Insights into the Catalytic Performance of Mesoporous H-ZSM-5-Supported Cobalt in Fischer–Tropsch Synthesis

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Mesoporous H-ZSM-5 (*meso*H-ZSM-5) was used as a carrier for a series of bifunctional Co-based catalysts for Fischer–Tropsch synthesis with ZrO₂ and/or Ru added as promoters. The reducibility of the catalysts was studied in detail by using temperature-programmed reduction and X-ray absorption spectroscopy. A comparison of the catalytic performance of Co/*meso*H-ZSM-5 and Co/SiO₂ (a conventional catalyst), after 140 h on stream, reveals that the former is two times more active and three times more selective to the C₅–C₁₁ fraction with a large content of unsaturated hydrocarbons, which is next to α -olefins. The acid-catalyzed conversion of *n*-hexane and 1-hexene,

as model reactions, demonstrates that the improvement in the selectivity toward gasoline range hydrocarbons is due to the acid-catalyzed reactions of the Fischer–Tropsch α -olefins over the acidic zeolite. The formation of methane over the zeolite-supported Co catalysts originates from direct CO hydrogenation and hydrocarbon hydrogenolysis on coordinatively unsaturated Co sites, which are stabilized as a consequence of a strong metal–zeolite interaction. Although the addition of either ZrO₂ or Ru increases the catalyst reducibility considerably, it does not affect the product selectivity significantly.

Introduction

Fischer–Tropsch synthesis (FTS) is one of the most important achievements of chemical industry in the 20th century. The depletion of fossil resources over the last few decades, the increasing price of crude oil, the rapid increase in methane reserves, and environmental concerns have generated a worldwide interest in practical applications of FTS-based technologies. Different types of fossil- (natural gas and coal) and renewable-based feedstocks can be converted into industrially relevant chemicals, such as lower olefins and alcohols as well as ultraclean fuels, through the FTS reaction.^[1] The latter case is already commercialized through the so-called low-temperature Fischer–Tropsch (LTFT; catalyzed by Co or Fe) and high-temperature Fischer–Tropsch (HTFT; catalyzed by Fe) processes.^[2] However, these technologies are economically feasible only at large scales^[3] and therefore process intensification is needed in applications with limited (and scattered) availability of feedstock (e.g., biomass) and/or space (e.g., offshore flare gas).

Both LTFT and HTFT reactors are followed by product upgrading units in which hydrocracking and/or isomerization of the products of FTS are performed.^[4] Therefore, one way to

attain the above-mentioned process intensification is to tune the FTS product selectivity to eliminate the demand for downstream conversion units.^[5]

Such efforts date to 1980s when combinations of zeolites with the FTS active phase were reported to “break” the classical Anderson–Schulz–Flory (ASF) product distribution.^[6] Since then, the integration of both Co- and Fe-based catalysts with various zeolite topologies has been studied at different levels, such as catalyst bed layers,^[7] physical mixtures of catalyst particles,^[8] and coated catalysts.^[9] A 7.5 wt% Co–0.2 wt% Ru catalyst supported on alumina-bound ZSM-5 has been reported recently to demonstrate a stable performance and high selectivity toward C₅–C₂₀ up to 1500 h on stream.^[10] Co is claimed to be present mainly on the alumina binder of this hybrid catalyst.

A systematic comparison of different Co–zeolite catalyst configurations reveals that the selectivity toward liquid hydrocarbons increases as the proximity between FTS and acid sites increases in these hybrid systems.^[11] Such a contact can be maximized by directly dispersing Co over the zeolite. Because high metal loadings are typically required in the catalyst formulations for FTS and zeolites lack a sufficient external surface area, the use of mesoporous zeolites as catalyst carriers gave promising results.^[12] On the one hand, the improved transport properties of hierarchically structured zeolites increase the selectivity toward liquid hydrocarbons,^[13] on the other hand, their high mesopore surface area improves dispersion at elevated metal loadings.^[11, 13–14] Insights into the catalytic performance of these bifunctional catalysts would enable us to fine-tune their product selectivity, which makes these catalysts attractive for practical applications.

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In an earlier work, we demonstrated that in an attempt to maximize the performance of bifunctional catalysts by steering the product selectivity toward liquid hydrocarbons, the topology of the zeolite and, most importantly, the number and strength of acid sites are key parameters.^[14] Herein, mesoporous H-ZSM-5-supported Co (≈ 20 wt%) catalysts are studied further. Special attention is given to thoroughly characterize metal reducibility and to its improvement upon promoter addition. Hydrocarbon conversion mechanisms over acid sites and Co are investigated by using the conversion of C6 as a model reaction. The effect of such reactions on the product selectivity and origins of methane formation over the zeolite-containing Co catalyst is discussed in detail. In all, through an advanced catalyst characterization along with a detailed catalyst assessment, a clear relationship is established between Co structural characteristics (if supported on the zeolite) and activity and selectivity in FTS.

Results and Discussion

Catalyst characterization

The total and mesopore surface area of H-ZSM-5 increases by 40 and 720 %, respectively, and its Si/Al ratio decreases from 41 to 22 after desilication with tetrapropylammonium hydroxide (TPAOH) owing to the creation of mesopores^[15] (Table 1).

