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Tunable isoparaffin and olefin yields in Fischer-Tropsch synthesis achieved by a novel iron based micro-capsule catalyst

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ABSTRACT

A novel iron based micro-capsule catalyst with interior Fe/Silica core and exterior H-ZSM-5 shell was synthesized via in-situ crystallization route on Fe/SBA-15 catalyst by using steam-assisted crystallization (SAC) process and evaluated for direct synthesis of middle isoparaffin from syngas in a fixed bed reactor. Structure characterization indicated that the size of micro-capsule catalyst was about 1-2 micrometer. According to activity test results, original Fe/SBA-15 catalyst exhibited a low selectivity of isoparaffin as 8.2 %. But the as-prepared micro-capsule catalyst achieved an excellent performance for isoparaffin synthesis with the selectivity up to 46.5 %. Meanwhile, the physical mixture catalyst (Fe/SBA-15 and H-ZSM-5) exhibited lower isoparaffin selectivity with 33.9 % than that of the micro-capsule catalyst. The spatial confinement effect of the micro-capsule catalyst played an important role for the high selectivity of isoparaffin synthesis.

Keywords: Fischer-Tropsch synthesis; Iron; Micro-capsule catalyst; Spatial confinement effect, Isoparaffin.

1. Introduction

The depletion of crude oil and the rapid growing demand of liquid fuels have attracted more interest in the synthesis of alternative fuels from the rich-reserved coal, natural gas and renewable biomass via Fischer-Tropsch synthesis (FTS) reaction [1]. Generally, FTS reaction mainly produces normal hydrocarbons and some building-block chemicals such as lower olefin, which can not directly be used as gasoline [2, 3]. Additional hydrocracking and isomerization steps are usually employed for the production of gasoline, especially isoparaffin in industry. But these steps increase the operating cost and complexity of the processes. Therefore, it is more desirable to synthesize gasoline components (rich in middle isoparaffin) from syngas without extra processes.

Bifunctional catalysts with the combination of the conventional FTS catalyst and acidic zeolite have been studied widely for direct synthesis of middle isoparaffin [4-11]. Until now, there are three kinds of bifunctional catalysts for direct synthesis of middle isoparaffin: physical mixture catalysts [12, 13], zeolite supported metal catalysts [14, 15], and capsule or coated catalysts with the conventional FTS catalyst core and zeolite shell [16-18]. The physical mixture catalysts usually have a relatively low selectivity of middle isoparaffin due to its random hydrocracking/isomerization of long chain hydrocarbons in acidic zeolite. Zeolite supported metal catalysts, as the active metal dispersed on acidic zeolite supports, exhibit a low reduction degree due to the strong metal support interaction (SMSI). Capsule or coated catalysts are more effective for isoparaffin synthesis because of the spatial confinement effect and unique pore structure of the zeolite shell, which can enforce effectively the hydrocracking/isomerization of long chain hydrocarbons. Cobalt based capsule catalysts have been studied extensively

for direct isoparaffin synthesis [19, 20]. Fe based catalysts have much lower cost and lower methane selectivity than Co based catalysts, which are proper candidates for capsule catalysts [21, 22]. Recently, our group reported a fused iron based capsule catalyst for isoparaffin synthesis, which was synthesized without organic template, giving a remarkable increase of isoparaffin/normal paraffin ratio compared to the core catalyst (fused iron) [23]. However, more works are still needed to further increase the catalytic activity and middle isoparaffin selectivity for iron based capsule catalyst, as well as enhancing the diffusion of products due to the fused iron without pore structure. In order to enhance the catalytic activity and the diffusion of products, iron based core catalyst with mesopore structure and large surface area is recommended. SBA-15 as an ordered mesoporous silica with large surface area, unique pore size and thermostability, is applied widely as model support for FTS reaction [24-28]. Furthermore, it has been proved that SBA-15 supported catalysts exhibited superior performance to compare with the traditionally disordered silica catalysts in FTS, such as the high activity and stability due to the confinement effect of ordered pore channels [29, 30].

