

## Utilization of Microporous and Mesoporous Materials as Supports of Cobalt Catalysts for Regulating Product Distributions in Fischer–Tropsch Synthesis

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The utilization of different types of microporous and mesoporous materials as the supports of cobalt catalyst for Fischer–Tropsch synthesis could produce hydrocarbon fuels with different distributions. Among various catalysts investigated, Co/ $\beta$  and Co/SBA-15 exhibited the highest selectivities to  $C_5$ – $C_9$  (gasoline fuel fraction) and  $C_{10}$ – $C_{20}$  (diesel fuel fraction) hydrocarbons, respectively.

Fischer–Tropsch (FT) synthesis is an important route for the production of hydrocarbon fuels from synthesis gas, which can be derived from coal and natural gas. The studies on catalyst development for the production of synfuels based on FT synthesis have received renewed interest because of the world-wide demand for the decrease in the dependency on oil.<sup>1</sup> Moreover, because the synfuels produced in FT synthesis can be sulfur-free, they may easily meet the stringent environmental requirements.<sup>2</sup> However, the products of FT synthesis usually follow the Anderson–Schultz–Flory distribution determined by the probability of chain growth, and the development of effective catalysts with desired product distributions is a very difficult task.<sup>3</sup> Many studies have indicated that the mean pore diameter of the catalyst support may affect the product distributions of FT synthesis.<sup>4</sup> Microporous and mesoporous materials possess ordered porous structures, and may thus be exploitable for regulating the product distribution. Microporous zeolites such as ZSM-5, NaX, and NaY, and mesoporous materials typified by MCM-41, MCM-48, and SBA-15 have been applied for FT synthesis.<sup>5,6</sup> However, the effect of the types of molecular sieve supports on product distributions still remains ambiguous since almost all of the current investigations focus only on a single molecular sieve as the catalyst support and the systematic comparisons of product distributions among different molecular sieve-supported Co catalysts under the same reaction conditions are very scarce. Moreover, high cobalt loading is generally used in the previous studies for obtaining high activity, but the high loading may cause a large proportion of Co species located outside the ordered pores. The present work aims to compare the catalytic performances of Co catalysts supported on different types of molecular sieves for FT synthesis under the same reaction conditions.

The following microporous materials (sodium-type zeolites) were used in this work: ZSM-5 (Si/Al = 100; pore dimension:  $a$ -axis  $0.55 \times 0.51 \text{ nm}^2$ ,  $b$ -axis  $0.53 \times 0.56 \text{ nm}^2$ ),  $\beta$  (Si/Al = 12.5; pore dimension:  $a$ ,  $b$ -axes  $0.73 \times 0.60 \text{ nm}^2$ ,  $c$ -axis  $0.56 \times 0.56 \text{ nm}^2$ ), mordenite (Si/Al = 9.3, pore dimension:  $0.65 \times 0.70 \text{ nm}^2$ ), and faujasite (NaY, Si/Al = 2.8, pore dimension:  $0.74 \times 0.74 \text{ nm}^2$ ).<sup>7</sup> HY and H-mordenite (hydrogen-type) zeolites prepared by ion-exchange of the Na-type samples with aqueous solution of  $\text{NH}_4\text{NO}_3$  (1 M), followed by drying and cal-

cination at 823 K, were also used as catalyst supports. The crystalline structure of each zeolite was confirmed by X-ray diffraction measurements. Mesoporous molecular sieves with hexagonal regularity including MCM-41 and SBA-15 were synthesized by the hydrothermal synthesis using hexadecyltrimethylammonium bromide and a triblock copolymer ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) as templates under the alkaline and acidic mediums, respectively.<sup>8</sup> A cubic mesoporous material with three-dimensional porous channels (i.e., SBA-1) was synthesized according to the procedure reported previously.<sup>9</sup> In each case, after the hydrothermal synthesis, the resultant solid was filtered, washed, dried, and finally calcined at 823 K in air.  $\text{N}_2$ -sorption measurements showed that the MCM-41, SBA-15, and SBA-1 synthesized here possessed sharp pore diameter distributions with the maxima at 3.2, 5.2, and 2.1 nm, respectively. The loading of cobalt was carried out using the conventional impregnation method. A low loading amount (5 wt %) was adopted to ensure the incorporation of most of the cobalt into the pores of molecular sieves. XRD measurements confirmed that the ordered porous structures of the MCM-41, SBA-15, and SBA-1 were sustained after the incorporation of Co.

FT synthesis was carried out with a fixed-bed reactor operated at 2.0 MPa. The catalyst (0.8 g) loaded in the reactor was first reduced in  $\text{H}_2$  flow at 673 K for 6 h. Then, a  $\text{H}_2$  and CO gas mixture ( $\text{H}_2/\text{CO} = 2$ ,  $20 \text{ mL min}^{-1}$ ) containing 4% Ar (as an internal standard) was introduced into the reactor after the temperature was decreased to 523 K. The products with carbon numbers lower than 5 were analyzed by on-line gas chromatography using Porapak Q and Molecular Sieve 5A as columns, and those with larger carbon numbers ( $\text{C}_6^+$ ) were collected by a cold trap during a 10-h reaction and were analyzed by a gas chromatograph equipped with a capillary column (AT PONA) and a flame ionization detector.

