



## Direct conversion of syngas to isoparaffins over hierarchical beta zeolite supported cobalt catalyst for Fischer-Tropsch synthesis



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### ABSTRACT

A hierarchical micro-meso-macroporous Beta zeolite (HB) was developed by a steam-assisted crystallization method and was employed for cobalt Fischer-Tropsch synthesis. Meso-macroporous silica (HS), alumina modified meso-macroporous silica (HAS) and conventional Beta zeolite (CB) were used for comparison. Structural characterization indicated that the as-synthesized HB exhibited nanosized Beta zeolite crystallites and a hierarchical micro-meso-macroporous structure. The HB supported catalyst showed very high isoparaffins selectivity because of the isomerization reaction at the strong acidic sites of the Beta zeolite, while due to its good macroporous structure, which is in favor of reducing the internal diffusion limitations, the methane selectivity was kept as low as HAS supported catalysts. In this paper, we use large particle catalysts for evaluation, which are very close to industrial condition. And the conclusions obtained may be very important for the design of new Fischer-Tropsch catalysts.

### 1. Introduction

As an important heterogeneous catalytic polymerization process, Fischer–Tropsch synthesis (FTS) is expected to produce super-clean fuel and valuable chemicals from various non-petroleum carbon resources such as coal, gas and biomass [1,2]. Among the reported FTS catalysts, due to its excellent properties such as high activity, low activity for the competing water gas shift (WGS) reaction and high selectivity of C<sub>5+</sub> hydrocarbons, supported cobalt catalyst is one of the most widely used catalyst for the low-temperature Fischer–Tropsch synthesis [3].

As the FTS product is believed to follow the Anderson–Schulz–Flory distribution, the product distribution is very wide and the desired hydrocarbon fractions (diesel and gasoline ranges) is not very high [4,5]. In order to produce diesel or gasoline, additional refining processes are usually required, which always significantly increase the cost and energy consumption [6,7]. Therefore, it is of great interest to design bifunctional catalyst for the FTS reaction to directly convert of syngas to hydrocarbons of certain carbon number and with a branched structure at the same time. In recent years, many research groups combined Fischer-Tropsch catalysts with zeolites to prepare bifunctional catalysts to increase the proportion of isoparaffins and middle distillate [8–10]. Zhang et al. prepared a series of ZSM-5/SBA-15 compound supported

cobalt catalysts [11]. The ZSM-5/SBA-15 composite supported catalysts showed superior catalytic performance as compared to the single material supported catalysts. However, in this system, the cobalt active sites are far away from the acid sites of the zeolite, so that a large amount of the product directly diffuses into the catalyst bed, losing the opportunity for further reforming. Capsule catalyst can overcome this problem well because the Fischer-Tropsch product formed inside the catalyst must pass through the zeolite shell, where sufficient hydrocracking and isomerization would occur [12]. Tsubaki et al. prepared a capsule catalyst by coating a H-ZSM-5 membrane onto the surface of the pre-shaped Co/SiO<sub>2</sub> pellet [13]. In the prepared capsule catalyst, the C<sub>10+</sub> hydrocarbons were suppressed completely and the selectivity of middle isoparaffins was considerably improved. However, in the capsule catalyst, microporous structure of the zeolite is very detrimental to the mass transfer of reactants and products, which leads to excessive cracking of the Fischer-Tropsch products, resulting in a large amount of gaseous products. In order to solve this problem, many researchers have prepared mesoporous zeolites, utilizing the mesoporous channels to solve the problem of mass transfer [14–16].

However, few researchers have applied zeolite with macroporous structures to cobalt-based Fischer-Tropsch synthesis. As we all know, in order to keep advisable pressure gradients and heat transfer,

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packed-bed Fischer-Tropsch synthesis reactors always require large pellet catalysts (1–3 mm), resulting in serious internal diffusion limitations, which would decrease Fischer-Tropsch synthesis rates and  $C_5+$  selectivity [17–19]. In our previous research, we have demonstrated that introducing of additional macropores is expected to be an effective way to reduce internal diffusion limitations in large pellet catalyst [20]. Many other researches have also demonstrated the effect of macropores on mass transfer and diffusion [21,22].

