

## Confinement Effect and Synergistic Function of H-ZSM-5/ Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> Capsule Catalyst for One-Step Controlled Synthesis

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**Abstract:** Dimethyl ether (DME) is an industrially important intermediate, as well as a promising clean fuel, but the effective production through traditionally consecutive steps from syngas to methanol and then to DME has been hindered by the poorly organized structure of the conventional physical mixture catalyst. Here, a novel zeolite capsule catalyst possessing a core-shell structure (millimeter-sized core catalyst and micrometer-sized acidic zeolite shell) was proposed initially through a well-designed aluminum migration method using the core catalyst as the aluminum resource and for the first time was applied to accomplish the DME direct synthesis from syngas. The selectivity of the expected DME on this zeolite capsule catalyst strikingly exceeded that of the hybrid catalyst prepared by the traditional mixing method, while maintaining the near-zero formation of the unexpected alkanes byproduct. The preliminary methanol synthesis reaction on the core catalyst and the following DME formation from methanol inside the zeolite shell cooperated concertedly and promoted mutually. This zeolite capsule catalyst with a synergetic confinement core-shell structure can be used to efficiently realize the combination of two and more sequential reactions with many synergistic effects.

### Introduction

Alternative energy sources have moved into the spotlight in recent years with soaring oil prices and dwindling resources.<sup>1</sup> In addition to utilization as an important chemical intermediate, DME is also very promising as a new energy source, being available for various purposes such as an LPG alternative, a fuel for power generation, synthetic diesel, and hydrogen resource for fuel cells.<sup>2–4</sup> Traditionally, DME can be produced through two methods. One is methanol dehydration on a single dehydration catalyst, where the methanol is separately made from syngas,<sup>5</sup> and another is a couple of consecutive reactions for DME direct synthesis from syngas on a hybrid catalyst, where the hybrid catalyst is a simple mixture of methanol synthesis catalyst and methanol dehydration catalyst.<sup>6</sup> The latter method is more thermodynamically favorable than the former because methanol synthesis is generally severely limited by thermodynamics and in situ conversion of the formed methanol to DME can enhance the maximum syngas conversion.<sup>6,7</sup>

However, previous studies paid more attention to the simply mechanical mixing of the two types of catalysts, improving catalyst lifetime, performance, or activity.<sup>8–10</sup> The effective structure combination of two active catalysts was not deeply studied until now.

In heterogeneous catalysis, the active chemical composition of a catalyst can work more efficiently only in combination with a well-organized structure.<sup>11–13</sup> A catalyst having a finely designed structure usually exhibits better catalytic performance.<sup>14</sup> Recently, a material study on nano- or micro-sized particles with a special core-shell structure has attracted tremendous interest.<sup>15</sup> The core-shell particles have broad promising application in many fields, such as drug delivery,<sup>16</sup> photonic devices,<sup>17</sup> and catalytic and separation processes.<sup>18</sup>

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Usually, the core-shell structure is made up of two or more varied materials, in which the different materials (organic and/or inorganic) are spatially separated in different locations, promoting mutually at the same time. In our previous reports, the zeolite capsule catalysts with a supported metallic core catalyst and a zeolite shell exhibited excellent properties for isoparaffin direct synthesis that are significantly different from their physical mixture analogy, which makes them better than the conventional hybrid catalyst usually used for the consecutive reactions.<sup>19,20</sup> However, it is difficult to prepare the defect-free H-type zeolite shell on the pure metallic catalyst, coprecipitated catalyst, or alloy catalyst without sodium hydroxide in the precursor synthesis solution, protecting the core catalyst from damage by hydrothermal treatment at the same time. Especially, the coprecipitated catalyst used here as the core generally has mechanical and chemical strength much weaker than that of a supported catalyst and can very easily be decomposed or dissolved in the hydrothermal synthesis process of zeolite membrane.

Herein, we report a millimeter-sized zeolite capsule catalyst possessing a special core-shell structure (a tricomponent core catalyst enwrapped by one layer of H-ZSM-5 zeolite shell) with a coprecipitated catalyst as core. Different from the traditional zeolite membrane preparation methods, such as in situ or seeding method using the aluminum-containing precursor solution for zeolite layer growth on various supports,<sup>21–23</sup> here an acidic H-ZSM-5 zeolite shell was directly prepared successfully through an unreported way of aluminum migration from the core catalyst body. The aluminum-containing core catalyst acted as the substrate for zeolite membrane growth and at the same time as the sole aluminum resource to construct the zeolite framework in the total synthesis process, resulting in the defect-free covering and tightly enwrapping of the zeolite shell on its surface. For the first time, this zeolite capsule catalyst was applied to accomplish a successive reaction, DME direct synthesis from syngas. The selectivity of the expected DME on this zeolite capsule catalyst strikingly exceeded that of the traditional hybrid catalyst (the simple blending of core catalyst and zeolite powder), while maintaining zero formation of the unexpected alkane byproducts. The encouraging results proved that this novel method for the preparation of H-type zeolite shell on aluminum-containing metallic catalyst was feasible and very reliable, effectively protecting the vulnerable metallic core catalyst from damage by the hydrothermal synthesis process and realizing the controlled synthesis of the target product on a single catalyst. The zeolite capsule catalyst preparation method reported here together with its application in DME controlled synthesis from syngas have the potential to inspire not only the zeolite membrane synthesis but also heterogeneous catalysis.

