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Sartipi, Gascon *et al.*

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Breaking the Fischer–Tropsch synthesis selectivity: direct conversion of syngas to gasoline over hierarchical Co/H-ZSM-5 catalysts†

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Sina Sartipi,* Kshitij Parashar, Michiel Makkee, Jorge Gascon* and Freek Kapteijn

We report the combination of Fischer–Tropsch catalyst with acid functionality in one single catalyst particle. The resulting bifunctional catalyst is capable of producing gasoline range hydrocarbons from synthesis gas in one catalytic step with outstanding activities and selectivities.

The Fischer–Tropsch synthesis (FTS) is a key step in the transformation of various non-petroleum carbon resources such as natural gas, coal, and biomass into clean hydrocarbon fuels as well as valuable chemicals. Since the FTS product spectrum is believed to follow the Anderson–Schulz–Flory (ASF) distribution, it is theoretically impossible to selectively synthesize hydrocarbon fractions in the diesel and/or gasoline ranges.¹ Therefore, the state of the art Gas-to-Liquid (GTL) processes are based on FTS followed by downstream conversion units (predominantly hydrocrackers in the case of Co-based FTS).² This layout is economically feasible once it is applied at large scale, but is less suitable for the production of liquid fuels from remotely dispersed syngas resources such as biomass and offshore flare gas.³

Recently, the combination of zeolites with FT catalysts in one reaction step has gained a great deal of attention as a tool for intensifying the GTL process. This approach aims to minimize the demands on the refining units, especially hydrocrackers, by maximizing the production of desired liquid fractions in FTS reactors. The use of acidic zeolites as FTS catalyst supports and/or as co-catalysts deviates from the ASF limitation, yielding products mainly in the gasoline range with high selectivities to isoparaffins.⁴ In these catalytic systems, the primary hydrocarbons, formed on the FTS active sites, migrate to the micropores of the zeolite where (hydro)cracking and isomerization occur. Nevertheless, the low external/mesopore surface area of zeolites, their poor mass transport properties

and the fast deposition of coke⁵ cause a number of limitations which are addressed in this contribution.

Along with the development of efficient methods to alleviate diffusion limitations in zeolites,⁶ the first examples of mesoporous zeolites as FT supports have been published very recently. Co supported on a slightly mesoporous zeolite Beta is reported to give a better FTS catalytic performance in terms of CO conversion with lower methane and higher C6+ selectivities. However, the improvement was insignificant in comparison with the unmodified Beta sample.⁷ A comprehensive study on 3 wt% Ru supported on desilicated ZSM-5 and Beta zeolites revealed that the activity for hydrocarbon reactions of FTS products correlates with the extent of support mesoporosity as well as with its acid strength.⁸ In spite of the promising results, it is fair to admit that Ru is not the preferred metal of choice for large scale applications due to volatile Ru-carbonyl formation under reaction conditions.⁹

In this contribution, the performance of Co-based FT catalysts supported on hierarchical H-ZSM-5 is presented. The performance of the new bifunctional catalyst is compared with Co supported on SiO₂ as a conventional FT catalyst. To create mesoporosity in the parent ZSM-5 (Zeolyst, CBV 8014; nominal Si/Al = 40), two different desilication procedures were followed: mesoH-ZSM-5(a) was obtained *via* alkaline treatment with a 1 M NaOH solution, while in the case of the mesoH-ZSM-5(o) sample, the organic base TPAOH was used as a desilicating agent (see ESI† for further details). The textural properties of these supports are presented in Table 1. Under similar treatment conditions, NaOH results in a more severe desilication than TPAOH, creating mesostructures with pore sizes and volumes very similar to the amorphous SiO₂ reference support. This difference is visible in the textural properties (Table 1) as well as in the TEM images of the corresponding catalysts (*cf.* Fig. S5e and f, ESI†). In line with previous observations,¹⁰ a more controlled desilication with TPAOH gives rise to more mesoporosity with pores in the range of 4–8 nm. MesoH-ZSM-5(o) shows a clear type IV hysteresis upon N₂ adsorption at 77 K (see Fig. S2, ESI†), suggesting a higher degree of hierarchy with large cavities communicated with smaller mesopores.

