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Tunable isoparaffin and olefin synthesis in Fischer–Tropsch synthesis achieved by composite catalyst

Chuang Xing [a,b], Jian Sun [a], Guohui Yang [a], Wenzhong Shen [c], Li Tan [a], Pengfei Zhu [a], Qinhong Wei [a], Jie Li [a], Masahiro Kyodo [a], Ruiqin Yang [b], Yoshiharu Yoneyama [a], Noritatsu Tsubaki [a,*]

[a] Department of Applied Chemistry, Graduate School of Engineering, University of Toyama, Gofuku 3190, Toyama 9308555, Japan
[b] 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
[c] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

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ABSTRACT

Hierarchical HZSM-5 zeolite with combined micropores and mesopores was synthesized by one-step approach with TPAOH and F127 as dual templates. The physical and acidic properties of the hierarchical HZSM-5 zeolite were characterized by XRD, N_2 adsorption–desorption isotherm, SEM, TEM, and NH_3-TPD techniques. The hierarchical HZSM-5 zeolite exhibited a significantly higher mesopore surface area and larger mesopore volume than that of the conventional HZSM-5. The prepared hierarchical HZSM-5 and conventional HZSM-5 zeolite supported cobalt catalysts were evaluated via Fischer–Tropsch synthesis (FTS) reaction to tune product selectivity. Compared with the conventional catalyst, the CO conversion of FTS reaction on the present catalyst increased significantly. Meanwhile, the C_{5+} selectivity and isoparaffin selectivity also increased. The C_{5-11} hydrocarbons with a lot of isoparaffin and olefin had become the main FTS products due to the optimized hydrocracking and isomerization afforded by the hierarchical pore structure, different from the conventional FTS hydrocarbons which were mainly composed of normal paraffin.

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1. Introduction

Zeolite, with high internal surface area, high thermal stability, unique micropore size, and intrinsic acidity, has been widely used as the shape-selective catalysts in oil refining and fine chemistry [1]. Unfortunately, the relatively small micropores strongly inhibit mass transfer of reactants and products in catalytic reactions [2,3]. In order to overcome this problem, the hierarchical zeolite as catalysts or catalyst supports has been studied widely. In recent years, different techniques were employed to synthesize hierarchical zeolite with combined micropores and mesopores, generally including steaming, acid leaching (dealumination) or base leaching (desilication), templating, chemical treatment and direct synthesis process [4]. For example, desilication has been studied deeply as a common method to generate mesoporous HZSM-5 zeolite [5]. Moreover, hierarchical zeolite is usually synthesized through nanocasting route on various templates, e.g. $CaCO_3$ [6], carbon black [7], carbon nanotubes [8], carbon nanofiber [9], ordered mesoporous carbon [10], carbon aerogels and polymer aerogels [11]. However, the troublesome preparation or high cost of the carbon template is still inevitable. Therefore, direct synthesis of mesoporous zeolite is one of the promising strategies to reduce the use of raw materials, energy and costs.

Fischer–Tropsch synthesis (FTS) reaction is a process to produce ultra clean liquid fuel via the transformation syngas ($CO + H_2$), which can be generated from many resources such as coal, biomass, nature gas and garbage [12]. The FTS products are mostly linear paraffin, whose distribution (from methane to long-chain hydrocarbons) obeys the Anderson–Schulz–Flory (ASF) law [13]. Middle hydrocarbons, with a range of C_{5-11}, particularly rich in isoparaffin and olefin, as gasoline-range liquid fuels with high octane value, are an important fuel in petrochemical industry. It is well known that acidic zeolite or other acidic supports present good performance for hydrocracking and isomerization to produce more isoparaffin as the ideal synthetic gasoline [14,15]. To obtain high selectivity of C_{5-11} hydrocarbons with high isoparaffin selectivity, several technologies such as conventional zeolite supported metal [16], physical mixture [17], two-step hydrocracking reaction [18] and a novel capsule catalyst [19] for middle isoparaffin synthesis via FTS have been investigated.

Here, we report a facile one-step synthesis of hierarchical HZSM-5 zeolite with TPAOH and F127 as dual templates, being applied in FTS reaction for direct middle isoparaffin synthesis. The overall synthetic route is illustrated in Fig. 1. In the first step, a homogeneous solution, including silicon source, aluminium source, water, micro- and meso-templates, was prepared and then the solution converted gradually