## Experimental Section

**Core Catalyst Preparation.** The core catalyst, tricomponent Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA), was prepared by the conventional oxalate

coprecipitation method.<sup>24</sup> An ethanol solution of oxalic acid was added rapidly to a mixed ethanol solution of copper, zinc, and aluminum nitrates (Cu/Zn/Al in molar ratio 45/20/10) at room temperature under vigorous stirring. The gel-like precipitate was aged at room temperature for 24 h and then separated by centrifuge. The drying process was conducted at 393 K for 6 h followed by calcination in air at 643 K for 1 h. Before the following utilization, the raw CZA catalyst was granulated into a new grain with the size of 0.85–1.70 mm.

**Zeolite Capsule Catalysts Preparation.** In this report, two different zeolite membrane hydrothermal synthesis methods were adopted to directly construct two types of H-type ZSM-5 zeolite shell onto the CZA catalysts. One was the traditional acidic H-ZSM-5 zeolite membrane synthesis method with the aluminum resource in the precursor solution. Another was the close-to-neutral Silicalite-1 zeolite membrane preparation method without an aluminum resource in the synthesis solution; here, the core CZA catalyst acted as the support and Al resource for H-ZSM-5 zeolite membrane growth simultaneously.

In preparation, the structure directed reagent TPAOH (tetrapropylammonium hydroxide, 10% in water), silica resource TEOS (tetraethyl orthosilicate, 95%), and aluminum resource (aluminum nitrate, 99.9%) were the Wako Co. products. Dehydrated ethanol (99.5%) and nitric acid (69%) were both purchased from Kanto Chemical Co. The first H-ZSM-5 zeolite shell was prepared on the CZA core catalyst using a traditional acidic H-ZSM-5 zeolite synthesis recipe of 0.48 TPAOH:2 TEOS:8 EtOH:120 H<sub>2</sub>O:0.025Al<sub>2</sub>O<sub>3</sub>. The second H-ZSM-5 zeolite shell was prepared by the close-to-neutral Silicalite-1 zeolite synthesis recipe of 0.48 TPAOH:2 TEOS:8 EtOH:120 H<sub>2</sub>O:0.24 HNO<sub>3</sub>. All reagents were mixed in a Teflon container with vigorous stirring at room temperature for 6 h. Then the CZA pellets (0.85–1.70 mm) were added into the precursor solutions, and the Teflon container was placed into the stainless steel autoclave for hydrothermal synthesis. Zeolite shell synthesis was performed in a rotation oven with the rotation rate of 2 rpm at 453 K for 72 h. Here, the rotation synthesis effectively prevented the cementation of catalyst pellets during the hydrothermal synthesis process, improving the integrity of the zeolite shell simultaneously. Without the rotation, for example, using a static autoclave instead, it was difficult to enwrap all core catalyst surfaces completely. The final samples were separated from the mother liquid and then were calcined at 773 K in air for 5 h, removing the organic template stored in the zeolite pores. The zeolite capsule catalyst obtained by this process using different synthesis methods were named as CZA-Z and CZA-S respectively, where the “Z” stands for the preparation using the H-ZSM-5 zeolite synthesis recipe and “S” means the synthesis utilizing the Silicalite-1 zeolite synthesis recipe. It is noted that no aluminum resource was adopted for CZA-S preparation. Moreover, it is very important that commonly used reagent containing NaOH, KOH, Cl<sup>-</sup>, or Br<sup>-</sup> cannot be used here for zeolite shell synthesis, as they will deactivate the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> core catalyst severely. For the same reason, Na-type or NH<sub>3</sub>-type zeolite membrane is not permitted for our zeolite capsule catalyst as ion-exchange to H-type zeolite will deactivate core catalyst. We must synthesize H-type capsule catalyst in one step.

**Hybrid Catalyst Preparation.** Self-made H-ZSM-5 (Si/Al = 163, atomic ratio) zeolite powder was used for the preparation of the physically mixed catalyst. This zeolite powder was physically well mixed with the CZA catalyst with a weight ratio of 1:10 and then granulated to 0.85–1.70 mm at 60 MPa pressure. This catalyst was named as CZA-M, where the “Z” means H-ZSM-5 zeolite and “M” means the mechanical mixture of H-ZSM-5 with CZA.

**Catalysts Characterization.** X-ray diffraction (XRD) patterns were collected using a Rigaku RINT 2400 X-ray powder diffractometer equipped with a Cu K $\alpha$  radiation source at 40 KV and 40

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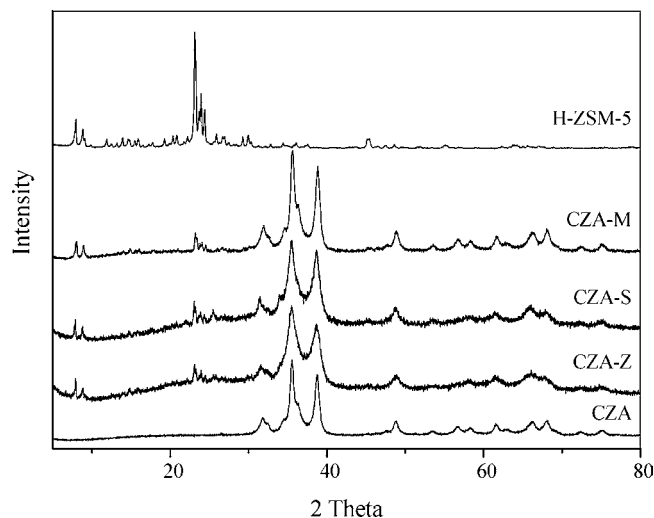
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**Figure 1.** XRD patterns of CZA, CZA-Z, CZA-S, CZA-M, and pure H-ZSM-5 zeolite.

mA. A JEOL JSM-6360LV scanning electron microscope (SEM) and JED-2300 energy dispersive spectroscopy (EDS) were used for SEM imaging and EDS analyzing on the catalyst surface and cross-section.