Zeolite with highly thermal stability, ordered structure, high acidity and shape selectivity, has been applied widely as heterogeneous catalysts in the traditional petroleum-related processes and fine chemical industries [31-33]. So far, the zeolite membrane coated core catalysts are usually prepared by the hydrothermal synthesis method [22, 34, 35] or physically adhesive method [16, 36]. However, the hydrothermal synthesis method produces generally a lot of waste water. Moreover, it also limits the design and preparation of the various zeolite shell coated core catalysts. The physically adhesive method is a facile process where the independent zeolite powders are directly pasted onto the core catalyst surface with adhesive. The prepared capsule catalysts by

using the physically adhesive method can not exhibit a very high selectivity of gasoline. For these reasons, the steam-assisted crystallization (SAC) process as a new method to prepare capsule catalysts is desired.

In our previous studies, the conventional capsule catalyst had the size scale of 1000-2000 micrometer [18, 34, 37]. It is a significantly technological interest to decrease the size of capsule catalyst. Herein, we designed the Fe base micro-capsule catalyst with unique size approximately 1-2 micrometer. The micro-capsule catalyst with Fe/Silica core and H-ZSM-5 zeolite shell via an in-situ crystallization route on Fe/SBA-15 catalyst by using the SAC process was first synthesized and applied in direct synthesis of isoparaffin from syngas via FTS reaction. The overall synthetic route is illustrated in Fig. 1. In the first step, iron precursor was impregnated over SBA-15 support (Fig. 1b). Subsequently, Fe/SBA-15 was dissolved partially in zeolite synthesis solution (Fig. 1c). After solvent evaporation, the obtained Fe/Silica dry gel (Fig. 1d) acted as silicon source of the capsule catalyst. Finally, the Fe/Silica core catalyst was coated by H-ZSM-5 zeolite through the SAC method (Fig. 1e, Fe/Silica/SZ).

Fig. 1. Synthesis schematic route of iron based micro-capsule catalyst.

2. Experimental Section

2.1 Catalyst preparation

The mesoporous SBA-15 was synthesized according to the procedure described by Zhao et al [38]. Briefly, 4.0 g of P123 (Pluronic P123, EO:PO:EO = 20:70:20, MW=5800, Aldrich) was dissolved in 30 g of deionized water, followed by the addition of 2 M HCl solution at 35 °C with stirring. Then, 8.5 g of tetraethyl orthosilicate (TEOS, 95.0 %, Wako) was added to the former solution. The obtained mixture was stirred at 35 °C for 20 h, subsequently kept in a closed Teflon vessel at 100 °C for 12 h. The solid product was filtered, washed with deionized water, dried at room temperature and calcined in air at 500 °C for 6 h with a heating rate of 1 °C/min.

The Fe/SBA-15 catalyst was prepared by impregnation of the SBA-15 support with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ethanol solution. The impregnated sample was first dried using rotary evaporator at 80 °C, and then further dried at 120 °C for 24 h. The dried sample was calcined at 450 °C under air for 4 h to obtain the Fe/SBA-15 catalyst. The final Fe content of the catalyst was 27 wt%.

The micro-capsule catalyst with Fe/Silica core and H-ZSM-5 zeolite shell was prepared by using an in-situ crystallization route on Fe/SBA-15 catalyst via SAC process [39], and denoted as Fe/Silica/SZ. Firstly, 1 g of Fe/SBA-15 was added to 0.026 g of aluminium isopropoxide, 10.72 g of distilled water and 3.26 g of TEOS under vigorously stirring to get a clear solution until get a sol. And then, 3.03 g of tetrapropylammonium hydroxide (TPAOH, 10%) was added dropwise into the sol. The sol was kept stirred until it become solidified gel. The resultant wet gel was aged at 60 °C for 8 h and subsequently dried at 90 °C for 12 h. Then, the as-prepared gel was transferred into a Teflon-lined stainless steel autoclave and crystallized by SAC method

at 160 °C for 18 h. The obtained sample was washed, filtrated repeatedly for several times and dried at 120 °C overnight. Finally, the dried sample was calcined at 500 °C in air for 5 h to obtain the micro-capsule catalyst. The conventional H-ZSM-5, as a physical mixture catalyst with Fe/SBA-15, was also synthesized by the same method but without Fe addition. For comparison, the physical mixture catalyst (denoted as Fe/SBA-15+SZ) was also prepared by the mechanical mixture of the conventional H-ZSM-5 and Fe/SBA-15 catalyst.

