

Preparation of SiO₂-encapsulated Fe@Mn catalyst for promoting the production of olefins-riched liquid fuels from syngas

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ABSTRACT

Energy conversion, energy efficiency and the study of producing liquid fuels from other carbon resources are getting an increasing attention, as the continue depletion of oil. In this paper, SiO₂-encapsulated Fe@Mn catalysts were prepared by Stöber method and applied for the production of olefins-riched liquid fuels from syngas. With the thickening of SiO₂ shell, the selectivity for liquid hydrocarbons (C₅⁺) presents a volcanic trend, which is the result of the balancing effect between hydrogen enrichment and spatial restriction of SiO₂ shell. The promotional effect of SiO₂ shell on the formation of C₅⁺ can be attributed to the confinement effect of SiO₂ shell, which prolongs the residence time of light hydrocarbons formed on Fe@Mn, enhancing the polymerization reaction for producing more C₅⁺ hydrocarbons. The C₅⁺ selectivity can reach 72% with 78% olefins in it, at CO conversion of 67%. However, the continued increase in the thickness of SiO₂ shell may lead to the enrichment of H₂ and increase the local H₂/CO ratio in the vicinity of the active metal, enhancing the hydrogenation reaction and suppressing the formation of C₅⁺ hydrocarbons.

Keywords: energy conversion, liquid fuels, olefins, SiO₂ shell, Fischer-Tropsch synthesis

1. INTRODUCTION

With the depletion of oil, an increasing attention has been paid on energy conversion, energy efficiency and the study of producing liquid fuels from other carbon resources. Fischer-Tropsch synthesis (FTS) is a process for the conversion of syngas (CO and H₂) to chemicals and liquid hydrocarbons, which can replace the petroleum refining process to synthesize various liquid fuels. The design of catalyst to optimize the selectivity of liquid fuels (C₅⁺ hydrocarbons) is the key to

improve FTS process and is the main concern in academia.

Olefins are important chemical materials for the production of valuable aromatics, lubricating oil and alcohols [1]. Mn is widely added in the FTS catalysts as a superior promoter to enhance the production of olefins. The electron transfer from Mn to Fe can promote the chemisorption of CO and suppress that of H₂, resulting in the formation of more olefin products [2].

The confinement effect of core-shell structure catalyst can enhance the polymerization reaction of light hydrocarbons to produce more liquid fuels [3]. However, specific morphologies, such as core-shell, nanotube or hollow shell structure can also enhance the adsorption of H₂ [4,5], which may promote the hydrogenation reaction and inhibit the formation of heavy hydrocarbons. Understanding whether the core-shell structure exhibits confinement effect or enrichment effect needs more discussion.

In this paper, SiO₂-encapsulated Fe@Mn catalysts with different shell thickness are prepared. A balancing effect between confinement effect and enrichment effect is exhibited, which results in a volcanic trend for C₅⁺ selectivity with the thickening of SiO₂ shell.

2. EXPERIMENTAL SECTION

2.1 Catalyst preparation

The preparation of Fe₃O₄@MnO₂ was referred to our previous report [2]. Ferrous sulfate and polyvinylpyrrolidone were dissolved in deionized water and the solution was heated to 90 °C. Sodium hydroxide and potassium permanganate were subsequently added. After aging for ten hours, the precipitate was washed and dried. The Fe/Mn molar ratio was 1:1.

SiO₂-encapsulated catalysts were prepared by Stöber method. The prepared Fe₃O₄@MnO₂ was

dispersed in ethanol. Then, x ml ($x = 0.25, 0.50, 0.75, 1.00$) tetraethoxysilane was added. After stirring for three hours, ammonia (5 mL) and deionized water (20 mL) were added. After stirring for four hours, the products were washed and dried. The obtained catalysts were denoted as Fe@Mn@Si- x .

2.2 Catalyst characterization

N_2 physisorption was conducted on Micromeritics ASAP 2010 instruments at -196 °C. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro diffractometer. Fourier transform infrared spectra (FT-IR) was performed on a NICOLET 5700 FTIR Spectrometer.

Hydrogen temperature programmed reduction (H_2 -TPR) was performed in a quartz tube. All catalysts were pretreated with N_2 at 350 °C for one hour. After cooling down to 80 °C, $5H_2/95N_2$ (30 mL/min) was introduced into the system. The H_2 -TPR was conducted by ramping the temperature to 800 °C (10 °C/min).

