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Impact of Hydrogenolysis on the Selectivity of the Fischer–Tropsch Synthesis: Diesel Fuel Production over Mesoporous Zeolite-Y-Supported Cobalt Nanoparticles**

Xiaobo Peng, Kang Cheng, Jincan Kang, Bang Gu, Xiang Yu, Qinghong Zhang, and Ye Wang**

Abstract: *Selectivity control is a challenging goal in Fischer–Tropsch (FT) synthesis. Hydrogenolysis is known to occur during FT synthesis, but its impact on product selectivity has been overlooked. Demonstrated herein is that effective control of hydrogenolysis by using mesoporous zeolite Y-supported cobalt nanoparticles can enhance the diesel fuel selectivity while keeping methane selectivity low. The sizes of the cobalt particles and mesopores are key factors which determine the selectivity both in FT synthesis and in hydrogenolysis of n-hexadecane, a model compound of heavier hydrocarbons. The diesel fuel selectivity in FT synthesis can reach 60 % with a CH_4 selectivity of 5 % over a Na-type mesoporous Y-supported cobalt catalyst with medium mean sizes of 8.4 nm (Co particles) and 15 nm (mesopores). These findings offer a new strategy to tune the product selectivity and possible interpretations of the effect of cobalt particle size and the effect of support pore size in FT synthesis.*

Fischer–Tropsch (FT) synthesis, a process for the conversion of syngas (CO/H_2) derived from nonpetroleum carbon resources such as natural gas (also shale gas), coal, and biomass, into hydrocarbon fuels and chemicals, has received renewed interest because of the growing global demand for liquid fuels and the depletion of petroleum. Extensive studies have been devoted to developing efficient catalysts for FT synthesis,[1] but the effective control of product selectivity remains one of the grand challenges. The FT products generally follow the Anderson–Schulz–Flory (ASF) distribution, which is unselective for the middle-distillate products.[1b] For example, the selectivities of products in gasoline (C_{5-11}) and diesel (C_{10-20}) fractions are limited to 45 and 39 %, respectively. Conventionally, the FT products are subjected to further hydrotreatment to increase liquid fuel selectivity. Compared to this two-stage process, the direct production of specific-range liquid fuels would be more energy and cost efficient.

Recently, bifunctional FT catalysts, which combine either ruthenium, cobalt, or iron nanoparticles for CO hydrogenation, and acid sites in a zeolite like H-ZSM-5 for hydrocracking, have been harnessed to enhance the C_{5-11} selectivity.[2,3] However, few studies have succeeded in the direct and selective production of C_{10-20} hydrocarbons,[4] even though the FT-based diesel fuel is known to possess many advantages such as low sulfur and aromatic content, and reduced NO_x and particulate matter emissions.[5] Herein, we report a new strategy to improve the C_{10-20} selectivity by effective control of hydrogenolysis.

We expected that the use of zeolite H-Y, having a weaker Brønsted acidity than H-ZSM-5, might cause milder hydrocracking of heavier primary hydrocarbons formed on FT metals and lead to higher C_{10-20} selectivity. However, the Co/H-Y catalyst did not show enhanced C_{10-20} selectivity compared to that of Co/SiO_2 and Co/Al_2O_3, which are two conventional FT catalysts, but its C_{21+} selectivity was lower because of the Brønsted acid catalyzed hydrocracking reaction (Table 1). Unexpectedly, the Co/Na-Y catalyst lacking Brønsted acidity (see Figures S1 and S2, and Table S1 in the Supporting Information) also exhibited lower C_{21+} selectivity. The data in Table 1 reveal that the use of mesoporous Y (meso-Y) significantly decreases the selectivity for the undesirable and lighter hydrocarbons, and increases that for diesel fuel. The C_{10-20} selectivity reached 60 % over the Co/Na-meso-Y catalyst, and is significantly higher than the maximum

Table 1: Fischer–Tropsch synthesis over some supported cobalt catalysts.[a]

Catalyst	CO conv. [%]	Hydrocarbon selectivity [%][b]					C_{iso}/C_n[c]
		CH_4	C_{2-4}	C_{5-9}	C_{10-20}	C_{21+}	
Co/SiO_2	37	6.6	5.2	16	44	28	0.3
Co/Al_2O_3	39	4.6	5.9	15	41	33	0.5
Co/H-Y	36	12	14	34	38	3.1	3.2
Co/Na-Y	35	9.7	11	26	46	6.2	0.4
Co/H-meso-Y	42	7.7	11	32	47	2.2	2.7
Co/Na-meso-Y	40	5.0	6.1	17	60	12	0.3

[a] Reaction conditions: catalyst (Co loading, 15 wt %), 0.50 g; 503 K; 2.0 MPa; H_2/CO 1:1; 20 mL min^{-1}; and time on stream is 12 h. [b] The selectivity was calculated on a molar carbon basis. [c] Molar ratio of isoparaffins to *n*-paraffins in C_{5-20}.

