

Supplementary Information

Oriented synthesis of target products in liquid-phase tandem reaction over a tripartite zeolite capsule catalyst

Guohui Yang,^a Hajime Kawata,^a Qihang Lin,^{a, b} Jingyan Wang,^a Yuzhou Jin,^a Chunyang
Zeng,^a Yoshiharu Yoneyama^a and Noritatsu Tsubaki^{a*}

^a Department of Applied Chemistry, School of Engineering, University of Toyama, Toyama
City 930-8555, Japan

^b Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen
University, Xiamen 361005, China

*Corresponding author: Noritatsu Tsubaki

E-mail: tsubaki@eng.u-toyama.ac.jp

Tel./Fax: +81-076-445-6846

Experimental

Preparing 5 wt% Ru/Al₂O₃ core catalyst

The core catalyst Ru/Al₂O₃ was prepared by incipient-wetness impregnation of γ -Al₂O₃ (JRC-ALO-6, Nikki-Universal Co., Ltd.; specific surface area: 180.0 m²·g⁻¹; pore volume: 0.93 cm³·g⁻¹; pellet size: 1.66 mm) with an aqueous solution of Ru(NO₃)₃ (Tanaka Kikinzoku Group). Here, the ruthenium loading amount of Ru/Al₂O₃ was 5 wt%. After the impregnation process, the catalyst precursor was first dried in air at 393 K for 12 h and then calcined in air at 673 K for 2 h. The final sample named Ru/Al₂O₃ was the core catalyst used for the following zeolite capsule catalyst preparation.

Tailor-made zeolite capsule catalyst

As our design, one layer of neutral Silicalite-1 zeolite shell was synthesized on the external surface of 5 wt% Ru/Al₂O₃ core catalyst pellets by using hydrothermal synthesis method. In this zeolite shell preparation process, the tetrapropylammonium hydroxide (TPAOH) was selected as the template and tetraethyl orthosilicate (TEOS) acted as the silica resources, both of these two reagents were the products of Wako Pure Chemical Industries, Ltd. The recipe of the precursor solution used for zeolite shell growth was 0.3TPAOH : 1.0TEOS : 120H₂O : 0.3NaOH (molar ratio). After the mixing of each reagents and then stirring for 6 h, the core catalyst Ru/Al₂O₃ (pellet size: 1.66 mm) was added into the precursor solution and aged at room temperature for 24 h. And then the precursor solution with core catalyst Ru/Al₂O₃ was sealed in a Teflon container by a stainless steel autoclave, followed by the hydrothermal synthesis at 453 K with 1 rpm rotation speed for 24 h. The used rotation synthesis could effectively prevent the cementation of catalyst pellets during the hydrothermal synthesis process, improving the integrity of zeolite shell simultaneously. The final sample was collected, washed until pH=7, calcined at 773 K in air for 5 h. Furthermore, it should be noted that some ion-exchange procedures on zeolite shell were absolutely forbidden in order to avoid the formation of acid sites. The obtained capsule catalyst had the special core-shell structure: one layer neutral Silicalite-1 zeolite shell enveloping core catalyst. The measured weight ratio of Silicalite-1 zeolite shell to core catalyst was 1 : 10.

Palladium doped zeolite capsule catalyst preparation

Palladium was doped into the zeolite shell of the capsule catalyst through incipient wetness impregnation method with an aqueous solution of Pd(NH₃)₂(NO₃)₂ (Tanaka Kikinzoku Group). The impregnated sample was dried at 373 K for 12 h and then calcined at 773 K for 5 h. The final Pd doped zeolite capsule catalyst obtained by this process was named as Ru/Al₂O₃-Pd/S and the Pd loading amount based on the Silicalite-1 zeolite shell weight was 2 wt%.

