



# Effect of hierarchical crystal structures on the properties of cobalt catalysts for Fischer–Tropsch synthesis



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## HIGHLIGHTS

- Mesoporous zeolites as FT supports were synthesized using double-template method.
- The catalyst with bimodal crystal structure showed higher C<sub>5–18</sub> selectivity.
- Higher C<sub>5–12</sub> selectivity over Co/ZSM-5 catalyst and higher C<sub>12–18</sub> selectivity over Co/SBA-15 catalyst were observed.
- Co loaded on hierarchical crystalline zeolite showed the lowest deactivated rate.

## ARTICLE INFO

### Article history:

Received 23 October 2015

Received in revised form 12 January 2016

Accepted 13 January 2016

Available online 21 January 2016

### Keywords:

Fischer–Tropsch synthesis

Hierarchical zeolites

Crystalline

Cobalt catalyst

## ABSTRACT

Mesoporous ZSM-5 was synthesized using double-template method and its application in Fischer–Tropsch synthesis (FTS) was studied. By comparison, ZSM-5 and SBA-15 were also prepared. The results demonstrated that the catalysts with bimodal structure and moderate acidity showed higher C<sub>5–18</sub> selectivity with relatively lower CH<sub>4</sub> selectivity, while higher C<sub>5–12</sub> selectivity over Co/ZSM-5 catalyst and higher C<sub>12–18</sub> selectivity over Co/SBA-15 catalyst were observed, respectively. Cobalt loaded on crystalline mesoporous ZSM-5 showed the lowest deactivated rate, which suggested that such bimodal structure was favor to the stabilization of cobalt particles. As a result of lower hydrothermal stability of mesoporosity, Co/SBA-15 catalyst had the fastest deactivation.

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## 1. Introduction

Fischer–Tropsch synthesis is an important technology for the transformation of various non-petroleum carbon resources into clean fuels, which has attracted great research interest due to the decline of petroleum reserves and requirement for clean fuels in recent years. Because of the high stability, high selectivity to linear paraffins, low water–gas shift (WGS) activity, and relatively low price, Co-based catalysts are often the choice for low temperature FTS [1,2].

Recently, zeolites with hierarchically porous structures have gained much attention. Because they combine the catalytic features of micropores and the improved accessibility for molecular transport within several porosities in a whole body, more effective solution to the mass transport problem can be offered compared

with conventional zeolites in catalyzed reactions [3–5]. Many hierarchically structured zeolitic materials have been successfully synthesized and used as novel supports in many catalytic reactions [6–9]. For example, Zhu et al. [10] investigated propanal converted into gasoline-range molecules over a series of HZSM-5 catalysts with controlled mesoporosity generated by desilication. Increasing the extent of desilication gradually reduced the aromatization and cracking reactions due to a reduction in the fraction of micropores and in the diffusion path length. Mildly desilicated samples exhibited the best stability on stream and inhibited coke formation. Wang et al. reported that the use of mesoporous ZSM-5 [11] and Beta [12] as supports could significantly improve product selectivity of a supported ruthenium catalyst in FTS. Ru/meso-ZSM-5 catalyst exhibited a higher selectivity for C<sub>5–11</sub> isoparaffins from syngas than that expected from the Anderson–Schulz–Flory (ASF) distribution. These results demonstrated that the support with mesoporous structure and moderate acidity played key roles in tuning the product selectivity in FTS. However, alkali post-treatment was used to prepare hierarchical zeolites, which usually

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generated isolated mesopores by extracting Si atoms in the framework [13–17] and easily resulted in irregular porous structure [11,18,19]. Therefore the design of multimodal porous zeolite with ordered and crystalline structures still remains a great challenge and its application in catalysis is evidently desirable. Here, the aim was to provide an efficient strategy to synthesize hierarchical zeolites with different mesopore sizes adjusted by using soft templates, and then their applications in FTS were studied. Meanwhile, ZSM-5 and SBA-15 were also applied for comparison.

## 2. Experimental

### 2.1. Sample preparation

All the reagents, including tetrapropylammonium hydroxide (TPAOH, 25 wt.%), aluminum isopropoxide (AIP, AR), tetraethylorthosilicate (TEOS, AR), cetyltrimethylammonium bromide solution (CTAB, AR), were purchased from Sinopharm Chemical Reagent Company (China). PEO–PPO–PEO (P123) was purchased from Aldrich.

ZSM-5 was prepared as follows: first, 2.409 g of sodium aluminate were dissolved in 37.8 ml of tetrapropylammonium hydroxide solution (25%), together with 65.5 ml of water and 0.191 g of sodium hydroxide, 20.2 g of TEOS were added to this solution. The suspension obtained was maintained under mechanical agitation for 2 h. The mixture was heated at 413 K and kept at this temperature for 72 h in hydrothermal vessel. The obtained solid by centrifugation was washed with deionized water and then dried at 333 K for 12 h. The sample was then calcined at 823 K for 5 h. Ion exchange was performed using 1 M solution of  $\text{NH}_4\text{NO}_3$  at 353 K for 4 h by two consecutive similar processes. After the ion exchange, the zeolite was filtered and washed with enough deionized water and after that dried in oven at 363 K overnight,  $\text{NH}_4$ -zeolite was calcined in the static air at 773 K for 3 h to obtain H-ZSM-5.