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[*] X. Peng,[+] Dr. K. Cheng,[+] Dr. J. Kang,[+] B. Gu, X. Yu,
Prof. Dr. Q. Zhang, Prof. Dr. Y. Wang
State Key Laboratory of Physical Chemistry of Solid Surfaces
Collaborative Innovation Center of Chemistry for Energy Materials
National Engineering Laboratory for Green Chemical
Productions of Alcohols, Ethers and Esters
College of Chemistry and Chemical Engineering
Xiamen University, Xiamen 361005 (China)
E-mail: zhangqh@xmu.edu.cn
wangye@xmu.edu.cn

[+] These authors contributed equally to this work.

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(39 %) expected from the ASF distribution. Moreover, the products over this catalyst were mainly *n*-paraffins, thus favoring the cetane number. Furthermore, our Co/Na-meso-Y catalyst was very stable (Figure 1). After 515 hours of reaction, the CO conversion and $C_{10–20}$ selectivity were 36 and 62 %, respectively, whereas the CH_4 and C_{2-4} selectivities were both as low as about 5 %. This performance is better than that reported for Ru/CNT, a more expensive catalyst which also shows excellent C_{10-20} selectivity.[4] The Co/Na-meso-Y catalyst is very promising for the selective production of diesel fuel from syngas.

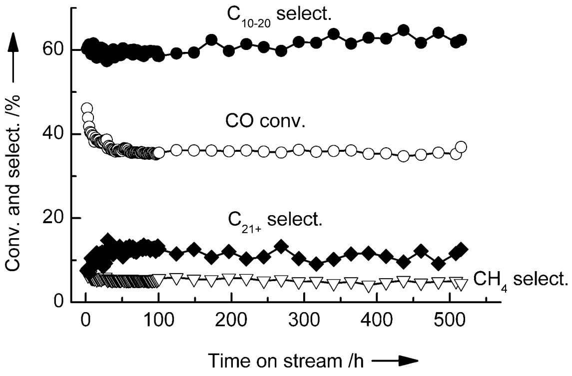

Figure 1. Stability of the Co/Na-meso-Y catalyst in FT synthesis. Reaction conditions: 0.50 g catalyst; 503 K; 2.0 MPa H_2/CO 1:1; 20 mL min^{-1}.

Alkali metal ions were reported as poisons of cobalt-based catalysts for FT synthesis because strong interactions between the alkali metal ions and the cobalt species could decrease the cobalt reducibility.[6] We confirmed the negative effect of the intentionally added Na^+ on the catalytic activity of the Co/SiO_2 (see Table S2). However, the FT activity for our Co/Na-Y or Co/Na-meso-Y catalyst was not low (Table 1). The interaction between Na^+ and the Co species in our catalyst is weak, probably because Na^+ in the cation-exchange positions of Na-Y or Na-meso-Y is mainly located inside the small cage and has interactions with the anionic zeolite framework.[7] The melt infiltration technique that we adopted for the loading of cobalt may also cause weak interactions between the cobalt species and the support.[8] We confirmed that the reduction of the cobalt species over the Co/Na-Y or Co/Na-meso-Y catalyst was not inhibited (see Table S3).

Our NH_3-TPD, pyridine-adsorption FT-IR and ^1H magic-angle spinning (MAS) NMR spectroscopic studies confirmed that no Brønsted acid sites existed for Na-meso-Y and Na-Y (see Figures S1 and S2, and Table S1). It is unusual that the Co/Na-meso-Y catalyst without Brønsted acidity can catalyze the selective formation of $C_{10–20}$ hydrocarbons with decreased C_{21+} selectivity. To unravel the nature of this unique observation, we performed the conversion of *n*-hexadecane, a model compound of heavier hydrocarbons, over our catalysts at the same temperature as that for FT synthesis. As expected, the Co/H-Y and Co/H-meso-Y, having Brønsted acidity, showed higher *n*-hexadecane conversions (Table 2). The main products obtained over the two catalysts were $C_{5–9}$ hydrocarbons with higher fractions of isoparaffins. This observation suggests a hydrocracking/isomerization mechanism involving carbocation intermediates over the catalysts having both metal and Brønsted acid sites.[2b,9] It is of interest that the catalysts without Brønsted acidity in Table 2 can also catalyze the conversion of *n*-hexadecane. In particular, the *n*-hexadecane conversion reached 94 % over the Co/Na-meso-Y catalyst. However, the product distributions were different: CH_4 and $C_{10–15}$ hydrocarbons were the main products when using the catalyst without Brønsted acidity (see Figure S3 for a comparison of detailed product selectivities over Co/H-meso-Y and Co/Na-meso-Y).