As discussed above, zeolite with macroporous structures is expected to be a kind of good support: on the one hand, the isoparaffins selectivity can be increased because of its rich acidic sites, on the other hand, internal diffusion limitations could be reduced due to its macroporous structures. In the present work, the performance of cobalt Fischer-Tropsch synthesis catalyst supported on a micro-meso-macroporous Beta zeolite was presented.

## 2. Experimental

### 2.1. Synthesis of supports and catalysts

Meso-macroporous silica monolith was prepared according to our previous report [23]. The prepared meso-macroporous silica monolith was then grinded into 10–20 mesh (800–1700  $\mu\text{m}$ ) and was noted as HS. The alumina modified meso-macroporous silica support was prepared by an incipient wetness impregnation method. According to the different loading amount of  $\text{Al}_2\text{O}_3$ , the prepared samples were noted as HAS ( $\text{Al}_2\text{O}_3$  loading of 0.8%) and HAS10 ( $\text{Al}_2\text{O}_3$  loading of 10%). The hierarchical Beta zeolite was prepared by steam-assisted crystallization (SAC) method using HS as precursor. The specific preparation process was as followed: A desired amount of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and NaOH was dissolved in a certain amount of TEOH solution (25 wt%). The as prepared HS was then impregnated into the solution described above. After ultrasonic for 10 min, dried at room temperature for 24 h and at 60 °C for 12 h, the mixture became a dry gel. The dry gel and  $\text{H}_2\text{O}$  (2 mL) were sealed in a Teflon-lined steel autoclave (150 mL), and crystallization was conducted at 150 °C for 3 days. The sample was removed, washed with water and dried at 60 °C for 6 h and then calcined at 550 °C for 6 h with a rate of 1 °C/min. The prepared sample was subjected to ion exchange for transformation into the H-form and noted as HB [24]. It should be noted that HB has similar Si/Al ratio to HAS. The conventional Beta zeolite with the similar Si/Al ratio to HB was purchased from Nanjing JCNANO. The same ion exchange procedure was taken for the conventional Beta zeolite, and was named as CB.

The resulted materials were used to prepare cobalt catalysts and noted as Co/HS, Co/HAS, Co/HAS10, Co/HB and Co/CB respectively.

### 2.2. Catalyst characterizations

A JSM-7001 F scanning electron microscope (SEM) was employed to observe the morphology of the supports, operating at 5.0–15.0 kV.

Nitrogen sorption was measured with a Micro Active for ASAP 2460 2.01 instrument at liquid nitrogen temperature. The specific surface areas of the samples were determined by the Brunauer–Emmett–Teller (BET) method. Mesoporous size distributions were obtained by applying the BJH formalism to the desorption branch of the isotherms. Microporous size distributions were obtained by the Horvath–Kawazoe (HK) method.

The phase structures of the catalysts was characterized by powder X-ray diffraction (XRD), performed at room temperature on a PANalytical Empyrean X'pert powder diffractometer operated at 50 kV and 50 mA with monochromatized  $\text{Cu K}\alpha$  radiation. The Scherrer's equation was used to calculate the average size of the  $\text{Co}_3\text{O}_4$  crystallite from the most intense  $\text{Co}_3\text{O}_4$  peak at  $2\theta = 36.9^\circ$  [[25]]. The average Co pellet size  $d_x$  in the reduced catalysts was then obtained from the corresponding  $\text{Co}_3\text{O}_4$  crystallite size by applying the relative molar volume correction  $d_x = 0.75 d(\text{Co}_3\text{O}_4)$ . Then, the  $\text{Co}^\circ$  metal dispersions can be

calculated using the equation:  $D = 96/d(\text{Co}^\circ)$  [26].

