carbides whose properties need to be understood. Theory can aid here by showing how the performance depends on the carbide composition, surface termination and promoters. Innovative synthesis approaches have already shown how to prepare much more active catalysts.

Nomenclature

ASF: Anderson–Schulz–Flory

CTO: Coal to olefins

CTL: Coal to liquid

DFT: Density functional theory

FTS: Fischer–Tropsch synthesis

GHSV: Gas hourly space velocity

GTL: Gas to liquid

HTFT: High temperature Fischer–Tropsch

LTFT: Low temperature Fischer–Tropsch

MOF: metal organic framework

MTO: Methanol to Olefins

NPs: Nanoparticles

RQ Fe: rapidly quenched skeletal iron

TOF: Turn over frequency

TON: Turn over number

TOS: Time on stream

WGS: Water gas shift

α : Chain growth probability

Acknowledgements The authors acknowledge with thanks, the permission of Dr. Ivo Pilot, Eindhoven University of Technology for offering *Figure 1*.

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