Table 2: The conversion of *n*-hexadecane over some supported cobalt catalysts.[a]

Catalyst	n-$C_{16}H_{34}$ conv. [%]	Product selectivity [%][b]				C_{iso}/C_n[c]
		CH_4	$C_{2–4}$	$C_{5–9}$	$C_{10–15}$	
Co/SiO_2	65	14	1.5	7.2	77	0.01
Co/Al_2O_3	58	14	0.6	4.4	81	0.01
Co/H-Y	98	0.9	26	73	0.5	2.7
Co/Na-Y	80	13	0.7	5.5	81	0.01
Co/H-meso-Y	99	0.8	24	65	11	2.2
Co/Na-meso-Y	94	9.4	0.5	4.6	85	0.03

[a] Reaction conditions: catalyst (Co loading, 15 wt %), 1.0 g; 503 K; H_2 at 2.0 MPa; 60 mL min^{-1}; n-$C_{16}H_{34}$ at 0.12 mL h^{-1}; time on stream is 12 h. [b] The selectivity was calculated on a molar carbon basis. [c] Molar ratio of isoparaffins to *n*-paraffins in $C_{5–15}$.

The hydrogenolysis of paraffins (in particular heavier paraffins), which may proceed through adsorbed hydrocarbon radical intermediates, can take place on group VIII metals.[2b,10] The successive demethylation at the terminal C–C bond is known to occur for cobalt-based catalysts, thus forming CH_4 and a heavier fragment.[10,11] The distributions of the products from *n*-hexadecane over the catalysts without Brønsted acidity (Table 2 and Figure S3) suggest a hydrogenolysis mechanism. Although the addition of Na^+ onto the Co/SiO_2 decreased its activity for hydrogenolysis (see Table S4), the Co/Na-meso-Y catalyst with Na^+ in the cation-exchange position showed high hydrogenolysis ability. Interestingly, not only the activity but also the selectivity for *n*-hexadecane hydrogenolysis could be tuned by changing the catalyst. The Co/Na-meso-Y demonstrated the highest C_{10-15} selectivity (Table 2). We speculate that this may account for its outstanding $C_{10–20}$ selectivity in FT synthesis.

The hydrogenolysis may increase the formation of CH_4 and has long been regarded as a negative contribution to FT synthesis.[2b,11,12] Our present work suggests that control of hydrogenolysis may improve the diesel fuel selectivity in FT synthesis. We performed further studies to gain deeper insights into key factors controlling the hydrogenolysis and the role of hydrogenolysis in determining the FT product selectivity.

Our characterizations clarified that the Co/Na-meso-Y catalyst had the smallest mean cobalt size (8.4 nm) among the catalysts in Table 2 (Table S3). This might be responsible for its high hydrogenolysis activity. To unveil the effect of the cobalt particle size, we synthesized Co/Na-meso-Y catalysts with mean cobalt particle sizes ranging from 4.9 to 27 nm, but with similar degrees of cobalt reduction (see Figure S4 and

Table S5). For FT synthesis, the change in the cobalt particle size resulted in a varied product selectivity along with slight changes in CO conversion (Figure 2a). In contrast, the *n*-hexadecane conversion decreased remarkably with an increase in the cobalt particle size (Figure 2b). Thus, the contribution of hydrogenolysis would be smaller in FT synthesis over the catalyst with a larger mean cobalt size, thus leading to higher C_{21+} selectivity. The decrease in the mean cobalt size from 27 to 8.4 nm enhanced the selective hydrogenolysis of *n*-hexadecane to $C_{10\text{-}15}$ hydrocarbons, and thus increased the $C_{10\text{–}20}$ selectivity in FT synthesis. A further decrease in the mean cobalt size from 8.4 to 4.9 nm increased the selectivities to CH_4 and $C_{5\text{-}9}$ and decreased that to $C_{10\text{-}15}$ hydrocarbons in *n*-hexadecane hydrogenolysis. Thus, the higher CH_4 and $C_{5\text{–}9}$ selectivities and the lower $C_{10\text{–}20}$ selectivity observed in FT synthesis over the catalyst with a smaller mean cobalt size should stem from the unselective hydrogenolysis. As a result, a maximum $C_{10\text{–}20}$ selectivity was obtained at a mean cobalt size of 8.4 nm. The phenomenon that a decrease in cobalt size below a critical value (6–10 nm) leads to an increase in CH_4 selectivity and a decrease in C_{5+} selectivity is known for FT synthesis.[1b,13] Our present work suggests that the change in the hydrogenolysis activity and selectivity with cobalt particle size can be one interpretation for this phenomenon.

