# Supplementary Information

# Facile synthesis of H-type zeolite shell on the silica substrate for tandem catalysis

Guohui Yang,[a] Ding Wang,[a] Yoshiharu Yoneyama,[a] Yisheng Tan[b] and Noritatsu Tsubaki*[a]

[a] Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan. Fax/Tel: +81-76-4456846; E-mail: tsubaki@eng.u-toyama.ac.jp

[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China.

## S1. Experimental section

**Core catalyst preparation.** The core catalyst used for zeolite capsule catalyst preparation is 10 wt% Pd/Silica catalysts. Silica pellets (Cariact Q-10, 0.85-1.7mm) are used as support for catalyst preparation by using incipient wetness impregnation method with $Pd(NH_3)_2(NO_3)_2$ as palladium resource. The fresh precursors are first dried in 393 K oven overnight, followed by its calcination in muffle at 673 K for 2 h. The final sample is the conventional 10 wt% Pd/Silica catalyst usually used for the study of methanol synthesis using syngas as feedstock.

**Tailor-made capsule catalyst by dual-layer method.** Silicalite-1 zeolite layer is first synthesized on the naked Pd/Silica, acting as an intermediate layer for H-ZSM-5 zeolite shell growth on its surface. The naked Pd/Silica and the Silicalite-1 zeolite synthesis solution with molar ratio of $2TEOS:0.48TPAOH:120H_2O:8EtOH:0.24HNO_3$ are sealed together in an autoclave undergoing hydrothermal synthesis. Crystallization temperature and time are 453 K and 24 h respectively. The Silicalite-1 zeolite layer coated core catalyst, as supports, will be used for the following H-ZSM-5 zeolite shell synthesis. The H-ZSM-5 zeolite shell synthesis solution has the molar ratio of $2TEOS:0.68\ TPAOH:120H_2O:8EtOH:0.24Al_2O_3$, in which the aluminium resource comes from $Al(NO_3)_3{\cdot}9H_2O$. This hydrothermal synthesis is performed at 453 K for 48 h. The final zeolite capsule catalyst named as $Pd/SiO_2$-SZ, after washing, drying and calcination, will

be used for the tandem catalysis reaction. The weight increment of this zeolite capsule catalyst is close to 20 wt% towards to the Pd/Silica core catalyst.

**Hybrid catalyst.** Pure H-ZSM-5 zeolite used for this hybrid catalyst preparation is prepared with the same recipe and synthesis procedures to zeolite capsule catalyst but without core catalyst. The obtained H-ZSM-5 catalyst and the crashed Pd/Silica is physically mixed well based on the weight ratio of 1:5 similar to the zeolite content of zeolite capsule catalyst Pd/Silica-SZ, and then granulated into the size range of 0.85-1.7mm. The new hybrid catalyst is named as Pd/Silica-M, where the "M" stands for the physical mixing of Pd/Silica with H-ZSM-5.

**Catalysts characterization.** An X-ray diffractometer (RINT 2400, Rigaku Co.) equipped with CuKα radiation is used to collect the XRD patterns of all catalysts. The physical morphology of catalysts is characterized by a scanning electron microscopy (SEM; JEOL, JSM-6360LV).

**Tandem catalysis reaction.** A pressurized flow-type reaction apparatus with a fixed-bed stainless steel reactor (ID 8 mm) is adopted for catalyst activity test. The catalyst is fixed in the middle of reactor, first reduced at 673 K in a flow of 100 % hydrogen for 3 h. And then the reaction is carried out at 523 K with 5.0MPa system pressure and $W_{Pd/Silica}/F_{syngas} = 20$ g·h·mol$^{-1}$. All of the effused products from the reactor are analyzed online in gaseous state by gas chromatograph. In order to get the reliable data with better precision, all of the catalysts (Pd/Silica, Pd/Silica-M and Pd/Silica-SZ) are tested for at least three times independently and the fresh catalyst is used in each time. The syngas conversion data presented in this communication for each kind of catalyst is the mean value of three times.

## S2. Results and discussion

Without the Silicalite-1 zeolite layer as intermediate, the authors had also investigated the direct H-ZSM-5 shell synthesis on the Pd/Silica core catalyst by using two different ways: 1) the direct synthesis and 2) the close-to-neutral synthesis. For the first case, the Pd/Silica core catalyst after hydrothermal synthesis suffers from lots of serious damages, not only on its surface but also in its internal section as shown by Fig. S1a and S1b in this supplementary information. As a reference, the corresponding SEM images of zeolite capsule catalyst Pd/Silica-SZ are also presented in Fig.S1c and S1d, where we can find that the synthesized zeolite shell enwraps core catalyst very well without damage or corrosion on the core catalyst. For the second case, according to our experiments, the close-to-neutral condition if used for H-ZSM-5 zeolite shell direct synthesis can not form

zeolite coating or zeolite powder on core catalyst at all. Instead of zeolite crystals, this type of hydrothermal synthesis process only generates a large number of gels.

