Preparation of Core-Shell Catalyst by *in situ* Growth Method in Water-in-Oil Microemulsion†

Y. Chen, T. Cao, Y. Wang, H. Xuan, Z.H. Zhou and S.J. Feng[*]

School of Materials Science and Chemical Engineering, Anhui Jianzhu University, Hefei 230022, P.R. China

*Corresponding author: E-mail: fengshaojie@ahjzu.edu.cn

A type of core-shell catalyst CuO-ZnO-Al₂O₃/ZSM-5 was prepared for direct synthesis of dimethyl ether from syngas. A water-in-oil microemulsion made up of liquid paraffin, Span 80 and water phase was used to prepare both the core and core-shell catalyst. The water phase was consisted of core growth medium for core preparation or core sol for core-shell preparation. The dispersion medium of core sol was the growth medium and shell would layer on the core directly. Transmission electron microscopic images showed the core particles were in nano-size and coated by shell successfully. EDS was used to test quality percents of Cu, Zn and Al. The crystal structure of core and shell was described by XRD. This original preparation method of *in situ* growth in microemulsion can give a novel inspiration to the core-shell constitute material which can realize the combination of two and more sequential reactions with many synergistic effects.

Keywords: Microemulsion, *in situ* growth, Core-Shell, Compound catalyst.

INTRODUCTION

Compound catalyst now is commonly studied in syngas reaction. Traditionally, the final production can be produced through two methods. One is an intermediate on a single catalyst, where the intermediate is separately made from syngas and the other is a couple of consecutive reactions for final production direct synthesis from syngas on a hybrid catalyst, where the hybrid catalyst is a simple mixture. Obviously improvement on efficiency in syngas productivity, catalyst lifetime, performance and activity can be realized by the latter methods because compound catalyst introduces synergistic and conjugate action between the consecutive chemical reactions so that the active chemical composition of a catalyst will work more efficiently[1-3]. It is predicted that the catalyst having a finely designed structure usually exhibits better catalytic performance[4]. However, previous studies paid more attention to the simple mechanical mixing of the different types of catalysts. The effective structure combination of different active catalysts was not studied in detail[5-7]. Catalyst with core-shell is expected to provide fixed active chemical composition and can be benefited to explain the reaction systems such as how the consecutive reactions couplings[8].

Here, a core-shell catalyst used for dimethyl ether (DME) produced from syngas directly was designed. Dimethyl ether is an industrially important intermediate, as well as a promising clean fuel[9,10]. One of produced methods of dimethyl ether is methanol dehydration on a single dehydrating catalyst, where the methanol is separately made from syngas and the other is a couple of consecutive reactions for dimethyl ether direct synthesis from syngas on a hybrid catalyst[11,12]. Among all the dimethyl ether synthesis catalysts, CuO-ZnO-Al₂O₃ compound oxide is commonly used for methanol synthesis catalyst and Zeolite Socony Mobile-Five (ZSM-5) or γ-Al₂O₃ for methanol dehydration catalyst[13-15].

Herein, we report a method for nano-sized catalyst possessing core-shell structure by using water-in-oil microemulsion. The whole procedure of preparation is described in **Scheme-I**. The core particles were prepared in a microemulsion with smaller water droplets consisted of metal nitrate solution while core-shell structure formed in a microemulsion with larger water droplets consisted of core particles and shell growth medium. The shell layer would direct deposit on the core particles by *in situ* growth method when precipitant was added into microemulsion. Different size of water droplets were obtained by adjusting the total amount of water phase. In fact, many researches on nanoparticle or core-shell material prepared by microemulsion have been reported in recent years in which both metal oxide and zeolite involved[16-21]. To the best of our knowledge, there are few reports on nanoparticle with core-shell material prepared by *in situ* growth method in microemulsion.
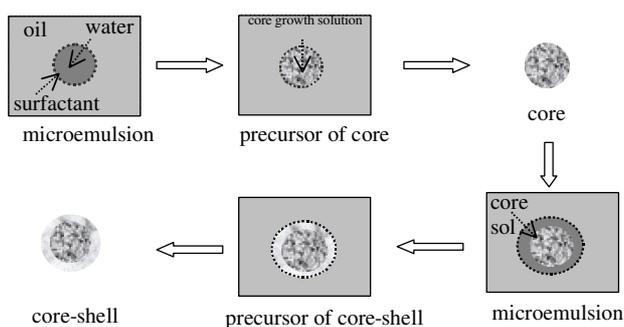
Scheme-I: Schematic diagram of the preparation of core-shell compound particle by *in situ* growth method in water-in-oil microemulsion

