Fischer–Tropsch Synthesis

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Mesoporous Zeolite-Supported Ruthenium Nanoparticles as Highly Selective Fischer–Tropsch Catalysts for the Production of C_5–C_{11} Isoparaffins**

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The Fischer–Tropsch (FT) synthesis is a key step in the transformation of various non-petroleum carbon resources, such as natural gas, coal, and biomass, into clean hydrocarbon fuels or valuable chemicals from syngas (H_2 and CO).[1] Although many catalysts have been developed,[1–8] some challenges still remain in the research area of FT synthesis. Selectivity control is one of the most attractive and difficult challenges.[2c] Over conventional FT catalysts, the hydrocarbon products generally follow the Anderson-Schulz–Flory (ASF) distribution, which is wide and unselective. The development of novel catalysts that can tune product selectivities would significantly improve the FT technology.

It is known that the use of an acidic zeolite as a catalyst support or as a co-catalyst in combination with the conventional FT catalyst can lead to high C_5–C_{11} selectivity owing to the hydrocracking of heavier FT products over the acid sites.[2c,4,9] In these catalytic systems, the primary hydrocarbon products formed on the active FT catalyst can migrate into the micropores of zeolites, where the hydrocracking occurs, and the products must diffuse out of the micropores. The slow transportation of products inside the long micropores of zeolites usually causes over-cracking, leading to high selectivity to undesirable light hydrocarbons (CH_4 and C_2–C_4 alkanes). The strong acidity of zeolites may also cause the over-cracking of hydrocarbon products.

Herein, we present a highly selective Fischer–Tropsch catalyst based on mesoporous zeolites. Hierarchical zeolites, that is, zeolites containing both micro- and mesopores, have attracted much attention as catalyst supports because of their efficient mass-transport property.[10–15] However, to date, there has been no report on the utilization of hierarchical zeolites for FT synthesis. We found that the use of mesoporous ZSM-5 (denoted as meso-ZSM-5), which was prepared by a simple NaOH treatment of H-ZSM-5, as the support could significantly improve the product selectivity of the supported ruthenium catalyst. Compared to cobalt and iron, ruthenium catalysts are known to have some unique features in FT synthesis despite the higher price of ruthenium, and are suitable for fundamental research to gain insights into the key to rational design of catalysts with controlled product selectivity.[2c,7] Herein, we demonstrate that both the mesoporous structure and the unique acidity of the meso-ZSM-5 play crucial roles in tuning the product selectivity in FT synthesis.

X-ray diffraction (XRD) measurements showed that the crystalline structure of ZSM-5 was sustained for the meso-ZSM-5 samples prepared by treating H-ZSM-5 (Si/Al = 26) using NaOH with concentrations of 0–2.0 mol dm^{-3} (0–2.0 M; Supporting Information, Figure S1). Argon physisorption studies confirmed the generation of mesopores in the ZSM-5 after NaOH treatment. The pore-size distributions derived from the Ar adsorption–desorption isotherms (Supporting Information, Figure S2) by using the Horváth–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) methods for the micropores and mesopores are shown in Figure 1. Apart from the micropores with diameters of about 0.55 nm (Figure 1 A),

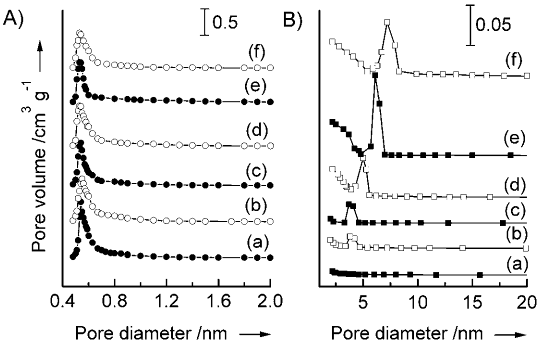

Figure 1. Pore-size distributions derived from the Ar adsorption–desorption isotherms using the HK (A) and the BJH (B) methods for meso-ZSM-5 prepared by NaOH treatment of H-ZSM-5 (Si/Al = 26) at 343 K. NaOH concentrations: a) 0, b) 0.1, c) 0.3, d) 0.5, e) 1.0, f) 1.5 M.

