# Direct Synthesis of Liquefied Petroleum Gas from Syngas over H-ZSM-5 Enwrapped Pd-based Zeolite Capsule Catalyst

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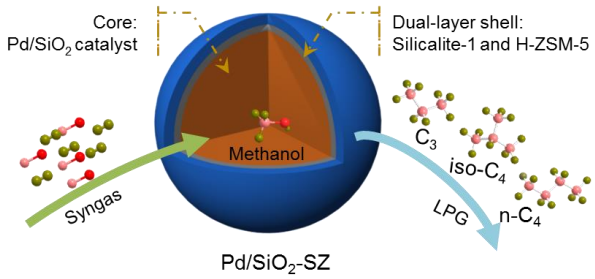
**Abstract:** The millimeter-sized zeolite capsule catalyst ($Pd/SiO_2$-SZ) with a core-shell structure was prepared by a developed dual-layer crystal growth method: coating Silicalite-1 and H-ZSM-5 zeolite orderly as double shells encapsulating the $Pd/SiO_2$ core catalyst. We employed the prepared $Pd/SiO_2$-SZ capsule catalyst for the direct synthesis of liquefied petroleum gas from syngas ($CO+H_2$). The $Pd/SiO_2$-SZ realized the highest LPG selectivity of 34.4% with CO conversion of 14.1%. The high performance of zeolite capsule catalyst $Pd/SiO_2$-SZ was attributed to the enforced mass transfer diffusion from inside to outside of the capsule catalyst.
**Keywords:** Zeolite capsule catalyst, Liquid petroleum gas, Syngas

## 1. Introduction

Currently, the global energy crisis and environmental contamination issues are greatly concerned in the world. More works about exploring green energy have been studied for several decades. For instance, liquefied petroleum gas (LPG), a mixture of propane and butane, is widely regarded as a promising candidate for fuel in household and industry fields due to its excellent chemical characteristic such as clean, renewable and easy storage [1]. LPG is mainly obtained from petroleum refining, natural gas and crude oil exploration [2]. The direct synthesis of valued-hydrocarbons from non-petroleum resource is a promising technology due to the declining of petroleum reserves. Here syngas from methane or biomass is used to obtain LPG.

In this paper, we developed a facile method for coating Silicalite-1 and H-ZSM-5 zeolite orderly as double shells on the $Pd/SiO_2$ pellet ($Pd/SiO_2$-SZ). The physical properties of zeolite capsule catalyst were determined by XRD and SEM characterization. The as-prepared $Pd/SiO_2$-SZ zeolite capsule catalyst was evaluated in the reaction of syngas direct conversion to LPG, as given in Scheme 1. The different reaction conditions of $Pd/SiO_2$-SZ zeolite capsule catalyst on catalytic performance were also investigated.




**Scheme 1.** Synthetic procedures of $Pd/SiO_2$-SZ zeolite capsule catalyst and its performance for LPG synthesis from syngas.

## 2. Experimental

### *2.1 Synthesis of $Pd/SiO_2$-SZ capsule catalyst*

We prepared the capsule catalyst by coating Silicalite-1 and H-ZSM-5 zeolite shells on the $Pd/SiO_2$ pellets successively. Firstly, the Silicalite-1 zeolite shell was first synthesized on the surface of $Pd/SiO_2$ pellets by hydrothermal synthesis as a protective layer. Then, the $Pd/SiO_2$-S catalyst was used as core catalyst for the successive H-ZSM-5 zeolite shell growth. The recipe of H-ZSM-5 zeolite synthesis solution was 2TEOS: 0.68TPAOH: $120H_2O$: 8EtOH: $0.024Al_2O_3$, where $Al(NO_3)_3{\cdot}9H_2O$ served as aluminum source. Firstly, the resulted solution was mixed by stirring for 4 h at room temperature to form homogeneous gel. The prepared $Pd/SiO_2$-S catalyst was immersed in this H-ZSM-5 synthesis solution and sealed in hydrothermal synthesis reactor at 453 K for 24 h. After crystallization, the product was filtrated by

centrifugation and washed by deionized water several times. Finally, the sample was obtained by drying at 393 K in oven for 12 h and calcination at 773 K in muffle for 5 h with heating rate of 1 K/min. The obtained capsule catalyst was denoted as $Pd/SiO_2$-SZ, where the S means Silicalite-1 shell and Z stands for H-ZSM-5 shell. The weight of zeolite shell encapsulating on the $Pd/SiO_2$-SZ catalyst was calculated to be 16.7 wt%.

