



# The delaminating and pillaring of MCM-22 for Fischer–Tropsch synthesis over cobalt



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## ABSTRACT

To investigate the effect of structural evolution of layered zeolite on the performance of Co/MCM-22 derived zeolites for Fischer–Tropsch (FT) synthesis, the MCM-22, MCM-36 and delaminated zeolite characterized by different arrangement of MWW nanosheets were prepared through directly calcination, pillaring and delaminating of the layered precursor of the MCM-22 (MCM-22(P)). The results show that the extent of reduction of cobalt was increased over Co-supported pillared and delaminated zeolites, and the activities of the catalysts (i.e., CO conversions) were increased in the order of Co/MCM-22 < Co/Al<sub>2</sub>O<sub>3</sub>–MCM-36 < Co/SiO<sub>2</sub>–MCM-36 < Co/delaminated zeolite. Compared to Co/MCM-22, the selectivity of CH<sub>4</sub> over Co-supported pillared and delaminated zeolites was decreased clearly. Moreover, Co-supported SiO<sub>2</sub>–MCM-36 and Al<sub>2</sub>O<sub>3</sub>–MCM-36 can effectively narrow the product distribution of FT synthesis showing clearly increased C<sub>4</sub>–C<sub>12</sub> selectivity. However, the selectivity of C<sub>21</sub>+ hydrocarbons over Co/delaminated zeolite was significantly increased. The results are well explained based on the structural and acidic properties of the MCM-22 derived zeolites together with the reduction behaviors of the catalysts.

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## 1. Introduction

The Fischer–Tropsch (FT) synthesis is a key technology for producing high quality ultra-clean fuels and high-value added fine chemicals from syngas originating from coal, natural gas and biomass [1]. Recently, FT synthesis has received increasingly worldwide attention in both industrial and academic domains because of the shortage of crude oil and the increasingly stringent environmental legislations on transportation fuels. However, as a result of the polymerization mechanism, the products of FT synthesis generally follow a statistical hydrocarbon distribution and nonselective to any specific product, which is known as the Anderson–Schulz–Flory (ASF) distribution [1–4]. Thus, the development of effective catalysts with controlled product selectivity is a difficult task and remains one of the biggest challenges.

Indeed, the cobalt is considered to be one of the most effective and industrially important catalysts for the FT synthesis due to its high activity, high resistance to deactivation, low water–gas

shift activity, and much lower price compared with noble metals [5]. Consequently, bifunctional catalysts, namely, combinations of cobalt with various solid acids for cracking and isomerizing the FT hydrocarbons, have been extensively studied in order to circumvent the ASF distribution and selectively produce gasoline or diesel-range hydrocarbons [6–9]. The solid acids investigated have mainly focused on zeolites. This strategy has proven to be very effective, and the traditional FT product distribution can be significantly changed with much increased selectivity to liquid fuels [10–12]. However, because of the microporous structure of the zeolite, the diffusion limitation in the micropores may cause higher local H<sub>2</sub>/CO ratios on the active metal surface because H<sub>2</sub> diffuses more quickly than CO, which results in the high CH<sub>4</sub> and C<sub>2</sub>–C<sub>4</sub> selectivities [13]. Moreover, the slow transportation of FT products inside the long micropores may cause over-cracking, which leading to higher selectivity to C<sub>2</sub>–C<sub>4</sub> lighter hydrocarbons. Furthermore, most of acid sites are located inside the narrow and long micropores, which would make more difficult in accessing these acid sites by primary heavier hydrocarbons, thus decreasing the efficiency of secondary reactions [10]. To solve these problems above, simple alkaline treatment method has been used to modify the porous structure, and the mesoporous zeolite with hierarchical porous

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structures are obtained [10,14,15]. Previous studies revealed that Co or Ru supported on the mesoporous zeolites can directly synthesize the gasoline or diesel-range hydrocarbons through FT synthesis [14,15]. However, the pore size and distribution of the mesoporous zeolites cannot be controlled very well using the alkaline treatment method [16].