Catalysis Engineering, Dept. Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. E-mail: S.Sartipi@tudelft.nl, J.Gascon@tudelft.nl

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Table 1 Textural properties of supports, obtained from N₂ physisorption at 77 K

Support	$S_{\text{meso}}^a/\text{m}^2 \text{ g}^{-1}$	$V_{\text{meso}}^b/\text{cm}^3 \text{ g}^{-1}$	$d_{\text{meso}}^c/\text{nm}$
SiO ₂	248	1.34	23–32
H-ZSM-5	52	0.08	nd ^d
MesoH-ZSM-5(a)	309	1.08	15–32
MesoH-ZSM-5(o)	414	0.52	4–8

^a Mesopore surface area obtained from *t*-plot. ^b Mesopore volume. ^c Mesopore diameter, derived from the adsorption branch employing the BJH method. ^d Not determined.

Temperature programmed NH₃ desorption profiles (Fig. S3, ESI†) show a maximum at around 700 K for both parent and mesoH-ZSM-5(a) supports which is characteristic of strong Brønsted acidity in H-ZSM-5.⁸ Moreover, a shoulder appears at around 550 K for mesoH-ZSM-5(a), corresponding to weaker acid sites which are predominantly present in the mesoH-ZSM-5(o).

All four supports mentioned in Table 1 were loaded with ca. 10 wt% Co *via* incipient wetness impregnation. FTS experiments were performed in a parallel six-flow unit (described in the ESI†) at 513 and 493 K, 15 bar and H₂/CO = 2 feed. CO conversion as well as carbon selectivity of different products on the catalysts (at 513 K) are compared in Fig. 1.

Fig. 1a shows that Co/SiO₂ and Co/H-ZSM-5 display similar CO conversion levels after 20 h; however, once mesoporosity is created in the zeolite support, the conversion increases considerably (by ca. 13 and 28% in the case of Co/mesoH-ZSM-5(a) and -(o), respectively) under similar process conditions. Time-on-stream evolution of CO conversion reveals that Co/H-ZSM-5 deactivates faster as compared with the mesoporous zeolite supported catalysts (Fig. 1a). TGA analysis of the spent catalysts gives comparable weight losses and patterns for the zeolite supported samples upon heat treatment in air (Fig. S6, ESI†). This result points to the formation of similar amounts and type of carbon residues on the spent zeolite containing catalysts, indicating that coke deposition cannot explain their different catalytic activities. In general, microporous zeolites are devoid of mesopore surface area, essential for an optimal dispersion of Co particles at high metal loadings. On the other hand, formation of metal clusters in the micropores is undesired, as Co particles smaller than 6 nm are not optimal for FTS in terms of activity and selectivity.¹¹ Therefore, the first advantage of introducing hierarchy in H-ZSM-5, for the current application, is providing the proper mesopore surface area to support Co particles of proper size in close vicinity to acid sites. TEM images (Fig. S5, ESI†) show that Co oxide crystallites of about 17 nm are located on the external surface of parent H-ZSM-5 particles, whereas considerably smaller Co crystallites are present in the mesoporous zeolite supports (see also Table S1, ESI†). Further, Co crystallites visibly tend to cluster more on the parent zeolite support (Fig. S5, ESI†). These Co agglomerates are prone to sinter which results in a lower time-on-stream stability of Co/H-ZSM-5 than that of the mesoporous zeolite supported catalysts at higher operating temperatures (Fig. 1).

Although after desilication by NaOH, mesoH-ZSM-5(a) was ion exchanged and the amount of Na in this support is lower than our detection limit (0.01 wt%), alkaline treatment is a less preferred route, as Na⁺ is a well-known poison for Co-based

Fig. 1 Time-on-stream (TOS) evolution of CO conversion during FTS at 513 K, 15 bar, H₂/CO = 2, $GHSV/m_{\text{STP}}^3 \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1} = 2.4$ (solid symbols) and 6.0 (open symbols) (a). Carbon selectivity of FTS products after 20 h on-stream at $GHSV/m_{\text{STP}}^3 \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1} = 2.4$ (b) and 6.0 (c); ■: *n*-paraffins, ///: sum of isoparaffins and olefins; O/P (C2–4): olefin to *n*-paraffin ratio of C2–C4, S_{CO_2} : CO₂ selectivity.

