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Designing core ($Cu/ZnO/Al_2O_3$)–shell (SAPO-11) zeolite capsule catalyst with a facile physical way for dimethyl ether direct synthesis from syngas

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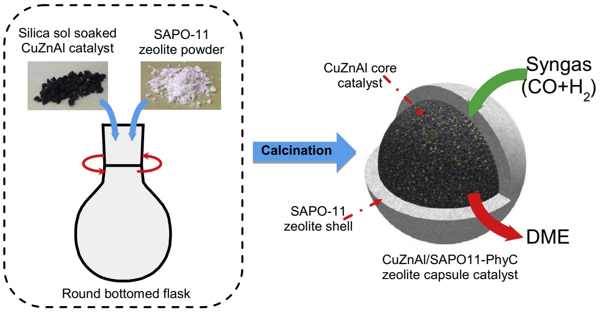
HIGHLIGHTS

- A new method for zeolite capsule catalyst preparation without hydrothermal synthesis.
- The new method was considerably simple and scalable.
- DME synthesis from syngas was efficiently realized on the prepared zeolite capsule catalyst.
- The confined reaction space of capsule catalyst facilitated the controlled synthesis of DME.

GRAPHICAL ABSTRACT



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ABSTRACT

Core–shell like zeolite capsule catalyst can effectively realize tandem catalysis process, like syngas → methanol → dimethyl ether (DME), but the general zeolite shell preparation requires high temperature and alkaline conditions, which severely limits the design, industrial production and application of zeolite capsule catalyst. In this report, we present a simple and scalable method, named physical coating (PhyC), to prepare zeolite shell without employing hydrothermal synthesis process. The demonstrated zeolite capsule catalyst, named CuZnAl/SAPO11-PhyC, has a $Cu/ZnO/Al_2O_3$ (CuZnAl) core catalyst and a PhyC-prepared silicoaluminophosphate-11 (SAPO-11) shell. This zeolite capsule catalyst CuZnAl/SAPO11-PhyC is characterized by XRD, SEM, EDS, N_2 adsorption and NH_3-TPD respectively. Tandem catalysis process of syngas to DME (STD) is carried out on this CuZnAl/SAPO11-PhyC zeolite capsule catalyst, comparing its catalytic performance with other general mixture catalyst of CuZnAl/SAPO11-M. The reaction results indicate that the zeolite capsule catalyst of CuZnAl/SAPO11-PhyC prepared by PhyC method can increase not only the syngas conversion, but also the selectivity of the desired DME, considerably better than the mixture catalyst of CuZnAl/SAPO11-M. The excellent catalytic performance of zeolite capsule catalyst CuZnAl/SAPO11-PhyC should be attributed to its special core–shell-like structure that provides a confined reaction field to the studied STD reaction, accelerating the syngas conversion to DME, at the same time suppressing the over-dehydration of DME to form other by-products.

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1. Introduction

Dimethyl ether (DME) is widely used as basic chemical feedstock for producing many downstream substances such as methyl acetate, acetaldehyde, acetic acid, etc. [1,2]. Moreover, DME is also known as one of the promising substitute of petroleum-based fuels [3]. Burning DME can effectively reduce the exhausting of environmental-unfriendly particular matters, like soot, SO_x and NO_x [4]. DME has high cetane number, which can help it to replace the general diesel fuel or act as liquefied petroleum gas (LPG) for cooking or power generation [5,6]. Therefore, designing more effective catalyst for the production or conversion of DME has gradually attracted more attentions.

Generally, DME is produced through two ways: one is methanol dehydration on a single acidic catalyst and another is a tandem catalysis process including the initial syngas to methanol synthesis and the followed methanol dehydration to form DME over mixture catalysts [7]. The later one-step process from syngas to DME, also named STD reaction, is more thermodynamically favorable than the first way of methanol to DME, due to the combination of two sequential reactions of methanol synthesis and methanol dehydration. The mixture catalysts for STD reaction usually comprise of a methanol synthesis catalyst (like Cu/ZnO, Cr/ZnO or Pd) and an acid catalyst (such as Al_2O_3 or H-ZSM-5 zeolite) [8–11]. Recently, some silicoaluminophosphate (SAPO) series zeolite, owing to their proper milder acidity property, also arose more research interests for DME production, starting from methanol or even CO_2-containing syngas [11–13].

The assembly style of the used mixture catalysts for STD reaction is physical mixing, that is, two types of different catalysts are simply mixed [14]. In STD reaction, methanol synthesis and methanol dehydration take place consequently on the mixture catalyst. However, since the simple preparation way, the obtained mixture catalysts in fact cannot facilely realize the precise control on the two sequential reactions: methanol synthesis from syngas and methanol dehydration to from DME. It is difficult for mixture catalyst to define the assigned reaction happening on a fixed position or a required catalyst, as well as suppressing the formation of undesired by-products through side reactions.

