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Precise construction on the structure of zeolite microcapsules

Jing Shi [a,b,*], Jia-Wei Teng [a], Yang-Dong Wang [a], Yi Tang [b], Zai-Ku Xie [c,**]

[a] Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China
[b] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China
[c] Sinopec, China Petroleum & Chemical Corporation, Beijing 100027, China

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ABSTRACT

In this paper, the precise construction on the structure of silicalite-1 microcapsules (S1) was specifically described. The interior carbon modifications and the outside mesoporous functionalizations were successfully conducted and each sample was characterized in detail. It was found that the carbon networks could be formed inside the zeolite microcapsules *via* the pretreatment of sugar injections. The uniformity of the distinct microcapsule could be regulated by adjusting the sugar concentrations. With the encapsulated Pt species inside the MSSs, the nano-particles could be dispersed well within the carbon network. On the other hand, during the fabrication of the mesoporous materials outside the microcapsules, the template and the acidity of the system could play an important role in determining the morphology of S1. Besides, the PDDA modification on the shell of S1 could help the combination of the meso-layer and the shell of S1 at nano-scale. The thickness of the outside mesopore could be modulated through the controlling of the silica content.

1. Introduction

Microporous zeolite and mesoporous materials are two families of inorganic porous matrix [1–3]. As we all known, mesoporous material refers to a particular kind of material with pore diameters between 2 nm and 50 nm [4]. Because of its large surface, low diffusion limit, excellent surface condensation ability [5–10], the mesoporous material has great potential in adsorption processes, shape separation, high efficient catalysis and nano-equipment applications *etc.* [11–16]. Compared to the simple mechanical mixture between micro- and meso-porous materials, the micro@-meso composite obtained from the chemical means could make their combination truly at nano-scale level [17]. In 2005, Yoon's research group synthesized a silicalite-1@mesoporous core–shell structure with the help of *n*-octadecyltrimethoxysilane (C_{18}-TMS) for the first time [18]. Although the outside mesoporous layer is not so uniformly dispersed, it was considered to be a new type of material with hierarchical pores distributed at the nano-scale. Since then, Ying *et al.* applied cetyltrimethylammonium bromide (CTAB) to fabricate the zeolite@mesoporous core–shell structures. They skillfully took advantage of the solubility of zeolite in alkaline solutions to release the silicon species as the growing source for the formation of outer mesopores [19]. Xu *et al.* also used CTAB as a template to produceTS-1@mesoporous after the modification of zeolite with poly(diallyldimethylammonium chloride) (PDDA). Following the adsorption of gold nano particles, this composite could perform well in the selective epoxidation reaction of propylene [20]. Recently, professor Zhao has developed a convenient way to led to a micro-meso-product of ZSM-5@SBA-15 with the P123 (PEO-PPO-PEO) as a template under acidic conditions [21] and explored it in menthol to propylene (MTP) reaction with fine catalytic performance. It could be concluded that the micro@meso core–shell structure has attracted more and more researchers due to its specific characters and structures. Another member in the mesoporous family is the porous carbon [22] with mesopores (2–50 nm) inside. Owing to its peculiar features such as the resistance to the acid or the alkalinity, the flexibility of the pore size and the large surface area [23–26], the mesoporous carbon has been widely used as an excellent support for the catalytic processes and electronic applications [27–30].

As an inorganic core–shell structure, the zeolite microcapsule is synthesized through assembling strategies of nano-seeds *via*

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[*] Corresponding author at: Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China.
[**] Corresponding author.
E-mail addresses: shij.sshy@sinopec.com (J. Shi), xzk@sinopec.com (Z.-K. Xie).

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layer-by-layer fabrication methods [31]. It has been demonstrated that the zeolite microcapsule could be used as an effective catalyst both in tandem reactions of fine chemical syntheses and kinetic dynamic reactions in biochemistry owing to its shape selectivity, screening and isolation effects [32,33]. The precise construction of zeolite microcapsules could not only provide the high-uniformity of dispersed Pt nanoparticles, the improved connectivity of meso- and micro-pores and the enlarged flexibility of the functionalization for its better performance in catalysis but also realize the integration of catalytic reactors in one composite. Our work mainly focused on the distinct modification of silicalite-1 microcapsule (denoted as S1) with interior meso-carbon and exterior mesopore, respectively, which enabled the possibility for second or even third modification of S1. Each functionalized S1 has been characterized in detail.