**Reaction and Analysis of Products.** Before the reaction, the catalyst was first reduced in situ at 493 K by a 5% H<sub>2</sub> in nitrogen flow (60 mL/min) for 10 h. Reactions were carried out in a down flow fixed-bed stainless steel reactor. The reaction conditions were 523 K, 5.0 MPa,  $W_{\text{CZA catalyst}}/F_{\text{syngas}} = 10 \text{ g}\cdot\text{h}/\text{mol}$ , and syngas (H<sub>2</sub> 59.22%, CO 32.60%, CO<sub>2</sub> 5.16%, Ar 3.02%). The effluent products from the heated line were first analyzed by an online gas chromatograph (Shimadzu, TCD, GC-8A) for CO and CO<sub>2</sub>, and then the tail gases were analyzed online using another gas chromatograph (Shimadzu, FID, GC-8A) for other products. All analysis lines and valves were heated to prevent possible condensation of the products before entering the gas chromatograph, ensuring reliable materials balance.

## Results and Discussion

**Capsule Catalysts Preparation and Characterization.** The tricomponent catalyst Cu/Zn/Al<sub>2</sub>O<sub>3</sub> (CZA) made by the coprecipitation method is a conventional catalyst usually used for methanol synthesis. In this report, it was selected as the core catalyst for preparation of the zeolite capsule catalysts. The bare CZA catalyst without hydrothermal treatment had a pellet size of 0.85–1.70 mm. For its X-ray diffraction (XRD) analysis, no crystalline peaks of H-ZSM-5 zeolite were observed, as shown in Figure 1. The surface scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis results in Figure 2 indicated that this CZA catalyst had the molar composition of Cu/Zn/Al = 61.90:24.50:13.60. It was very similar to its original bulk ratio in this catalyst preparation recipe. The hybrid catalyst named as CZA-M was prepared by mixing CZA catalyst with pure H-ZSM-5 (Si/Al = 163) zeolite powder. The XRD peaks assigned to CZA or H-ZSM-5 zeolite can be distinguished by comparing the XRD patterns of CZA-M with pure H-ZSM-5 zeolite or bare CZA core catalyst independently in Figure 1.

In this report, two different methods for zeolite membrane preparation were adopted to construct two types of H-ZSM-5 zeolite shell directly on the millimeter-sized CZA core catalyst. For the first type of zeolite shell preparation, the traditional acidic H-ZSM-5 zeolite synthesis method using the aluminum-containing precursor solution, but without sodium hydroxide,

was adopted to directly coat a H-ZSM-5, not Na-ZSM-5, shell onto the CZA core catalyst surface. The obtained catalyst, denoted as CZA-Z, was separated from the mother liquid, washed, and calcined, removing the template settled in the zeolite pores. The XRD pattern of this CZA-Z zeolite capsule catalyst in Figure 1 identified the classic X-ray diffraction peaks of H-ZSM-5 zeolite in the ranges of  $2\theta = 5\text{--}10$  and  $21\text{--}25$ , indicating that H-ZSM-5 zeolite had crystallized on the CZA core catalyst successfully.<sup>25</sup>

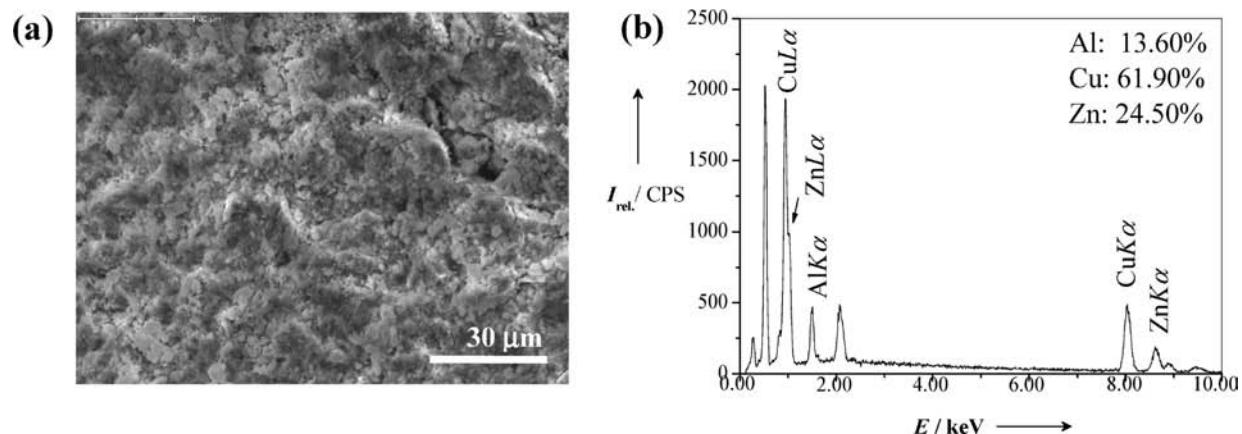
The surface SEM image and EDS analysis of CZA-Z in Figure 3a and b gives the surface morphology and elemental composition of zeolite shell. After this zeolite shell preparation, the surface of CZA core catalyst had been homogeneously covered by one layer of randomly oriented H-ZSM-5 zeolite crystals. The average size of zeolite crystals of the zeolite shell was about 1  $\mu\text{m}$ . The surface EDS analysis result in Figure 3b presented that the Si/Al ratio of zeolite shell was about 32. The signals of Cu and Zn on the zeolite shell surface were zero, which proved that this H-ZSM-5 zeolite shell was compact and integrated, indicating that this zeolite shell preparation method was successful. Figure 3c and d shows the cross-section SEM image and EDS line analysis results of CZA-Z zeolite capsule catalyst, respectively. A well-intergrown zeolite shell had enwrapped the CZA core catalyst perfectly. The related EDS line analysis along the white line in the SEM image exhibited the change of element signals from the zeolite shell to the catalyst core part. The Si K $\alpha$  signal increased in the zeolite shell and then decreased sharply at the interface between zeolite shell and core catalyst, indicating the change from zeolite shell to core catalyst, as well as identifying that the thickness of zeolite shell was about 3.9  $\mu\text{m}$ . The Al K $\alpha$  signal kept a stable level in both the zeolite shell and the core catalyst. For Cu K $\alpha$  and Zn K $\alpha$ , they were close to zero in the zeolite shell, which suggested that there was no obvious weight loss for the active species of core catalyst during this hydrothermal synthesis process.