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

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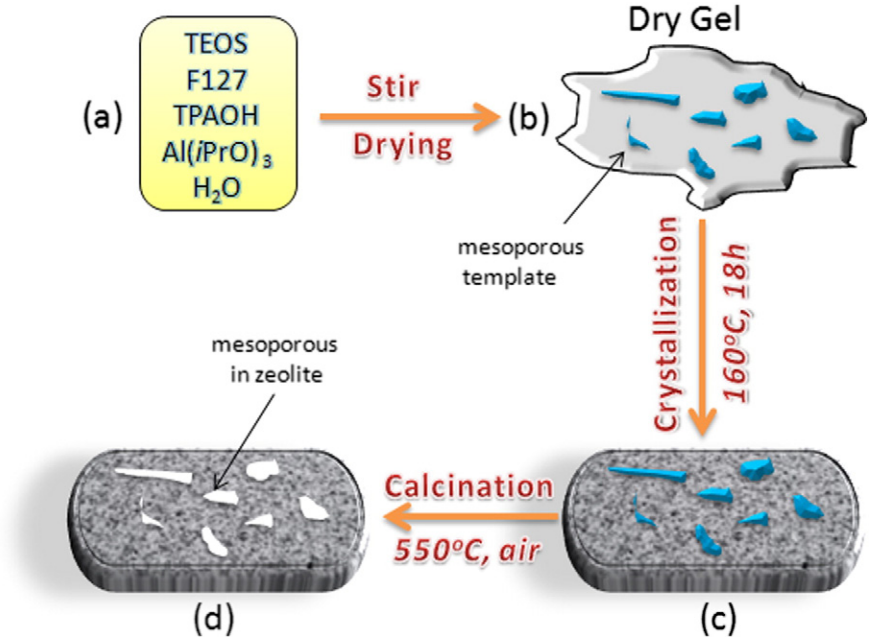

Fig. 1. Schematic depiction of the hierarchical zeolite preparation procedure.

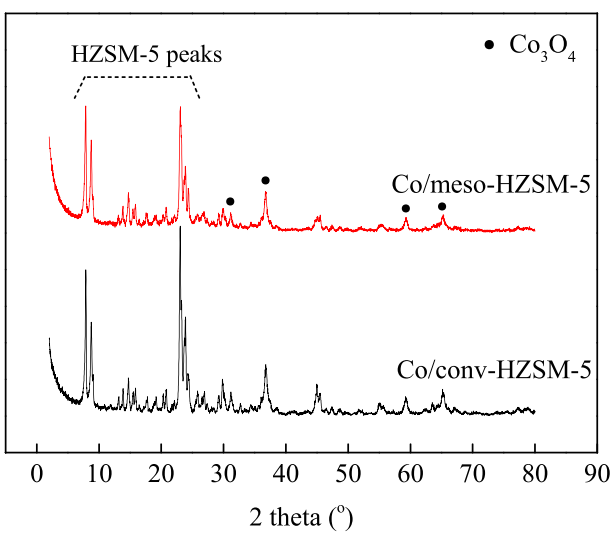

Fig. 2. XRD patterns of Co/conv-HZSM-5 and Co/meso-HZSM-5.

into dry gel as in Fig. 1(b), followed by crystallization in a water-steaming environment as in Fig. 1(c). Finally, the micro- and meso-templates were removed through calcination in air.

2. Experimental section

2.1. Catalyst preparation

The hierarchical HZSM-5 zeolite was prepared by a mixed aqueous solution of aluminium isoporpoxide, pluronic F127 (Sigma, MW = 12600), tetraethylorthosilicate (TEOS) and distilled water under continuous stirring to get a clear solution. Then, tetrapropylammonium hydroxide (TPAOH) was added dropwise to the solution, and continued stirring at 40 °C to form a gel. The molar ratio of the resultant gel was 0.5 Al_2O_3:50 SiO_2:0.6 F127:6 TPAOH:2400 H_2O. The gel was aged at 60 °C, and dried at 90 °C overnight. Finally, the solid gel was transferred to Teflon-lined reactor and crystallized by steam-assisted crystallization (SAC) method at 160 °C for 18 h. The product was washed, dried and calcined at 550 °C for 5 h. The hierarchical HZSM-5 zeolite was denoted as meso-HZSM-5. A conventional HZSM-5 zeolite (conv-HZSM-5), as a reference catalyst, was also prepared by the same method but without F127 addition.

The FTS catalysts with the Co loading amount of 10 wt.% were prepared by an incipient wetness impregnation method on conv-HZSM-5 and meso-HZSM-5 supports with the aqueous solution of cobalt nitrate. Then the wet catalysts were dried at 120 °C overnight and calcined in air at 400 °C for 2 h. These catalysts were denoted as Co/conv-HZSM-5 and Co/meso-HZSM-5, respectively.

Table 1
Summary of the textural properties of different samples.

Sample	S(m^2/g)[a]			V(cm^3/g)			XRD (nm)[g]	Acidic amount (mm/g)
	Total	Micropore[b]	Mesopore[c]	Total[d]	Micropore[e]	Mesopore[f]	Co_3O_4	
conv-HZSM-5	615	415	200	0.48	0.23	0.25	16.1	2.02
meso-HZSM-5	578	286	292	0.78	0.16	0.62	12.7	2.26

[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 estimated from the adsorbed amount at $P/P_0 = 0.995$.
[e] Micropore volume evaluated by the *t*-plot method.
[f] Mesopore volume calculated as $V_{Meso} = V_{Total} - V_{Micro}$.
[g] Co_3O_4 crystallite size derived from XRD, applying the Scherrer equation.

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