We designed a type of core-shell catalyst, CuO-ZnO-Al$_2$O$_3$/ZSM-5. Methanol was expected to be synthesized inside of the compound catalyst because ZSM-5 is porous and syngas would directly pass through the pores and act inside on CuO-ZnO-Al$_2$O$_3$ to form CH$_3$OH. Then dimethyl ether could be obtained as CH$_3$OH spreading out of the shell structure ZSM-5. Different from the traditional shell layer preparation methods, such as the secondary growth method or hydrothermal method, here the surface modified of core was kept away and mild operating condition was used.

The obtained results demonstrate shell layer can directly deposit on core in spite of the different crystal form between CuO-ZnO-Al$_2$O$_3$ and ZSM-5. It is feasibility of this approach and potential of the microemulsion reaction method for the synthesis of particles with core-shell structure.

EXPERIMENTAL

Preparation of core: The microemulsion was prepared by mixing the appropriate amount of surfactant (Span-80) (8 mL), oil phase (liquid paraffin, 60 mL) and water phase (metal nitrate aqueous solution, 2 mL). The mixture was stirred (vortex) at 60 ºC to get a homogeneous, transparent and fluid isotropic phase.

The water phase was made up of Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ aqueous solution with the Cu:Zn:Al atomic ratio of 5:4:1 (eq. quality percentage of Cu:52.17 %, Zn:43.48 %, Al:4.35 %).

The microemulsion was kept stirring for 12 h and a small amount of sodium carbonate solution (2 mL, 1 M) was added under vigorous stirring for another 24 h to precipitate metal ions. The metal oxides precursor were formed in the water phase and separated from the microemulsion by unstabilizing the microemulsion with hot ethanol followed by centrifugation at 4000 rpm for 10 min. The particles were filtered and washed thoroughly with hot ethanol and deionized water. After the drying at 100 ºC overnight and calcination at 500 ºC for 3 h were carried out successively, core CuO-ZnO-Al$_2$O$_3$ can be obtained.

Preparation of core-shell: The core-shell catalyst was also formed in microemulsion. Different to core preparation, here the water phase was made up of core sol instead of metal nitrate solution. Other operating conditions such as reaction temperature, stirring time, washing and dry process of precursor was the same as core preparation.

The core sol was made up of CuO-ZnO-Al$_2$O$_3$ (30 mg), TEOS (1.7 mL), isopropyl alcohol (1.6 mL) and aqueous solution of Al(NO$_3$)$_3$ (0.6 mL, 1 M). The mixture of TPAOH (0.9 mL) and NaOH aqueous solution (0.03 g NaOH dissolved in 1.2 mL deionized water) was used as precipitant. Calcinations process was at 400 ºC for 3 h.

Charactrization: The size and morphology of the core-shell catalyst were imaged using a transmission electron microscope (JEOL-2010, Japan). The quality percent of Cu, Zn and Al in core catalyst was measured using the transmission electron microscope (JEOL-2010, Japan). X-Ray diffraction (XRD) patterns were collected using X-ray powder diffracto-meter equipped with a CuK$_\alpha$ radiation source at 40 kV and 200 mA (MXPAHF, Japan).