For the second type of zeolite shell preparation, the traditional Silicalite-1 zeolite synthesis method was utilized to construct zeolite shell on CZA core catalyst. No aluminum in the precursor synthesis solution was the specific feature of this preparation process. The Al used to construct the framework of H-ZSM-5 zeolite shell here would be extracted from the CZA core catalyst during the hydrothermal synthesis process, as designed. The obtained zeolite capsule catalyst by this preparation method was named as CZA-S, where the “S” means this Silicalite-1 zeolite synthesis method. The XRD pattern of CZA-S zeolite capsule catalyst is presented in Figure 1. This sample exhibited the MFI structure with major peaks located at  $2\theta = 7.9, 8.9$  and the characteristic triplet at  $2\theta = 23.5$ , confirming the formation of zeolite with MFI structure on the CZA core catalyst. In addition, some comparable peaks of CZA-S catalyst to that of the bare CZA catalyst were observed in the range of  $2\theta = 30\text{--}40$ , indicating that the CZA core catalyst was still stable after this hydrothermal synthesis treatment.

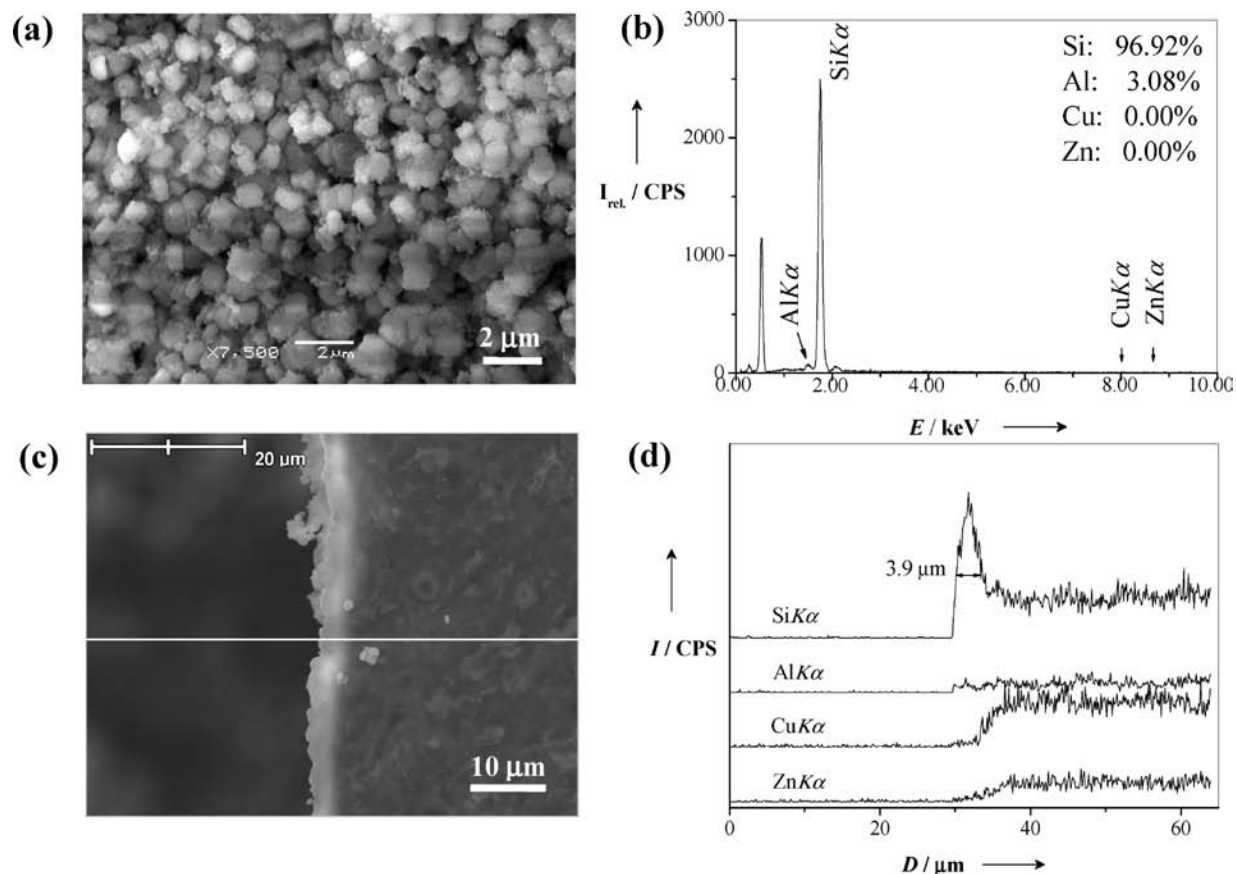
Zeolite shell surface morphology and elemental composition of CZA-S zeolite capsule catalyst are shown in Figure 4a and 4b, respectively. The average size of zeolite crystal constructed this zeolite shell was much larger than that of CZA-Z zeolite capsule catalyst as above, probably because of the special zeolite synthesis solution for CZA-S preparation without aluminum

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**Figure 2.** (a) Surface SEM image and (b) EDS analysis of the bare CZA core catalyst.