Hybrid catalyst preparation

For comparison, a hybrid catalyst had also been prepared by mixing 2 wt% Pd loaded Silicalite-1 zeolite powder with the crushed 5 wt% Ru/Al₂O₃ core catalyst. Here, the pure Silicalite-1 zeolite powder used for the preparation of 2 wt% Pd/Silicalite-1 was synthesized using the same recipe, hydrothermal synthesis and calcined conditions with that of zeolite capsule catalyst preparation mentioned above. The 2 wt% palladium loaded Silicalite-1 zeolite powder was obtained by the similar incipient wetness impregnation way to that of the Ru/Al₂O₃-Pd/S catalyst preparation as above, but without core catalyst pellets. After fully mixing of Pd/Silicalite-1 with Ru/Al₂O₃ catalyst, the obtained mixture was granulated under 60 MPa into the size range of 0.85-1.70 mm. And it should be noted that the final hybrid catalyst, named Ru/Al₂O₃-Pd/S-M, has the weight ratio of Pd doped zeolite towards Ru/Al₂O₃ catalyst same to that of the zeolite capsule catalyst Ru/Al₂O₃-Pd/S.

Catalyst characterization

XRD patterns were collected using a Rigaku RINT 2400 X-ray powder diffractometer equipped with a Cu K α radiation source at 40 kV and 40 mA. JEOL JSM-6350LV scanning electron microscope (SEM) equipped with a JEOL JED-2300 energy dispersive X-ray spectroscopy (EDS) was used to analyze the catalysts surface, cross-section morphology and their elemental composition information. In order to

determine the Ru state on the core catalyst before and after hydrothermal synthesis process, X-ray photoelectron spectra (XPS) was used to analyze the catalysts surface. The XPS spectra were recorded on a Thermo ESCALAB 250 Xi, and the binding energy was corrected by taking C1s line at 284.5 eV as an internal standard. In addition, another catalyst analyzer BELCAT-B-TT (Bel Japan Inc.) was also employed to perform H₂ temperature-programmed reduction (H₂-TPR) on catalysts, whereby to further determine the Ru reducibility before and after hydrothermal synthesis process.

Catalysts activity test

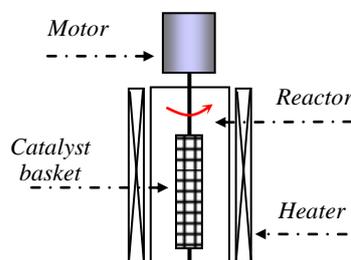
Before the reaction, all the catalysts were reduced by a flow of 100 % hydrogen with the rate of 60 ml·min⁻¹ at 673 K for 10 h, followed by passivating with 1 % oxygen diluted with nitrogen at room temperature for 1 h. The 20 ml of 20 wt% glycerol aqueous solution was first loaded in the stainless autoclave and then 1.0 g catalyst was fixed in the catalyst basket made by stainless steel net. Same with previous studies^[S1-6], here, water also acted as both of the solvent and by-product in the total reaction system. The reaction temperature and H₂ pressure were 473 K and 0.3 MPa respectively. The rotating rate of catalyst basket was 120 rpm. All of the products were analyzed by gas chromatograph. The gas products collected with a gas pack from the cooling reactor were analyzed by the Shimadzu GC-8A gas chromatograph with a flame ionization detector (FID, column: Gaskuropack 54 + Porapak Q). The liquid products were analyzed by Shimadzu GC-2014 gas chromatograph (FID, Capillary column: InertCap 5). All of the products selectivity given in this report was calculated in carbon molar base. The glycerol conversion and products selectivity are calculated through the following equations:

$$\text{Conversion (\%)} = \frac{C_{\text{mol}} \text{ of glycerol (before)} - C_{\text{mol}} \text{ of glycerol (after)}}{C_{\text{mol}} \text{ of glycerol (before)}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{C_{\text{mol}} \text{ of specific product}}{\text{Overall } C_{\text{mol}} \text{ of products}} \times 100\%$$

Results and discussion

For the catalyst performance evaluation in liquid-phase reaction system, in this report, we initially present a modified spinning basket reactor. This special reactor can effectively facilitate the utilization of zeolite capsule catalyst in liquid-phase chemical reaction, avoiding possible damage on zeolite shell from the collision between zeolite capsule catalyst and usual reactor impeller, thereby keeping the integrity of zeolite shell during the total reaction process. The followed Scheme S1 shows the schematic diagram of spinning basket reactor used for glycerol conversion on zeolite capsule catalyst.