RESULTS AND DISCUSSION

The water droplets for core preparation were expected to be as small as possible to obtain CuO-ZnO-Al$_2$O$_3$ particles with small size. On one hand, the small core will be easy to suspend steadily in shell growth medium to form core sol which acted as the water phase in the microemulsion used for core-shell preparation. On the other hand, smaller particle may show better compatibility for shell deposition inspite of different crystal type between core and shell. In addition, the size of water droplets for *in situ* growth would be adjusted between core size and the largest size for stable microemulsion. The total water phase amount here was 4 mL for core preparation and 6 mL for core-shell structure preparation, amount of precipitant included.

Fig. 1 shows that the core CuO-ZnO-Al$_2$O$_3$ is well disper-sed with size below 30 nm. The shell layer grows successfully around core particle but has no clear edge. The reason why shell layer was adhesion each other instead of well dispersed may result from element migration. Concretely, Al$_2$O$_3$ and ZnO in core were dissolved partially with the action to Na$_2$CO$_3$ (used in core preparation) or NaOH (used in core/shell preparation) and migrate outside to shell growth medium. Thus the mass ratio of Cu: Zn: Al in the core would not keep consistent before and after the core coating. EDS analysis of the core (Fig. 2) shows the quality percentage of Cu, Zn and Al in the core after coating. Zn % and Al % in core CuO-ZnO-Al$_2$O$_3$/ZSM-5 were 33.84 and 4.1 % in the core. Compared with the initial percentage in core growth medium (Cu: 52.17 %, Zn: 43.48 %, Al: 4.35 %), it can be concluded that there was quality loss of Al and Zn in core after coating, as demonstrated the migration of these two elements. The Al content in shell growth medium may have an effect on dispersion of core-shell structure because amorphous aluminum oxide formed during calcination caused rough surface of the shell and adhered each other.

The core sol in microemulsion may restructure with the joint action of surfactant, stirring and Brownian motion which may cause some core particles escaped from sol and suspended in oil phase while some shell growth medium existed as a form of new droplets in the microemulsion. So when the precipitant agent was added, core-shell structure formed in the droplets consisted of core sol while particle without core in the droplets consisted of shell growth medium only. Particles composed of ZSM-5 with core-shell structure are also shown in TEM images (Fig. 1).
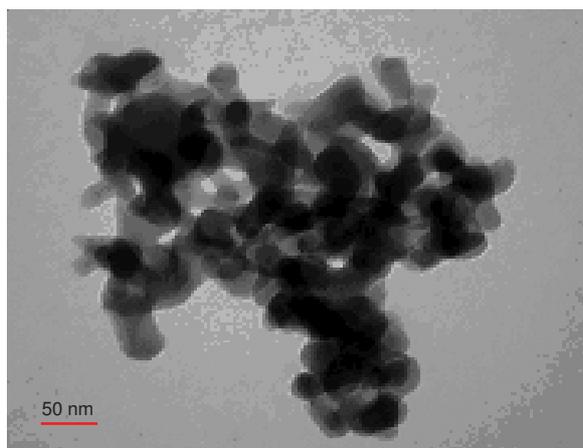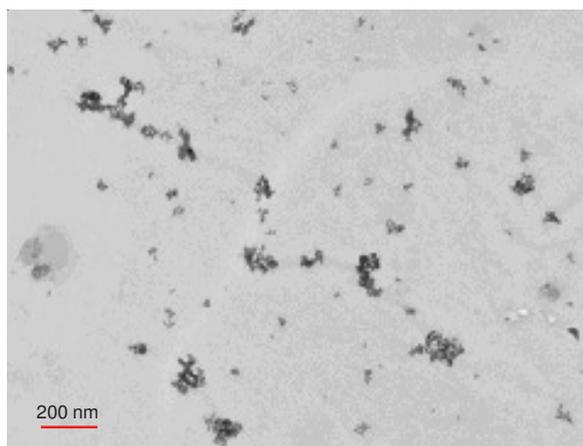
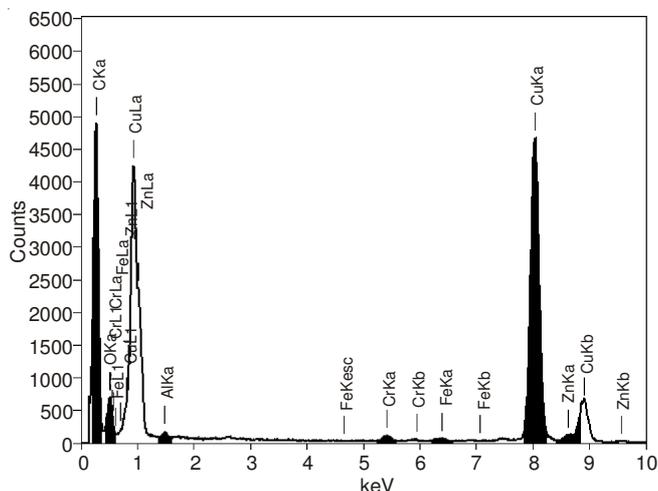Fig. 1. TEM images for CuO-ZnO-Al$_2$O$_3$/ZSM-5 catalyst