FT catalysts where trace amounts can result in the loss of activity.¹² Under similar process conditions, CO conversion over Co/mesoH-ZSM-5(o) is almost 15% higher than that over Co/mesoH-ZSM-5(a) (Fig. 1a). Since no major differences are observed between Co crystallite sizes of these two catalysts (see Table S1 and Fig. S5, ESI†), we attribute this difference in activity to the effect of Na traces.

Fig. 1b shows that Co/SiO₂ and Co/H-ZSM-5 produce a considerably different product spectrum at similar conversion levels.

In contrast to Co/SiO₂, formation of C₂₁+ (waxes) is eliminated on Co/H-ZSM-5 (see also Fig. 2) and gasoline range hydrocarbons are produced, but with increased C₁–C₄ selectivities. Methane selectivity on Co/H-ZSM-5 is almost three times higher than that on Co/SiO₂. Due to the higher diffusivity of H₂ (than that of CO), the local H₂ concentration in the zeolitic particle is higher than that in the mesoporous SiO₂. The higher intra-particle H₂/CO ratio contributes to an enhanced CH₄ production over the Co/H-ZSM-5 catalyst.¹³

Comparison of the Co/H-ZSM-5 and Co/mesoH-ZSM-5(a) performances under iso-conversion conditions reveals that the selectivity to gasoline cut (C₅–C₁₁) is higher for the mesoporous sample and that to C₁ is lower (*cf.* Fig. 1b and c). This selectivity improvement over Co/mesoH-ZSM-5(a) is attributed to reduced diffusion limitations, which eliminate the overexposure of the FT hydrocarbons to strong acid sites and keep the local H₂/CO closer to bulk conditions inside the catalyst particle. Indeed, the positive effect of reduced diffusion limitations in hierarchical zeolites is known to increase the yield towards middle distillates with a decreased coke formation.¹⁴

Fig. 2 compares the FTS product distributions (molar fractions) over conventional and bifunctional catalysts. Under the applied process conditions, long chain hydrocarbons (waxes) are formed on Co/SiO₂ according to an ASF distribution with a chain growth probability (α) of 0.87. In contrast, a clear deviation from ASF distribution is observed for H-ZSM-5 supported catalysts, resulting in a cut-off above C₁₁, breaking the Fischer–Tropsch synthesis ASF distribution at the upper limit of gasoline cut, as longer hydrocarbons are more prone to conversion reactions.¹⁵ The reduced wax production on the zeolite containing samples is confirmed by TGA analysis of the spent catalysts where their weight loss is *ca.* 8 times lower than that of the spent Co/SiO₂ (Fig. S6, ESI†). In line with other reports,¹⁶ the methane level, higher than that of the ASF distribution, implies that a secondary reaction of CO hydrogenation takes place (in addition to FTS) for all the Co catalysts. As compared to Co/SiO₂, the higher CH₄ molar fraction obtained over Co/zeolite catalysts (see inset in Fig. 2), and their lower olefin selectivity (see insets in Fig. 1b and c), reveals that this hydrogenation functionality is more pronounced in the case of zeolite supported catalysts.

Fig. 2 FTS product distribution (molar fractions) over catalysts after 20 h on-stream at 513 K, 15 bar, H₂/CO = 2 and GHSV = 2.4 m_{STP}³ kg_{cat}^{−1} h^{−1}; α : chain growth probability, y_{C1} : methane molar fraction.