2.3 Catalytic tests

The catalytic tests were conducted in a fixed-bed reactor using 0.5 g catalysts mixed with 0.5 g quartz sand. All catalysts were reduced in H_2 (33.3 ml/min) at atmospheric pressure and 350 °C for ten hours. The FTS reactions were conducted at 2.0 MPa and 320 °C for thirty hours under syngas ($5N_2/47.5H_2/47.5CO$, 33.3 ml/min). Gaseous hydrocarbons were detected by a gas chromatograph (FULI GC 97). Liquid hydrocarbons were collected through a hot trap (50 °C) combined with a cold trap (5 °C) and detected by another gas chromatograph (FULI GC 97). The carbon balance was between 94% and 96%.

3. RESULTS AND DISCUSSION

3.1 Characterizations of the catalysts

Textual properties of the catalysts are shown in **Fig. 1** and **Table 1**. The Fe@Mn catalyst presents type IV isotherms with H3 hysteresis loop, implying the two-dimensional plate-shaped structure (**Fig. 1a**). After the encapsulation of SiO_2 , the isotherms exhibit no obvious change, suggesting that the incorporation of SiO_2 shell has little influence on the pore structure of Fe@Mn. The pore size distribution demonstrates the existence of mesopores around $10\sim 30$ nm (**Fig. 1b**). While the mesopores above 30 nm may be attributed to the voids between the aggregated Fe@Mn nanoparticles [6]. The mesopores above 30 nm decrease rapidly as the increase of SiO_2 content, which may be attributed to

that the encapsulation of SiO_2 reduces the voids between the aggregated Fe@Mn nanoparticles. The BET specific surface area displays an increasing trend as the increase of SiO_2 content, possibly because the amorphous SiO_2 possesses a rougher structure (**Table 1**). The total pore volume gradually decreases as the increase of SiO_2 content, which may be attributed to the reduction of mesopores produced by the aggregation of Fe@Mn nanoparticles.

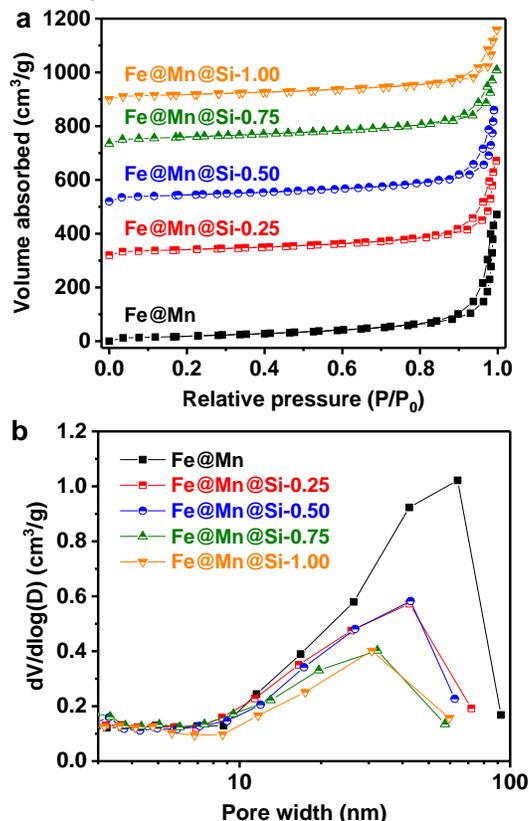


Fig. 1. N_2 adsorption/desorption isotherms (a) pore size distribution (b) of the catalysts.

Table 1. Textural properties of zeolites

Sample	S_{BET} ($m^2 \cdot g^{-1}$) ^a	V_{total} ($cm^3 \cdot g^{-1}$) ^b	S_{pore} (nm) ^c
Fe@Mn	73	0.73	22
Fe@Mn@Si-0.25	79	0.55	19
Fe@Mn@Si-0.50	91	0.52	18
Fe@Mn@Si-0.75	95	0.42	16
Fe@Mn@Si-1.00	99	0.40	15

^a BET surface area.

^b Total pore volume, $P/P_0 = 0.986$.

^c Average pore size.

XRD patterns of the catalysts are shown in **Fig. 2**. The diffraction peaks at 2θ value of 29.9° , 35.3° , 43.1° , 53.4° , 57.0° , 62.6° are attributed to Fe_3O_4 species, and the diffraction peak at 2θ value of 40.6° is attributed to MnO_2 species, confirming the formation of Fe_3O_4 and

MnO₂. [2] After the encapsulation of SiO₂, the diffraction peaks exhibit no obvious change, suggesting that the incorporation of SiO₂ shell has little influence on the crystal structure of Fe@Mn.

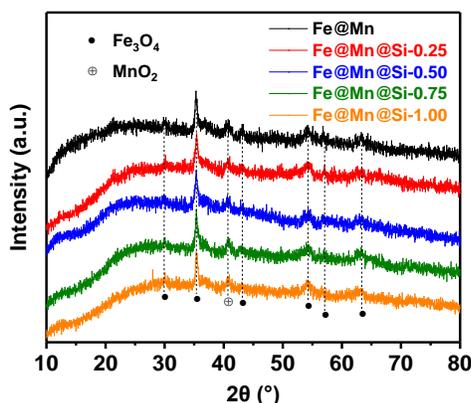


Fig. 2. XRD patterns of the catalysts.