Fig. 2. EDS analysis of CuO-ZnO-Al$_2$O$_3$/ZSM-5 catalyst

In fact, core-shell catalyst with different crystal between core and shell is often prepared by not *in situ* growth method but the secondary growth method. Before shell disposition, core particle will be modified for shell adsorption on core surface[22-28]. But here we got no modification and the shell disposition was forced directly on the core surface in a small space of water droplet, the core particle acting as seed, as is *in situ* growth method in water in oil microemulsion. XRD spectra (Fig. 3) exhibited the ZSM-5 with sharp peak located at 2θ = 21.9. The wide peak in the range of 2θ = 5-15 indicated Al$_2$O$_3$ existing in the sample as form of amorphous. Peaks

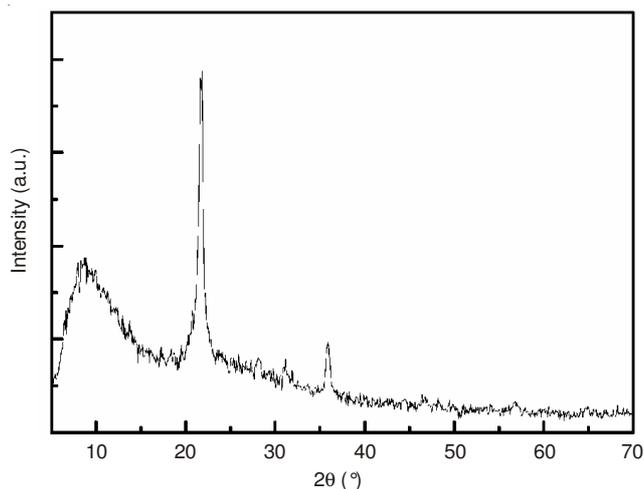

Fig. 3. XRD spectra of CuO-ZnO-Al$_2$O$_3$/ZSM-5 catalyst

observed at 2θ = 31.8 and 2θ = 35.8 confirmed the formation of crystal ZnO and CuO crystal, respectively. Characteristic peaks at 2θ = 7.9, 8.5 of ZSM-5 may be masked by the wide peaks of Al$_2$O$_3$ existed here. Other characteristic peaks such as 2θ = 14.8, 17.8 of ZSM-5 and 2θ = 38.8, 48.7, 58.4, 61.6 of CuO can not be identified clearly may be caused by the super-position peak or preferred orientation of crystal.

Conclusion

A kind of core-shell compound catalyst CuO-ZnO-Al$_2$O$_3$/ZSM-5 was synthesised by *in situ* growth method in micro-emulsion. The core particle was of nano size and coated by shell successfully. Shell layer was adhered each other because of aluminum migration. Size of water droplet adjusted by changing the total amount of water phase was realized here. And the water droplets made up of core growth medium was smaller than that made up of core sol. Crystal growth orientation also can be influenced by the water droplet, as can be deduced from XRD spectra. In addition, it is clear that the original preparation method of *in situ* growth in microemulsion can give a novel inspiration to the core-shell constitute material.

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