Table 1. Textural and chemical properties of the supports used for catalyst preparation for FTS.							
Support	Treatment sequence	S [m ² g ⁻¹]		V [cm ³ g ⁻¹]			Si/Al ^[a]
		Total ^[b]	Meso ^[c]	Total ^[d]	Micro ^[e]	Meso ^[f]	
SiO ₂	none	290	250	1.35	0.02	1.34	n.a.
H-ZSM-5	none	460	50	0.26	0.18	0.08	41
mesoH-ZSM-5(o)	TPAOH	650	430	0.68	0.10	0.58	22
mesoH-ZSM-5	TPAOH/HNO ₃	690	470	0.67	0.09	0.58	41
ZrO ₂ /mesoH-ZSM-5	TPAOH/HNO ₃ /impregnation	600	410	0.57	0.08	0.48	n.d.

[a] Obtained from ICP-OES; [b] BET surface area; [c] Mesopore surface area obtained by using the *t*-plot method applied to the N₂ isotherm; [d] Total pore volume; [e] Micropore volume obtained by using the *t*-plot method; [f] Mesopore volume calculated as $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

Moreover, the mesopore volume of mesoH-ZSM-5(o) is approximately 7 times larger than that of H-ZSM-5. This increase is at the cost of a slight decrease in micropore volume (0.18 and 0.10 cm³g⁻¹ for H-ZSM-5 and mesoH-ZSM-5(o), respectively), which indicates a minor collapse of the zeolite structure under basic conditions.^[16] Nevertheless, the XRD patterns of the corresponding catalysts (Figure S1) confirm that the characteristic MFI structure is preserved after desilication.^[17] The surface area and pore volume of mesoH-ZSM-5 are barely altered with respect to those of mesoH-ZSM-5(o); however, the zeolite Si/Al ratio is readjusted to the original value (41) after acid treatment (Table 1). It was shown earlier that (the used) treatment with 1 M HNO₃ is effective only in removing the extra-frame-

Figure 1. NH₃-TPD profiles (10 K min⁻¹) of H-ZSM-5 zeolites. NH₃ was adsorbed at 473 K.

work aluminum species and does not leach out aluminum from the H-ZSM-5 framework.^[13b]

The temperature-programmed desorption of ammonia (NH₃-TPD) profile of H-ZSM-5 shows the characteristic peak of strong Brønsted acidity^[12a] at approximately 700 K (Figure 1). This “high-temperature” peak is initiated by a tail at lower temperatures, which originates from weaker Lewis acid sites.^[13b] Although mesoH-ZSM-5(o) does not show any desorption of NH₃, mesoH-ZSM-5 shows a profile similar to that of H-ZSM-5 (notably, the peak at temperatures above 800 K corresponds to framework collapse, not to strong acidity).^[14] We conclude that the initial treatment with TPAOH results in the partial ion exchange of the framework protons, which are recovered after acid treatment and calcination. The quantification of acidity through pyridine adsorption (Table 2) shows that the Brønsted acid density of

Table 2. Acid-type densities of H-ZSM-5 zeolites obtained through pyridine adsorption.				
Support	Brønsted acid		Lewis acid	
	[μmol g ⁻¹]	[μmol μmol ⁻¹ Al]	[μmol g ⁻¹]	[μmol μmol ⁻¹ Al]
H-ZSM-5	138	0.35	37	0.09
mesoH-ZSM-5	74	0.18	38	0.09

mesoH-ZSM-5 is lower than that of H-ZSM-5; nevertheless, the concentrations of Lewis acid sites are equal for both samples. The addition of ZrO₂ slightly modifies the acidic properties of supports: the high-temperature peak shifts slightly to lower temperatures in the NH₃-TPD profile of ZrO₂/mesoH-ZSM-5

Table 3. Textural and chemical properties of the catalysts for FTS.

Catalyst	S [m ² g ⁻¹]		V [cm ³ g ⁻¹]			d _{Co} ^[a] [nm]	Co loading [wt %] ^[b]		
	Total ^[c]	Mesopore ^[d]	Total ^[e]	Micropore ^[f]	Mesopore ^[g]		Co	Ru	Zr
Co/SiO ₂	200	180	0.89	0.01	0.88	16	18.6	n.a.	n.a.
Co/mesoH-ZSM-5(o)	440	270	0.45	0.07	0.38	11	20.7	n.a.	n.a.
Co/mesoH-ZSM-5	510	310	0.50	0.08	0.41	10	23.8	n.a.	n.a.
10 wt % Co/mesoH-ZSM-5	560	370	0.55	0.08	0.47	10	10.7	n.a.	n.a.
CoRu/mesoH-ZSM-5	460	290	0.40	0.07	0.33	10	17.7	0.3	n.a.
Co/ZrO ₂ /mesoH-ZSM-5	420	260	0.37	0.07	0.30	12	18.0	n.a.	3.5
CoRu/ZrO ₂ /mesoH-ZSM-5	430	270	0.39	0.07	0.32	13	17.8	0.3	3.7

[a] Co crystallite size calculated by using $d(\text{Co}^0) = 0.75 \times d(\text{Co}_3\text{O}_4)$, in which $d(\text{Co}_3\text{O}_4)$ is determined from XRD analysis by applying the Scherrer equation; [b] Obtained from ICP-OES; [c] BET surface area; [d] Mesopore surface area obtained by using the t -plot method applied to the N₂ isotherm; [e] Total pore volume; [f] Micropore volume obtained by using the t -plot method; [g] Mesopore volume calculated as $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

(4.6 wt % Zr). Moreover, a shoulder appears at approximately 550 K, which indicates a considerable increase in the Lewis acidity of this sample owing to the presence of ZrO₂^[18] (Figure 1).

All the mesoporous supports given in Table 1 were loaded with 18–24 wt % of Co (Table 3), except 10 wt % Co/mesoH-ZSM-5, which was prepared with a lower Co loading of 10.7 wt %. In addition, 0.3 wt % Ru-promoted catalysts were prepared over mesoH-ZSM-5 and ZrO₂/mesoH-ZSM-5 supports. The N₂ physisorption results reveal that at least 70% of the micropore volume is maintained after the impregnation of the active phase (cf. Tables 1 and 3).