*2.2 Catalytic performance evaluation*

The catalytic performance in the synthesis of LPG from syngas over various catalysts was carried out in a fixed-bed steel reactor with inner diameter of 6 mm. Prior to the test, all catalysts were reduced in the reactor for 10 h at 673 K with $H_2$. After cooling to room temperature, syngas containing $CO_2$, with a $H_2/CO$ molar ratio of 2, was introduced into the reactor. Then, the reaction was conducted under the required conditions as follows: $H_2/CO=2$, 5 MPa, $W_{catalysts}/F_{syngas}$= 10 $g \cdot h \cdot mol^{-1}$ and reaction temperature of 623 K.

## 3. Results and discussion

The catalytic performances of $Pd/SiO_2$, $Pd/SiO_2$-S, $Pd/SiO_2$-SZ and $Pd/SiO_2$-M catalysts in LPG synthesis reaction, are listed in Table 1. The $Pd/SiO_2$-SZ zeolite capsule catalyst shows CO conversion of 14.1%, which is higher than $Pd/SiO_2$-S capsule catalyst but it is lower than $Pd/SiO_2$ core catalyst and $Pd/SiO_2$-M mixture catalyst. The zeolite shell covers partial active sites on the surface of $Pd/SiO_2$ core catalyst, which may lead to the lower CO hydrogenation activity of zeolite capsule catalyst than that of $Pd/SiO_2$ core catalyst. The exposed active sites on $Pd/SiO_2$-M catalyst result in higher CO conversion in LPG synthesis. Moreover, the products distribution exhibits a significant difference among these catalysts, as compared in Table 1. $Pd/SiO_2$-SZ zeolite capsule catalyst realizes as high as 34.4% LPG selectivity with little amount of MeOH and DME. The LPG selectivity of $Pd/SiO_2$-SZ catalyst is much higher than that of $Pd/SiO_2$-M catalyst. The reaction environment suitable for LPG synthesis can be fabricated in the confined structure of $Pd/SiO_2$-SZ zeolite capsule catalyst with the advantage of the promoted mass and heat transfer.

**Table 1** Catalysts activity and products distribution over different catalysts.[a]

| Catalysts[b] | Conv. (%) | | Selectivity (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | CO | $CO_2$ | MeOH | DME | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $C_5H_{12}$ | others[c] | LPG |
| $Pd/SiO_2$ | 14.4 | 12.7 | 76.9 | 3.2 | 15.3 | 1.9 | 1.2 | 0.6 | 0.4 | 0 | 1.8 |
| $Pd/SiO_2$-S | 12.9 | 11.8 | 12.9 | 24.1 | 59.8 | 2.9 | 0.2 | 0 | 0 | 0 | 0.2 |
| $Pd/SiO_2$-M | 20.3 | 10.2 | 6.9 | 17.8 | 39.8 | 17.2 | 8.1 | 5.2 | 3.1 | 2.0 | 13.3 |
| $Pd/SiO_2$-SZ | 14.1 | 10.7 | 2.2 | 2.0 | 24.3 | 33.1 | 27.8 | 6.7 | 2.5 | 1.6 | 34.4 |

[a] Reaction conditions：623 K, 5.0 MPa, 4 h, $W_{catalysts}/F_{syngas}$= 10 $g \cdot h \cdot mol^{-1}$, syngas: $H_2/CO/CO_2/Ar$=62.78/29.3/4.95/2.97. [b] Weight of catalysts (core catalyst weight is the same): $Pd/SiO_2$-0.5 g, $Pd/SiO_2$-S-0.6 g, $Pd/SiO_2$-SZ-0.6 g, $Pd/SiO_2$-M-0.6 g. [c] Others mainly consist of $C_6$ and $C_7$ hydrocarbons.

## 4. Conclusions

In summary, a $Pd/SiO_2$-SZ zeolite capsule catalyst is prepared by a developed dual-layer growth method. The catalyst characterization demonstrates that the $Pd/SiO_2$-SZ zeolite capsule catalyst has millimeter-sized core-shell structure with a compact H-ZSM-5 shell. $Pd/SiO_2$-SZ zeolite capsule catalyst is used to investigate the catalytic performance of direct LPG synthesis from syngas. In contrast to the naked $Pd/SiO_2$ core catalyst and the mixture catalyst $Pd/SiO_2$-M, the zeolite capsule catalyst shows excellent LPG selectivity. The LPG selectivity on this $Pd/SiO_2$-SZ zeolite capsule catalyst reaches 34.4% with CO conversion of 14.1%. The unexpected superior performance of $Pd/SiO_2$-SZ zeolite capsule catalyst is ascribed to the tailor-made core-shell-like structure, which provides a confined reaction environment for LPG direct synthesis from syngas. The new findings in this study are beneficial to designing core-shell-like catalysts for LPG direct synthesis from syngas, and the presented catalyst preparation method in this paper can be also extended to other tandem catalysis processes.

## References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