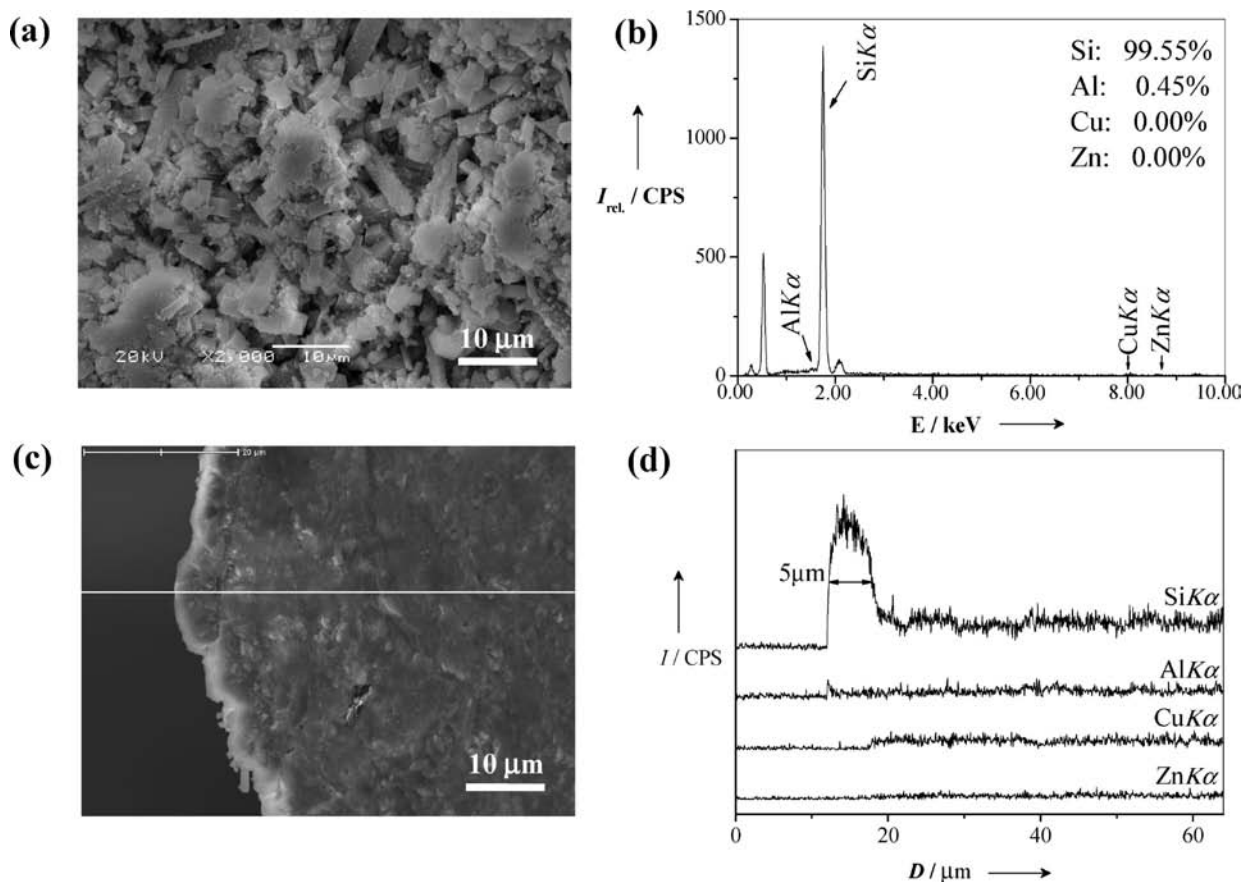
**Figure 3.** (a) Surface SEM image and (b) surface EDS analysis; (c) cross-section SEM image and (d) EDS line analysis of the zeolite capsule catalyst CZA-Z.

resource, in conjunction with the lower pH value.<sup>26,27</sup> In addition, there were no pinholes and cracks on the zeolite shell, which indicated that this hydrothermal synthesis process was successful. Surface EDS analysis on the zeolite shell gave zero signals of Zn and Cu, suggesting that this zeolite shell was compact and well integrated as well. The most interesting finding was the Al content in the zeolite shell. Actually, it was not zero despite the close-to-neutral Silicate-1 zeolite synthesis method for zeolite shell preparation. Nonzero Al signal, together with

the XRD pattern of CZA-S in Figure 1, confirmed that the zeolite shell of the CZA-S catalyst had the MFI zeolite structure and belonged to a H-ZSM-5 zeolite membrane. The surface Si/Al ratio of this zeolite shell was 221, as listed in Table 1, much higher than that of the conventional H-ZSM-5 zeolite powder usually used for DME direct synthesis from syngas. However, the total acid amount of this zeolite capsule catalyst was similar to that of hybrid catalyst CZA-M (see Figure S1, Table S1 in Supporting Information). These should be attributed to the aluminum-containing CZA core catalyst used here. It acted as the substrate and aluminum resource simultaneously for zeolite shell growth, which could lead to a concentration gradient of Al in the zeolite shell.<sup>22</sup> The cross-section SEM

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**Figure 4.** (a) Surface SEM image and (b) surface EDS analysis; (c) cross-section SEM image and (d) EDS line analysis of the zeolite capsule catalyst CZA-S.