The average Co crystallite size, as calculated from the XRD data, is the largest for Co/SiO₂ (16 nm) and similar for all zeolite-supported catalysts (10–13 nm) (Table 3). According to TEM analysis, Co particles form clusters over amorphous SiO₂, which results in an inhomogeneous distribution of the FTS active phase on this support (Figure 2a). This spatial distribution is to some extent improved in the zeolite-supported catalysts; yet, regions with higher Co concentration can be observed in all the TEM micrographs (Figure 2b–d).

The dark-field TEM images (Figure 3) of Co/SiO₂ and mesoH-ZSM-5 supports show smaller Co particles that are dispersed more over mesoH-ZSM-5 than over Co/SiO₂. Any Co particle can hardly be observed at the outer surface (edge) of the zeolite crystallites, which indicates that most of the FTS active phase is introduced into the mesopore space of mesoH-ZSM-5.

The temperature-programmed reduction by H₂ (TPR-H₂) profiles of supported Co catalysts are shown in Figure 4. The classical two-step reduction of Co₃O₄ via CoO to Co⁰^[19] occurs for Co/SiO₂ below 800 K. A sharp peak at approximately 550 K is also observed in the profile of Co/mesoH-ZSM-5, which is followed by two broad peaks: one at 600–900 K and the other above 900 K. The latter two peaks merge in the case of CoRu/mesoH-ZSM-5 and form a large peak at approximately 700 K with a shoulder at approximately 600 K. Moreover, the onset temperature of reduction and the positions of the peak maxima shift by approximately 100 K to lower temperatures, which suggests that the presence of Ru increases the rate of Co reduction. Co/ZrO₂/mesoH-ZSM-5 demonstrates a pattern similar to that of Co/mesoH-ZSM-5, although it is apparent that

hydrogen consumption above 900 K has decreased upon ZrO₂ addition. These results reveal that the reducibility of Co is lower over H-ZSM-5 than over amorphous SiO₂ owing to a stronger metal-support interaction. In addition, the presence of multiple reduction peaks on zeolite-supported catalysts indicates Co species with different reactivities.

Degrees of reduction, as calculated from the total consump-

Figure 2. Quasi in situ TEM images of FTS catalysts after reduction in H₂ at 773 K for 13 h. Scale bars = 50 nm.

tion of H₂, are listed in Table 4. Co is fully reduced over SiO₂, whereas the degree of reduction is 67% for Co/mesoH-ZSM-5. With the addition of either Ru or ZrO₂, this value increases considerably and reaches above 90%. Different mechanisms have been proposed for the promoting effects of precious metals (Ru) and ZrO₂. Small amounts of Ru in the catalyst composition promote H₂ spillover and thus increase the rate of reduction.^[20]

Table 4. Degree of reduction of the catalysts for FTS obtained by using TPR-H₂.

Catalyst	Degree of reduction [%]
Co/SiO ₂	> 95
Co/mesoH-ZSM-5	67
CoRu/mesoH-ZSM-5	92
Co/ZrO ₂ /mesoH-ZSM-5	> 95
CoRu/ZrO ₂ /mesoH-ZSM-5	> 95

Figure 3. a, b, c) Quasi in situ dark-field TEM images of Co/SiO₂ and d, e, f) Co/mesoH-ZSM-5, both after reduction in H₂ at 773 K for 13 h. Scale bars = a, d) 50 nm, b, e) 20 nm, and c, f) 10 nm.

Figure 4. TPR-H₂ profiles (5 K min⁻¹) of fresh catalysts for FTS.

ZrO₂ forms an intermediate layer between the metal and the support, which reduces the metal-support interaction.^[21] Such mechanistic differences are indicated by the observed changes in the TPR-H₂ profiles of CoRu/mesoH-ZSM-5 and Co/ZrO₂/mesoH-ZSM-5 compared with those of Co/mesoH-ZSM-5.

The reducibility and coordination of Co on zeolite-supported catalysts were also studied by using X-ray absorption spectroscopy (XAS). The extended X-ray absorption fine structure (EXAFS) Fourier transform and X-ray absorption near-edge structure (XANES) spectra of fresh and activated catalysts as well as reference compounds at Co K-absorption edges are shown in Figure 5.

The EXAFS data of fresh (supported) Co species are characterized by the presence of two peaks, which are characteristic of Co–O and Co–Co coordination, respectively. The Co–O coordination can still be observed in the EXAFS spectrum of the activated Co/mesoH-ZSM-5 catalyst, demonstrating an incomplete reduction of Co, which is in agreement with the TPR-H₂ results. In contrast, activated Co/ZrO₂/mesoH-ZSM-5, CoRu/ZrO₂/mesoH-ZSM-5, and CoSiO₂ catalysts all have a local atomic structure similar to that of the Co foil, which confirms a full reduction of Co.

The XANES spectra of Co/ZrO₂/mesoH-ZSM-5 and CoRu/ZrO₂/mesoH-ZSM-5 are characterized by a pre-edge peak at approximately 7710 eV, arising from the 1s→3d transition, which is only quadrupole allowed for coordination sites without centric symmetry, and an edge peak at 7717 eV.^[22] According to the edge position, Co₃O₄ is the major Co phase in these promoted catalysts; this observation is in agreement with the XRD and TPR-H₂ results. After activation, the XANES spectra of Co/ZrO₂/mesoH-ZSM-5 and CoRu/ZrO₂/mesoH-ZSM-5 resemble that of the Co foil. The slight difference can be due to the metal-support interactions that can induce a perturbation on the electronic structure and hence on the spectral features.^[22c]

The results obtained from XAS are consistent with the improved reducibility and degree of reduction of Co upon promotion with ZrO₂ (Table 4), which reveal that Ru addition to the ZrO₂-promoted catalyst is not necessary for activation temperatures above 773 K.

