

Pore size-controlled synthesis of molecular sieves and their difference in catalytic properties for Fischer–Tropsch synthesis

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Received: 7 February 2015 / Accepted: 8 April 2015 / Published online: 17 May 2015
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Abstract Three molecular sieves with different pore size distributions, i.e., mesopore (Al-MCM-41), micropore (ZSM-5) and hierarchical pore (HPMS), were synthesized under hydrothermal condition and characterized by N₂ adsorption–desorption. Three cobalt-loaded catalysts, i.e., Co/Al-MCM-41, Co/ZSM-5 and Co/HPMS, were prepared by impregnating cobalt nitrate onto three molecular sieves, respectively, and characterized by X-ray diffraction, scanning electron microscopy, and H₂ temperature-programmed reduction (H₂-TPR). The H₂-TPR results show that the reduction temperature of Co/HPMS is lower than those of Co/Al-MCM-41 and Co/ZSM-5, indicating that Co/HPMS has a better catalytic activity. The selectivity of three catalysts for Fischer–Tropsch synthesis was evaluated in a fixed-bed reactor, and the results show that the pore structure is of important influence on the product distribution. Co/HPMS exhibits significantly good selectivity of C_{5–11} and C_{12–18} hydrocarbons (up to 25.6 and 27.7 %, respectively), much higher than those of Co/Al-MCM-41 and Co/ZSM-5, due to the confinement effect of micropore and good diffusibility for long-chain hydrocarbons of mesopore in Co/HPMS.

Keywords Hierarchical porous molecular sieve · Fischer–Tropsch synthesis · Cobalt-based catalyst

Introduction

The limited reserves of crude oil and sudden/large changes of oil price caused by unpredictable oil crises seriously impact on the economic development of the society. Hence, seeking an alternative way to produce liquid fuels is necessary. Conversion of coals, natural gas and/or biomass to liquid hydrocarbons via gasification and subsequent Fischer–Tropsch synthesis (FTS) is an attractive method to obtain high-quality liquid fuels. Furthermore, FTS-derived fuels have excellent combustion properties and lead to a reduction of pollution emission [1, 2]. Unfortunately, FTS could produce a wide range of hydrocarbons, such as gaseous hydrocarbons, gasoline, diesel and wax depending on catalyst and reaction conditions [3, 4]. The Anderson-Schulz-Flory (ASF) distribution for FTS was put forward to predict the fraction of product at each carbon number [5, 6]. According to ASF distribution, the maximum selectivity for gasoline-range products is *ca.* 48 % [7]. Hence, the selectivity of the catalyst should be the key parameter to be optimized for FTS, and the enhancement of C₅₊ selectivity and suppression of methane selectivity are quite crucial [8].

Some drawbacks of common porous supports, such as low hydrothermal stability of mesoporous molecular sieve (e.g., Al-MCM-41) and narrow pore structure of microporous zeolite (e.g., ZSM-5), limit their application in FTS. Hierarchical porous molecular sieve (HPMS) has regular structure and high hydrothermal stability, and could overcome the drawbacks of Al-MCM-41 and ZSM-5. Hence, it is an important approach to control the FTS product distribution via suitable catalyst using HPMS as a

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support. Coppens et al. [9] pointed out that hierarchically structured porous supports are of great importance to catalysis because the pore texture at different length scales can be beneficial to reduce the transport limitations of catalyst.

Since the discovery of FTS in 1923, the common-used catalysts are Co [3, 6–8, 10], Fe [5, 11, 12], Ru [13–15], and bimetallic Co and Fe [16, 17]. Due to their good activity and selectivity, Co-loaded catalysts are often the choice for the low-temperature FTS [2, 10]. In this paper, three Co-loaded catalysts (i.e., Co/Al-MCM-41, Co/ZSM-5 and Co/HPMS) with different pore size distributions (PSDs) were prepared and the influence of PSD on the catalytic properties for FTS was preliminarily investigated.

Experimental

Synthesis of HPMS

16 g tetrapropylammonium hydroxide (TPAOH) and *ca.* 0.36 g aluminium isopropoxide (AIP) were dissolved into 95 g deionized water, and then magnetically stirred for 2.5 h to obtain a solution. 32 mL tetraethoxysilane (TEOS) was added into the solution, and then stirred for 24 h to afford a precursor solution A (PS_A).