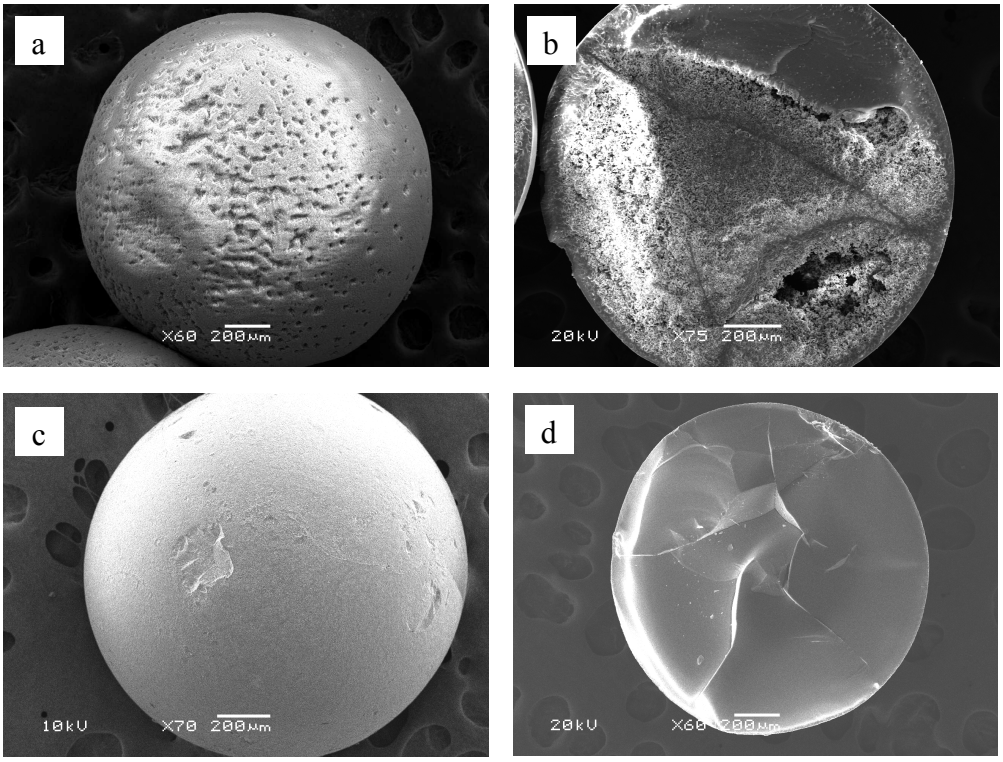


**Fig. S1** a) surface and b) cross-section SEM images of Pd/Silica after H-ZSM-5 zeolite shell direct synthesis; c) surface and d) cross-section SEM images of Pd/Silica-SZ zeolite capsule catalyst

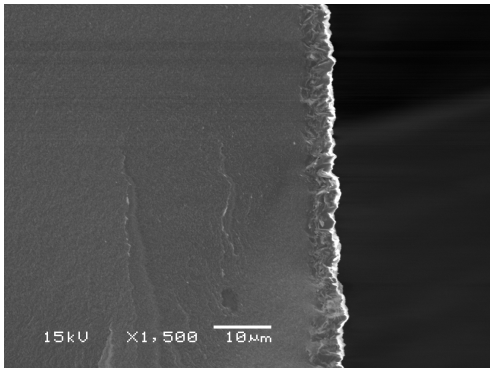


**Fig. S2** Cross-section SEM image of Pd/Silica-S

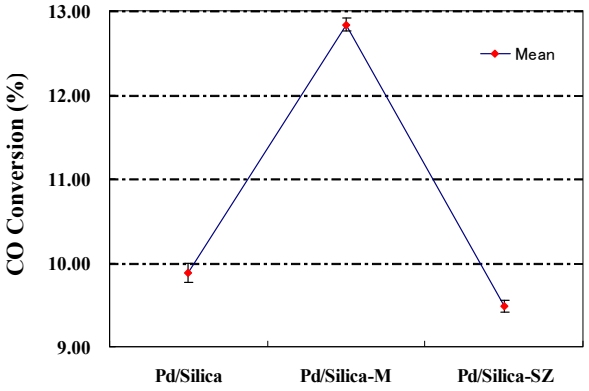


**Fig. S3** Graph of catalysts CO conversion with error bars