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修饰晶种法合成 MFI 型分子筛膜包覆的活性炭颗粒

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摘要: 由于分子筛膜的分离和催化作用, 分子筛膜包覆的传统催化剂颗粒可以实现高效的催化过程. 活性炭颗粒作为一种常用的催化剂载体, 由于其表面的憎水性和不平整, 在不规则活性炭颗粒表面直接水热合成包覆一层分子筛膜非常困难. 为了克服上述缺点, 本文采用一种勃姆石凝胶修饰的晶种法在活性炭颗粒表面合成连续的分子筛膜. 以勃姆石溶胶为前驱体, 在活性炭颗粒表面通过喷涂预先形成一层相对平整的勃姆石凝胶层以改善活性炭表面. 在随后的晶种涂覆过程中, 晶种分散液加入部分勃姆石溶胶为胶粘剂, 所得的晶种层覆盖载体完全, 与载体结合牢固, 无需焙烧处理. 将晶种涂覆后颗粒在旋转动态水热 175 °C 处理 6 h, 得到分子筛膜包覆的活性炭颗粒, 所得材料分别用 X 射线衍射和扫描电镜进行表征. 包覆的分子筛膜为 MFI 结构, 厚度约为 5 μm . 对比实验表明, 没有勃姆石溶胶修饰的活性炭颗粒上不能成膜. 这种勃姆石凝胶修饰晶种法为在各种惰性载体上合成分子筛膜提供了便捷的方法.

关键词: 晶种法; 喷涂; 勃姆石溶胶; 分子筛膜; 活性炭颗粒

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Synthesis of MFI-Type Zeolite Membrane Encapsulated Activated Carbon Particles Using a Modified Seeded Method

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Abstract: Zeolite membranes with their advantageous separation and catalytic properties can be coated on traditional catalysts to achieve highly effective performance. It is difficult to coat zeolite membranes onto activated carbon (AC) particles, a commonly used catalyst support, because of the hydrophobic and rough surfaces of AC. To overcome these shortcomings, a boehmite gel modified seeded method was developed to synthesize MFI-type zeolite membrane encapsulated AC particles. By using the spray-coating process, the boehmite sol precursor was introduced in a gel layer on the AC surface to provide a smooth surface for seed dispersion and a binder for seed fixation. The obtained seed layer was dense and firm even without calcination. After 6 h rotary hydrothermal synthesis, continuous zeolite membrane encapsulated AC particles were obtained. The synthetic membrane type and the composite material morphologies were elucidated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The results indicate that MFI-type zeolite membrane has a thickness of 5 μm . For comparison, on AC particles without boehmite gel modification, no continuous membrane forms. Our boehmite gel modified seeded strategy provides an efficient way to prepare zeolite membranes on different inert supports.

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Key Words: Seeded method; Spray-coating; Boehmite sol; Zeolite membrane; Activated carbon particle

1 Introduction

Supported zeolite membrane has attracted increasing interest due to its potential application in separation, catalytic reactor, electrical insulator, etc.¹⁻³ Traditionally, zeolite membrane is prepared on surface of disk or tubular supports made of materials such as porous Al_2O_3 , SiO_2 , and ceramic.^{4,5} Recently, much effort has been devoted to coat a zeolite membrane shell on the surface of catalyst particles. Taking advantage of the molecular sieving ability of zeolite membrane shell, better selectivity and superior reusability of the catalysts can be achieved.^{6,7} For example, MFI-type zeolite capsule catalysts were prepared for adjusting the products distribution of Fischer-Tropsch synthesis as well as realizing the combination of sequential reactions from syngas (CO/H_2) to methanol and then to dimethyl ether.⁸⁻¹²

There are two main methods to synthesize zeolite membrane on the supports: *in-situ* hydrothermal synthesis and secondary growth on seeded supports. Compared to the oxides supports, due to the hydrophobic surface of activated carbon (AC), it is more difficult to coat zeolite membranes on AC by using *in-situ* hydrothermal process. Thus, methods like surface oxidation, impregnation with silicon atoms or adding hydrophilic montmorillonite clay were employed to increase the nucleation site carbon-based materials to facilitate zeolite synthesis on.^{13,14} Also, concentrated nitric acid treatment was an efficient way to form membrane on carbon-based materials.¹⁵ Generally, a long time is needed for *in-situ* zeolite membrane synthesis on the support. For instance, as reported in literature,¹⁶ it takes 48 h to coat a zeolite membrane on AC particles. Moreover, the recipes used in a given support usually do not apply to the others due to their varying surface properties of different support materials.