2.2 Catalyst characterization

The nitrogen sorption experiments were performed at -196 °C on a 3Flex analyzer (Micromeritics Co.). The surface area of samples was determined by the Brunauer-Emmett-Teller (BET) method. The pore size distributions in the mesoporous region were obtained by Barrett-Joyner-Halenda (BJH) method, and that in the microporous region were determined by the Horváth-Kawazoe (HK) method. Micropore volume and surface area were evaluated by the *t*-plot method.

Small-angle X-ray diffraction (SARD) patterns were carried out on a Bruker D8 Advance powder diffraction system with CuK α radiation (40 kV, 40 mA). The wide-angle X-ray diffraction (XRD) patterns were characterized by a Rigaku D/max-2550 V diffractometer with CuK α radiation (40 kV, 40 mA) in the 2θ angle ranging from 5 to 80°.

The surface morphology of samples was characterized with a scanning electron microscopy (SEM, JEOL, JSM-6360LV).

Transmission electron microscopy (TEM) measurements were performed on JEOL JEM-2100 UHR at an acceleration voltage of 200 kV to analyze the morphology of samples.

Ammonia temperature programmed desorption (NH₃-TPD) experiments were conducted in a flow apparatus on a BELCAT-B-TT (BEL Co.) instrument. In a typical NH₃-TPD experiment, 0.03 g of catalyst was first loaded in a quartz reactor in flowing He at 150 °C for 1 h and then the followed adsorption was performed by using the 5 % NH₃ in helium flow with a rate of 20 mL/min at 80 °C for 20 min. The desorption process proceeded first by treatment of saturated catalyst at 80 °C for 30 min and then the gas desorption step was implemented with the increased temperature from 80 °C to 800 °C at the rate of 5 °C/min in flowing He (20 mL/min) atmosphere.

2.3 Isoparaffin direct synthesis reaction

FTS reaction was carried out using a pressurized stainless steel fixed-bed reactor with H₂/CO ratio of 1:1 and W/F of 10 gh/mol. Prior to reaction, the catalyst was loaded in the center of reactor and reduced in-situ at 400 °C in a flow of H₂/CO (1:1, 80 ml/min) for 10 h, and then cooled down to 300 °C under N₂ flow. During the reaction, gaseous products were online analyzed by two gas chromatographs (Shimadzu, GC-8A and Shimadzu, GC-14B). Liquid products from an ice trap were analyzed by an offline gas chromatograph (Shimadzu GC-2014, FID).

3. Results and Discussion

3.1 Structures of the micro-capsule catalyst

3.1.1 XRD analysis

The XRD patterns of the calcined SBA-15, Fe/SBA-15 and Fe/Silica/SZ are presented in Fig. 2. The SBA-15 sample exhibits three diffraction peak at $2\theta = 0.9^\circ$, 1.6° , and 1.8° (Fig. 2a), which indicates the well hexagonal pore structure of SBA-15 [40]. However, Fe/Silica/SZ micro-capsule catalyst has no any peaks in the small-angle X-ray diffraction, indicating that the SBA-15 structure was destroyed during catalyst preparation. After impregnation with iron, the diffraction peaks of Fe_2O_3 appear as shown in Fig. 2b. For the micro-capsule catalyst Fe/Silica/SZ, the appearance of XRD reflections at $2\theta=23\text{-}25^\circ$ is the characteristic feature of MFI zeolite, which confirms the existence of H-ZSM-5 zeolite in this capsule catalyst.

Fig. 2. XRD patterns of SBA-15, Fe/SBA-15 and Fe/Silica/SZ.

3.1.2 Pore properties

The pore structures of the SBA-15 support, Fe/SBA-15 and Fe/Silica/SZ catalysts are characterized by the N₂ sorption analysis. The N₂ adsorption-desorption isotherms and pore size distributions are showed in Fig. 3 while the calculated pore parameters are summarized in Table 1. SBA-15 presents a typical type IV isotherm with a H1

hysteresis loop, indicating uniform tubular mesopores. After the loading of iron, the N_2 adsorption capacity decreased gradually. It means that the loaded iron partially blocked mesopores of the SBA-15. However, the Fe/Silica/SZ micro-capsule catalyst exhibits a significant uptake at the relative pressure (P/P_0) of 0.4-0.9, indicating the existence of a broad mesoporous distribution. In addition, an adsorption at $P/P_0=0.95-1.0$ is also observed for Fe/Silica/SZ, indicating the presence of macropores. The macropores may come from the aggregated zeolite particles.

