Catalysis Communications 55 (2014) 53–56

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

Completed encapsulation of cobalt particles in mesoporous H-ZSM-5 zeolite catalyst for direct synthesis of middle isoparaffin from syngas

Chuang Xing [a,b], Wenzhong Shen [c], Guohui Yang [b], Ruiqin Yang [a], Peng Lu [b], Jian Sun [b], Yoshiharu Yoneyama [b], 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, 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 8 January 2014
Received in revised form 10 June 2014
Accepted 17 June 2014
Available online 26 June 2014

Keywords:
Fischer–Tropsch synthesis
Encapsulation
Mesoporous zeolite
Isoparaffin

ABSTRACT

The completed encapsulation cobalt clusters inside the channels of mesoporous H-ZSM-5 zeolite catalyst was synthesized using mesoporous carbon as a hard template and evaluated in Fischer–Tropsch synthesis (FTS) for direct synthesis of middle isoparaffin. The characterization and catalytic performance tests revealed that the acid sites of mesoporous zeolite tuned FTS product distribution. The isoparaffin selectivity of Co/MZ was 34.6% to become the main FTS products because of the optimized hydrocracking and isomerization function of the mesoporous structure of H-ZSM-5 support. The novel route of catalyst preparation, first reported here, can also be extended into other clean fuel synthesis fields.

1. Introduction

Fischer–Tropsch synthesis (FTS), a clean synfuel technology from carbon monoxide and hydrogen, is carried out by using some metals, like ruthenium, cobalt, nickel or iron, as active components to produce linear paraffin with a wide distribution range. However, the main products of common FTS reaction are linear paraffin and α-olefin, which severely follow the known Anderson–Schulz–Flory (ASF) law [1]. Recently, the synthesis of branched hydrocarbons with high octane value, as the substitute of gasoline (C_{5-11}), has gained more attentions [2–5]. In order to tune the FTS product distribution, acid sites are usually introduced into catalyst supports for the hydrocracking and isomerization on the initial FTS products [6]. As reported previously, the physical mixture approach and two-step hydrocracking reaction for the direct synthesis of middle isoparaffin through FTS reaction were presented and investigated [7]. In addition, a new concept of zeolite capsule catalyst with a special core-shell structure was developed by our group, realizing the direct synthesis of middle isoparaffin with high selectivity, completely depressing the formation of heavy hydrocarbons [8]. However, due to the microporous properties, it is hard to get satisfied diffusion efficiency for both reactants and products on the zeolite-based catalysts. In order to overcome this disadvantage of poor diffusion, mesoporous materials as catalysts or catalyst supports have been studied deeply in recent years [9]. Bi-functional catalysts that composed of the conventional FTS catalysts and acidic zeolite have been reported for the direct synthesis of middle isoparaffin. Sartipi et al. recently studied deeply that mesoporous H-ZSM-5 zeolite supported Co catalyst for direct synthesis C_5–C_9 isoparaffin, which exhibited higher isoparaffin selectivity as well as FTS activity than the conventional catalysts [10–14]. Some metallic particles, however, deposited still on the surface of zeolite by employing the general impregnation way (See Fig. S1 in Supplementary material).

In this work, the completed encapsulation of cobalt clusters inside the channels of mesoporous H-ZSM-5 zeolite was designed by using mesoporous carbon as a hard template and applied for middle isoparaffin direct synthesis from syngas via FTS reaction. The overall synthetic route is illustrated in Fig. 1 (catalyst preparation see Supplementary material). First, mesoporous carbon (Fig. 1(c), denoted MC) was synthesized using furfuryl alcohol (FA) as a carbon source, Al-doped SBA-15 (Al-SBA-15, Fig. 1(b)) as a hard template, followed by removing Al-SBA-15 hard template with 10% HF. Co/MC (Fig. 1(d)) was prepared by the impregnation method. Co/MC was directly adopted as a hard template for the mesopore formation in zeolite, while the carbon template and organic template were removed in air. The residual metallic cobalt clusters from Co/MC were deposited in mesoporous zeolite (Co/MZ, 10 wt.% Co, Table S1).

---

[*] Corresponding author at: Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan. Tel./fax: +81 76 445 6846.
E-mail address: tsubaki@eng.u-toyama.ac.jp (N. Tsubaki).

http://dx.doi.org/10.1016/j.catcom.2014.06.018

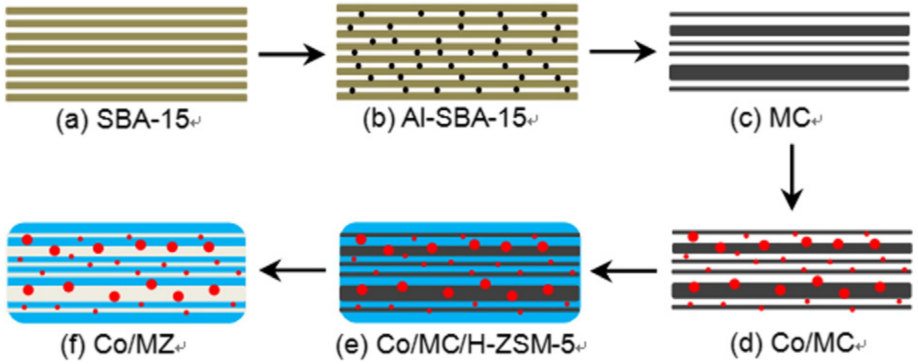

Fig. 1. Illustration of the synthesis procedure of the completed encapsulating cobalt clusters in the mesoporous H-ZSM-5 zeolite: a) SBA-15; b) Al-SBA-15 (Al doped SBA-15); c) MC (mesoporous carbon); d) Co/MC (MC surface-deposited cobalt nanoparticles); e) Co/MC/H-ZSM-5 composite (coating of H-ZSM-5 on Co/MC); f) Co/MZ (mesoporous zeolite completed encapsulating cobalt particles after removing the template).