Table 1 compares the catalytic properties of cobalt catalysts using various types of microporous and mesoporous materials as the supports. As a reference, the catalytic result over the cobalt catalyst supported on a non-porous fumed silica (Cab-O-Sil) was also shown in Table 1. The Co/Cab-O-Sil showed rather broad product distributions. Hydrocarbons with  $\text{C}_1$ – $\text{C}_{30}$  were all produced and the selectivity to  $\text{C}_{21}^+$  (wax fraction) was approximately 25% over this catalyst under our reaction conditions. When molecular sieves were applied as the supports for cobalt, the selectivity to  $\text{C}_{21}^+$  decreased significantly and became lower than 1.0% in many cases. It is of particular interest to note that the pore dimensions of the molecular sieve supports exert a significant influence on the product distributions. The microporous material-supported catalysts exhibited lower selectivities to  $\text{C}_{10}$ – $\text{C}_{20}$  but higher ones to  $\text{C}_5$ – $\text{C}_9$  hydrocarbons except for the Co/Na-mordenite. When zeolite  $\beta$  was used as the support, the

**Table 1.** Catalytic performances of Co catalysts supported on various molecular sieves for FT synthesis

Catalyst <sup>a</sup>	CO conversion /%	Selectivity/% <sup>b</sup>				$\alpha^c$
		C <sub>1</sub> –C <sub>4</sub>	C <sub>5</sub> –C <sub>9</sub>	C <sub>10</sub> –C <sub>20</sub>	C <sub>21</sub> <sup>+</sup>	
Co/Na-ZSM-5	78	38	43	15	<1.0	0.53
Co/Na-beta	47	29	48	22	<1.0	0.60
Co/Na-mordenite	43	35	19	34	8.0	0.88
Co/H-mordenite	39	29	46	24	<1.0	0.72
Co/NaY	47	34	39	24	1.1	0.77
Co/HY	41	35	37	27	<1.0	0.74
Co/SBA-1	61	26	31	38	2.4	0.83
Co/MCM-41	86	30	37	30	<1.0	0.79
Co/SBA-15	92	20	36	40	<1.0	0.81
Co/Cab-O-Sil <sup>d</sup>	41	16	28	31	~25	0.83

<sup>a</sup>Cobalt content was 5.0 wt % except for Co/Cab-O-Sil. <sup>b</sup>Other products were mainly CO<sub>2</sub>. <sup>c</sup> $\alpha$  is the chain growth probability and has been evaluated from the slope of the curve of  $\ln M_n$  versus  $n$ , where  $M_n$  and  $n$  are the molar fraction of each hydrocarbon product and the carbon number, respectively. <sup>d</sup>Cobalt content was 2.0 wt %.

selectivity to C<sub>5</sub>–C<sub>9</sub> hydrocarbons could reach 48%. The Co/NaY and Co/HY did not show distinct differences in product distributions as well as CO conversions. However, as compared with the Co/Na-mordenite, the Co/H-mordenite exhibited a significantly higher selectivity to C<sub>5</sub>–C<sub>9</sub> hydrocarbons at the expense of those to C<sub>10</sub>–C<sub>20</sub> and C<sub>21</sub><sup>+</sup>. Thus, the porous structure and the acidity of zeolite support may both affect the product distributions. On the other hand, the mesoporous molecular sieve-supported Co catalysts favored the formation of C<sub>10</sub>–C<sub>20</sub> hydrocarbons. We obtained the highest selectivity to C<sub>10</sub>–C<sub>20</sub> hydrocarbons over the Co/SBA-15 catalyst.

We have characterized the Co/beta and Co/SBA-15 with XRD, TEM, and H<sub>2</sub>-TPR. The reduction degrees evaluated on the basis of H<sub>2</sub>-TPR were 33 and 69% at 673 K for the Co/beta and Co/SBA-15, respectively. For both catalysts before reduction, our characterization results suggest that a large proportion of cobalt species are located in the porous channels of zeolite beta or SBA-15. This allows us to suggest that the effect of the pore dimensions on the product distributions observed here may stem from the limitation of the reaction spaces to some extent. The limitation of the reaction spaces may restrain the growth of the carbon chain, and thus inhibits the formation of hydrocarbons with carbon numbers larger than 20 for all the molecular sieve-supported catalysts listed in Table 1. For the zeolite-supported catalysts, the secondary conversions of C<sub>10</sub>–C<sub>20</sub> and C<sub>21</sub><sup>+</sup> to C<sub>5</sub>–C<sub>9</sub> hydrocarbons may also occur in addition to the restraint of the reaction space. The acidity of the zeolite may affect such secondary transformations as observed in the case of Co/H-mordenite. It should be noted that a few recent papers have reported that the coating of a zeolite membrane on Co/SiO<sub>2</sub> or the combination of Co/SiO<sub>2</sub> with Pd/beta can lead to the formation of middle isoparaffins with high selectivities.<sup>10</sup> In our case, we also found that the proportion of *n*-paraffins in the hydrocarbon products tended to be lower when the zeolite-supported catalyst was used.

In summary, we have found that the use of different types of molecular sieves as supports of cobalt catalysts can modify the product distributions of FT synthesis. In general, zeolites favor the production of C<sub>5</sub>–C<sub>9</sub> hydrocarbons (gasoline fuel fraction), whereas the mesoporous materials are promising for the production of diesel fraction synfuels (C<sub>10</sub>–C<sub>20</sub> hydrocarbons).

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