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which is typical for ZSM-5, mesopores with sizes of 3.8–7.2 nm also appeared in the meso-ZSM-5 samples (Figure 1 B). The generation of mesopores was further confirmed by the transmission electron microscopy (TEM) measurements (Supporting Information, Figure S3). The extraction of a small part of framework silicon is expected to occur during the NaOH treatment,[12,13] leading to an interconnected network of micropores and mesopores.

The acidity of the meso-ZSM-5 and of H-ZSM-5 was investigated by ammonia temperature-programmed desorption (NH_3-TPD) studies. Two NH_3 desorption peaks were observed for each sample in the NH_3-TPD experiment, with NH_3 adsorption at 373 K (Figure 2 A). The lower-temperature peak centered at 480–500 K is known to arise from the weakly held (probably hydrogen-bonded) NH_3 molecules, but not the NH_3 molecules on acid sites.[16] For H-ZSM-5, the higher-temperature peak observed at about 720 K can be ascribed to the strong Brønsted acid sites.[16] For our meso-ZSM-5, a peak at 580-605 K, which could be attributed to weaker acid sites, was observed. To eliminate the influence of the weakly held NH_3 molecules, we also measured the acidity by NH_3-TPD with NH_3 adsorption at 473 K. Figure 2 B confirms that the strength of the acidity of the meso-ZSM-5 is significantly weaker than that of H-ZSM-5. The strength of the acid site is slightly dependent on the concentration of NaOH used for the preparation of meso-ZSM-5; the higher NaOH concentration led to slightly weaker acidity.

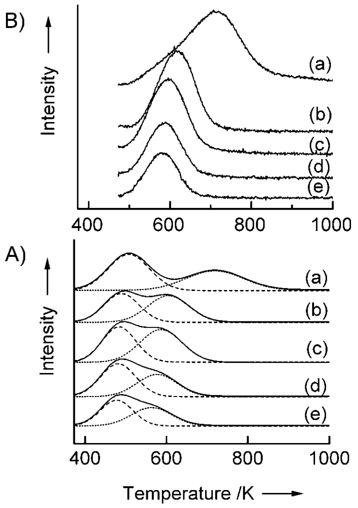

Figure 2. NH_3-TPD profiles for the meso-ZSM-5 prepared by NaOH treatment of H-ZSM-5 at 343 K. A) NH_3 adsorption at 373 K; B) NH_3 adsorption at 473 K. NaOH concentrations: a) 0, b) 0.1, c) 0.5, d) 1.0, e) 1.5 M.

We further investigated the nature of the acid sites over the meso-ZSM-5 by FTIR spectroscopy of adsorbed NH_3. An band at 1455 cm^{-1}, corresponding to the Brønsted acid site,[17] was observed for the H-ZSM-5, but this band became significantly weaker for the meso-ZSM-5, and instead, an IR band at 1635 cm^{-1}, which could be ascribed to the Lewis acid site,[17] clearly appeared (Supporting Information, Figure S4). Thus, Lewis acid sites mainly exist over our meso-ZSM-5 samples.

Ruthenium catalysts loaded on the meso-ZSM-5 were characterized by various spectroscopic techniques. The H_2 temperature-programmed reduction (H_2-TPR) revealed that the ruthenium species in all of the catalysts could be reduced almost completely into metallic ruthenium at 573 K (Supporting Information, Figure S5), which was used for catalyst reduction before reaction. TEM showed that the mean sizes of ruthenium particles in these catalysts were quite similar and were in a range of 6.5–7.7 nm (Supporting Information, Figure S6). The dispersions of ruthenium in these samples evaluated by a H_2–O_2 titration technique[18] were 0.18–0.23 (Supporting Information, Table S1), corresponding to Ru sizes of 7.3–5.7 nm by using the following relationship: ruthenium particle size = 1.32/(ruthenium dispersion).[19] We have demonstrated previously that ruthenium particles with a mean size in this range were beneficial to FT synthesis.[7]