**Table 1.** Catalyst Properties and Catalytic Performance in STD Reaction<sup>a</sup>

catalyst	Si/Al <sup>b</sup>	zeolite (%)	CO conversion (%)	selectivity (%)		
				MeOH	DME	others
CZA			44.02	98.38	0.50	1.12
CZA-Z <sup>c</sup>	32	7.60	5.59	3.41	96.59	0.00
CZA-S <sup>d</sup>	221	9.63	30.40	21.43	78.57	0.00
CZA-M <sup>e</sup>	163	10.0	58.07	57.29	40.51	2.20

<sup>a</sup> Reaction conditions: 523 K, 5.0 MPa,  $W_{CZA}/F_{\text{syngas}} = 10 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$ . Syngas: H<sub>2</sub>/CO/CO<sub>2</sub>/Ar = 59.22/32.60/5.16/3.02. <sup>b</sup> Si/Al ratio of zeolite shell or zeolite powder. <sup>c</sup> “Z” means the H-ZSM-5 synthesis method. <sup>d</sup> “S” stands for the Silicalite-1 synthesis method. <sup>e</sup> “M” means the physical mixing of CZA with H-ZSM-5 zeolite powder.

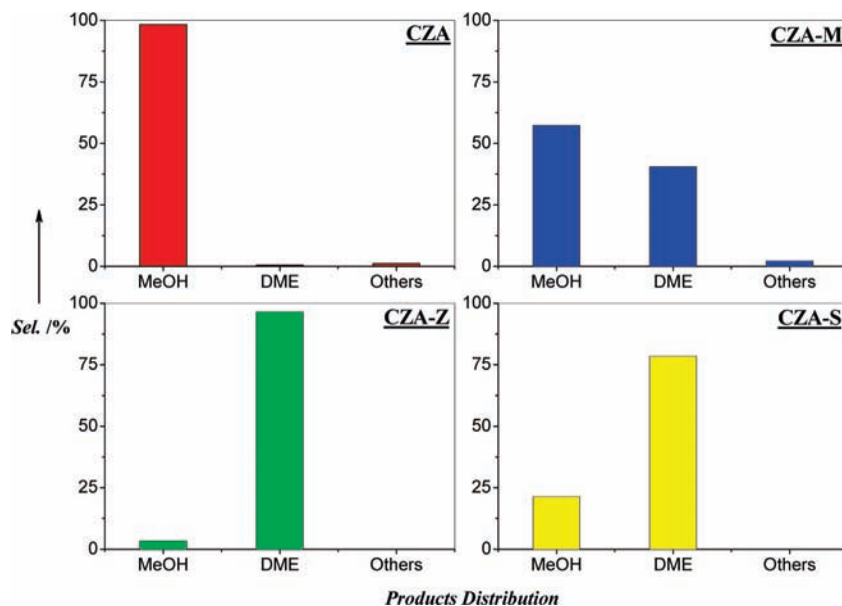
image and EDS line analysis of CZA-S zeolite capsule catalyst are shown in Figure 4c and 4d, respectively. In the SEM image, the zeolite shell could be distinguished easily and was also in a good state, enwrapping the CZA core catalyst. The signal intensity of Si K $\alpha$ , Cu K $\alpha$ , and Zn K $\alpha$  in the EDS line analysis result gave a change similar to that of CZA-Z zeolite capsule catalyst along the direction from the zeolite shell to the core catalyst, but the thickness of the zeolite shell was 5  $\mu\text{m}$  here. It is noteworthy that the Al K $\alpha$  signal in the zeolite shell also was not zero, even if the synthesis solution for the CZA-S preparation did not contain any aluminum resource. For the aluminum constructing the final H-ZSM-5 zeolite shell, it must come from the core catalyst, the sole aluminum resource in this total hydrothermal synthesis process. Accordingly, it can be concluded that the hydrothermal synthesis solution without Al resources could

also form H-ZSM-5 zeolite shell with lower aluminum content on aluminum-containing supports.

Both of the zeolite shell preparation methods, acidic zeolite synthesis and close-to-neutral zeolite synthesis, can realize the formation of a complete, well-intergrown acidic zeolite shell on the CZA core catalyst. Here, the realization of core catalyst enwrapped tightly by one layer of zeolite shell should be attributed to the aluminum-containing CZA core catalyst. The aluminum migrated from the aluminum supports and was incorporated into the MFI zeolite framework.<sup>22,28</sup> At the same time, a transition layer of zeolite crystals with aluminum-containing supports could be formed at the interface area between the zeolite shell and CZA core catalyst. These factors ensured the integrity of zeolite capsule catalyst even if undergoing calcination and the following catalysis reaction. In addition, the zeolite shells prepared by two different methods had different structural properties, not only in regard to the element composition but also the shell thickness, as well as zeolite loading amount and acidic sites distribution shown in NH<sub>3</sub>-TPD curves (Supporting Information). Therefore, only by an ordinary method, with/without the initial aluminum resource in precursor solution, the physical and chemical properties of zeolite capsule catalyst could be dominated well.

**Capsule Catalysts Activity.** The direct conversion from syngas to dimethyl ether (STD reaction) was the application of zeolite capsule catalysts CZA-Z and CZA-S. The bare CZA catalyst and hybrid catalyst CZA-M were also performed under the same

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**Figure 5.** Products distribution of the CZA catalyst, zeolite capsule catalyst CZA-Z and CZA-S, and the hybrid catalyst CZA-M.

reaction conditions as references. The catalyst activity is summarized in Table 1. The hybrid catalyst CZA-M consisted of two types of catalysts, CZA and zeolite catalyst, for different reactions, respectively. In the STD reaction on this hybrid catalyst, the formed methanol on the CZA catalyst was randomly converted to DME on the zeolite catalyst via its dehydration reaction, which broke the thermodynamic equilibrium of the reaction from syngas to methanol on CZA catalyst, enhancing the CO conversion from 44.02% (on single CZA catalyst) to 58.07%. It is well-known that the reaction combination of methanol synthesis with its in situ dehydration to DME is thermodynamically more favorable than either occurring solely.<sup>6</sup> The results obtained on this hybrid catalyst CZA-M also proved it.