Scheme S1. Schematic diagram of spinning basket liquid-phase reactor for glycerol conversion on zeolite capsule catalyst.

The synthesized shell of core-shell-dopant tripartite capsule catalyst is a multifunctional and composite Silicalite-1 zeolite shell with microporous structure. It also differs from the conventional pure Silicalite-1 zeolite. In this report, the zeolite shell synthesis was performed on the Al contained supports of Al₂O₃,

which can migrate a small quantity of Al from substrates into zeolite shell structure ^{[S7], [S8]}, positively improving the hydrophilic property of formed zeolite shell ^[S9-S11], but only resulting in a very few of ignorable acidic sites if without the additional ion-exchange process. In addition, the synthesized zeolite shell had also performed another doping process with palladium as guest, acting as the hydrogenation catalyst to hydrogenate the diffused acetol into the desired 1,2-propanediols. Here, the doped zeolite shell can further boost the hydrophilic property of zeolite shell ^[S12]. Furthermore, the adopted reaction temperature of 473K, very higher than the most used temperature for zeolite membrane separation process, has another positive effect on the diffusion of hydrophilic reactants and products passing through the zeolite shell of capsule catalyst ^[S13]. All these favorable factors can significantly ensure the smooth diffusion of glycerol reactant and generated products passing through zeolite shell without obvious restraint.

The zeolite capsule catalyst lifetime is also one of the key factors that affect the potential use of this core-shell structured catalyst in wide liquid-phase catalysis process, as well as the possibility of its commercial development. The life test of zeolite capsule catalyst was performed by the recycled use of the same catalyst for several fresh reactions. In brief, the glycerol conversion over one Ru/Al₂O₃-Pd/S was repeated for three times. After one experiment, the used zeolite capsule catalyst was taken out from the catalyst basket of reactor, followed by catalyst drying at 393 K for 10 h. And then the dried zeolite capsule catalyst was used for the next experiment. Here, with the assistance of well-designed catalyst basket in reactor, it is very facile to realize the recovery ratio of the used zeolite capsule catalyst beyond 99 %, that is, the loss of the zeolite capsule catalyst after the reaction was close to zero. In addition, the experimental results are presented in Fig. S1, from which we can find that the conversion of glycerol and selectivity of every product remained almost constant despite three times of catalyst recycle.

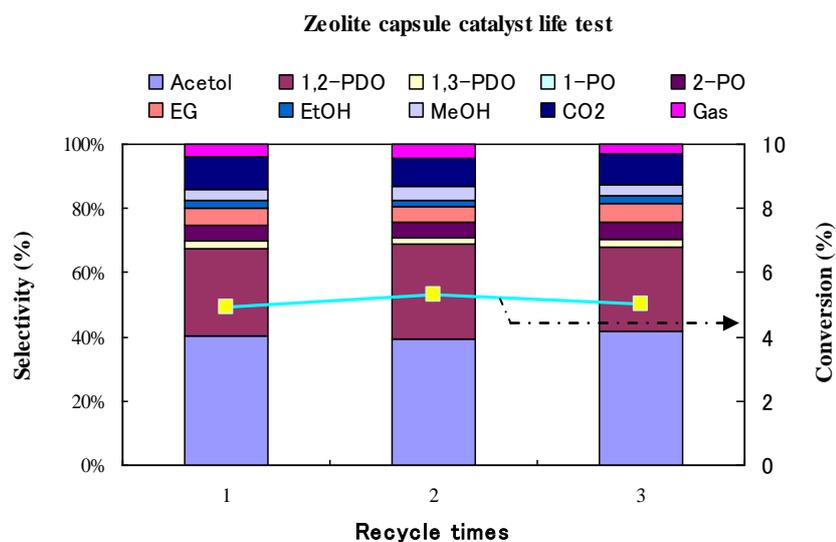


Fig. S1. The life test of zeolite capsule catalyst Ru/Al₂O₃-Pd/S in the glycerol conversion through the liquid-phase tandem catalysis process.

