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A hierarchically spherical Co-based zeolite catalyst with aggregated nanorods structure for improved Fischer–Tropsch synthesis reaction activity and isoparaffin selectivity



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ABSTRACT

A hierarchically spherical Co based zeolite catalyst with aggregated nanorods structure (simplified as Co/AN-Z) was prepared by an in-situ self-assembly crystallization route of Co/SBA-15 under hydrothermal synthesis environment. The obtained Co/AN-Z catalyst with uniformly sized zeolite microspheres with 0.5–1 μm was evaluated for improved Fischer–Tropsch synthesis (FTS) reaction activity and isoparaffin selectivity. The selectivities of isoparaffin and C_{5–11} hydrocarbons were higher with a narrower product distribution as well as CH₄ and C₁₂₊ selectivities were lower on the Co/AN-Z catalyst than those on the commercial HZSM-5 supported Co catalyst (Co/HZSM-5) for FTS reaction. The demonstrated route of the hierarchically spherical Co based zeolite catalyst can be extended to synthesize bifunctional catalyst and expected to find a new approach for tandem reaction.

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1. Introduction

Zeolite crystals with inherent micropores, high acidity, uniform micropore size and shape selectivity have been widely applied as heterogeneous catalysts or catalyst supports in the petrochemical and fine chemical industries [1]. However, its microporous texture strongly limits mass transfer of reactants and products in catalytic reactions. Hierarchical zeolite containing both micro- and mesopores has been developed to improve its diffusion performances. Recently, most works in the literature focused on synthesizing hierarchical zeolite by non-templating and templating approaches [2]. Dealumination or desilication is a common non-templating

method, including steaming, leaching and chemical treatment to introduce mesopores on pristine zeolite [3]. Although the non-templating method can successfully create mesopores, accompanying the wastes also are produced by a reduction in pore-wall crystallinity. Hierarchical zeolite is also usually synthesized through templating method by using various templates, e.g. CaCO₃ [4], carbon nanoparticles [5], carbon nanotubes [6], carbon nanofiber [7], carbohydrate feedstocks [8], carbon aerogels and polymer aerogels [9]. However, the process complexity or high cost of template is still inevitable.

Since ordered mesoporous materials were first synthesized in 1990s, providing a potential to enhance diffusion ability with uniform mesopores, which have widespread application in materials synthesis [10]. In recent years, ordered mesoporous zeolite has been developed widely by using ordered mesoporous carbon or silica sources as templates [11]. Tsapatsis et al. reported that a series of ordered mesoporous cubic zeolite was synthesized using three dimensional mesoporous carbon as template [12]. Ryoo and co-workers investigated the synthesis of ordered mesoporous MFI

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zeolite using CMK-type mesoporous carbon as template through the dry-gel synthesis method [13]. However, it is still a big challenge to fabricate zeolite with highly ordered mesoporous structure so far [14]. More recently, hierarchical zeolite composite materials from the synthetic precursors with zeolite beta seeds and SBA-15 were studied widely by using a self-assembly process [15,16]. The functional Fe_3O_4 @ZSM-5 microspheres through an in-situ crystallization route were developed and evaluated for middle hydrocarbons synthesis via Fischer–Tropsch synthesis (FTS) reaction by Zhao group [17].

SBA-15, as an ordered mesoporous materials with large surface area, unique pore size and excellent thermostability, was usually used as an inert support for FTS reactions [18–22]. Furthermore, it has been proved that the catalysts using ordered mesopore silica as support exhibited superior performance due to the confinement effect of ordered pores, such as the high activity and stability, compared to that using the traditional porous silica as support in FTS [22]. It is known that the FTS products obey the Anderson–Schulz–Flory (ASF) law for conventional Co-based catalysts, such as Co/SiO_2 , $\text{Co}/\text{Al}_2\text{O}_3$ and Co/TiO_2 [23–26]. In our previous studies, the capsule catalyst with core/shell structure (such as $\text{Co}-\text{SiO}_2/\text{HZSM}-5$), as bifunctional catalyst for direct synthesis of middle isoparaffin with high octane value via FTS reaction, was successfully synthesized, realizing a sharp anti-ASF law product distribution [27,28]. However, the capsule catalysts possess a large particle diameter of 1–2 mm and inhomogenous pore size, thus there is significant technological interest in reducing the particle size of bifunctional catalyst to improve the FTS reaction activity and isoparaffin selectivity.

In this work, a hierarchically spherical Co based zeolite catalyst with aggregated nanorods structure realized through an in-situ self-assembly crystallization route, was designed and evaluated by FTS reaction. The overall synthetic route is illustrated in Fig. 1. First, $\text{Co}/\text{SBA}-15$ (Fig. 1b) was prepared by impregnation method with cobalt nitrate solution. And then, a synthesis solution of sodium aluminate, tetrapropylammonium hydroxide (TPAOH) and deionized water was impregnated into $\text{Co}/\text{SBA}-15$ under vigorously stirring. The $\text{Co}/\text{SBA}-15$ was dissolved to form the rodlike $\text{Co}/\text{SBA}-15$, subsequently in-situ self-assembled and crystallized under hydrothermal synthesis condition, forming spherical Co based zeolite catalysts with aggregated nanorods structure ($\text{Co}/\text{AN}-\text{Z}$, Fig. 1d).