Fig. 3. N_2 sorption isotherms of SBA-15, Fe/SBA-15 and Fe/Silica/SZ.

As shown in Table 1, it can be seen that the SBA-15 support exhibits large surface area of $993 \text{ m}^2/\text{g}$ and large pore volume of $1.17 \text{ cm}^3/\text{g}$. After impregnation with iron, the surface ($560 \text{ m}^2/\text{g}$) area and pore volume ($0.59 \text{ cm}^3/\text{g}$) are distinctly lower than those of SBA-15. Further coating with H-ZSM-5 zeolite on Fe/Silica (Fe/Silica/SZ) results in a remarkable increase of microporous surface area from 161 to $240 \text{ m}^2/\text{g}$, suggesting an in-situ crystallization transformation of SBA-15 silicon source during SAC process.

Moreover, the average pore size of Fe/Silica/SZ is 3.6 nm, indicating the formation of mesopores in the capsule catalyst structure.

Table 1

Summary of the textural properties of different samples.

Sample	S(m ² /g) ^a		V(cm ³ /g)		Average pore size
	Total	Micropore ^b	Total ^c	Micropore ^d	
SBA-15	993	161	1.17	0.07	4.7
Fe/SBA-15	560	127	0.59	0.06	4.2
Fe/Silica/SZ	449	240	0.41	0.12	3.6

^a BET surface area.

^b Microporous surface area evaluated by the *t*-plot method.

^c Total pore volume calculated by single point method at P/P₀ = 0.99.

^d Micropore volume evaluated by the *t*-plot method.

The pore size distributions (PSD) of SBA-15, Fe/SBA-15 and Fe/Silica/SZ samples are displayed in Fig. 4. As shown in Fig. 4a, the micropore PSD of Fe/Silica/SZ calculated by the HK method shows a peak centered at 0.59 nm, which is in accordance with the microporosity of the H-ZSM-5 zeolite. Both of SBA-15 and Fe/SBA-15 exhibit a broad microporosity PSD within the micropore range, which derives from the intrawall porosity of SBA-15. The mesopore PSD of samples is calculated by the BJH method. SBA-15 exhibits uniform mesopores and narrow PSD centered at 6.2 nm (Fig. 4b). After Fe doped into SBA-15 (Fe/SBA-15), it exhibits two mesopores of 3.8 and 6.2 nm due to the partial blockage of the pores by Fe clusters. For Fe/Silica/SZ catalyst, a similar pore size at 3.8 nm is also observed, indicating the formation of mesopores.

Fig. 4. Pore size distributions of samples: (a) micropore region (b) mesopore region.

3.1.3 Morphology and surface composition analysis

The morphologies of samples are characterized by SEM, and the results are showed in Fig. 5. The SEM image of SBA-15 (Fig. 5a) shows very uniform rodlike morphology, which is in good agreement with the result obtained by the small-angle XRD analysis, confirming successful synthesis of high-quality SBA-15 silica. The

micro-capsule catalyst Fe/Silica/SZ, with Fe/Silica as core and H-ZSM-5 as shell, was prepared by an in-situ crystallization transformation of SBA-15 as silicon source during SAC process. As shown in Fig. 5b, Fe/Silica/SZ reveals the presence of aggregates of worm-like H-ZSM-5 crystals. The TEM image of Fe/Silica/SZ (Fig. 5c) shows that the mesoporous channels are disordered, indicating the destroyed SBA-15 structure during catalyst preparation.

Fig. 5. SEM images of (a) SBA-15 and (b) Fe/Silica/SZ and TEM image of (c) Fe/Silica/SZ.

3.2 NH₃-TPD characterization

The acidic property of the micro-capsule catalyst was measured by NH₃-TPD. The NH₃-TPD profiles of Fe/SBA-15 and Fe/Silica/SZ are shown in Fig. 6. There is no obvious NH₃ desorption peak in Fe/SBA-15 sample, indicating that Fe/SBA-15 catalyst has no remarkable acidic sites. Two distinct NH₃ desorption peaks appear in micro-capsule catalyst Fe/Silica/SZ. The desorption peaks above 400 °C can be assigned to the desorption of NH₃ from strong B and L sites [41]. The desorption peaks below 400 °C can be attributed to NH₃ from weak acidic sites (weak B and L sites) or physically adsorbed ammonia. The abundant acidic sites of the micro-capsule catalyst are mainly provided by the H-ZSM-5 shell, which are very important to yield middle isoparaffin.