In order to observe the active component distributions and morphology of the catalysts, transmission electron microscopy (TEM) was employed, operated at 200 kV with an JEOL: JEM-2010 FEF microscope.

The acid strength of the samples was determined by  $\text{NH}_3$  temperature programmed desorption method. The samples (50 mg) were pre-treated at 200 °C in Ar flow (30 mL/min) for 2 h to remove the adsorbed  $\text{H}_2\text{O}$  in the samples. After the sample was cooled to 80 °C, the gas was switched to a  $\text{NH}_3/\text{Ar}$  mixture (10 vol%  $\text{NH}_3$ , 30 mL/min) for 30 min. Then pure Ar was introduced again to purge the physically adsorbed  $\text{NH}_3$  for 30 min. Then the programmed temperature desorption was conducted by increasing the temperature from 80 °C to 800 °C at a ramp rate of 10 °C/min in an Ar flow (30 mL/min). The desorbed  $\text{NH}_3$  was detected by a mass spectrometer.

The Pyridine IR of the samples were determined on a Nicolet Magna 550 infrared spectrometer. After grinding into below 200 mesh, the samples (20 mg) were mixed with potassium bromide and pressed into a translucent wafer, then connected to the vacuum system. Samples were first evacuated at 400 °C for 3 h under a vacuum of  $1.33 \times 10^{-3}$  Pa, then cooled to room temperature. The sample was then followed to adsorb pure pyridine vapor under static conditions for 30 min. The system was heated up to 150 °C, maintained for 60 min to remove the excess pyridine, then the Py-IR spectra were collected after the temperature reduced to room temperature.

The reduction behaviors of the different catalysts were studied by  $\text{H}_2$  temperature-programmed reduction ( $\text{H}_2$ -TPR) using a Zeton Altamira AMI-200 unit. 50 mg samples were initially flushed with high purity argon (30 mL/min) at 120 °C for 2 h to remove  $\text{H}_2\text{O}$  in the catalysts. When the system cooled down to 50 °C, a gas consisting of 5%  $\text{H}_2$  in Ar was switched on and the temperature was increased to 960 °C with a heating rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) spectra were obtained on an AXIS ULTRA DLD spectrometer equipped with a hemispherical electron energy analyzer. The C 1s line (284.6 eV) was taken as a reference to calibrate the binding energies (BEs).

Al MAS NMR was carried out on a Bruker AVANCE III 600 MHz superconducting nuclear magnetic spectrometer, operating at 156.3 MHz for aluminum using a Chemagnetics 2.5-mm HX MAS probe. Magic angle spinning (54.7°) was carried out at a rotation speed of 12 kHz using a 4 mm diameter zirconium tube.  $\text{Al}(\text{NO}_3)_3$  aqueous solution (1.0 M) was used as a standard sample to measure chemical shifts.

A Nicolet Magna 750 infrared spectrometer supplied with a MCT detector was used to record diffuse reflectance FTIR spectra with a resolution of 8  $\text{cm}^{-1}$  and accumulation of 64. The catalysts were first reduced in situ for 6 h under atmospheric pressure with a stream of high hydrogen (> 99.99%) at 400 °C, then the system cooled down to 30 °C. High purity CO (> 99.99%) was introduced for 30 min. Then the system was purged with argon for 10 min to remove gaseous CO.

### 2.3. Fischer–Tropsch synthesis catalytic evaluation

Fischer–Tropsch synthesis catalytic evaluation was carried out according to our previous study [1].

## 3. Results and discussion

### 3.1. Morphology and texture of the samples

Fig. 1 shows that HS, HAS and HAS10 have a honeycomb-like structures with interconnected macropores. The conventional Beta zeolite presents irregular globular shape, and does not exist macroporous structure. HB obtained by steam-assisted crystallization method still retains the macroporous structure, at the same time a large number of zeolites nanocrystallites can be found inside and outside the

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