Catalytic performance

Lower hydrocarbons (C₃–C₅) are detected in the product streams upon feeding C₆ (in a mixture with H₂) over mesoH-ZSM-5 (Figure 6). C₆ conversion increases from 4% to 96% if *n*-hexane is replaced by 1-hexene in the feed stream. This dif-

Figure 5. a–e) Fourier-transformed EXAFS (Co K-edge, not phase corrected) and f) XANES spectra of fresh and activated catalysts for FTS (reduced quasi in situ in H_2). Spectra f correspond to Co_2O_3 (1), Co^0 (2), fresh $Co/ZrO_2/mesoH-ZSM-5$ (3), activated $Co/ZrO_2/mesoH-ZSM-5$ (4), fresh $CoRu/ZrO_2/mesoH-ZSM-5$ (5), and activated $CoRu/ZrO_2/mesoH-ZSM-5$ (6).

ference in conversion implies that olefins are much more reactive in the acid-catalyzed reactions over the zeolite support. Hydrocarbon conversion reactions over *mesoH-ZSM-5* do not lead to methane formation. However, nearly full conversion of *n*-hexane and a 99% methane selectivity are obtained by incorporating Co into *mesoH-ZSM-5*. These results reveal that hydrocarbon hydrogenolysis is predominant over Co.

In FTS, the cobalt time yield (CTY) of $Co/mesoH-ZSM-5$ is almost two times higher than that of Co/SiO_2 (Figure 7). At the same time, calculations assuming spherical Co particles with diameters equal to those reported in Table 3 show that the ratio of CO turnover frequencies between $Co/mesoH-ZSM-5$ and Co/SiO_2 is approximately 1.1, which is in line with the general belief that Co-based FTS is not structure sensitive if particles are larger than 6–10 nm.^[23] The initial activity of $Co/mesoH-ZSM-5$ increases with the addition of either Ru or ZrO_2

to the catalyst composition. However, CTYs of all the zeolite-supported catalysts become similar after approximately 80 h on stream.

The carbon selectivities to different FTS product ranges over promoted and unpromoted catalysts are shown in Figure 8. Under the applied process conditions, Co/SiO_2 is highly selective to C_{21+} (wax). Wax production is suppressed considerably over the zeolite-containing catalysts, which results in higher carbon selectivity toward gasoline range hydrocarbons (C_5 – C_{11}) as well as to C_1 . A comparison of $Co/mesoH-ZSM-5$ and $CoRu/mesoH-ZSM-5$ catalysts under isoconversion conditions shows a minor effect of Ru in terms of altering the catalyst product distribution (Figure 8). In general, the selectivity toward C_1 (S_{C_1}) decreases only slightly by introducing Ru and/or ZrO_2 .

A detailed analysis of liquid products formed over $Co/mesoH-ZSM-5$ (in the FTS reaction) shows a large fraction of unsaturated hydrocarbons, other than α -olefins, in the sample (Figure 9). (Notably, a contribution of aromatics plus oxygenates to the liquid products was < 0.3 wt %.)

The time on stream (TOS) evolution of CO conversion (X_{CO}) during 140 h on stream demonstrates that the stability of $Co/mesoH-ZSM-5$ in terms of activity is comparable to that of Co/SiO_2 (Figure 10). Methane selectivity is fairly constant over Co/SiO_2 during 140 h on stream ($\approx 6\%$), whereas it increases from 11 to 14% with time as X_{CO} decreases by 9% over $Co/mesoH-ZSM-5$. Once the catalytic activity is restored after regeneration, S_{C_1} decreases again (Figure 10). In contrast to $Co/mesoH-ZSM-5$, no C_4 isomers are produced over Co/SiO_2 . The iso-to-normal C_4 ratio (I/N (C_4)) over the former catalyst decreases with TOS and reaches a steady-state level after approximately 80 h on stream. The I/N (C_4) of the reactivated catalyst is similar to that of the fresh catalyst, which indicates that the acid sites are re-covered.

To investigate the effect of conversion level on S_{C_1} over the zeolite-supported catalyst, X_{CO} was varied by changing the space velocities at different H_2/CO ratios of 1 and 2. Data reported in Table 5 indicate that increasing the H_2 concentration

Figure 6. Conversion and product selectivities in C6 hydroconversion over mesoH-ZSM-5 and CoRu/mesoH-ZSM-5. Data were collected after 20 h on stream at 513 K, 15 bar, $H_2/C_6=9.0$, $N_2/H_2=2.0$, and $SV=13 \text{ mol}_{C_6} \text{ kg}_{cat}^{-1} \text{ h}^{-1}$. Either *n*-hexane or 1-hexene was included in the feed stream, as indicated in the legend.

Figure 9. Selectivity distribution of liquid hydrocarbons formed over Co/mesoH-ZSM-5. Liquid products were collected after 140 h on stream at 513 K, 15 bar, $H_2/CO=1$, $GHSV=12 \text{ m}_{STP}^3 \text{ kg}_{cat}^{-1} \text{ h}^{-1}$ and were analyzed by 2D GC. The associated 2D chromatogram is presented in Figure S2.