Fig. 6. NH₃-TPD profiles of SBA-15 and Fe/Silica/SZ samples.

3.3 FTS reaction properties

The FTS results and product distributions of Fe/SBA-15, micro-capsule catalyst Fe/Silica/SZ and a physical mixture catalyst Fe/SBA-15+SZ for isoparaffin synthesis

were tested in a fixed bed reactor, as compared in Table 2 and Fig. 7. The CO conversion of Fe/Silica/SZ is 57.6 %, slightly lower than that of Fe/SBA-15 (68.5 %), which is mainly ascribed to the partial coverage of Fe active sites by the H-ZSM-5 shell [42]. According to Fig. 7 and Table 2, Fe/SBA-15 exhibits a broad product distribution up to C₁₇, but the isoparaffin selectivity is only 8.2 %, with a high selectivity of olefin up to 49.2 %. For Fe/Silica/SZ micro-capsule catalyst, extremely high isoparaffin selectivity with 46.5 % is obtained. Meanwhile, the selectivity of olefin decreases significantly to 16.8 %. Surprisingly, according to the product distributions (Fig. 7), the light olefin (C₂₋₄) selectivity decreases suddenly after doping acidic zeolite into Fe/SBA-15 (Fe/Silica/SZ and Fe/SBA-15+SZ), which may be the transformation of a partial FTS products from light olefin to middle isoparaffin. For Fe/Silica/SZ, the hydrocracking and isomerization of the formed C₁₂₊ hydrocarbons by the acidic sites on H-ZSM-5 shell may contribute to improve isoparaffin selectivity. It is noted that the increase of CH₄ and CO₂ selectivity are very small after the coating of H-ZSM-5 shell on Fe/Silica core catalyst. This might be due to the small size and thin shell of the micro-capsule catalyst. On the case of physical mixture catalyst (Fe/SBA-15+SZ), a broad product distribution and relatively low isoparaffin selectivity (33.9 %) are achieved. It is clear that certain amount of C₁₂₊ fractions (Fig. 7) is still produced, up to C₁₆ hydrocarbons, in the physical mixture catalyst, due to the lack of spatial confinement effect.

Table 2Catalytic performance of various catalysts for FTS^a.

Catalysts	Conv./%	Sel./%								
	CO	CO ₂	CH ₄	C ₂₋₄	C ₅₊	C _n	C ₌	C _{iso}	C ₌ /C _n ^b	C _{iso} /C _n ^c
Fe/SBA-15	68.5	37.0	12.8	23.1	51.0	42.6	49.2	8.2	1.65	0.40
Fe/Silica/SZ	57.6	37.3	15.3	5.8	62.7	36.7	16.8	46.5	0.79	3.71
Fe/SBA-15+SZ	63.6	43.8	19.2	2.5	54.1	56.0	10.1	33.9	0.27	1.67

^a Reaction conditions: Catalyst weight, 0.5 g; T, 300 °C; P, 1.0 MPa; H₂/CO, 1; W/F, 10 gh/mol.^b C₌/C_n is the ratio of olefin to paraffin of C₂₊.^c C_{iso}/C_n is the ratio of olefin to paraffin of C₄₊. **Fig. 7.** FTS product distributions of catalysts:*yellow, n-paraffin; gray (slash), olefin; cyan (perpendicular), isoparaffin.*

According to the structure characterization and performance tests, the schematic diagram of middle isoparaffin synthesis over the micro-capsule catalyst is illustrated in Fig. 8. Syngas first passes through the mesoporous channels of core to contact the active sites, where normal paraffin and olefin are formed. The formed light olefin and long chain paraffin subsequently convert to isoparaffin by the catalysis with the acidic sites of H-ZSM-5 shell. High selectivity of middle isoparaffin is realized with the help of spatial confinement effect of H-ZSM-5 shell. The mesoporous channels of

micro-capsule catalyst core (Fe/Silica) can offer a high diffusion rate of reactants and products. Moreover, the H-ZSM-5 micropores shell with acidic sites affords to hydrocrack and isomerize heavy hydrocarbons, simultaneously tuning the product selectivity.