As the amorphous SiO₂ presents no obvious diffraction peak in the XRD patterns, FT-IR spectra is further used to characterize the properties of amorphous SiO₂ (**Fig. 3**). The vibration peaks at 3430, 2925 and 1632 cm⁻¹ observed on all the catalysts are attributed to the adsorbed water [7]. After the encapsulation of SiO₂, new vibration peaks at 793, 960, 1081, 1221 cm⁻¹ are detected, which are attributed to Si-O-Si and Si-OH [8], confirming the incorporation of SiO₂ into Fe@Mn. Especially, as the increase of SiO₂ content, the intensity of the vibration peaks attributed to SiO₂ gradually increase, suggesting the gradually thickening SiO₂ shell.

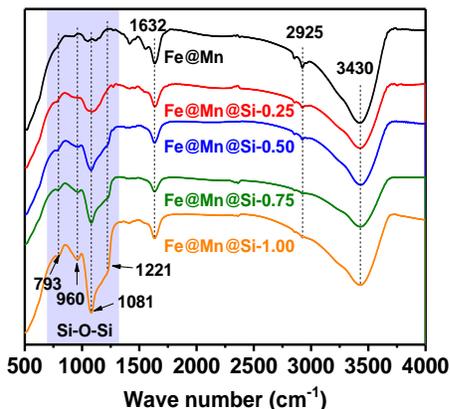


Fig. 3. FT-IR spectra of the catalysts.

Reduction behavior of the catalysts is shown in **Fig. 4**. The reduction peaks at 200-400°C and above 600°C are attributed to the reduction process of Fe₃O₄ to FeO and FeO to Fe, respectively [2]. And the middle reduction peak at 400-600°C is attributed to the reduction of MnO₂. As the increase of SiO₂ content, the reduction peak of FeO to Fe shifts to lower temperature, suggesting that the reduction of iron

oxides is promoted by the thickening SiO₂ shell. The previous report [9] claimed that SiO₂ suppressed the reduction of iron oxides in silica-supported catalyst. The contradictory result may be attributed to that the silica-coated catalyst can enhance the adsorption of H₂ and increase the local H₂/CO ratio in the vicinity of the active metal compared to the silica-supported catalyst [4,10].

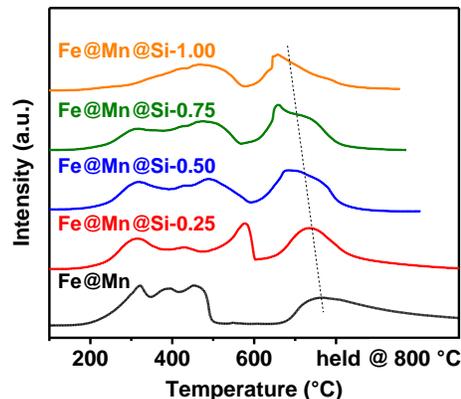


Fig. 4. H₂-TPR of the catalysts.

3.2 Catalytic performances of the catalysts

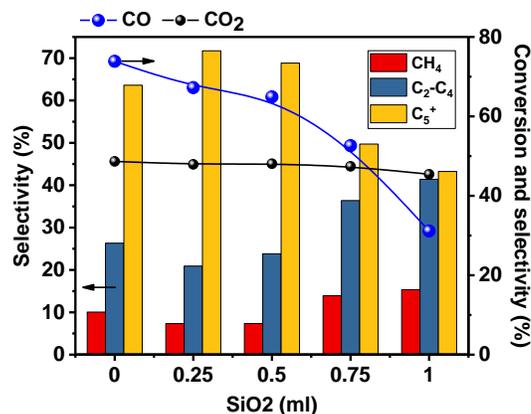


Fig. 5. Catalytic performances of the catalysts.

The catalytic performances of Fe@Mn catalysts with different SiO₂ loadings are shown in **Fig. 5**. CO conversion exhibits a decreasing trend as the increase of SiO₂ loading, which may be attributed to that the thickening SiO₂ shell hinders the adsorption of CO on the iron carbide active sites. With the thickening of SiO₂ shell, the selectivity for C₅⁺ hydrocarbons present a volcanic trend. The slight addition of SiO₂ shifts the products distribution towards heavy hydrocarbons, which may be attributed to the confinement effect of the SiO₂ shell. The SiO₂ shell prolongs the residence time of light hydrocarbons formed on Fe@Mn, enhancing the polymerization reaction for producing heavy hydrocarbons [3]. However, the continued increase in the thickness of the SiO₂ shell will enhance

the adsorption of H₂ and increase the local H₂/CO ratio in the vicinity of the active metal [4,10], leading to the shift of products towards light hydrocarbons and the decrease of olefins selectivity (Fig. 6).