Figure 7. TOS evolution of the CTY during FTS at 513 K, 15 bar, $H_2/CO=1$, and $GHSV=12 \text{ m}_{STP}^3 \text{ kg}_{cat}^{-1} \text{ h}^{-1}$.

Figure 8. Carbon selectivity toward products of FTS after 140 h on stream. In each carbon number group from left to right: Co/SiO₂, Co/mesoH-ZSM-5, CoRu/mesoH-ZSM-5, CoRu/mesoH-ZSM-5, Co/ZrO₂/mesoH-ZSM-5, and CoRu/ZrO₂/mesoH-ZSM-5. Experiments were performed at 513 K, 15 bar, and $H_2/CO=1$.

Figure 10. TOS evolution of CO conversion (X_{CO}), methane (C1) selectivity, and I/N (C4) over a) Co/SiO₂ and b) Co/mesoH-ZSM-5 during FTS at 513 K, 15 bar, $H_2/CO=1$, and $GHSV=12 \text{ m}_{STP}^3 \text{ kg}_{cat}^{-1} \text{ h}^{-1}$. Solid symbols correspond to the first reaction run; open symbols correspond to the second reaction run over in situ reactivated catalysts (in H_2 at 773 K for 13 h).

Table 5. CO conversion and carbon selectivity to products of FTS over Co/mesoH-ZSM-5 after 22 h on stream at 513 K, 15 bar total pressure, and different feed composition H_2/CO ratios and space velocities.

H_2/CO	$GHSV$ [$\text{m}_{STP}^3 \text{ kg}_{cat}^{-1} \text{ h}^{-1}$]	X_{CO} [%]	S [%]					
			C1	C2–C4	C5–C11	C12–C20	C21+	CO_2
1	4.8	48	10	12	62	12	1	3
1	12	42	12	14	56	16	1	1
2	12	83	17	15	51	15	0	2
2	24	55	20	17	48	14	0	1

by changing the H_2/CO ratio from 1 to 2 results in 5–10% increase in S_{C1} . Furthermore, this value is higher at lower X_{CO} for both H_2/CO ratios.

Discussion

The acid-catalyzed hydroconversion of C6 confirms that hydrocracking is feasible under the applied LTFT process conditions (Figure 6), which is consistent with the literature.^[7b,8a] This finding explains the increased selectivities to liquid fractions over the H-ZSM-5-containing catalysts (Figure 8). A close contact between the metal for FTS and acid sites is reported to be of crucial importance in this respect.^[11] If acid site domains are in the vicinity of FTS sites at a nanometer scale, α -olefins, which are the primary products of FTS, may crack or isomerize before they are hydrogenated. The closer these sites, the higher the probability for cracking to occur. The conversion of 1-hexene is much higher than that of *n*-hexane over *meso*H-ZSM-5 (Figure 6). The classical mechanism of such acid-catalyzed reactions, through the rearrangement of a secondary carbocation into a protonated dialkylcyclopropane, increases the degree of branching of hydrocarbons.^[24] Because FTS may mainly produce linear α -olefins, a considerable fraction of other unsaturated hydrocarbons shown in Figure 9 are formed over the acid sites.

Ru has (*de*)hydrogenation activity, which promotes the acid-catalyzed hydrocarbon reactions.^[25] At the same time, Ru increases the reducibility of small Co particles (Figure 4), which are active for hydrogenolysis.^[26] Thus, Ru promotes hydrogenolysis (indirectly) and, in the absence of CO, this reaction over the 20 wt% Co catalyst is prevalent (Figure 6). As a consecutive reaction, hydrogenolysis may even convert the products of the acid-catalyzed reactions into C1 (and C2).

The higher activity of Co/*meso*H-ZSM-5 compared with that of Co/SiO₂ (Figures 7 and 10) is a result of a smaller Co crystallite size (Table 3 and Figure 3). Both catalysts demonstrate a similar TOS stability in terms of CO conversion. Sintering is an important cause for the deactivation of Co-based catalysts for FTS^[27] and can be suppressed by maximizing the spatial distribution of active phase particles over the support surface.^[27b,28] Therefore, the availability of accessible surface area is an advantage in the design of stable catalysts (supported on mesoporous H-ZSM-5) for FTS.^[13a] The representative TEM images in Figures 2 and 3 show that the Co distribution in the mesopores of the hierarchical zeolite is slightly better than that in amorphous SiO₂.

The TPR-H₂ and EXAFS results (Figure 5) reveal that the addition of promoters (Ru and/or ZrO₂) increases the reducibility and degree of reduction of smaller cobalt oxide crystallites over *meso*H-ZSM-5. Although large Co particles do not reoxidize in the FTS reaction environment, the reoxidation of smaller crystallites (<4 nm) starts in an early course of the reaction.^[29] Therefore, the CTY of the promoted catalysts, which is initially higher, reaches values similar to that of the unpromoted catalysts after a gradual decrease (Figure 7). The fact that both Co/ZrO₂/*meso*H-ZSM-5 and CoRu/ZrO₂/*meso*H-ZSM-5 (with similar Co loadings and crystallite sizes; Table 3) present fairly identical

values and trends in the TOS evolution of CTY (Figure 7) supports the EXAFS data in the sense that the addition of ZrO₂ is sufficient to fully reduce Co by using the activation method.