MCM-22 with MWW topology is one of the most interesting zeolite structures synthesized in the past decade. More importantly, the precursor of the MCM-22, i.e., MCM-22(P), is a two-dimensional layered material formed by parallel and ordered zeolitic layers perpendicular to the *c*-axis. Each individual MWW-type nanosheet has a thickness of 2.5 nm and contains a 10 member-ring (MR) sinusoidal channel present along the plane *ab* [17]. Thus, the layered MCM-22(P) can be swollen, pillared, and exfoliated under suitable conditions, which results in the pillared and delaminated materials characterized by the different arrangement of the MWW nanosheets [18]. For the pillaring of MCM-22(P), the oxide “pillars” in the interlayer avoids the covalent connection between the consecutive inorganic MWW nanosheets. Thus, additional new mesoporous with adjustable pore size can be generated in the interlayer space. More importantly, this intercalation process not only increase the accessibility to internal acidic sites of microporous zeolites, but also incorporates additional active sites located in the interlayer of MWW nanosheets [18,19]. Moreover, for the delaminating of MCM-22(P), the randomly separated individual MWW nanosheets in a random arrangement can be obtained. Thus, the delaminating process results in high external surface area and greater accessibility of acidic sites over MWW nanosheets. More importantly, compared to the MCM-22 with 3D structure, the individual MWW nanosheets short the diffusion paths of the products [18–22], which would suppress the formation of undesired products due to the over-cracking of the intermediates.

Herein, based on these understandings, in this work, MCM-22, a series of pillared and delaminated zeolite with unique structural properties from the different arrangement of the MWW nanosheets were comparatively studied as supports for FT synthesis over cobalt. The results indicate that the pillaring and delaminating of the layered zeolite precursor results in the increase of the CO conversions and decrease of the selectivity of CH<sub>4</sub>. Moreover, the selectivity of C<sub>4</sub>–C<sub>12</sub> ranged liquid hydrocarbons was increased clearly. The experimental results are well explained based on the characterizations of by X-ray diffraction (XRD), hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR), and NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD).

## 2. Experimental

### 2.1. Synthesis of MCM-22 derived zeolite

MCM-22(P) zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 50 was synthesized by hydrothermal crystallization according to the reported procedure [23]. Typically, 0.15 g of NaAlO<sub>2</sub> (Sinopharm Chemical Reagent Co., Ltd.) and 0.18 g of NaOH (Sinopharm Chemical Reagent Co., Ltd.) were dissolved in 25.2 g of deionized H<sub>2</sub>O. Subsequently, 1.09 g of hexamethylenimine (HMI) (Aldrich) and 4.67 g of silica (LUDOX AS-40, Aldrich) were added to this solution while stirring for 30 min. The resulting gel was introduced into a 50 mL rotating Teflon-lined steel autoclave, and heated at 150 °C for 7 days. After quenching the autoclaves in cold water, the samples were centrifuged and washed thoroughly with deionized water until pH < 9.0. The resulting white solid was dried at 60 °C overnight. A portion of this MCM-22(P) was calcined in air at 580 °C for 3 h to obtain MCM-22.

The swelling of MCM-22(P) was prepared using the method described by Corma et al., [20]. 5.0 g of typically aqueous slurry

of MCM-22(P) (20 wt.% solids) was mixed with 56.0 g of an aqueous solution of 10 wt.% hexadecyltrimethyl-ammonium bromide (CTAB) and 6.1 g of an aqueous solution of 40 wt.% tetrapropylammonium hydroxide (TPAOH). The mixture was allowed to stir at 80 °C for 16 h. A portion of the swelling mixture recovered after 16 h of swelling was subjected to the ultrasonication for 2 h to exfoliate the layers, and subsequently acidified until pH < 2 to collect the particles. The resulting white solid was dried overnight at 60 °C. After calcination at 540 °C under nitrogen atmosphere for 2 h and finally at 540 °C under air atmosphere for 5 h, delaminated zeolite was obtained.