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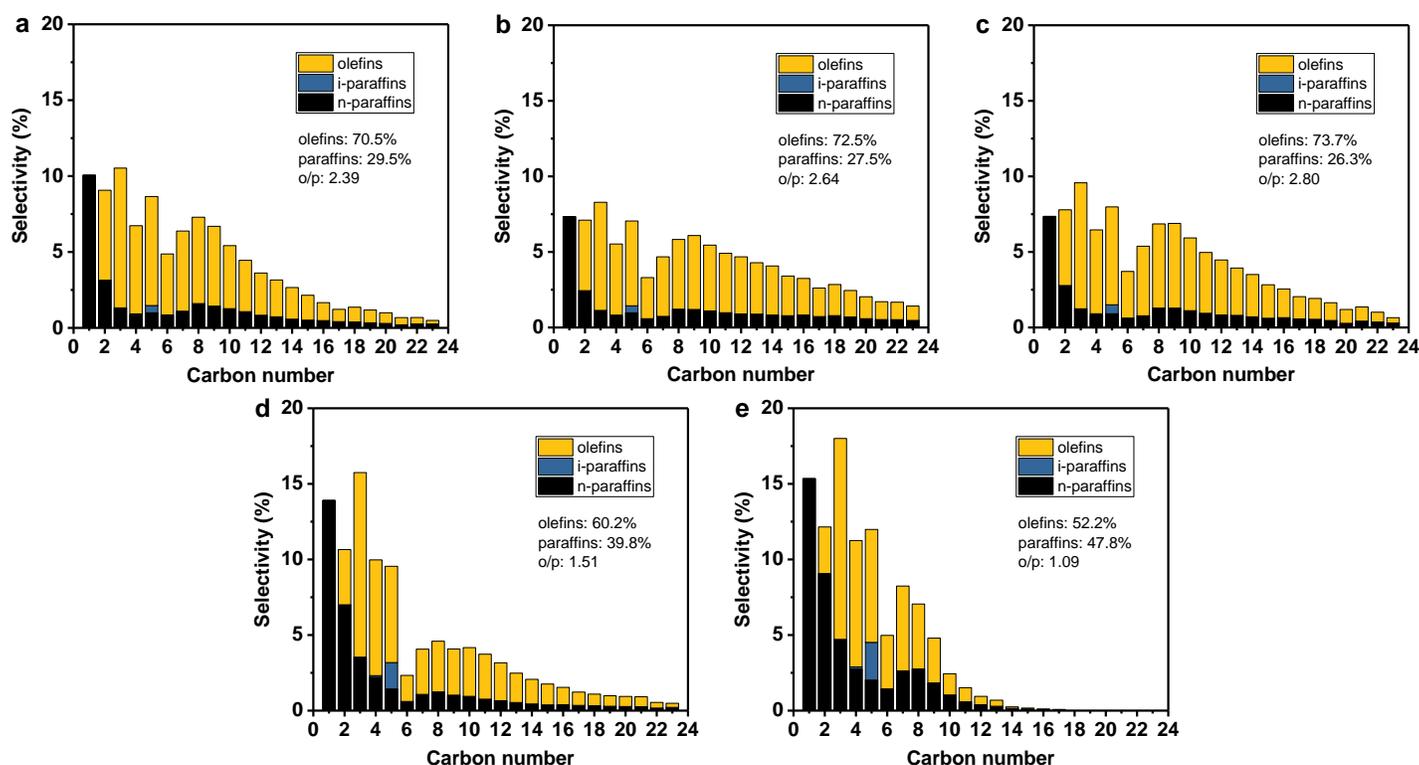


Fig. 6. Detailed hydrocarbons distribution of the catalysts. Fe@Mn (a), Fe@Mn@Si-0.25 (b), Fe@Mn@Si-0.50 (c), Fe@Mn@Si-0.75 (d), Fe@Mn@Si-1.00 (e).

4. CONCLUSIONS

SiO₂-encapsulated Fe@Mn catalysts were prepared by Stöber method. The encapsulation of SiO₂ shell promotes the formation of liquid fuels. The enhanced C₅⁺ selectivity can be attributed to the confinement effect of SiO₂ shell, which prolongs the residence time of light hydrocarbons formed on Fe@Mn, enhancing the polymerization reaction for producing C₅⁺ hydrocarbons. However, the continued increase in the thickness of SiO₂ shell will lead to the enrichment of H₂ and increase the local H₂/CO ratio in the vicinity of the active metal, enhancing the hydrogenation reaction and suppressing the formation of C₅⁺ hydrocarbons.

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