The carbon selectivity toward C1 over Co/*meso*H-ZSM-5 is more than two times larger than that over Co/SiO₂ (Figure 8). The possible sources for such a high methane selectivity are as follows: (1) a poor catalyst reducibility, (2) a low chain growth probability (α) in FTS, (3) acid-catalyzed hydroconversion reactions, and (4) side reactions over Co. Sources 1 and 2 increase the rate of methane formation through FTS, whereas in the case of sources 3 and 4, other reactions generate C1 along with FTS. The contribution of each source is discussed below:

- 1) Figure 8 shows that promoter addition and reducibility enhancement do not significantly change the methane selectivity.
- 2) In line with previous reports,^[11,13–14] the fractional molar distribution of products of FTS has a nonlinear shape for the H-ZSM-5-containing catalysts (Figure S3a). The only exception is Co/*meso*H-ZSM-5(*o*), which is devoid of strong Brønsted acidity (Figure 1) and represents a linear ASF product distribution, which is similar to the case of Co/SiO₂. A “break” in the ASF product selectivity at about C12 (Figure S3a) can be translated into a lower α for higher hydrocarbons, which can eventually increase the formation of methane. The S_{C1} of Co/*meso*H-ZSM-5 is 2% higher than that of Co/*meso*H-ZSM-5(*o*) at isoconversion (Figure S3b).
- 3) No methane was detected during the conversion of C6 over the bare zeolite (Figure 6), which agrees with the general belief that the (hydro)cracking mechanism over acid sites does not lead to C1.^[24] Furthermore, if overcracking inside the zeolite pores was the main origin of the large production of methane over the Co-containing catalysts, then Co/*meso*H-ZSM-5(*o*) should have represented a much lower carbon selectivity toward C1. However, the catalytic performance results shown in Figure S3 rule out this possibility. Therefore, alleviating the effect of the above-mentioned sources (1–3) may lower S_{C1} (over Co/*meso*H-ZSM-5) only by a few percent at maximum.
- 4) Among Fe and Co, the hydrogenation activity of Co is stronger.^[30] The Co-based catalysts for FTS are more sensitive (than Fe) to changes in the process conditions^[30] (such as temperature and H_2/CO ratio). Moreover, the C1 level is typically higher for Co-based catalysts than what is anticipated by extrapolating the ASF distribution to $n=1$ (Figure S3a). In the case of our zeolite-supported Co catalysts, both direct CO hydrogenation to methane ($CO + 3H_2 \rightarrow CH_4 + H_2O$) and hydrogenolysis are expected to occur because both side reactions become important on smaller Co particles. This is a result of the larger H_2 coverage over lower index surface crystallographic planes or steps and corners^[31] (of which the density increases as Co crystallite size decreases).^[32] Hydrogenolysis is a structure-sensitive reaction that will compete with direct CO hydrogenation over the small metal particles.^[33] Although this reaction could be suppressed at low CO conversions owing to competitive CO adsorption,^[34] it can be observed from Figure 6

that in the absence of CO, the zeolite-supported Co converts hydrocarbons into methane in a yield of 99% at 513 K.

In line with our previously reported CO adsorption results,^[13b] the TPR-H₂ results reveal that the nature and thus the reactivity of Co sites is more heterogeneous over the zeolite-supported catalysts than over Co/SiO₂ (Figure 4). We conclude that owing to the strong Co–zeolite interaction (Figure 4), lower coordinated Co sites are stabilized over the zeolite support. Therefore, this catalyst is sensitive to changes in H₂ concentration as well and demonstrates an increased selectivity toward C1 as the H₂ concentration is higher at lower conversion levels (Table 5). This observation explains why in contrast to Co/SiO₂, *S*_{C1} increases with time over Co/mesoH-ZSM-5 with a decrease in CO conversion (Figure 10).

At similar conversion levels, a catalyst with a lower Co loading of 10.7 wt% has 4% more selectivity toward C1 (Figure S3b). At a lower Co loading, more defects are expected on the metal crystallites; therefore, this result further confirms the above-mentioned hypothesis on the main source of methane formation over the zeolite-supported Co catalysts.

Conclusions

Mesoporous H-ZSM-5 (*mesoH*-ZSM-5) is prepared through base and acid treatments of a commercial ZSM-5 zeolite (Si/Al = 40). The base treatment with tetrapropylammonium hydroxide increases the mesopore surface area considerably and deactivates the Brønsted acidity of the zeolite. The decreased Si/Al ratio, caused by zeolite desilication, is set back to the original value through the succeeding treatment with HNO₃, which also regenerates the Brønsted acidity. If loaded with Co, the resulting *mesoH*-ZSM-5-supported Co catalyst is much more active than the conventional Co/SiO₂ catalyst. After 140 h on stream, Co/*mesoH*-ZSM-5 is three times more selective to the C5–C11 fraction than is Co/SiO₂. A large contribution of unsaturated hydrocarbons, other than α -olefins, to the liquid products as well as the conversion of *n*-hexane and 1-hexane indicate that the improved selectivity toward the gasoline fraction owes to the secondary acid-catalyzed reactions of Fischer–Tropsch α -olefins over the zeolite.

With the addition of either Ru or ZrO₂ promoters, the reducibility of zeolite-supported Co increases considerably, which leads to an increased initial catalytic activity. Nevertheless, promoters do not affect the product distribution significantly. The TPR-H₂ and CO adsorption results reveal that the reactivity of Co is diverse as supported on mesoporous H-ZSM-5. In this respect, a large contribution of lower coordinated Co sites promotes methane formation through the direct hydrogenation of CO and hydrogenolysis and makes the catalyst sensitive to changes in H₂ concentration in terms of selectivity toward C1.