2. Experimental

2.1. The interior modification of S1 with meso-carbon

The mesoporous silica spheres (MSSs) were fabricated according to our previous work [32]. Then, 0.5 g of MSSs was impregnated in sugar solutions with different concentrations and stirred at room temperature for 12 h. After heated to 100 °C, this solution was kept stirring for 12 h and at 150 °C for 6 h. Finally, the solid products were collected by filtration and fully carbonized at 900 °C for 6 h under argon to obtain the MSSs with carbon inside (C-MSS). The samples of C-MSS-1, C-MSS-2 and C-MSS-3 were prepared with the sugar concentration at 20 wt%, 40 wt% and 60 wt%, respectively. The above products were then added into an HF solution to remove the carbon template. After washing and drying, the samples of C-HSM-1, C-HSM-2 and C-HSM-3 were obtained respectively. We used C-MSS-2 as a representative for the hydrothermal treatment and modified its surface with the zeolite seeds as the literature indicated [32]. This seeded C-MSS-2 was then dropped into the precursor solution with a molar ratio ofTPABr:H_2O:NaOH = 18:2000:0.2 and heated to 90 °C for 8 h. After cooling down to room temperature, the solids were collected by filtration and the interior carbonized S1 (C-HSM-4) was obtained by further washing with demineralized water and drying at the 80 °C. The process for the carbonization was illustrated in Fig. 1.

2.2. The introduction of Pt into the S1

0.5 g of MSSs was modified with an amine-group [32] and then dropped into the precursor containing both sugar (40 wt%) and $HPtCl_4$ (3 wt%). The solution was heated to 100 °C and stirred for 12 h, and then to 150 °C for 6 h. The carbonization was conducted at 900 °C under argon and the MSSs with Pt and carbon inside (Pt-C-MSS) were obtained. After assembling the silicalite-1 seeds *via* the layer-by-layer method on the Pt-C-MSS, the seeded samples were added to the precursor solution as the procedure described in Section 2.1 and heated to 90 °C for 8 h. The hollow solids (Pt-C-HSM) were collected by filtration and then washed and dried for further characterizations.

2.3. The outside modification of S1 with mesopore

Using P123 as the template: To prepare the precursor for mesopore modification: 0.039 g of P123 was first dissolved in 20 mL of HCl, followed by the addition of 0.116 g of $MgSO_4$ and 0.1 g of S1. After 30 min of ultrasonic treatment, 0.05 g of TEOS was added slowly to the above solution and kept stirring for 24 h at room temperature. Then the solution was treated at 90 °C for 8 h and the modified zeolite microcapsules (S1@meso-1) were finally calcinated at 550 °C for 6 h to remove the organic template.

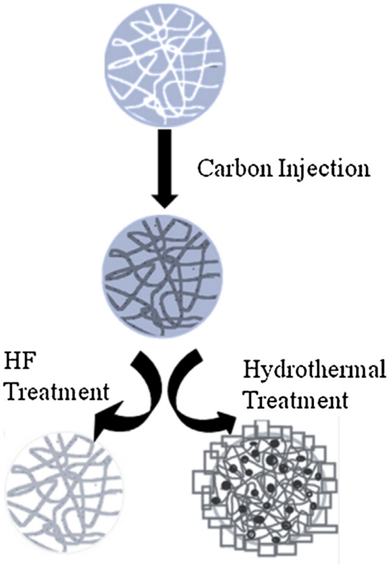

Fig. 1. Schematic illustration of the formation of C-HSMs

Using CTAB as the template: 0.1 g of the prepared S1 was added to a PDDA solution (0.3 wt%) and stirred for 30 min. After centrifugation, the solids were washed and dried, then dropped into a CTAB solution. Afterwards, 0.3 g of ammonium hydroxide (28 wt%) was injected to adjust the acidity of the CTAB solution. Certain amount of TEOS was added drop wise to the solution with vigorous stirring, and the agitation was kept for 6 h after the addition. After treated at 90 °C for 8 h, the white solids were collected by filtration and the final S1@meso was obtained by washing, drying and calcinating at 550 °C for 6 h. The samples of S1@meso-2 and S1@meso-3 were prepared with the corresponding TEOS content at 5 wt% and 10 wt%, respectively.

2.4. Characterization

The solid products were characterized by powder X-ray diffraction (XRD) on an Rigaku D/max-IIA equipment with Cu Kα radiation for the determination of phase purity and crystallinity of the samples. It worked at the condition of 40 kV, 40 mA with a scanning rate of 0.02°/min (2θ). Scanning Electron Microscopy (SEM) images were taken from anXL30E equipment of FEI Company. Transition electron microscopy (TEM) and energy dispersive spectrometer (EDS) were taken from a JEOL JEM-2010 equipment. Nitrogen adsorption and desorption data were obtained from a Micromeritics ASAP-2000.

3. Results and discussion

3.1. The interior carbonization of S1

The MSSs were carbonized with different concentrations of sugar as shown in the SEM images shown in Fig. 2. It can be seen that the original sphere morphology of MSSs was reserved with its diameter at around 1.5 μm (Fig. 2A–D). At a high concentration of sugar at 60 wt%, the spheres were connected with each other and formed a bulky solid easily (Fig. 2E and F).

The C-MSSs were treated with an HF solution to remove the silica sphere and the corresponding samples of C-HSM-1, C-HSM-2 and C-HSM-3 were obtained. As shown in Fig. 3, the spheres were