Catalysis Today 251 (2015) 41–46

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

Chuang Xing[a,b], Jian Sun[b], Qingjun Chen[b], Guohui Yang[b], Nobuyoshi Muranaka[b], Peng Lu[b], Wenzhong Shen[c], Pengfei Zhu[b], Qinhong Wei[b], Jie Li[b], Jianwei Mao[a], Ruiqin Yang[a], Noritatsu Tsubaki[a,b,*]

[a] *Zhejiang Provincial Key Lab for Chem. & Bio. Processing Technology of Farm Product, School of Biological and Chemical Engineering, Zhejiang University of Science and Technology, Hangzhou 310023, PR China*
[b] *Department of Applied Chemistry, Graduate School of Engineering, University of Toyama, Gofuku 3190, Toyama 9308555, Japan*
[c] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China*

ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form
24 September 2014
Accepted 1 October 2014
Available online 4 November 2014

Keywords:
Fischer–Tropsch synthesis
Iron
Micro-capsule catalyst
Spatial confinement effect
Isoparaffin

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 μm. 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.

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 cannot 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 in 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

---

[*] Corresponding author. Tel.: +81 76 445 6846; fax: +81 76 445 6846.
E-mail address: tsubaki@eng.u-toyama.ac.jp (N. Tsubaki).

http://dx.doi.org/10.1016/j.cattod.2014.10.022
0920-5861/© 2014 Elsevier B.V. All rights reserved.

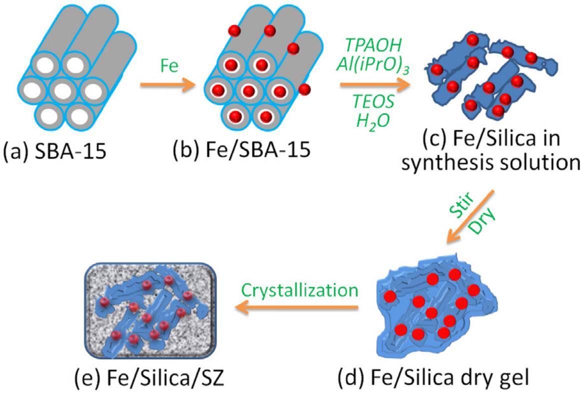

Fig. 1. Synthesis schematic route of iron-based micro-capsule catalyst.

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, and 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 cannot 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 μm [18,34,37]. It is a significant technological interest to decrease the size of capsule catalyst. Herein, we designed the Fe base micro-capsule catalyst with unique size approximately 1–2 μm. 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 the 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).

2. Experimental

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 $Fe(NO_3)_3 \cdot 9H_2O$ 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 aluminum isopropoxide, 10.72 g of distilled water and 3.26 g of TEOS under vigorous 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 catalysts.

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 Cu Kα radiation (40 kV, 40 mA). The wide-angle X-ray diffraction (XRD) patterns were characterized by a Rigaku D/max-2550 V diffractometer with Cu Kα 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 (NH_3-TPD) experiments were conducted in a flow apparatus on a BELCAT-B-TT (BEL Co.) instrument. In a typical NH_3-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% NH_3 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