Alternatively, the secondary growth can also form supported zeolite membrane. First the zeolite crystal seeds are deposited on the substrates, and upon sequential hydrothermal treatments under the appropriate conditions the seeds grow to form a continuous membrane, even when the crystallization conditions are not optimum.¹⁷ The key factor of this method is to deposit and fix a continuous seed layer on the surface of supports. For this purpose, cation polymer has been used to modify the surface properties of oxide supports.¹⁸ Considering the different shapes of carbon-based materials, seeded methods like slip-casting and electrophoretic deposition were employed.^{19,20}

However, when using irregular catalyst particles as the support to coat zeolite membrane, there is another big challenge that the particle is always millimeter-sized and its surface is uneven, which makes the fixation and deposition of a seed layer become difficult. In this work, we present an efficient method by pre-coating activated carbon particles with a boehmite gel layer and then growing the membrane with seeds subsequently.

2 Experimental

2.1 Zeolite membrane preparation

2.1.1 Seed synthesis

Unless special statement, the chemicals used in this work were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Crystal seeds were prepared according to the method reported in literature.²¹ 5.0 g of fumed silica (A200, Degussa, Germany) was added to the solution of 0.27 g of sodium hydroxide (NaOH, AR) and 20.0 mL of $1 \text{ mol} \cdot \text{L}^{-1}$ tetrapropyl ammonium hydroxide solution (TPAOH, Wuhan Chi-Fei chemical Co., Ltd.). The mixture was stirred for 24 h at room temperature and then was transferred to a 100 mL Teflon-lined autoclave and placed in an oven with static at 125°C for 8 h. After the treatments of cooling, washing, and filtering, the obtained powders were dried at 120°C for 10 h.

2.1.2 Seeded process

The irregular coconut shell based AC particles (20–40 mesh) were dried at 70°C overnight in a vacuum oven, followed by boehmite gel coating using the spray-coating method. Boehmite sol ($0.36 \text{ mol} \cdot \text{L}^{-1}$) was prepared by the Yoldas process,²² using aluminum isopropoxide (CP) as the precursor. Prior to coating, the pre-weighted AC particles were soaked with ethanol (the mass ratio of ethanol/AC is 0.3). Filling the pores of AC with ethanol would prevent boehmite gel from entering into the inner pores of AC particles. Then the boehmite sol was sprayed carefully on dispersed AC particles with a 100 mL plastic sprayer bottle, after then the AC particles were dried at 45°C for 1 h. This procedure was repeated several times until the mass ratio of AlOOH/AC reached 0.06. After that, 0.1 g of seeds and 1.0 g of boehmite sol ($0.36 \text{ mol} \cdot \text{L}^{-1}$) were dispersed in 9.0 g of ethanol and followed by ultrasonic treatment for 30 min. Then the mixture was sprayed on 5.0 g of boehmite gel coated AC particles with the aforementioned way. For comparison, bare AC particles were seeded with the similar way.

2.1.3 Hydrothermal synthesis

For membrane synthesis, a solution was made by mixing 2.26 g of TPAOH (25.0% (w) in water, Wuhan Chi-Fei Chemical Co., Ltd.) and 0.44 g of NaOH in 28.0 g of de-ionized water. After magnetic stirring at room temperature for 30 min, 3.47 g of tetraethyl orthosilicate (TEOS, AR) was added drop-by-drop to the solution under stirring. The obtained solution has a mole ratio of $\text{SiO}_2:0.67\text{NaOH}:0.17\text{TPAOH}:100\text{H}_2\text{O}:4\text{EtOH}$. After stirring for 8.0 h, the clear solution was divided into two equal parts and mixed with 0.5 g of gel coated seeded AC and 0.5 g of no alumina sol modified AC particles, respectively. Then the mixtures were transferred to a Teflon-lined autoclave and kept under static condition for 0.5 h at room temperature. Crystallization was carried out in a rotation oven with

a rotary speed of $2 \text{ r} \cdot \text{min}^{-1}$ at 175°C for 6 h.

2.2 Characterization

X-ray diffraction (XRD) patterns were determined on an X-ray diffractometer (XRD-6000, Shimadzu, Japan), using Cu K_α radiation, with a working voltage of 40 kV and a current of 40 mA. Apart from the scanning electron microscopy (SEM) of seeds obtained from Carl Zeiss Ultra55 (Germany), the morphologies of the other samples were examined by Hitachi TM-1000 (Japan).

3 Results and discussion

The synthesized crystal seeds were confirmed with XRD and SEM, as shown in Fig.1. XRD pattern of the sample has a good agreement with the characteristic diffraction peaks of silicalite-1 (PDF card 45-0737). Elliptic and twin crystals with a size about 500 nm are observed from the inserted micrograph. Combined with the XRD results, it suggests that uniform silicalite-1 seeds are synthesized successfully, which are often used for the preparation of MFI-type (TS-1, ZSM-5, Silicalite-1) membrane.