About 2.3 g NaOH was dissolved into 210 g deionized water to give an alkaline solution, and then *ca.* 6.3 g cetyltrimethylammonium bromide (CTAB) was put into the alkaline solution under stirring for 0.5 h to gain a transparent, slightly bubble solution B (BS_B). The BS_B was slowly added into the PS_A, and then stirred for 4 h to give a white gel. The white gel was transferred into a Teflon-lined autoclave, and then heated to 373 K for 24 h and subsequently heated to 453 K for 48 h. After the autoclave was cooled to room temperature, the reaction mixture was filtrated. The resulting filter cake was repeatedly washed with distilled water to remove the excess Na⁺, dried at 353 K for 24 h and then calcined in air at 773 K for 6 h to afford HPMS.

Synthesis of ZSM-5 and Al-MCM-41

About 0.8 g NaOH was placed into the PS_A and then stirred for 4 h. The resulting solution was heated to 373 K for 48 h and then filtrated to afford a filter cake 1 (FC₁).

6.3 g CTAB was added into 310 mL, 0.42 mol L⁻¹ NaOH aqueous solution and then stirred for 0.5 h to afford a solution. 30 g TEOS was added into the solution and stirred for 12 h, and then *ca.* 0.36 g AIP was placed into the solution and stirred for 2.5 h to afford a white gel. The gel was heated to 413 K for 48 h and then filtrated to obtain a filter cake 2 (FC₂).

The FC₁ and FC₂ were repeatedly washed with distilled water, dried at 353 K for 24 h and then calcined at 773 K for 6 h to afford ZSM-5 and Al-MCM-41, respectively.

Preparation of Co/HPMS, Co/ZSM-5 and Co/Al-MCM-41

The catalysts were prepared by impregnating cobalt nitrate onto HPMS, ZSM-5 and Al-MCM-41, respectively. The weight ratio of metallic cobalt to each support is 15 %. After impregnation, three resulting mixtures were dried at 373 K for 24 h and calcined in air at 673 K for 6 h to give Co/HPMS, Co/ZSM-5 and Co/Al-MCM-41, respectively.

Characterization

The textural properties of supports were carried out on a Gold APP V-sorb 4800P N₂ adsorption/desorption analyzer at 77 K. The PSD and specific area were calculated by the density functional theory (DFT) and Brunauer–Emmett–Teller (BET) method, respectively. The total pore volume was determined by converting the amount of N₂ adsorbed at the relative pressure of 0.99 to the volume of liquid adsorbate.

The X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku RINT 2000 X-ray diffractometer with a Cu K α radiation. The tube current and voltage are 100 mA and 40 kV, respectively. The scanning rate and step-length are 5° min⁻¹ and 0.02°, respectively. Scanning electron microscopy (SEM) was conducted using a Hitach S-4500 scanning electron microscope with an accelerating voltage of 20 kV. Temperature-programmed reduction with hydrogen (H₂-TPR) was carried out using a Micromeritics Auto-Chem 2920 instrument with a thermal conductivity detector. 1 g catalyst was loaded and pre-treated under N₂ at 423 K for 2 h. After cooling to room temperature, the catalyst was heated to 1073 K at the rate of 20 K min⁻¹ under H₂ atmosphere.

The catalytic performance for FTS was tested in a fixed-bed reactor (10 mm inner diameter and 500 mm length). About 0.8 g catalyst was diluted with 3.2 g carborundum, placed into the reactor, and then reduced by H₂ at 673 K for 6 h and subsequently cooled to 393 K under H₂ flow. The CO and H₂ with volume ratio of 1:2 were reacted in the reactor under 2 MPa and 513 K. The vent gas was analyzed with an Agilent 7820A gas chromatograph.

Results and discussion

PSD of the supports

Figure 1 shows N₂ adsorption/desorption isotherms of ZSM-5, Al-MCM-41 and HPMS. All of isotherms belong to type IV. ZSM-5 is a microporous molecular sieve with a few mesopores. By contrast, Al-MCM-41 is a mesoporous molecular sieve with a few microporous. As for HPMS, the