For the CZA-Z zeolite capsule catalyst, its CO conversion was 5.59%, much lower than that of the bare CZA catalyst. The CZA-Z zeolite capsule catalyst was prepared by the acidic zeolite synthesis solution with aluminum resource. Possibly, the lower catalytic activity should be attributed to some damage on the core CZA catalyst during the hydrothermal synthesis process, such as dissolution of Cu or Zn, by the formation of a coordinated compound between TPAOH and Cu or Zn, or weakening interaction between Cu and Zn by TPAOH when the aluminum resource existed in the precursor solution, which led to the change of composition and structure of the core CZA catalyst. However, as a new method to overcome the problem of CZA-Z synthesis, the CZA-S zeolite capsule catalyst prepared by a close-to-neutral Silicalite-1 zeolite synthesis method, where HNO<sub>3</sub> was added to lower the pH value of TPAOH-containing synthesis solution, without aluminum resource, stopping formation of coordinated compounds, exhibited remarkably enhanced catalytic activity compared with the CZA-Z zeolite capsule catalyst, as shown in Table 1. The CO conversion of CZA-S reached 30.40%, which indicated that the close-to-neutral Silicalite-1 zeolite synthesis method could effectively reduce the damage from synthesis solution to core catalyst.

In addition, for the lower catalytic activity of zeolite capsule catalysts compared with bare CZA catalyst and hybrid catalyst CZA-M, another factor that some active sites of the core catalyst were partially covered by zeolite crystals should also be

considered. In the hydrothermal process, part of the synthesis solution entered the core catalyst pores and then crystallized into zeolite over some active sites of core catalyst, and the ease of Cu species reduction can essentially control the catalyst activity.<sup>29</sup> However, increasing metal content of the core catalyst or extending contact time of the reactant with zeolite capsule catalyst can enhance CO conversion very easily.

**Reaction Products Distribution.** Table 1 also gives the product selectivity on the bare CZA catalyst, hybrid catalyst CZA-M, and zeolite capsule catalysts CZA-Z and CZA-S. The corresponding products distribution patterns are compared in Figure 5. For CZA catalyst, the highest methanol selectivity of 98.38% was obtained, and DME was only a tiny product with a selectivity of 0.50%. Light hydrocarbons, such as methane and C<sub>2+</sub>, could be found in the final products. In the case of CZA-M, the selectivity of DME reached 40.51% along with a sharp decrease of methanol selectivity compared with the single CZA catalyst. However, there was only random contact between methanol and the active sites of zeolite catalyst in the hybrid catalyst CZA-M during STD reaction, which was decided by hybrid catalyst structure (simply mechanical blend of CZA with zeolite catalyst). As a result, only a fairly ordinary selectivity for DME was obtained, accompanied by the existence of unexpected alkanes in the final products.

Different from the physically mixed catalyst, zeolite capsule catalysts had a special core-shell structure in which the zeolite shell wrapped the core catalyst perfectly, which offered an inevitable way, passing through the zeolite shell, for methanol to escape from the zeolite capsule catalyst. Here, all of the methanol must contact the H-ZSM-5 zeolite shell. Capsule catalyst CZA-Z was prepared by the acidic H-ZSM-5 zeolite synthesis method. Its zeolite shell had higher acidic intensity but slightly lower zeolite loading amount compared with another zeolite capsule catalyst CZA-S. In the STD reaction on CZA-Z catalyst, the DME selectivity reached 96.59% together with zero alkanes byproduct, probably benefiting from the high acidic intensity and thinner zeolite shell thickness of capsule catalyst.

(29) Prasad, P. S. S.; Bae, J. W.; Kang, S. H.; Lee, Y. J.; Jun, K. W. *Fuel Process. Technol.* **2008**, *89*, 1281–1286.