Experimental Section

Amorphous SiO₂ (CARIACT Q-10) with surface area and pore volume of 293 m² g^{−1} and 1.35 cm³ g^{−1}, respectively, was provided

by Fuji Silysia Chemical Ltd (Japan). ZSM-5 zeolite in the ammonium form with a nominal Si/Al ratio of 40 was purchased from Zeolyst (CBV 8014) and calcined at 823 K for 5 h to obtain H-ZSM-5. TPAOH (1 M), HNO₃ (70 wt%), ruthenium(III) nitrosyl nitrate (1.5 wt%), and zirconyl nitrate (5 wt%) solutions as well as the cobalt(II) nitrate hexahydrate salt were purchased from Sigma–Aldrich. All chemicals were used without any further purification.

Mesoporous H-ZSM-5 was prepared through base and acid treatments, as described earlier.^[13b] In brief, desilication was performed in TPAOH aqueous solution (1 M) placed in a capped vessel (volume_{base solution}/weight_{zeolite} = 8.0 cm³ g^{−1}) and at 343 K for 1 h under stirring in an oil bath. This treatment was followed by immediate quenching in an ice water bath and centrifugation to separate the zeolite powder from the solution. The residue of the desilicating agent was removed from the zeolite crystallites through subsequent redispersion in deionized water and centrifugation cycles until neutral pH was reached. The samples were then kept overnight at 333 K followed by drying at 393 K for 12 h and calcination at 823 K for 5 h. After heat treatments, the mesoporous H-ZSM-5 samples were acid treated in aq. HNO₃ (1 M; volume_{acid solution}/weight_{zeolite} = 28.6 cm³ g^{−1}) at 343 K for 2 h under stirring in an oil bath. After quenching, the samples were washed thoroughly with deionized water, dried, and calcined similarly as after the above-mentioned desilication method. Mesoporous H-ZSM-5 before acid treatment was labeled as *mesoH*-ZSM-5(o), and the acid-washed zeolite was labeled as *mesoH*-ZSM-5.

The catalysts for FTS were prepared through incipient wetness impregnation. All the supports were dried overnight at 393 K before impregnation. To study the promoting effect of ZrO₂, a fraction of *mesoH*-ZSM-5 was loaded with Zr ($\approx$ 5 wt%) by using a zirconyl nitrate solution. This sample was then kept overnight in a desiccator at RT, dried at 393 K for 12 h, and calcined at 823 K for 5 h; the resulting sample was labeled as ZrO₂/*mesoH*-ZSM-5. Amorphous SiO₂, *mesoH*-ZSM-5(o), *mesoH*-ZSM-5, and ZrO₂/*mesoH*-ZSM-5 were used as carriers and loaded with Co ($\approx$ 20 wt% or 10 wt% in one case for each sample) by using aqueous cobalt(II) nitrate hexahydrate solutions as precursors. To investigate Ru as a catalyst promoter, ruthenium nitrosyl nitrate was added to the precursor solution and co-impregnated with Co to obtain a Ru loading of 0.3 wt%. After impregnation, the samples were dried in a desiccator at 393 K as explained above. Then, the catalysts were calcined at 673 K for 2 h. All the above-mentioned drying and calcination steps were performed at a heating rate of 2 K min^{−1} and under static air conditions.

N₂ physisorption was performed in an Autosorb 6B unit (Quantachrome Instruments) at liquid nitrogen temperature (77 K). Before the experiment, the samples ($\approx$ 0.1 g) were degassed overnight in an Autosorb Degasser unit (Quantachrome Instruments) under vacuum at 623 K.

Elemental analysis was performed with Perkin–Elmer Optima instruments. The samples were digested in an acid mixture. After dilution, analysis was performed by using inductively coupled plasma optical emission spectrometry (ICP–OES).

The XRD patterns were recorded in Bragg–Brentano geometry with a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye position-sensitive detector. Measurements were performed at RT by using monochromatic CoK α (λ = 1.788970 Å) radiation at 2θ = 5° and 90°. All patterns were background subtracted to eliminate the contribution of air scatter and possible fluorescence radiation.

NH₃-TPD was measured with an AutoChem II chemisorption analyzer (Micromeritics). The zeolite-containing samples (≈ 0.2 g) were first degassed under He flow at 673 K for 1 h and then saturated with NH₃ at 473 K during 1 h by using a flow of 1.65 % NH₃ in He. The gas mixture was then switched back to He, and the sample was purged at 473 K for 1 h to remove the weakly adsorbed NH₃ molecules until no NH₃ was detected. Temperature-programmed desorption was subsequently recorded under He flow from 473 to 873 K. All flow rates were adjusted to 25 cm³_{STP} min⁻¹ and the heating rates were 10 K min⁻¹ during different stages of the experiment.

The amount of Brønsted and Lewis acid sites in H-ZSM-5 and mesoH-ZSM-5 were evaluated by using pyridine adsorption, which was performed with a Nicolet 6700 FT-IR spectrometer (Thermo Scientific) equipped with a MCT-B detector. A zeolite sample (≈ 0.05 g) was pressed at 1132 kg cm⁻² for 5 s to form a self-supporting wafer of 1.5 cm diameter. The sample was then degassed at 673 K for 2 h under vacuum [2×10^{-5} mbar (1 bar = 100 kPa)]. Pyridine vapor was added stepwise to the sample at a known volume and pressure. After each step, the sample was heated at 433 K to allow diffusion of the probe molecules and then cooled to RT for spectra collection.^[35] This method was repeated to estimate the extinction coefficient until no further increase was observed in the areas of adsorbed pyridine upon pyridine addition. Finally, the sample was heated at 433 K under vacuum and the final spectrum was recorded at RT. During each measurement, 128 scans were recorded in 1000–4000 cm⁻¹ range at a resolution of 4 cm⁻¹. The degassed sample was recorded as a background spectrum.

