[Letter]

Novel Three-component Zeolite Capsule Catalyst for Direct Synthesis of Isoparaffin

Montree Thongkam ^{†1), †2)}, Guohui Yang ^{†1)}, Tharapong Vitidsant ^{†2)*}, and Noritatsu Tsubaki ^{†1)*, †3)}^{†1)} Dept. of Applied Chemistry, Graduate School of Engineering, University of Toyama,
Gofuku 3190, Toyama 930-8555, JAPAN^{†2)} Dept. of Chemical Technology, Faculty of Science, Chulalongkorn University,
Bangkok 10330, THAILAND^{†3)} JST, CREST, Sanbancho 5, Chiyoda-ku, Tokyo 102-0075, JAPAN

(Received March 23, 2009)

One zeolite capsule catalyst with core(Co/Al₂O₃)/shell(H-beta membrane) structure was prepared and used for isoparaffin direct synthesis *via* FTS reaction. Based on this core/shell zeolite capsule catalyst, a novel palladium painted zeolite capsule catalyst with three-component core (Co/Al₂O₃)/shell (H-beta membrane)/paint (Pd) structure was designed. In the isoparaffin synthesis on this three-component zeolite capsule catalyst, the olefins effused from the zeolite capsule catalyst were *in-situ* hydrogenated effectively, mostly converted to isoparaffin.

Keywords: Isoparaffin, Zeolite, Microencapsulation, Three-component structure, Hydrogenation

1. Introduction

Recently, more attention has been focused on the production of light isoparaffin *via* FTS reaction because of its wide foreground as synthetic gasoline alkylate. Zeolite was the effective catalyst for cracking and isomerization reaction¹⁾. The physically mixed catalyst of conventional FTS catalyst and zeolite can not decompose the heavy hydrocarbons in the final FTS products completely²⁾. Previous work of our group had represented a novel catalyst with a core/shell structure³⁾. Herein, we presented a catalyst with a new core (Co/Al₂O₃) and new shell (H-beta membrane). And then, a three-component zeolite capsule catalyst with the core (Co/Al₂O₃)/shell (H-beta membrane)/paint (Pd) structure was prepared by loading palladium on the H-Beta zeolite shell. In the synthesis reaction, the selectivity of light isoparaffin was increased effectively using only this single three-component zeolite capsule catalyst.

イソパラフィンの直接合成用三成分ゼオライトカプセル型触媒

Montree Thongkam^{†1,2)}, 楊 國輝^{†1)}, Tharapong Vitidsant^{†2)*},

椿 範立^{†1,3)*}

^{†1)} 富山大学工学部, 930-8555 富山市五福 3190

^{†3)} 科学技術振興機構 CREST, 102-0075 東京都千代田区三番町 5

* Corresponding author, E-mail: tsubaki@eng.u-toyama.ac.jp;

Tharapong.V@Chula.ac.th

2. Experimental

The conventional FTS catalyst 5 wt% Co/Al₂O₃ was prepared by the incipient wetness impregnation of γ -Al₂O₃ (JRC-ALO-6, 0.35-0.85 mm) with Co(NO₃)₂·6H₂O solution. The zeolite membrane synthesis recipe for H-Beta zeolite capsule catalyst preparation was 48.24SiO₂:17.40TEAOH:1.0Al₂O₃:519.3H₂O. Tetraethylammonium hydroxide (TEAOH) was the template. Hydrothermal synthesis was performed on the Co/Al₂O₃ at 428 K with rotation rate of 2 rpm for 24 h. The final zeolite capsule catalyst after the calcination at 823 K for 8 h was named Co/Al₂O₃-B. The zeolite capsule catalyst without calcination was used to prepare the three-component zeolite capsule catalyst by incipient wetness impregnation method with dinitrodiammine palladium aqueous solution. The three-component zeolite capsule catalyst with 2.5 wt% Pd loading, named Co/Al₂O₃-Pd/B, was obtained after calcination at 823 K for 8 h.