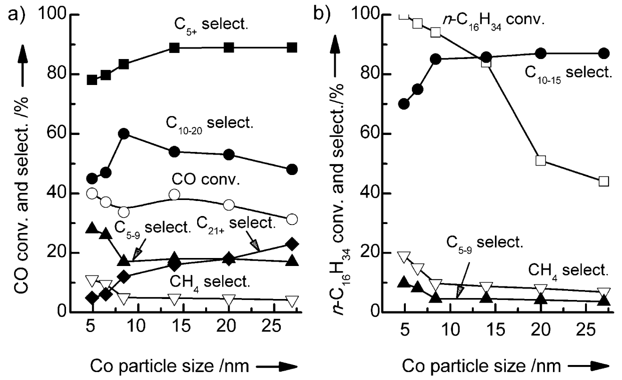

Figure 2. Effect of cobalt particle size on catalytic behaviors of the Co/Na-meso-Y catalysts. a) FT synthesis. b) *n*-$C_{16}H_{34}$ conversion. The reaction conditions for the two reactions are the same as those used for the data collected in Tables 1 and 2.

To extend the insights obtained from the Co/Na-meso-Y catalysts to other catalytic systems, we also prepared the Co/Na-Y and Co/SiO_2 catalysts with different mean cobalt sizes (see Figure S5 and Table S6) and investigated their catalytic behaviors. The smaller cobalt particles favored *n*-hexadecane hydrogenolysis for both series of catalysts (see Table S7). Upon increasing the mean size of the cobalt particles, the selectivity for $C_{10\text{-}15}$ increased and those for CH_4 and $C_{5\text{-}9}$ hydrocarbons decreased (see Table S7). These trends resembled those for the Co/Na-meso-Y catalysts (Figure 2b). However, Co/Na-Y (Co size, 8.4 nm) and Co/SiO_2 (Co size, 7.1 nm), which gave *n*-hexadecane conversions of greater than or equal to 90%, showed significantly higher CH_4 and $C_{5\text{–}9}$ selectivities and lower $C_{10\text{-}15}$ selectivity (Table S7) than those of Co/Na-meso-Y (Co size, 8.4 nm), which had a similar *n*-hexadecane conversion (Table 2). For FT synthesis, only the Co/Na-meso-Y catalyst exhibited significantly enhanced $C_{10\text{–}20}$ selectivity (Figure 3). Furthermore, compared to the ideal ASF distribution with a chain growth probability (α) of 0.9, which was gained by assuming that the $C_{3\text{–}10}$ products over these catalysts followed the ASF rule (Figure S6), the three catalysts showed lower C_{21+} selectivity and higher CH_4 selectivity (Figure 3), thus confirming that the hydrogenolysis occurred in FT synthesis over all these catalysts. The outstanding $C_{10\text{–}20}$ selectivity in FT synthesis and $C_{10\text{–}15}$ selectivity in *n*-hexadecane hydrogenolysis for the Co/Na-meso-Y catalyst may suggest the role of mesoporous structure.

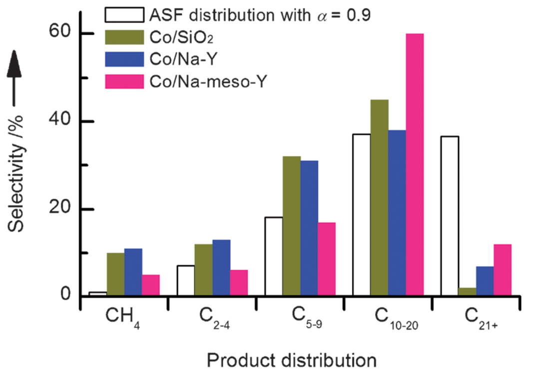

Figure 3. Comparison of product selectivities for FT synthesis over cobalt catalysts loaded on SiO_2, Na-Y, and Na-meso-Y (mean Co sizes = 7.1, 8.4, and 8.4 nm, respectively). The selectivity from ASF distribution (α = 0.9) is also displayed.