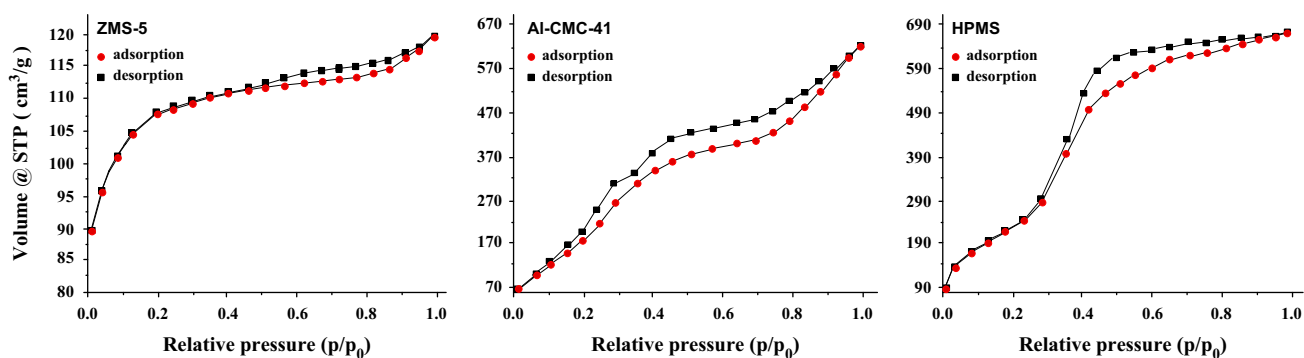


Fig. 1 Adsorption/desorption isotherms of N_2 on three supports

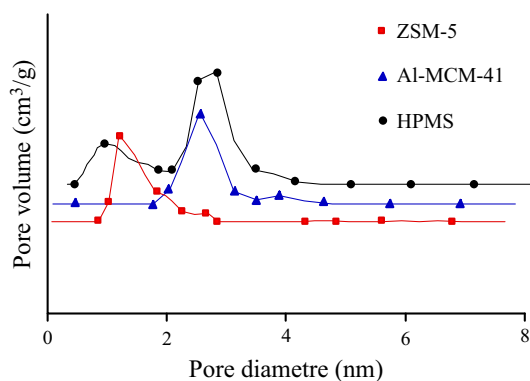


Fig. 2 PSDs of three supports

Table 1 Textural parameters of three supports

Support	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
ZSM-5	382.4	0.178	1.85
Al-MCM-41	1167.6	1.035	2.86
HPMS	1010.6	1.856	2.69

step rise in the range of $0 < P/P_0 < 0.3$ corresponds to filling of micropores with N_2 and the sharp inflection in the range of $0.3 < P/P_0 < 0.8$ indicates the capillary condensation of N_2 in mesopores. These facts indicate HPMS is a typical micro-mesoporous material.

The PSDs of HPMS, ZSM-5 and Al-MCM-41 were calculated from the adsorption branch of the N_2 sorption isotherms using the DFT model and displayed in Fig. 2. The pore sizes of ZSM-5 and Al-MCM-41 are *ca.* 1.85 and 2.86 nm, respectively. HPMS has two kinds of pore size, i.e., around 1.5 and 3.0 nm, with the average pore size of *ca.* 2.69 nm. Hence, HPMS is a molecular sieve with micropore and mesopore at the same time.

Texture properties of HPMS, ZSM-5 and Al-MCM-41 are listed in Table 1. The BET surface areas of HPMS,

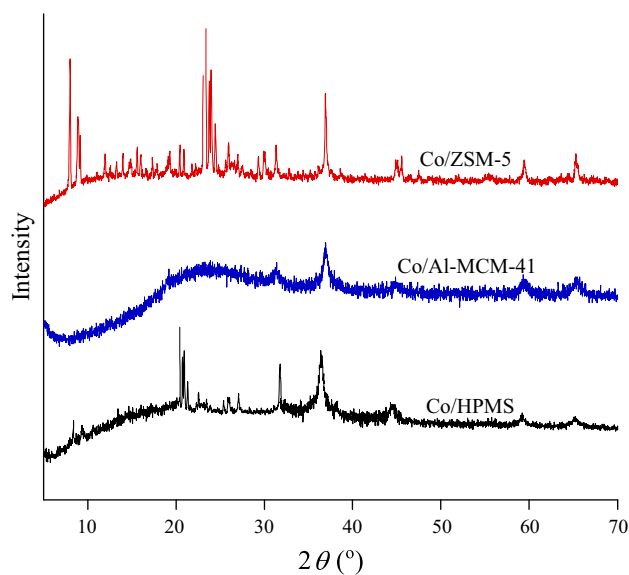


Fig. 3 XRD patterns of three cobalt-loaded catalysts Co/ZSM-5 Co/HPMS

ZSM-5 and Al-MCM-41 are 1010.6, 382.4 and 1167.6 m^2/g , respectively. The specific pore volume of HPMS is much higher than those of ZSM-5 and Al-MCM-41, which is beneficial to loading process of the Co-based precursor and diffusion of reaction products.