3. Results and Discussion

The catalysts of conventional FTS catalyst Co/Al₂O₃, zeolite capsule catalyst Co/Al₂O₃-B and three-component zeolite capsule catalyst had been characterized by XRD

(Rigaku, RINT 2400), SEM (JEOL, JSM-6360LV) and EDS (JEOL, JED-2300) analysis. The XRD analysis of zeolite capsule catalyst Co/Al₂O₃-Pd/B identified the emergence of H-Beta zeolite on the core catalyst of Co/Al₂O₃.

Fig. 1 (A) Cross Section SEM Image and (B) EDS Line Analysis of Co/Al₂O₃-Pd/B

Figures 1A, 1B shown the cross-sectional SEM image of Co/Al₂O₃-Pd/B and its EDS line analysis. In **Fig. 1A**, a compact beta zeolite shell coated on the Co/Al₂O₃ surface can be observed clearly, and there was no crack or pinhole on the zeolite shell. The EDS line analysis in **Fig. 1B** showed that the radial distribution of SiKa increased suddenly while the AlKa dropped slightly at the interface of substrate with zeolite shell, indicating the phase change from Co/Al₂O₃ to H-beta, proving the complete coverage of H-beta zeolite membrane onto Co/Al₂O₃ core.

To ascertain the performance of H-Beta zeolite capsule catalyst Co/Al₂O₃-B and three-component zeolite capsule catalyst Co/Al₂O₃-Pd/B, the conventional FTS catalyst of 10 wt% Co/Al₂O₃ was also tested. **Table 1** presented the reaction performance of these catalysts. Zeolite capsule catalyst Co/Al₂O₃-B gave a lower CO conversion than that of Co/Al₂O₃, probably because of the partial coverage of Co active sites on the core by zeolite crystal during the hydrothermal synthesis process. For

Co/Al₂O₃-Pd/B, the palladium loaded on the surface of Co/Al₂O₃-B might partly decrease the syngas diffusion rate while passing through the zeolite shell. As a result, Co/Al₂O₃-Pd/B exhibited the lowest catalyst activity of 32.35 % than other catalysts.

Table 1 Reaction Performances of Zeolite Capsule Catalyst, Three-component Zeolite Capsule Catalyst ^{a)}

Catalyst	Conv.[%] CO	Select. [%]		C _{iso} /C _n ^{b)}	C ₌ /C _n ^{c)}
		CH ₄	CO ₂		
Co/Al ₂ O ₃	97.60	22.11	11.09	0.20	0.16
Co/Al ₂ O ₃ -B	85.25	11.45	3.08	0.38	0.74
Co/Al ₂ O ₃ -Pd/B	32.35	10.81	0.00	0.96	0.23

^{a)} Reaction conditions: 523 K, 1.0 MPa, H₂/CO = 2, W_{Co/Al₂O₃}/F_{CO+H₂}=15g·h/mol.

^{b)} C_{iso}/C_n is the ratio of *iso*-paraffin to *n*-paraffin of C₄₊.

^{c)} C₌/C_n is the ratio of olefin to *n*-paraffin of C₂₊.

For the isoparaffin synthesis, Co/Al₂O₃ gave the lowest C_{iso}/C_n ratio of 0.20, although with the highest catalytic activity. For Co/Al₂O₃-B, the C_{iso}/C_n ratio was 0.38, proving its effectiveness for isoparaffin direct synthesis with the spatial consecutive reaction model. However, the selectivity of olefins increased along with the production of isoparaffin undergoing the cracking reaction. Based on the hydrogenation of olefins by the palladium loaded on the zeolite shell, three-component zeolite capsule catalyst Co/Al₂O₃-Pd/B with the core/shell/paint structure exhibited the highest isoparaffin selectivity of 0.96. All the reactions, FTS, cracking, isomerization and hydrogenation can be accomplished simultaneously only using this single catalyst. Three-component H-beta zeolite capsule catalyst with core/shell/paint structure explored a new way for simple synthesis of multiple step reactions.

References

- 1) Feller, A., Guzman, A., Zuazo, I., Lercher, J. A., *J. Catal.*, **224**, 80 (2004).
- 2) Tsubaki, N., Yoneyama, Y., Michiki, K., Fujimoto, K., *Catal. Commun.*, **4**, 108(2003).
- 3) He, J., Liu, Z., Yoneyama, Y., Nishiyama, N., Tsubaki, N., *Chem. Eur. J.*, **12**, 8296 (2006).