The irregular AC particle and boehmite gel coated AC particle are shown in Fig.2A and Fig.2B, respectively. The irregular AC particle has an uneven surface and possesses some visible pores with sizes up to ten microns. A smoother surface is obtained after coating a boehmite gel layer onto AC particles. And the majority of visible pores are covered by boehmite gel. For AC particles, it is difficult to directly deposit a dense seed layer on this uneven surface. After the seeded process, most of the seeds are located onto the low-lying place of surface (see Fig.2C). Instead, a uniform seeded surface is obtained on gel

Fig.1 XRD pattern and SEM image of crystal seeds

pre-coated AC surface (see Fig.2D). It seems that the gel pre-coated layer provides a flat surface for seed dispersion.

Representative results after hydrothermal treatment are shown in Fig.3. Only sporadic crystals attached onto the AC surface are observed on boehmite gel free seeded AC particles. In addition, some zeolite powders mixed with AC particles are obtained in final products, implying that the seeds on AC surface are not firm and would shed during the rotary hydrothermal treatment. In comparison, as shown in Fig.3B, the boehmite gel pre-coated AC particles are wrapped by a continuous zeolite membrane. No zeolite powders mixed with the final particles are found with naked eyes. With the boehmite sol mixed in seeded solution, it seems that all seeds are firmly attached onto the surface of particles. Owing to the firm seed layer, the nucleation in the synthesis solution is totally suppressed, so nearly all precursors in zeolite solution preferentially participate in seed growth for membrane formation.

Fig.2 Surface SEM images of (A) AC particle; (B) boehmite gel coated AC particle; (C) AC surface after seeded operation; (D) gel coated AC surface after seeded operation

Fig.3 Overall surface SEM images of (A) AC and (B) boehmite gel pre-coated AC after hydrothermal synthesis for 6 h

X-ray diffraction was used to identify the membrane and its evolution from boehmite gel coated AC particles. As shown in Fig.4, broad peaks at 24.2° and 43.5° are generated by the AC particles, suggesting that some graphitized micro-crystal carbon exists in AC.²³ The peak at 48.9° in the diffraction patterns is assigned to the gel layer (alumina oxide hydroxide) onto AC surface.²⁴ For seeded gel pre-coated particles, besides the diffraction peaks derived from AC particles, characteristic peaks of silicalite-1 at $2\theta=23.2^\circ$, 23.8° , 24.4° are also observed. After hydrothermal treatment for 6 h, the composite presents some much stronger characteristic peaks of MFI-type zeolite. Note that the diffraction peak at 48.9° for AlOOH shown in Fig.4c is not obvious as shown in Fig.4(a, b), this phenomenon is possibly because the boehmite gel layer is covered by the mem-

Fig.4 XRD patterns of (a) boehmite gel coated AC particles, (b) seeded on gel pre-coated AC particles, and (c) seeded particles after hydrothermal treatment for 6 h

Fig.5 SEM images of (A) top view and (B) cross view for zeolite membrane wrapped particles after hydrothermal treatment

brane. The other possibility is that the gel layer may be partial dissolution in alkaline solution during hydrothermal synthesis.

The top-view and corresponding cross-section view of the membrane are shown in Fig.5. As shown in Fig.5A, after hydrothermal treatment, the seed layer has grown into a continuous membrane. Some crystals grow epitaxially out of the underlying compact membrane. This phenomenon is most likely caused by the disorder arrangement of the seeds, which is in agreement with the morphology of seed layer. From the cross-sectional view, a membrane with a thickness of about $5\ \mu\text{m}$ is observed (see Fig.5B), which is without giving any consideration of the irregular epitaxial growth of partial crystals. Obviously, a continuous membrane is formed by using the boehmite gel modified seeded method. Based on the above characterization, the function of boehmite gel layer can be illustrated in Fig.6. One is offering a flat surface on the particles, the other one is a binder for fixing seeds. The interaction between AC

Fig.6 Schematic illustration of the boehmite gel modified secondary synthesis procedure

surface and gel layer mainly involves physical bonding force, including the wedge force generated due to the rough AC surface.²⁵

4 Conclusions

MFI-type zeolite membrane enwrapped AC particles were successfully fabricated using a boehmite gel modified seeded method. The pre-coated gel layer gives a more flat surface than that of AC, with which the seeds can be well dispersed. Boehmite gel is also used for seeds anchoring in the synthesis. This method provides an efficient way for coating zeolite membrane onto the carbon materials or the other inert supports, which can extend the promising application of the membranes for gas separation and catalytic processes.

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