Limiting the FT product spectrum to C₅–C₁₁ cut has often been reported in the literature over bifunctional FT catalysts. Researchers predominantly ascribed this phenomenon to the (hydro)cracking activity of the acid function.^{8,12,17,18} In contrast to the hydrocracking of petroleum-derived feeds, where the aromatic content of the feed determines the processing conditions, hydrocracking of low-temperature FT (LTFT) waxes (often referred to as ‘mild hydrocracking’) is less demanding. The optimal process temperature of mild hydrocrackers is *ca.* 100 K higher than that of the LTFT.^{3,15,19} Comparison of various catalytic systems reveals that the key factor, determining the product distribution over bifunctional FT catalysts, is the close vicinity of the FT active phase to the acid functionality. In that sense, hybrid catalyst particles (such as the so-called ‘core-shell’ catalysts¹⁷) are more effective than physical mixtures which perform in turn better than the layered beds of FT and acid catalyst particles.²⁰

An even more intimate contact between the FT and acid sites increases the chance of primary olefinic FT products to adsorb on the acid sites for further hydrocracking and isomerization reactions.²¹ The operating temperature window of isomerization overlaps better with that of the LTFS than hydrocracking, and considerable amounts of branched hydrocarbons are produced over our zeolite containing catalysts, in good agreement with the literature.^{8,12,17,18} Formation of skeletal and double bond isomers that do not re-incorporate into the chain growth process as fast as linear hydrocarbons would prevent the formation of waxes simply by lowering the α , but without any contribution of hydrocracking, the isomerization alone cannot explain the nonlinear break in the ASF distribution observed in Fig. 2. Our results show that the *iso-to-normal* butane ratio increases by one order of magnitude from 0.02 over Co/SiO₂ to 0.24 over Co/mesoH-ZSM-5(a) (513 K, 15 bar, H₂/CO = 2, GHSV = 2.4 m_{STP}³ kg_{cat}^{−1} h^{−1}). C₄ isomers are typically formed during acid catalyzed cracking reactions, and not produced to a large extent in skeletal isomerization at the above-mentioned temperature.¹⁹ Therefore, this result already indicates that some hydrocracking reactions take place over our zeolite containing catalysts.

In order to investigate the feasibility of acid catalyzed reactions under FTS process conditions and space velocities (as those described in Fig. 1 and 2), mesoH-ZSM-5(a) was subjected to a mixture of *n*-hexane, H₂ and N₂. As depicted in Fig. 3, both hydrocracking and hydroisomerization occur under reaction conditions, with C₄ as the major product. It is also important to mention that together with isomerization and cracking products, higher hydrocarbons (C₈–C₁₀) were also found among the products (Fig. S8, ESI†), demonstrating that C₆ first dimerizes and then cracks to C₄, C₅, C₈ and C₇. These results together with the fact that larger hydrocarbons are even more reactive (than C₆) for hydrocarbon conversion reactions¹⁵ explain the cut-off shown in Fig. 2 where the molar fraction of hydrocarbon products drops as their carbon number increases. The similar formation level of C₆ isomers (Fig. 3) implies that the effect of isomerization reactions on the product slate of bifunctional catalysts should not be neglected either, as mentioned earlier. Gas-phase hydroprocessing experiments with hydrocarbon

Fig. 3 Product yields of *n*-C6 hydroprocessing over mesoH-ZSM-5(a) at different temperatures, 15 bar, $H_2/n\text{-C6} = 9.0$, $N_2/H_2 = 2.0$ and $WHSV = 359.7 \text{ mol kg}_{\text{cat}}^{-1} \text{ h}^{-1}$.

model compounds show that hydrocracking reactions take place in the presence of CO and H_2O as well.^{20,22}

It is also important to notice that compared to the large amounts of methane formed over the FTS catalysts, this product was not detected when feeding *n*-hexane to mesoH-ZSM-5(a) in the absence of Co. This observation suggests that formation of C1 does not directly correlate with the support acidity but is related to the direct CO hydrogenation and/or hydrogenolysis reactions at the metal sites.²³ Our current research focuses on identifying the methane formation mechanism(s) and the corresponding sites.

Conclusions

The combination of FTS activity and acid functionality and a high degree of mesoporous hierarchy results in catalysts that produce gasoline range hydrocarbons from syngas in one step with selectivities close to 60%. This high selectivity towards gasoline is the result of the cooperative action of the different active sites that are in close vicinity. Introduction and control of mesoporosity in the zeolite support turned out to be a crucial parameter in increasing the yield towards C5–C11, as well as the catalyst activity and stability.

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