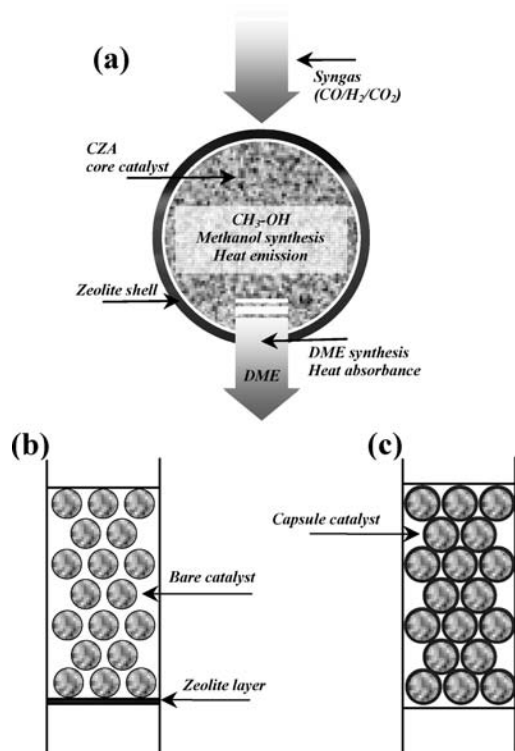


The strongly acidic sites ensured that almost all methanol formed on the core catalyst could be converted into DME, while the thinner zeolite shell thickness offered a short residence time for DME within the zeolite shell, inhibiting the formation of alkanes by DME further dehydration. Another zeolite capsule catalyst CZA-S was prepared using a close-to-neutral zeolite synthesis method that exerted less damage to core catalyst, and the CZA core catalyst acted in situ as the aluminum resource during hydrothermal synthesis process. The zeolite shell of CZA-S had a lower zeolite loading amount and similar acid amount compared with the physically mixed catalyst CZA-M (Supporting Information) but higher weight increment and greater thickness (5  $\mu\text{m}$ ) than zeolite capsule catalyst CZA-Z. In the STD reaction on the CZA-S zeolite capsule catalyst, there was still zero selectivity for the alkane byproducts as shown in Table 1, but the DME selectivity reached 78.57%, nearly twice that of the hybrid catalyst CZA-M even if the latter was prepared using the H-ZSM-5 zeolite with similar acid amount and larger weight proportion. Also, it was only slightly lower than that of the CZA-Z zeolite capsule catalyst, possibly due to the low acidic intensity and smaller acid amount together with the insufficient distance offered by the zeolite shell for methanol dehydration, leading to the partial conversion of the methanol to DME. It is referred that increasing the acidic sites intensity, density, and thickness of the zeolite shell of CZA-S, which will be easily realized only by controlling the hydrothermal synthesis conditions or recipe, can further reduce the selectivity of methanol, thereby enhancing the selectivity of DME.

## Discussion

The STD reactions on the zeolite capsule catalyst CZA-Z and CZA-S exhibited a completely different product distribution compared with that on the bare CZA and hybrid CZA-M catalyst, realizing an exclusive DME selectivity, very low methanol selectivity, and zero byproduct formation simultaneously, as shown in Figure 5. The outstanding capability of the capsule catalyst should be attributed to its specific core-shell structure. For hybrid catalyst CZA-M, there was no spatially confined effect between the methanol synthesis reaction and methanol dehydration reaction, demonstrating that these two consecutive reactions occurred independently and randomly. As a result, a part of the methanol formed on the methanol synthesis catalyst could escape from the catalyst bed directly without undergoing dehydration on zeolite catalyst. In addition, the random nature of the process also demonstrated that some DME may get more opportunities to be further dehydrated on the zeolite catalyst or transformed to alkanes or alkenes. However, the zeolite capsule catalysts with the core-shell structure might control the occurrence of the two reactions in a consecutive order. As illustrated in Scheme 1a, the feed gas first passed through the zeolite shell to enter the core catalyst, where the methanol was produced on the core catalyst. Then the methanol formed in the core catalyst must go through the zeolite shell to escape, which ensured that all of the methanol had enough opportunities to contact the active sites of the H-type zeolite shell, to be converted into the expected products. As a result, the selectivity for DME was increased sharply. Moreover, the zeolite shell had a fixed position, uniform thickness, and homogeneous property, which made it an equal opportunity provider to each methanol molecular that diffused from the core catalyst, improving the conversion from methanol to DME concertedly, while suppressing its further dehydration to generate the alkane or alkene byproducts simultaneously. From the

**Scheme 1.** (a) Schematic Diagram Showing DME Direct Synthesis from Syngas on a Single Zeolite Capsule Catalyst, (b) Schematic Diagram of the Bare Catalyst with Zeolite Layer Loading in Reactor in the Form of a Dual Layer, and (c) Zeolite Capsule Catalysts in Reactor



viewpoint of energy efficiency, it should be mentioned that the reaction heat from the exothermic methanol synthesis on the core catalyst could be in situ recycled inside the zeolite capsule by the DME synthesis from methanol on the zeolite shell to protect the catalyst lifetime from overheating.

It should also be noted that this capsule method, with a zeolite shell wrapping the millimeter-sized core catalyst, provided a new method to avoid the difficulty of large-area membrane preparation due to the easy formation of pinholes or cracks. Especially, the ratio of membrane surface area to catalyst bed volume of the zeolite capsule catalyst was extremely high compared to that of a dual-layer method or other membrane reactor configurations, providing excellent catalysis and separation since each core catalyst is wrapped by the zeolite shell, as illustrated in Scheme 1b and c.

## Conclusions

Two direct preparation methods were demonstrated to fabricate two types of H-ZSM-5 zeolite capsule catalyst with a tailor-made millimeter-sized catalyst core and microsized zeolite shell. One method was the traditional acidic H-ZSM-5 zeolite synthesis, and another was a close-to-neutral Silicate-1 zeolite synthesis using the core catalyst as the aluminum provider. The latter method explored a facile, reliable synthetic method for acidic zeolite membrane growth on an aluminum-containing support and effectively reduced the damage from zeolite precursor solution to substrates during the hydrothermal synthesis process. In the consecutive reactions of DME direct synthesis from syngas, zeolite capsule catalysts exhibited an extreme selectivity for DME compared with the conventional hybrid catalyst, suppressing the further dehydration of DME to form alkane/alkene byproducts. This concept of a zeolite capsule

catalyst with the effect of an equilibrium shift, shape selectivity, and synergetic confinement is therefore promising to be widely used for many consecutive reactions such as multiple-step organic synthesis. In addition, it is clear that the original preparation method of the acidic H-ZSM-5 zeolite shell using a close-to-neutral Silicalite-1 zeolite synthesis method on an aluminum-containing substrate can give a novel inspiration to the science of zeolite membranes.

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**Supporting Information Available:** Further characterization and detailed discussion on the concentration and strength of acid sites of bare CZA catalysts, zeolite capsule catalyst CZA-S, CZA-Z, and hybrid catalyst CZA-M by the temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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