Fig. 8. Schematic diagram of middle isoparaffin synthesis over micro-capsule catalyst.

4. Conclusions

A novel micro-capsule catalyst with interior Fe/Silica core and exterior H-ZSM-5 shell was firstly designed and performed for direct synthesis of middle isoparaffin from syngas. The as-prepared micro-capsule catalyst Fe/Silica/SZ achieved an excellent performance of isoparaffin selectivity with 46.5 %. The mesoporous channels of micro-capsule catalyst core (Fe/Silica) can offer a high diffusion rate of reactants and products, while the H-ZSM-5 micropores shell with acidic sites affords to hydrocrack and isomerize heavy hydrocarbons, simultaneously tuning the products selectivity. The spatial confinement effect of the H-ZSM-5 zeolite shell acted as an important role for the improvement of isoparaffin selectivity. The newly developed heterogeneous catalyst preparation method reported here will be also widely applied in designing other similar micro-capsule catalyst for varied tandem catalysis processes.

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References

- [1] Q. Zhang, J. Kang, Y. Wang, *ChemCatChem* 2 (2010) 1030-1058.
- [2] C. Xing, W. Shen, G. Yang, R. Yang, P. Lu, J. Sun, Y. Yoneyama, N. Tsubaki, *Catal. Commun.* 55 (2014) 53-56.
- [3] X.H. Li, X.H. Liu, Z.W. Liu, K. Asami, K. Fujimoto, *Catal. Today* 106 (2005) 154-160.
- [4] K. Cheng, J. Kang, S. Huang, Z. You, Q. Zhang, J. Ding, W. Hua, Y. Lou, W. Deng, Y. Wang, *ACS Catal.* 2 (2012) 441-449.
- [5] S. Sartipi, M. Alberts, V.P. Santos, M. Nasalevich, J. Gascon, F. Kapteijn, *ChemCatChem* 6 (2014) 142-151.
- [6] S. Sartipi, K. Parashar, M.J. Valero-Romero, V.P. Santos, B. van der Linden, M. Makkee, F. Kapteijn, J. Gascon, *J. Catal.* 305 (2013) 179-190.
- [7] S. Sartipi, M. Makkee, F. Kapteijn, J. Gascon, *Catal. Sci. Technol.* 4 (2014) 893-907.
- [8] J. Sun, W. Niu, A. Taguchi, T. Abe, Y. Yoneyama, N. Tsubaki, *Catal. Sci. Technol.* 4 (2014) 1260-1267.
- [9] J. Sun, X. Li, A. Taguchi, T. Abe, W. Niu, P. Lu, Y. Yoneyama, N. Tsubaki, *ACS Catal.* 4 (2014) 1-8.
- [10] J. Kang, K. Cheng, L. Zhang, Q. Zhang, J. Ding, W. Hua, Y. Lou, Q. Zhai, Y. Wang, *Angew. Chem. Int. Ed.* 50 (2011) 5200-5203.
- [11] Q. Zhang, K. Cheng, J. Kang, W. Deng, Y. Wang, *ChemSusChem* 7 (2014) 1251-1264.
- [12] Y. Yoneyama, J. He, Y. Morii, S. Azuma, N. Tsubaki, *Catal. Today* 104 (2005) 37-40.
- [13] X. Li, K. Asami, M. Luo, K. Michiki, N. Tsubaki, K. Fujimoto, *Catal. Today* 84 (2003) 59-65.
- [14] J. Sun, C. Xing, H. Xu, F. Meng, Y. Yoneyama, N. Tsubaki, *J. Mater. Chem. A* 1 (2013) 5670-5678.
- [15] S.H. Kang, J.H. Ryu, J.H. Kim, I.H. Jang, A.R. Kim, G.Y. Han, J.W. Bae, K.S. Ha, *Energy Fuel* 26 (2012) 6061-6069.
- [16] G. Yang, C. Xing, W. Hirohama, Y. Jin, C. Zeng, Y. Suehiro, T. Wang, Y. Yoneyama, N. Tsubaki, *Catal. Today* 215 (2013) 29-35.