Besides the reaction results presented in the main text of this report, all the catalysts had also been evaluated under different reaction conditions. The influence of varied reaction pressure on the 1,2-PDO selectivity over three different types of catalyst had also been supplied, as showed by Fig. S2. For all the catalysts, the 1,2-PDO selectivity increased as a function of reaction pressure from 0.3 MPa to 8 MPa, implying that higher reaction pressure is helpful to glycerol conversion to 1,2-PDO. For the hybrid catalyst Pd/Al₂O₃-Pd/S-M, it had also showed better ability on synthesizing 1,2-PDO especially under higher reaction pressure, even comparable to that of zeolite capsule catalyst at 8 MPa. But the zeolite capsule catalyst Pd/Al₂O₃-Pd/S remains its outstanding ability, as before, on the directed synthesis of the

desired 1,2-PDO in this liquid-phase tandem catalysis process, benefitting from its special core-shell structure.

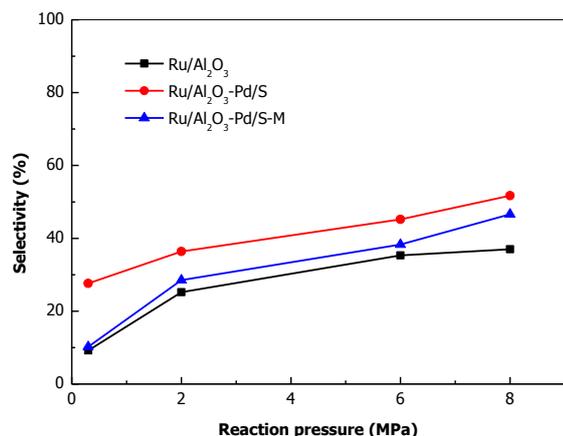


Fig. S2. The 1,2-PDO selectivity on three different types of catalyst, the naked core catalyst Ru/Al₂O₃, zeolite capsule catalyst Ru/Al₂O₃-Pd/S and hybrid catalyst Ru/ Al₂O₃-Pd/S-M as a function of reaction pressure.

Reference

- [S1] C. Montassier, J. C. Ménézo, L. C. Hoang, C. Renaud and J. Barbier, *Journal of Molecular Catalysis*, 1991, **70**, 99-110.
- [S2] I. Furikado, T. Miyazawa, S. Koso, A. Shima, K. Kunimori and K. Tomishige, *Green Chemistry*, 2007, **9**, 582-588.
- [S3] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. DellaPina, *Angewandte Chemie International Edition*, 2007, **46**, 4434-4440.
- [S4] Y. Zheng, X. Chen and Y. Shen, *Chemical Reviews*, 2008, **108**, 5253-5277.
- [S5] A. Brandner, K. Lehnert, A. Bienholz, M. Lucas and P. Claus, *Topics in Catalysis*, 2009, **52**, 278-287.
- [S6] Y. Nakagawa and K. Tomishige, *Catalysis Science & Technology*, 2011, **1**, 179-190.
- [S7]. Y. Yan, M. E. Davis and G. R. Gavalas, *Industrial & Engineering Chemistry Research*, 1995, **34**, 1652-1661.
- [S8]. D. E. Beving, A. M. P. McDonnell, W. Yang and Y. Yan, *J Electrochem Soc*, 2006, **153**, B325-B329.
- [S9]. B. Cekova, D. Kocev, E. Kolcakovska and D. Stojanova, *Acta periodica technologica*, 2006, 83-87.
- [S10]. R. Xiong, S. I. Sandler and D. G. Vlachos, *The Journal of Physical Chemistry C*, 2011, **115**, 18659-18669.
- [S11]. R. Xiong, S. I. Sandler and D. G. Vlachos, *Langmuir*, 2012, **28**, 4491-4499.
- [S12]. W. Hoelderich, *Studies in Surface Science and Catalysis*, 1988, **41**, 83-90.
- [S13]. M. Kanezashi and Y. S. Lin, *The Journal of Physical Chemistry C*, 2009, **113**, 3767-3774.