We further synthesized Na-meso-Y samples with different mesopore sizes (see Figures S7 and S8, and Table S8) and prepared Co/Na-meso-Y catalysts possessing similar mean cobalt sizes using the Na-meso-Y samples (see Figure S9 and Table S9). Figure 4 shows that the size of the mesopores does not affect CO or *n*-hexadecane conversions but exerts significant influence on product selectivities. The selectivities for CH_4 and $C_{5\text{-}9}$ decreased and that for C_{10+} ($C_{10\text{–}20}$ or $C_{10\text{–}15}$) hydrocarbons increased in both reactions with an increase in

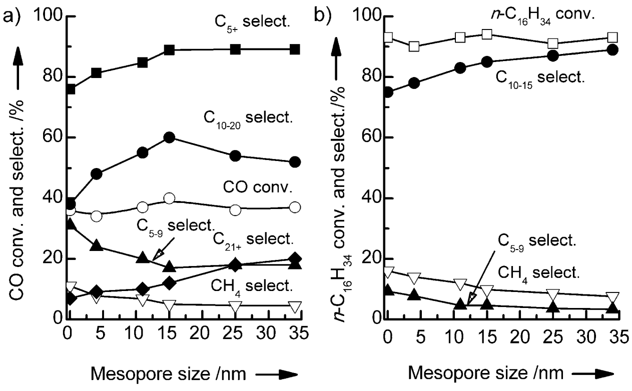

Figure 4. Effect of the size of the mesopores on the catalytic behaviors of the Co/Na-meso-Y catalysts. a) FT synthesis. b) *n*-$C_{16}H_{34}$ conversion. The reaction conditions for the two reactions are the same as those used for the data collected in Tables 1 and 2.

the mesopore size up to 15 nm. We speculate that the increase in the mesopore size accelerates the mass transport and suppresses the successive demethylation. Thus, the mesopores may contribute to tuning the FT product selectivity by influencing the degree of successive demethylation of the heavier primary hydrocarbons. These insights could be extended to Co/SiO_2, a more general catalyst. Our studies for the Co/meso-SiO_2 catalysts, which were prepared using SiO_2 of different mesopore sizes (see Figure S10 and Table S10) and possessed similar mean cobalt sizes (6.6–8.5 nm; Table S10), also showed that the larger pore size favored the C_{10-15} selectivity in *n*-hexadecane hydrogenolysis (see Table S11) and the C_{10-20} selectivity in FT synthesis (see Table S12). However, the enhancement in either the $C_{10–15}$ or $C_{10–20}$ selectivity, by increasing the pore size for the Co/meso-SiO_2, was much less significant than that for the Co/Na-meso-Y catalysts. This outcome suggests that the Co/Na-meso-Y catalyst is unique for selective production of diesel fuel owing to its high selectivity in the hydrogenolysis of heavier hydrocarbons.

In conclusion, we have demonstrated that the hydrogenolysis of heavier hydrocarbons occurs over supported cobalt catalysts under FT reaction conditions and exerts significant effects on the product selectivity. It has been clarified that the cobalt nanoparticle size and the support mesopore size are key factors which determine the activity and selectivity of hydrogenolysis. Our work has provided a first example to significantly enhance the diesel fuel selectivity in FT synthesis by effectively controlling the hydrogenolysis. A maximum C_{10-20} selectivity of about 60 % has been achieved over a Co/Na-meso-Y catalyst with medium-sized cobalt particles and mesopores. The present work also offers possible interpretations of the effects of the cobalt particle size and the support pore size in FT synthesis.

Experimental Section

Mesoporous zeolite Y was synthesized by post-treating zeolite Y with a sequential dealumination and desilication method.[14] The supported Co catalysts were typically prepared by a melt infiltration technique.[8] FT synthesis was performed in a fixed-bed reactor using syngas (H_2/CO 1:1) with a pressure of 2 MPa at 503 K. The conversion of *n*-hexadecane was performed in the same reactor at 503 K under a H_2 pressure of 2 MPa. See the Supporting Information for experimental details.

Keywords: cobalt · heterogeneous catalysis · hydrogenolysis · nanoparticles · zeolites

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