- [17] J. Bao, J. He, Y. Zhang, Y. Yoneyama, N. Tsubaki, *Angew. Chem. Int. Ed.* 47 (2008) 353-356.
- [18] J. He, Z. Liu, Y. Yoneyama, N. Nishiyama, N. Tsubaki, *Chem. Eur. J.* 12 (2006) 8296-8304.
- [19] Y. Jin, R. Yang, Y. Mori, J. Sun, A. Taguchi, Y. Yoneyama, T. Abe, N. Tsubaki, *Appl. Catal. A Gen.* 456 (2013) 75-81.
- [20] X. Li, J. He, M. Meng, Y. Yoneyama, N. Tsubaki, *J. Catal.* 265 (2009) 26-34.
- [21] C. Xing, G. Yang, D. Wang, C. Zeng, Y. Jin, R. Yang, Y. Suehiro, N. Tsubaki, *Catal. Today* 215 (2013) 24-28.
- [22] B. Sun, G. Yu, J. Lin, K. Xu, Y. Pei, S. Yan, M. Qiao, K. Fan, X. Zhang, B. Zong, *Catal. Sci. Technol.* 2 (2012) 1625-1629.
- [23] Q. Lin, G. Yang, X. Li, Y. Yoneyama, H. Wan, N. Tsubaki, *ChemCatChem* 5 (2013) 3101-3106.
- [24] Y. Wang, M. Noguchi, Y. Takahashi, Y. Ohtsuka, *Catal. Today* 68 (2001) 3-9.
- [25] J.P. Hong, P.A. Chernavskii, A.Y. Khodakov, W. Chu, *Catal. Today* 140 (2009) 135-141.
- [26] Q. Cai, J.L. Li, *Catal. Commun.* 9 (2008) 2003-2006.
- [27] Y. Ohtsuka, Y. Takahashi, M. Noguchi, T. Arai, S. Takasaki, N. Tsubouchi, Y. Wang, *Catal. Today* 89 (2004) 419-429.
- [28] L.A. Cano, M.V. Cagnoli, N.A. Fellenz, J.F. Bengoa, N.G. Gallegos, A.M. Alvarez, S.G. Marchetti, *Appl. Catal. A Gen.* 379 (2010) 105-110.
- [29] J. Panpranot, J.G. Goodwin Jr., A. Sayari, *J. Catal.* 211 (2002) 530-539.
- [30] J. Panpranot, J.G. Goodwin Jr., A. Sayari, *J. Catal.* 213 (2003) 78-85.
- [31] X. Meng, F.S. Xiao, *Chem. Rev.* 114 (2014) 1522-1544.
- [32] L.H. Chen, X.Y. Li, J.C. Rooke, Y.H. Zhang, X.Y. Yang, Y. Tang, F.S. Xiao, B.L. Su, *J. Mater. Chem.* 22 (2012) 17381-17403.
- [33] M.S. Holm, E. Taarning, K. Egeblad, C.H. Christensen, *Catal. Today* 168 (2011) 3-16.
- [34] G. Yang, N. Tsubaki, J. Shamoto, Y. Yoneyama, Y. Zhang, *J. Am. Chem. Soc.* 132 (2010) 8129-8136.
- [35] G. Yang, M. Thongkam, T. Vitidsant, Y. Yoneyama, Y. Tan, N. Tsubaki, *Catal. Today* 171 (2011) 229-235.
- [36] K. Pinkaew, G. Yang, T. Vitidsant, Y. Jin, C. Zeng, Y. Yoneyama, N. Tsubaki, *Fuel* 111 (2013) 727-732.
- [37] G. Yang, Kawata, Q. Lin, J. Wang, Y. Jin, C. Zeng, Y. Yoneyama, N. Tsubaki, *Chem. Sci.* 4 (2013) 3958-3964.
- [38] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* 279 (1998) 548-552.
- [39] J. Zhou, Z. Hua, Z. Liu, W. Wu, Y. Zhu, J. Shi, *ACS Catal.* 1 (2011) 287-291.
- [40] Q.Q. Hao, Y.H. Zhao, H.H. Yang, Z.T. Liu, Z.W. Liu, *Energy Fuel* 26 (2012) 6567-6575.
- [41] F. Lonyi, J. Valyon, *Micropor. Mesopor. Mater.* 47 (2001) 293-301.

- [42] G. Yang, J. He, Y. Zhang, Y. Yoneyama, Y. Tan, Y. Han, T. Vitidsant, N. Tsubaki, *Energy Fuel* 22 (2008) 1463-1468.

Graphical abstract

Fe based Micro-Capsule catalyst