XRD analysis of the catalysts

As shown in Fig. 3, all the catalysts present the diffraction peaks at $31.2, 36.8, 44.8, 59.4$ and 65.3° , suggesting that the catalysts contain the face-centered cubic spinel of crystalline Co_3O_4 . The Co/ZSM-5 shows the strongest cobalt diffraction peak, while Co/Al-MCM-41 shows the weakest one, which is probably caused by partial collapse of the periodic mesoporous structure during cobalt loading process. The intense diffraction peaks exist in Co/HPMS at $23.1, 23.9$ and 25.5° , which is characteristic of the long-range ordered ZSM-5 structure.

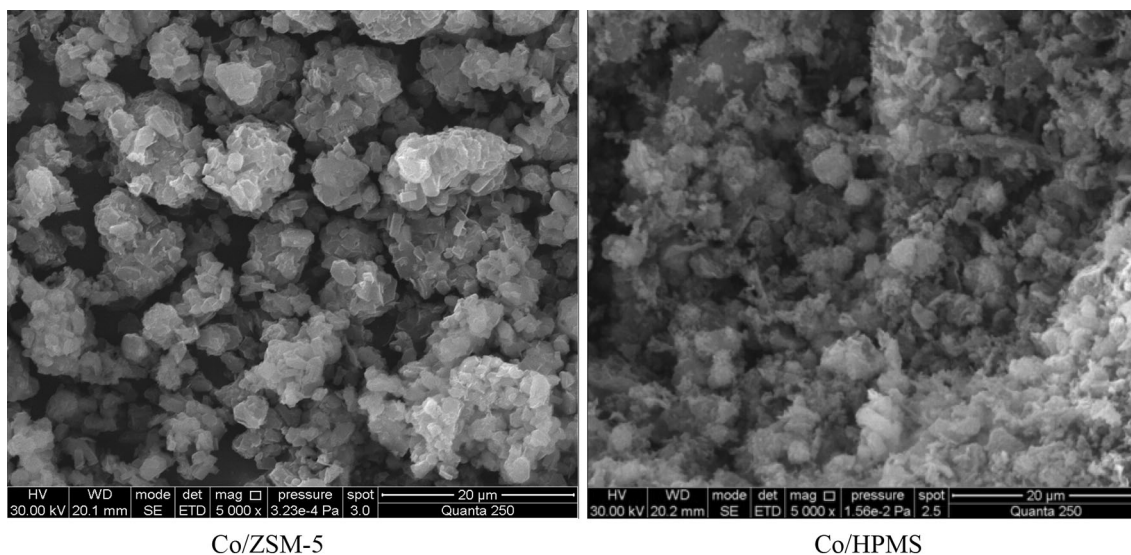


Fig. 4 SEM images of Co/ZSM-5 and Co/HPMS

The morphology of the catalysts

Figure 4 displays the morphologies of Co/ZSM-5 and Co/HPMS. Co/ZSM-5 shows a uniform rod-like crystalline phase, while Co/HPMS has a quite different morphology. The SEM pictures indicate that the HPMS should not be the aggregates of ZSM-5 or mechanical mixture of ZSM-5 and mesoporous molecular sieve. It could be assumed that mesoporous channel in Co/HPMS should be assembled by the microporous structure unit. Hence, Co/HPMS have higher thermal stability and stronger acidity than conventional amorphous mesoporous materials.

H₂-TPR analysis of the catalysts

As Fig. 5 shows, two distinct reduction peaks at around 400 and 610 °C in Co/Al-MCM-41 are related to the reduction reactions of $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ and $\text{CoO} \rightarrow \text{Co}$, respectively. This result indicates the existence of a high metal–support interaction in Co/Al-MCM-41. The reduction temperature of the cobalt oxide in Co/HPMS is *ca.* 390 °C and slightly lower than that of Co/ZSM-5. These facts indicate that Co/HPMS has a weak metal–support interaction and absence of the hardly reducible cobalt phase.