2. Experimental

2.1. Catalyst preparation

The SBA-15 was synthesized by a similar method described elsewhere using P123 (Pluronic P123, EO/PO/EO = 20/70/20, MW = 5800, Aldrich) as structure directing agent and tetraethyl

orthosilicate (TEOS, 95.0%, Wako) as silicon source under acidic conditions [29,30]. The obtained solution was first stirred at 35 °C for 20 h, and then kept in a closed Teflon vessel at 100 °C for 12 h. After washing with deionized water, the solid product was dried at room temperature and calcined in air at 550 °C for 6 h.

$\text{Co}/\text{SBA}-15$ catalyst was prepared by incipient wetness (IW) impregnation of the SBA-15 support with the aqueous solution of cobalt nitrate. The impregnated solid was subsequently dried at 120 °C overnight and calcined at 400 °C for 2 h. The final Co content was 10 wt.% in $\text{Co}/\text{SBA}-15$ catalyst.

The aggregated nanorods zeolite loaded Co catalysts were prepared by an in-situ self-assembly process under hydrothermal synthesis conditions and denoted as $\text{Co}/\text{AN}-\text{Z}$ [31]. In brief, a mixture solution of water, sodium aluminate and TPAOH was impregnated into the $\text{Co}/\text{SBA}-15$ catalyst with the final molar ratio of $\text{Al}_2\text{O}_3:\text{SiO}_2:\text{Na}_2\text{O}:\text{H}_2\text{O}:\text{TPAOH}$ of 1:100:4:4800:18. The mixture was first stirred at room temperature for 12 h, subsequently crystallized by hydrothermal synthesis method at 180 °C for 24 h. The obtained sample was centrifuged, filtered and washed with deionized water for several times, subsequently dried at 120 °C overnight and finally calcined at 500 °C in air for 5 h. The Na-type ZSM-5 was further exchanged with NH_4NO_3 solution and then calcined at 500 °C for 5 h to get the H-type zeolite. The 10 wt.% Co catalyst with a commercial HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$, Mizuzawa Co.) as support was also prepared by IW method, as reference catalyst, and denoted as $\text{Co}/\text{HZSM}-5$.

The aggregated nanorods of ZSM-5 (AN-Z) were prepared with the same procedure of $\text{Co}/\text{AN}-\text{Z}$ catalyst without Co addition. The AN-Z supported Co catalyst ($\text{Co}/\text{IW}-\text{AN}-\text{Z}$) with 10 wt% loading amount was prepared by conventional incipient wetness impregnation method with an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Finally, the wet catalyst was dried at 120 °C overnight and then calcined in air at 400 °C for 2 h.

2.2. Catalyst characterization

Small-angle X-ray scattering (SAXS) patterns were acquired on a Bruker D8 Advance powder diffraction system with $\text{Cu}-\text{K}\alpha$ radiation and scanning 2θ from 0.6° to 5.0°. Wide-angle X-ray diffraction (XRD) patterns were characterized using a Rigaku D/max-2550 V diffractometer with $\text{Cu}-\text{K}\alpha$ radiation in the 2θ angel ranging from 5° to 80°, operated at 40 kV and 40 mA.

Total surface area of samples was determined by the Brunauer–Emmett–Teller (BET) method using a 3Flex analyzer (Micromeritics Instrument Co.). The pore size distribution in the mesoporous region was obtained by Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherms, and that in the microporous region was determined by the Horvath–Kawazoe (HK) method. The surface area and volume of micropore were measured by the t -plot method.

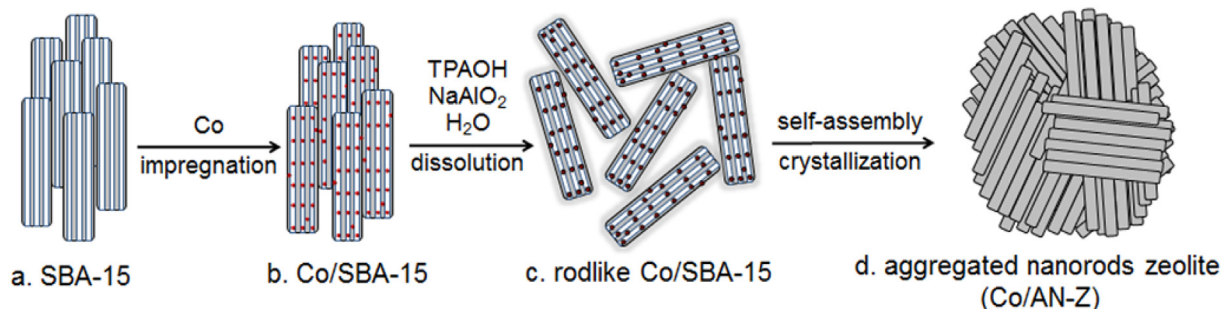


Fig. 1. The overall synthetic route of spherical Co based zeolite catalyst with aggregated nanorods structure.

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