In order to overcome these disadvantages of mixture catalyst, a novel concept of designing catalyst with a core–shell-like structure, named capsule catalyst, was presented, and the prepared zeolite capsule catalyst has proved its premier ability for lots of tandem catalysis processes, including STD reaction [15–19]. The zeolite capsule catalyst is capable of increasing the desired products selectivity by giving severe space confinement to the intermediates and final products in tandem catalysis process [20].

Core–shell like zeolite capsule catalyst, in comparison with the general mixture catalyst, can realize tandem catalysis process more effectively and protect core catalyst from the harsh reaction environments [21–23], but the hydrothermal synthesis process usually used for zeolite shell preparation is rather complex and must be operated carefully, which severely limits the industrially scalable preparation and application of zeolite capsule catalysts. Therefore, in this report, we develop a simple and scalable method, named physical coating (PhyC), to overcome this obstacle. This PhyC method is a considerably simple method to prepare the zeolite capsule catalyst without special equipment. With the assistance of PhyC method, without using direct hydrothermal synthesis process, we can facilely construct a well-organized zeolite shell enwrapping core catalyst to get a core–shell-like capsule catalyst.

The demonstrated zeolite capsule catalyst, named CuZnAl/SAPO11-PhyC in this report, is a core–shell-like silicoaluminophosphate-11 (SAPO-11) zeolite shell encapsulated $Cu/ZnO/Al_2O_3$ (CuZnAl) catalyst. It is characterized by XRD, SEM, EDS, N_2 adsorption and NH_3-TPD. The tandem catalysis process of one-step syngas to dimethyl ether (STD) is investigated on this CuZnAl/SAPO11-PhyC zeolite capsule catalyst, comparing its catalytic performance with another general mixture catalyst.

2. Experimental

2.1. Catalyst preparation

2.1.1. Silicoaluminophosphate-11 synthesis

Silicoaluminophosphate-11 (SAPO-11) was synthesized by hydrothermal synthesis method. The SAPO-11 was prepared with the recipe of $1.2Al_2O_3$:$3.0H_3PO_4$:$0.6SiO_2$:2.0 Di-n-propylamine (DPA): $100H_2O$. Firstly, the aqueous H_3PO_4 (85%, Chemerion Reagent) was slowly added into the solid aluminium isopropoxide (99%, Sigma–Aldrich). The mixture was stirred for 2 h until a homogenous white solution was obtained. Then certain amount of DPA was added slowly into this mixture under vigorous stirring for 3 h. Finally, the silica sol (LUDOX 40 wt% suspension, Aldrich) was mixed with the above mixture and was further stirred for another 6 h. The final sample was transferred into a Teflon container capped with a stainless steel autoclave and then placed into the hydrothermal unit (DRM-420DA, Hiro Company, Japan). The zeolite crystallization process was performed at 180 °C for 48 h. After crystallization, the product was separated from the mother liquid by centrifuge, dried at 120 °C overnight, followed by calcination in a muffle oven at 500 °C for 2 h to eliminate the organic template in zeolite.

2.1.2. $Cu/ZnO/Al_2O_3$ (CuZnAl) catalyst preparation

The $Cu/ZnO/Al_2O_3$ (CuZnAl) catalyst, a tri-component catalyst consisting of Cu, Zn and Al (Cu/Zn/Al = 6:3:1 mol ratio), was prepared by a conventional oxalate co-precipitation method [17,24,25]. The nitrates of copper, zinc and aluminum were dissolved in ethanol to get solution (A), and the oxalic acid was dissolved by ethanol independently to get another solution (B). Two solutions of (A) and (B) were mixed rapidly at room temperature under vigorous stirring. And then the formed gel-like precipitate performed ageing treatment at room temperature for 24 h. After ageing step, the precipitate was separated by centrifuge, dried at 120 °C for 6 h, followed by calcination in muffle oven at 370 °C for 1 h. Finally, the obtained sample was compressed and granulated into the fixed pellet size in 0.85–1.70 mm. The prepared catalyst was named CuZnAl catalyst and used as core catalyst for zeolite capsule catalyst preparation.

2.1.3. Zeolite capsule catalyst preparation by physical coating (PhyC) method

We developed a new physical coating (PhyC) method to prepare zeolite capsule catalyst without employing hydrothermal synthesis, as illustrated by Fig. 1. A certain amount of silica sol (Ludox: 40 wt%, Aldrich) was diluted by 1.5 times deionized water and then used as adhesive. The CuZnAl core catalyst was immersed in the diluted silica sol for a while, and then it was mixed with the as-prepared SAPO-11 zeolite powder in a round bottomed flask, followed by vigorously shaking until the formation of an integrated zeolite shell on the external surface of CuZnAl core catalyst. This procedure could be repeated for several times to realize the desired zeolite shell thickness. The obtained sample was finally calcined at 500 °C for 2 h to strengthen the zeolite shell. The obtained zeolite capsule catalyst, named CuZnAl/SAPO11-PhyC, had a core–shell structure in which the CuZnAl core catalyst was encapsulated by a well-prepared SAPO-11 zeolite shell. The weight ratio of zeolite shell to core catalyst in capsule catalyst was about 1:5. The contact intensity between core and shell was considerably higher. Even after several