Mesoporous ZSM-5 was prepared as the similar procedure of ZSM-5. The difference is that cetyltrimethylammonium bromide solution (CTAB), prepared with CTAB/TEOS molar ratio of 0.1 and 0.2, respectively, was added after homogenization of mixtures at initial stage and continued to be agitated for 2 h at room temperature. The synthesized materials were named as MZ-1 and MZ-2 corresponding to CTAB/TEOS molar ratio of 0.1 and 0.2, respectively. In the other sample preparation, 2.409 g of sodium aluminate were dissolved in 37.8 ml of tetrapropylammonium hydroxide solution (25%), together with 65.5 ml of water and 0.191 g of sodium hydroxide, 20.2 g of TEOS were added to this solution in one beaker. A certain amount of CTAB and PEO–PPO–PEO (P123) with 210.5 g of water was added in another beaker, maintained under mechanical agitation for 2 h. Two solutions were mixed and agitated for 24 h. After that, they were heated at 413 K for 72 h in hydrothermal vessel. The obtained solid by centrifugation was washed with deionized water and then dried at 333 K for 12 h. The sample was then calcined at 823 K for 5 h. Ion exchange was performed using 1 M solution of  $\text{NH}_4\text{NO}_3$  at 353 K for 4 h by two consecutive similar processes. After the ion exchange, the zeolite was filtered and washed with enough de-ionized water and after that dried in oven at 363 K overnight,  $\text{NH}_4$ -zeolite was calcined in the static air at 773 K for 3 h to obtain meso-H-zeolite named as MZ-3.

SBA-15 was synthesized according to the procedure: 4.0 g of P123 was stirred with 30 ml of deionized water, 30 g of 2 M HCl solution and 4.4 g of TEOS at 303 K for 24 h, then transferred into a Teflon bottle heated at 373 K for 24 h. The solid was filtered, washed and calcined at 773 K for 4 h.

The supported cobalt catalysts were prepared by initial wetness impregnation method. 3.0 g of different supports were completely wetted with deionized water to evaluate the corresponding volume. Then, cobalt nitrate was dissolved into the required deionized water to impregnate the supports with the loading of 15 wt.%. The catalysts were then dried under temperature of 333 K and calcined at 673 K for 4 h. The obtained catalysts were named Co/ZSM-5 catalyst, Co/MZ-1 catalyst, Co/MZ-2 catalyst, Co/MZ-3 catalyst, Co/SBA-15 catalyst, respectively.

### 2.2. Characterization

The textural properties of catalysts were determined by nitrogen adsorption, carried out at 77 K, in a micromeritics equipment. The surface area was calculated using Brunauer–Emmett–Teller (BET) method. The pore size distribution was determined by NLDFT method.

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker B5005 diffractometer using Cu K $\alpha$  radiation. The mean  $\text{Co}_3\text{O}_4$  crystallite sizes were deduced from the XRD data using the Scherrer equation.

TPR was carried out in a U-tube quartz reactor at the ramp rate of 10 K/min in the 5%  $\text{H}_2/\text{Ar}$  (vol.) flow of 30 ml  $\text{min}^{-1}$ . The  $\text{H}_2$  consumption was monitored with TCD using the reduction of CuO as the standard. The reduction percentage of the cobalt oxides at temperatures less than 673 K was calculated from TPR profiles. The ratio between the  $\text{H}_2$  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  $\text{Co}_3\text{O}_4$ ), was reported as the degree of reduction.

Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) was performed with a Chem TPR/TPD instrument (Quantachrome). Approximately 80.0 mg catalyst was activated for 1 h at 773 K heating with a ramp of 10 K  $\text{min}^{-1}$ . After cooling to 473 K, pure ammonia was passed through the sample. The desorption of the ammonia was accomplished by purging helium with a flow of 20 ml  $\text{min}^{-1}$  and raising the temperature to 1073 K. Total acidity of the catalyst which may correspond to Brønsted and Lewis sites was measured by a thermal conductivity detector (TCD).

Si/Al ratio of zeolite samples was measured by ICP-OES (Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing).

Scanning electron microscopy (SEM) was performed on a FEI QuantaTM 250. Samples were coated with a layer of gold using an Edwards S150A sputter coater, to make them conductive prior to imaging.

TEM micrographs were obtained from a Tecnai G20 (FEI-2012, LaB6) with an accelerating voltage of 200 kV. Each sample powder was dispersed in absolute ethanol, dropped on a carbon-coated copper grid, dried and transferred into TEM chamber.

The surface carbon concentration on used catalysts were determined using X-ray photoelectron spectroscopy (XPS) performed on a Physical Electronics Company Quantum-2000 Scanning ESCA Microprobe spectrometer with a Al K $\alpha$  monochromatized line (1486.6 eV).

Catalysts were evaluated in a pressured fixed-bed reactor at 2 MPa, 1000  $\text{h}^{-1}$  with the  $\text{H}_2/\text{CO}$  ratio of 2 after reduction at 673 K for 10 h. Wax was collected with a hot trap and the liquid products were collected in a cold trap after 24 h on-stream. The gas effluents were analyzed on-line by using Carbosieve-packed column with TCD. The gas hydrocarbons were analyzed on-line using Porapack-Q column with FID. Oil and wax were analyzed off-line in OV-101 capillary columns. 5%  $\text{N}_2$  was added to syngas as an internal standard. The carbon balance and mass balance were  $100 \pm 5\%$ .

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