Catalytic activity of the catalysts for FTS

As displayed in Fig. 6, the CO conversion yield over Co/HPMS at 230 °C is obviously higher than those of Co/Al-MCM-41 and Co/ZSM-5. The high CO reactivity over Co/HPMS could highly depend on the relatively high dispersion of the cobalt active phase which results in a high

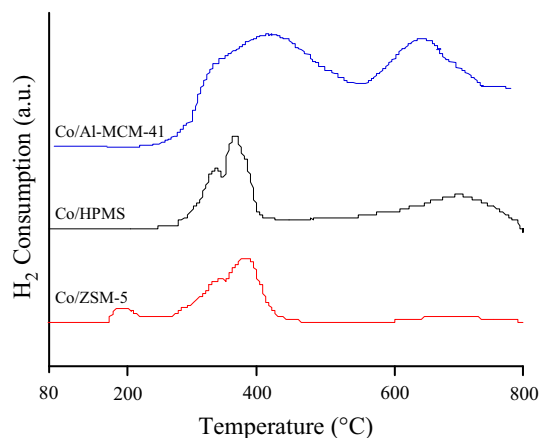


Fig. 5 H₂-TPR curves of three cobalt-loaded catalysts

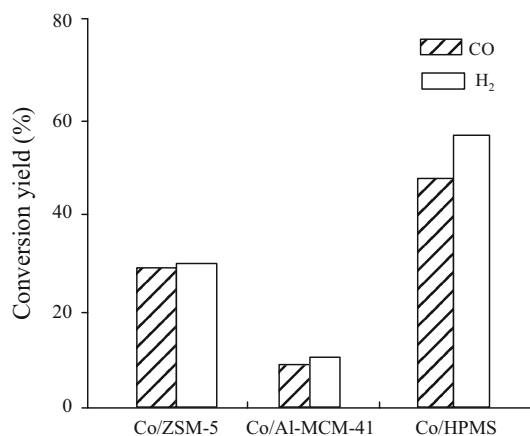


Fig. 6 Conversion yields of CO and H₂ over different catalysts

Table 2 Selectivity of three cobalt-loaded catalysts for FTS

Catalyst	S(C ₁) (%)	S(C _{2–4}) (%)	S(C _{5–11}) (%)	S(C _{12–18}) (%)	S(C ₁₈₊) (%)
Co/ZSM-5	67.39	14.91	10.22	6.76	0.71
Co/Al-MCM-41	6.16	6.82	13.17	25.11	48.74
Co/HPMS	23.45	6.04	25.55	27.71	17.25

Reaction conditions: 2 Mpa, 230 °C, H₂/CO molar ratio of 2, gas hourly space velocity of 1102 h⁻¹

active surface and low reduction temperature of Co/HPMS. Co/Al-MCM-41 with the highest reduction temperature is difficult to be reduced due to the strong metal–support interaction. Hence, the CO conversion yield over Co/Al-MCM-41 is the lowest.

Selectivity of the catalysts for FTS

Table 2 lists the hydrocarbons selectivity of Co/HPMS, Co/Al-MCM-41 and Co/ZSM-5. Methane and C_{2–4} hydrocarbons selectivities of Co/HPMS are 23.45 and 6.04 %, respectively, which are obviously lower than those of Co/ZSM-5 (67.39 and 14.91 %, respectively). C_{5–18} hydrocarbons selectivity of Co/HPMS is 53.26 %, which is much higher than that of Co/ZSM-5 (16.98 %). Additionally, Co/Al-MCM-41 has the lowest methane selectivity and the highest C₁₈₊ selectivity mainly due to its large pore size. However, CO conversion yield over Co/Al-MCM-41 is less than 10 %, quiet lower than that of Co/HPMS (*ca.* 55 %). The results suggest that Co/HPMS is a suitable catalyst for FTS. To be concluded, the PSD has a significant influence on product selectivity of catalyst.

Conclusions

Three molecular sieves with different PSDs, including Al-MCM-41, ZSM-5 and HPMS, were prepared under hydrothermal condition. Pore size of HPMS is mainly distributed at *ca.* 1.5 and 3.0 nm. PSD of the catalyst seriously impact on the catalytic selectivity. C_{5–18} hydrocarbons selectivity of Co/HPMS is 53.26 %, far higher than that of Co/ZSM-5 (16.98 %). The prepared catalyst with hierarchical pore could enhance well the selectivity of gasoline and diesel, which provide a promising way to produce high-quality fuels.

Acknowledgments This work was subsidized by National Natural Science Foundation of China (Grant 21106177).

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