TEM was performed with an FEI Tecnai TF20 microscope using a carbon-coated Cu grid. Before analysis, the samples were reduced in an H₂ flow of 80 cm³_{STP} min⁻¹ at 773 K for 13 h (heating rate = 2 K min⁻¹) and transferred to the grid in a glove box. For the introduction of the samples into the microscope, a transfer unit was used to prevent any contact with air.

TPR-H₂ was performed with a homemade equipment. The Co-containing samples (≈ 0.1 g) were subjected to a 7.4 % H₂ flow of 27 cm³_{STP} min⁻¹ in Ar in a temperature-controlled reactor. The reactor temperature was ramped from RT to 1223 K (heating rate = 5 K min⁻¹), and the H₂ consumption was monitored with a thermal conductivity detector. Water was removed with a Perma Pure membrane dryer. Calibration was performed with CuO (Alfa Aesar), and total H₂ consumption values were obtained from TPR-H₂ patterns. The ratio between the H₂ consumption and the corresponding theoretical value, calculated for the full reduction of each catalyst (assuming all Co atoms to be initially in the form of Co₃O₄), was reported as the degree of reduction.

XAS was performed at beamline X18A of National Synchrotron Light Source in Brookhaven National Laboratory (NY, USA). The beamline used the Si(111) channel-cut monochromator and provided an energy range of 5–25 keV. All the measurements were performed at RT in the transmittance mode. Incident and transmitted X-rays were detected with ion chambers. EXAFS and XANES data were collected on the K edge of Co. All Co-containing samples were measured against the Co foil used as a reference. In typical XAS experiments, the powder samples were placed into a 1.27 cm stainless steel washer and sealed from both sides with the Kapton tape. This configuration enabled us to keep the sample thickness constant. Air-sensitive samples (i.e., activated catalysts) were loaded into a dedicated cell. The cell consisted of an airtight stainless steel chamber equipped with two Kapton windows for the beam passing and a clamped cap for loading. The sample

holder was located in the middle of this cell under N₂ atmosphere in a glove box and sealed. The EXAFS data were processed by Athena (version 0.8.056). The background subtraction was performed by using the automated single-variable fit implemented in Athena. The Fourier transform of the reciprocal space data was performed by using the Hanning window in the k range of 2–10 Å⁻¹.

The acid-catalyzed reactions were performed in a fixed-bed stainless steel reactor with *n*-hexane and 1-hexene as hydrocarbon model compounds. The fresh catalyst particles (0.250 g, 100–212 µm in size) were fixed in the reactor (3.9 mm inner diameter) between quartz wool plugs. The samples were treated overnight under H₂ flow at 673 K and atmospheric pressure. After cooling the samples to 513 K, the pressure was increased to 15 bar, and subsequently, a mixture of C₆, H₂, and N₂ was fed to the reactor (space velocity (SV) = 13 mol_{C₆} kg_{cat}⁻¹ h⁻¹, H₂/C₆ = 9.0, and N₂/H₂ = 2.0). After 20 h on stream, the product was analyzed on-line at 363 K with a CompactGC (Interscience) equipped with a PoraBOND Q column (10 m × 0.32 mm) and a flame ionization detector (FID) and using He as the carrier gas.

FTS experiments were performed on a six-flow fixed-bed micro-reactor setup, as described elsewhere.^[11] For all experiments, the fresh catalyst (0.250 g, 100–212 µm in size) was diluted with SiC of similar size to attain a constant bed volume of approximately 1.3 cm³. Catalysts were activated in situ before the FTS reaction by H₂ at 773 K for 13 h at atmospheric pressure followed by cooling to 453 K under H₂ flow. After increasing the pressure to the process value (15 bar), CO was gradually introduced into the feed stream at 453 K to reach its final concentration (H₂/CO = 1 or 2) in 1 h. Subsequently, the reactor was heated to the process temperature (513 K).

To regenerate the catalysts, CO was excluded from the feed and the operating pressure was decreased to atmospheric pressure under H₂ flow. Upon increasing the reactor temperature to 773 K, the samples were reactivated in situ (as described) and a second FTS experiment was started as per the above-mentioned method. All the above heating and cooling steps were performed at a heating rate of 2 K min⁻¹.

During FTS experiments, heavy hydrocarbons (waxes) were collected with gas/liquid separators at 448 K and the reaction pressure. After expanding the product flow to atmospheric pressure by using back pressure controllers, lighter hydrocarbons and water were collected in cold traps at approximately 278 K. After separation from water, these liquid hydrocarbons as well as the waxes were weighted, dissolved in CS₂, and analyzed offline with a simulated distillation (SIMDIS) gas chromatograph (Hewlett-Packard HP 5890, Series II) equipped with an FID and HP-1 column (7.5 m × 0.53 mm; film thickness = 2.65 µm) and using He as carrier gas. During the analysis, the oven temperature was ramped from 35 to 350 K (ramp rate = 14 K min⁻¹) and maintained at the final temperature for 5 min. N₂, CO, and CO₂ as well as light hydrocarbons in the gas phase were analyzed on-line with a CompactGC (Interscience) equipped with three columns and detectors in parallel and using He as a carrier gas. In the first column (Carboxen-1010, 10 m × 0.32 mm), N₂, CO, CH₄, and CO₂ were separated at 333 K and analyzed with a thermal conductivity detector. In the second column (Al₂O₃/KCl, 10 m × 0.32 mm) and detection with an FID, separation between all C1–C4 components was achieved at 434 K. In the third column (RTX-1, 0.5 µm, 15 m × 0.32 mm), C5–C10 hydrocarbons were separated at 353 K and analyzed with an FID.

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