Figure 3 shows the catalytic performances of the meso-ZSM-5-supported ruthenium catalysts (Ru loading 3 wt %) for the conversion of syngas with a H_2/CO ratio of 1.0, which is close to the ratio of syngas derived from coal or biomass. The Ru/H-ZSM-5 catalyst provided a CO conversion of 25 % and selectivities for CH_4, C_2–C_4, C_5–C_{11}, and C_{12}–C_{20} hydrocarbons of 15 %, 37 %, 47 %, and 0.7 %, respectively, and the molar ratio of isoparaffins to *n*-paraffins (denoted as C_{iso}/C_n) in the C_5–C_{11} range was 2.7. The low selectivity to $C_{\geq 12}$ hydrocarbons and the high C_{iso}/C_n values are consistent with the expectation that the acid sites over H-ZSM-5 can catalyze the secondary reactions, that is, hydrocracking and isomerization, but the selectivities to CH_4 and C_2–C_4 alkanes, which are undesirable products, are too high. The use of meso-ZSM-5 as the support significantly decreased the selectivities to CH_4 and C_2–C_4 and increased that to C_5–C_{11} hydrocarbons.

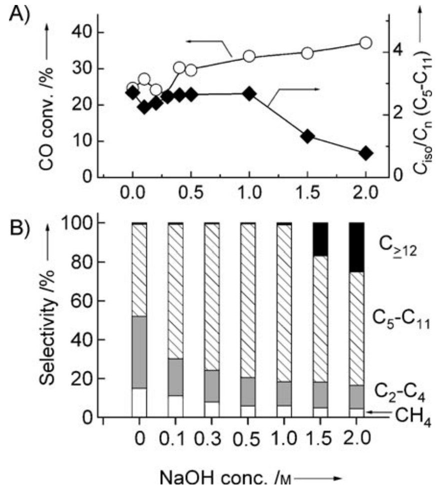

Figure 3. A) CO conversion and C_{iso}/C_n and B) selectivity of Ru catalysts loaded on meso-ZSM-5 prepared by treating H-ZSM-5 with different concentrations of NaOH. Reaction conditions: catalyst 0.5 g, H_2/CO = 1.0, temperature 533 K, pressure 2MPa, total flow rate 20 mL min^{-1}, time on stream 12 h.

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The product selectivity also depended on the concentration of NaOH used for meso-ZSM-5 preparation. For the meso-ZSM-5 prepared using 0.5 or 1.0 M NaOH, the CH_4 and C_2–C_4 selectivities decreased to about 6.0 % and 12–14 %, respectively, while the C_5–C_{11} selectivity increased significantly to about 80 %. Further increases in NaOH concentration to above 1.0 M decreased the selectivity to C_5–C_{11} and increased that to $C_{\geq 12}$ hydrocarbons. CO conversion also increased with a rise in NaOH concentration, possibly owing to the enhanced mass transport in the meso-ZSM-5. The increase in NaOH concentration from 0 to 1.0 M only slightly affected C_{iso}/C_n, but a further increase in NaOH concentration markedly decreased the C_{iso}/C_n. The higher $C_{\geq 12}$ selectivity and the lower C_{iso}/C_n value at NaOH concentrations above 1.0 M can be explained by the weak acidity of these catalysts. In short, the ruthenium catalyst loaded on meso-ZSM-5 prepared using a proper NaOH concentration can produce C_5–C_{11} hydrocarbons with a selectivity of about 80 % at a CO conversion of 30–35 %, and C_{iso}/C_n in the C_5–C_{11} range is about 2.7. To our knowledge, this is the highest selectivity to gasoline-range hydrocarbons achieved to date by FT synthesis.