Another portion of the swelling mixture was filtered, washed with distilled water and dried at 60 °C. The resulting powder was mixed with the pillaring agent tetraethylorthosilicate (TEOS) to prepare the SiO<sub>2</sub> pillared sample. Typically, 1.0 g of swollen MCM-22(P) powder was mixed with 5.0 g of TEOS, stirred for 24 h at 35 °C under nitrogen atmosphere, then filtered, and dried at room temperature. The dried solid was hydrolyzed with water at pH = 8 tuned by NaOH at 35 °C for 5 h, and then filtered, dried at room temperature. After calcination at 540 °C under nitrogen atmosphere for 5 h and finally at 540 °C under air atmosphere for 12 h, SiO<sub>2</sub>-MCM-36 was obtained.

The pillaring solution of alumina was prepared by using Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as the pillar precursor according to our previous report [3]. Typically, 0.11 mol/L of Na<sub>2</sub>CO<sub>3</sub> solution was slowly added to 0.10 mol/L of Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution, and then under vigorous stirring at 60 °C, until an OH<sup>-</sup>/Al<sup>3+</sup> molar ratio of 2.2 was reached. The alumina polycation was obtained after aging at 60 °C for 24 h. Subsequently, the alumina pillaring agent was added dropwise into a 2 wt.% of suspension of the MCM-22(P). The final suspension was stirred at 60 °C for 6 h and further aged for 24 h. After this, the suspension was centrifuged, washed with deionized water until no chloride could be detected, and dried at 60 °C. After calcined at 540 °C for 5 h under nitrogen atmosphere and finally at 540 °C for 12 h under air atmosphere, the Al<sub>2</sub>O<sub>3</sub>-MCM-36 was obtained. All of the zeolites obtained in this work were ion-exchanged with NH<sub>4</sub><sup>+</sup> in a 1 mol L<sup>-1</sup> of NH<sub>4</sub>NO<sub>3</sub> aqueous solution for three times. The NH<sub>4</sub><sup>+</sup>-exchanged zeolites were calcined again in air at 550 °C for conversion to the H<sup>+</sup>-ionic form.

### 2.2. Preparation of catalysts

The catalysts with a metallic cobalt loading of 20 wt.% were prepared by the incipient impregnation method. The cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.0%) was used as the cobalt precursor. The catalysts were dried at 120 °C for 12 h, and then calcined at 200 °C for 2 h in air by programmed heating with the rate of 2 °C min<sup>-1</sup>.

### 2.3. Characterization techniques

N<sub>2</sub> adsorption–desorption isotherms were measured with BelSorp-Max (Bel Japan Inc.) at –196 °C. The samples (ca. 150 mg) were previously outgassed at 300 °C for 5 h. The surface area was estimated by the BET method. The size distributions of micropores and mesopores were calculated based on the Horvath–Kawazoe (H–K) and Barret–Joyner–Hallender (BJH) method by using the data of adsorption branches, respectively.

XRD patterns were obtained at room temperature on a Rigaku D/Max-3c X-ray diffractometer using monochromatized Cu/Kα radiation (40 kV, 40 mA). The samples were scanned with a step size of 0.02° and speed of 8° min<sup>-1</sup>. The average crystallite size of Co<sub>3</sub>O<sub>4</sub> over the calcined catalysts was estimated using (3 1 1) diffraction peaks (2θ at about 37.0°) according to the Scherrer's equation  $d = 0.9\lambda / B \cos\theta$ , where *d*, λ, *B*, and θ are crystallite size, Cu Kα wavelength, full width at half-maximum intensity (FWHM) in radians, and Bragg's diffraction angle. The crystal size of the metal-

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