2. Result and discussion

The small-angle XRD patterns of the calcined SBA-15 and Al-SBA-15 samples are showed in Fig. S2. Both of the samples exhibit a very intense diffraction peak at $2\theta = 1.1°$, which can be ascribed to a hexagonal symmetry [15]. There is no obvious difference between SBA-15 and Al-SBA-15 at the small-angle. For the Co/MZ sample, the wide-angle powder pattern in region of $2° < 2\theta < 80°$ is given in Fig. 2. A series of diffraction peaks are the specific crystal of H-ZSM-5 zeolite at the range of $2\theta = 7$–$9°$ and 23–25°, which confirms the MFI structure of Co/MZ sample. The crystallization particles are CoO, rather than Co_3O_4, with the size of 3.1 nm for Co/MC. It is possible that the Co_3O_4 was reduced to CoO by mesoporous carbon during calcination process (350 °C under Ar flow for 3 h). For the Co/MZ, the intensity of Co_3O_4 crystallization peaks is clearly weaker than that of mesoporous zeolite. The size of Co_3O_4 crystallite is about 5 nm.

The BET surface areas and pore volumes of mesoporous samples are listed in Table 1. As compared to the Co/SBA-15, the BET surface area and total pore volume of the calcined Co/Al-SBA-15 decrease obviously. However, Co/Al-SBA-15 exhibits micropore volume of 0.08 cm^3/g due to the doped aluminium and cobalt in SBA-15. MC was synthesized through the carbonization of FA using Al-SBA-15 as a template, which exhibits a large BET surface area and mesopore volume. Moreover, no micropore volume is detected to this sample. It is clear that the micropore and mesopore surface areas of Co/MZ catalyst are 255 and 153 m^2/g respectively, indicating the coexistence of micropores and mesopores. Co/MZ catalyst has a smaller mesopore volume (0.17 cm^3/g) than other samples. The decrease of surface area and pore volume of Co/MZ catalyst derives from the partial blockage of pores by cobalt clusters and/or the partial collapse of the mesoporous structure [16].

Fig. 3 shows the nitrogen sorption isotherms of the SBA-15, Al-SBA-15, MC and Co/MZ samples. A H1 hysteresis loop of typical IV isotherm clearly appears on SBA-15 and Al-SBA-15, which is a typical adsorption phenomenon for mesoporous materials with 2D-hexagonal structure [17]. Nitrogen sorption isotherm of MC also exhibits type IV with a pronounced hysteresis loop, indicating that the mesopores are formed. However, Co/MZ catalyst exhibits a broad mesoporous distribution. The prepared MC has bigger BET surface area (1540 m^2/g) and pore volume (1.48 m^3/g). It can act as mesoporous scaffolds for zeolite crystallization inside its body, and only few parts of its mesopores are possibly blocked by some zeolite synthesis solution for the formation of the mesoporous zeolite [18].

The TEM images of Co/MZ are showed in Fig. 4. The TEM image in Fig. 4(a) illustrates that single crystal within mesopores is created by the combustion of MC template. It reveals that the residual cobalt clusters from Co/MC are completely deposited inside the mesoporous channels of zeolite. Fig. 4(b) gives a representative TEM image of cobalt particles with the size of 3–5 nm, which is slightly larger than the mean pore size of MC due to the Co_3O_4 aggregation under calcination process.

FTS reaction performances of the different cobalt-containing mesoporous catalysts are presented in Table 2. The CO conversion of Co/MZ is lower than that of Co/SBA-15 catalyst under the same reaction conditions, which is attributed to its low reduction degree (Table S2, see

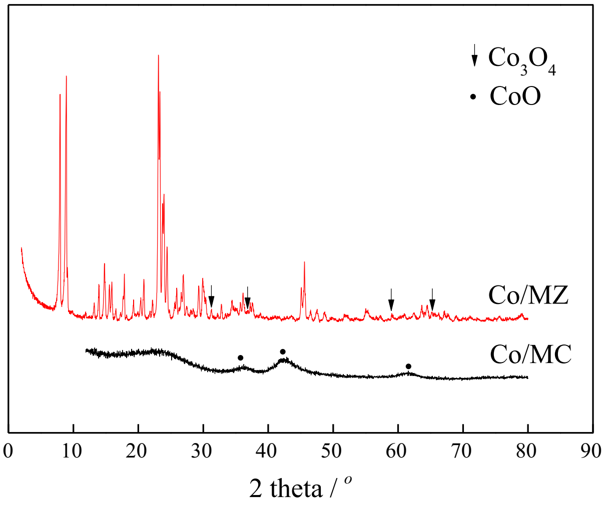

Fig. 2. XRD patterns of Co/MC and Co/MZ catalysts.

Table 1
Summary of the textural properties of different samples.

Sample	$S(m^2/g)$[a]			$V(m^3/g)$		
	Total	Micropore[b]	Mesopore[c]	Total[d]	Micropore[e]	Mesopore[f]
Co/SBA-15	787	0	787	1.12	0	1.12
Co/Al-SBA-15	536	150	386	0.65	0.08	0.57
MC	1540	0	1540	1.48	0	1.48
Co/MZ	408	255	153	0.31	0.14	0.17

[a] BET surface area.
[b] Microporous surface area evaluated by the *t*-plot method.
[c] Mesoporous surface area evaluated by the *t*-plot method.
[d] Total pore volume calculated by single point method at $P/P_0 = 0.995$.
[e] Micropore volume evaluated by the *t*-plot method.
[f] Mesopore volume calculated as $V_{Meso} = V_{Total} - V_{Micro}$.