Our characterizations using H_2-TPR, TEM, and H_2–O_2 titrations suggest that the reduction degree and the ruthenium particle size in the Ru/H-ZSM-5 and the Ru/meso-ZSM-5 catalysts are almost the same. Thus, it is reasonable to conclude that the meso-ZSM-5 itself plays crucial roles in enhancing the C_5–C_{11} selectivity. Our studies have revealed that the main features of the meso-ZSM-5 are the hierarchical porous structure (Figure 1) and the weakened acidity (Figure 2). It is reported that the alkaline treatment of H-ZSM-5 may not significantly decrease the acidity because the alkaline treatment mainly results in the partial desilication.[13] We clarified that the Na^+ ions were exchanged into the cationic sites of the meso-ZSM-5 samples during the NaOH treatment (Na^+ contents were 1.6–1.9 wt % in the meso-ZSM-5; see the Supporting Information, Experimental Details), leading to the decreased acidity. This may also be the reason that the Lewis acid sites mainly exist over our meso-ZSM-5 (Supporting Information, Figure S4). The ion exchanging of the meso-ZSM-5 samples (NaOH concentrations used for preparation: 0.1 and 0.5 M) with NH_4^+ followed by drying and calcination (the obtained samples denoted as H-meso-ZSM-5) could recover or partially recover the strong Brønsted acidity (Supporting Information, Figure S7). Table 1 shows that these H-meso-ZSM-5-supported ruthenium catalysts can also provide higher C_5–C_{11} selectivities (58.8 % and 70.3 %) than the Ru/H-ZSM-5 catalyst (47.2 %). Thus, we believe that the hierarchical structure of the H-meso-ZSM-5-supported catalysts plays a role in enhancing the C_5–C_{11} selectivity by decreasing CH_4 and C_2–C_4 selectivities. However, the ruthenium catalysts loaded on the H-meso-ZSM-5 showed relatively lower C_5–C_{11} selectivities than those loaded on the meso-ZSM-5 with weaker Lewis acidity. This result suggests that the stronger Brønsted acidity may cause over-cracking to C_1–C_4 hydrocarbons, whereas the relatively weaker Lewis acidity of the meso-ZSM-5 is beneficial to the selective production of C_5–C_{11} hydrocarbons during the hydrocracking of primary FT products.

Table 1: Comparison of the catalytic behavior of Ru catalysts loaded on ZSM-5 or meso-ZSM-5 with different acidities and porous structures for FT synthesis.[a]

Catalyst[b]	CO conv. [%]	Selectivity [%]				C_{iso}/C_n
		CH_4	C_{2-4}	C_{5-11}	$C_{\geq 12}$	
Ru/Na-ZSM-5	24.6	5.6	15.3	51.7	27.4	0.8
Ru/H-ZSM-5	24.7	15.0	37.1	47.2	0.7	2.7
Ru/meso-ZSM-5, 0.1 M	27.2	11.2	19.0	69.1	0.7	2.1
Ru/H-meso-ZSM-5, 0.1 M	33.0	14.3	26.8	58.8	0	2.2
Ru/meso-ZSM-5, 0.5 M	29.6	5.9	14.6	79.0	0.5	2.7
Ru/H-meso-ZSM-5, 0.5 M	26.4	7.0	22.7	70.3	0	2.7

[a] Reaction conditions: catalyst 0.5 g, $H_2/CO = 1.0$, temperature 533 K, pressure 2 MPa, total flow rate 20 mL min^{-1}, time on stream 12 h. [b] The concentration given after meso-ZSM-5 or H-meso-ZSM-5 denotes the concentration of NaOH used for meso-ZSM-5 preparation.

Table 2: Comparison of catalytic behaviors of Ru catalysts loaded on ZSM-5 or meso-ZSM-5 with different acidities and porous structures for hydrocracking of *n*-hexadecane.[a]

Catalyst[b]	*n*-$C_{16}H_{34}$ conv. [%]	Selectivity [%]			
		CH_4	C_{2-4}	C_{5-11}	C_{12-15}
Ru/Na-ZSM-5	37.2	0	44.2	54.6	1.2
Ru/H-ZSM-5	99.2	15.7	47.9	36.3	0.1
Ru/meso-ZSM-5, 0.1 M	95.4	7.7	29.5	60.6	2.3
Ru/H-meso-ZSM-5, 0.1 M	99.9	4.9	40.1	54.2	0
Ru/meso-ZSM-5, 0.5 M	99.7	0.1	36.2	63.8	0
Ru/H-meso-ZSM-5, 0.5 M	99.5	1.2	37.8	60.6	0.3

[a] Reaction conditions: catalyst 0.5 g, feed of *n*-$C_{16}H_{34}$ 0.010–0.045 mL min^{-1}, flow rate of H_2 30 mL min^{-1}, temperature 533 K, pressure 2 MPa, time on stream 10 h. [b] The concentration given after meso-ZSM-5 or H-meso-ZSM-5 denotes the concentration of NaOH used for meso-ZSM-5 preparation.

Table 1 also suggests that, as compared to the Ru/Na-ZSM-5, which shows a higher $C_{\geq 12}$ selectivity (27.4 %), the Ru/meso-ZSM-5 catalysts are effective in the hydrocracking of $C_{\geq 12}$ hydrocarbons, although the meso-ZSM-5 samples possess mainly Lewis acidity. To confirm the hydrocracking ability of the Ru/meso-ZSM-5, we performed the conversion of *n*-hexadecane over these catalysts. Table 2 shows that the hydrocracking of *n*-hexadecane proceeds rapidly over the Ru/meso-ZSM-5, whereas the Ru/Na-ZSM-5 showed a remarkably lower hydrocracking activity. This result is possibly due to the difference in the strength of acidity between Na-ZSM-5 and the meso-ZSM-5 (Supporting Information, Figure S7). The product selectivities in the hydrocracking reactions over Ru/meso-ZSM-5 and the Ru/H-meso-ZSM-5 were different from those over the Ru/H-ZSM-5; the C_5–C_{11} selectivity was significantly higher over the former catalysts, particularly Ru/meso-ZSM-5, 0.5 M or Ru/H-meso-ZSM-5, 0.5 M with larger mesopores. Thus, the presence of larger mesopores may play a key role in improving the C_5–C_{11} selectivity in the hydrocracking of *n*-hexadecane. Our observation is consistent with a recent finding that the use of hierarchical zeolite Y containing larger mesopores instead of conventional zeolite Y could decrease the selectivity to light products (C_1–C_5

alkanes) in the hydrocracking of *n*-hexadecane.[20] Mesopores are beneficial for the rapid mass transfer of hydrocracking products, suppressing the consecutive cracking. Moreover, as compared to the H-meso-ZSM-5 possessing stronger acidity, the use of meso-ZSM-5 with weaker acidity afforded higher C_5–C_{11} selectivity in hydrocracking.

In conclusion, we have succeeded in preparing a highly selective Ru/meso-ZSM-5 catalyst for the production of C_5–C_{11} isoparaffins from syngas. The C_5–C_{11} selectivity reaches about 80% with a ratio of isoparaffins to *n*-paraffins of about 2.7. This C_5–C_{11} selectivity is significantly higher than that expected from the ASF distribution (maximum ca. 45%). We propose that the hierarchical porous structure and the unique acidity of the meso-ZSM-5 both play important roles in enhancing the selectivity to C_5–C_{11} and decreasing that to light hydrocarbons (CH_4 and C_2–C_4 alkanes). Using *n*-hexadecane as a model molecule, we have demonstrated that the hydrocracking of heavier hydrocarbons proceeds quickly over our meso-ZSM-5-supported ruthenium catalysts possessing mainly Lewis acidity. The large mesopores and also the weak acidity could suppress the consecutive cracking, leading to significantly high selectivity to C_5–C_{11} hydrocarbons. Using the insights obtained herein, we have very recently succeeded in developing an industrially applicable Co/meso-ZSM-5 catalyst that can similarly catalyze the selective production of C_5–C_{11} hydrocarbons.

Experimental Section

meso-ZSM-5 was prepared using a simple alkaline treatment method. Briefly, after treatment in NaOH aqueous solutions with different concentrations at 343 K, the solid zeolite was recovered by filtration, washing with deionized water, drying, and calcination in air at 573 K. The supported Ru catalysts were prepared by an impregnation method. XRD, Ar physisorption, H_2-TPR, H_2–O_2 titration, TEM, NH_3-TPD and NH_3-adsorbed FT-IR spectroscopic techniques were used for characterizations. FT synthesis was performed on a fixed-bed flow reactor operated at 2 MPa. The products were analyzed by gas chromatography. The selectivity was calculated on a carbon basis. See the Supporting Information for further experimental details.

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