



Synthesis of b-oriented TS-1 zeolite membranes with high performance in the oxyfunctionalization of n-hexane

Xiaodong Wang, Jing Yan, Wei Huang*

Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan, 030024, China

ARTICLE INFO

Article history:

Received 2 April 2012

Received in revised form 18 January 2013

Accepted 18 January 2013

Available online 31 January 2013

Keywords:

b-Orientation

Zeolites

Membranes

Secondary growth

Oxyfunctionalization

n-Hexane

ABSTRACT

The b-oriented TS-1 zeolite membranes were synthesized with higher reproducibility by a simple secondary growth method, in which the membranes grew from b-oriented seed layers obtained by ultrasonication–electrostatic adsorption. The membranes demonstrated excellent catalytic performance in the oxyfunctionalization of n-hexane with a high average reaction rate of $1423 \text{ mol m}^{-3} \text{ h}^{-1}$.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Zeolite films have been widely synthesized due to their great potential applications as catalytic membranes, chemical sensors, corrosion-resistant coatings, and microelectronic devices [1–3]. TS-1 zeolite membranes with MFI topology have drawn more attention. Owing to the introduction of Ti atom into the framework, TS-1 zeolite possesses a variety of special features. In addition to the molecular sieving effect, TS-1 membranes catalyze oxidative reactions as well, including selective oxidation of alcohols [4], epoxidation of alkenes [5], hydroxylation of aromatics [6], oxyfunctionalization of n-hexane to hexanols and hexanones [7], and photocatalytic oxidation [8].

The channel system in the MFI-type structures is three dimensional: straight channels with an pore opening of $0.56 \times 0.54 \text{ nm}$ along its b axis and sinusoidal channels with a pore opening of $0.51 \times 0.55 \text{ nm}$ along its a axis. The b-channels and a-channels are interconnected with each other, so the c-direction is a tortuous pathway. The straight channel along the b-axis is the fast diffusion pathway, thus the b-oriented MFI film is most pursued. However, all the TS-1 films and membranes reported are randomly oriented, except in the works of Lee et al. [9] and Wang et al. [10]. By using an in situ hydrothermal reaction method, Lee et al. [9] prepared b-oriented TS-1 film on glass modified by poly(ethylene oxide) (PEO). And also with in

situ hydrothermal reaction method, Wang et al. [10] obtained b-oriented TS-1 films on $\alpha\text{-Al}_2\text{O}_3$ substrates modified by chitosan.

Compared to the in situ hydrothermal reaction, secondary growth offers significant advantages such as better control over membrane microstructure (thickness, orientation), higher reproducibility, and a wider range of hydrothermal synthesis conditions leading to continuous film formation by using seed layer. Generally, oriented seed layer can grow to be oriented zeolite membrane by hydrothermal reaction [11,12]. In this paper, we present a simple secondary growth method to synthesize b-oriented TS-1 membranes. The method involves preparing b-oriented TS-1 seed layers by ultrasonication–electrostatic adsorption with flat seeds, thinner in b-axis, then growing the seed layers into b-oriented TS-1 membranes. Because the isoelectric points of $\alpha\text{-Al}_2\text{O}_3$ and TS-1 crystal grains are $\text{pH} = 9$ and $\text{pH} \approx 3$, respectively [13,14], adjusting the seed solution to $\text{pH} = 8$ can make the surface of the substrate possess a positive charge and the surface of the seeds possess a negative charge. When the seeds attach to the substrate surface with their biggest a–c planes, the electrostatic attraction between them is the strongest, and the system is most stable. Ultrasonic oscillation gives the seeds a driving force to adjust themselves until their a–c planes are attached to the substrate surface, thus the b-oriented TS-1 seed layer was obtained.

2. Experimental details

2.1. Preparation of b-oriented TS-1 membranes on alumina substrates

The substrates used in our experiments were porous $\alpha\text{-Al}_2\text{O}_3$ disks prepared in-house with a thickness of 2 mm and a diameter of

* Corresponding author. Tel./fax: +86 351 6018073.

E-mail address: huangwei@tyut.edu.cn (W. Huang).

20 mm, the average pore size and porosity of which were ca. 0.2 μm and ca. 45%, respectively. The substrate was first treated by using acid and basic solutions, followed by ultrasonic treatment in acetone, and then transferred into a desiccator for further use.

The flat TS-1 seeds, thinner in b-axis, were prepared by hydrothermal reaction [15]. At first, 10 ml of tetraethylorthosilicate (TEOS, 98%, Aldrich) was hydrolyzed in a solution of tetrapropylammonium hydroxide (TPAOH, 20% aqueous solution, Aldrich, 6.83 ml) and 61 ml of deionized distilled water under vigorous stirring for 5 h. Then, 0.13 g of tetrabutylorthotitanate (TBOT, 97%, Aldrich) in isopropyl alcohol (99.7%, Tianjin Chemical Company, 2.85 g) was added dropwise to the solution in a nitrogen hood. The molar ratio of the final gel was Si/Ti/TPAOH/ H_2O = 1:0.008:0.14:77. The resulting solution was placed in a water bath at 353 K for 0.6 h to evaporate the alcohol formed during the hydrolysis of TEOS and TBOT. Thereafter, some deionized distilled water was added to make up for the volume lost in evaporation. 30 ml of the synthesis solution was then transferred into a Teflon-lined stainless steel autoclave. The autoclave was placed in a preheated oven. Hydrothermal reaction was carried out at 453 K for 48 h. Afterwards, the autoclave was removed and cooled down to room temperature. The sample was removed, rinsed with deionized distilled water, and dried at room temperature.

The b-oriented TS-1 seed layers were prepared on $\alpha\text{-Al}_2\text{O}_3$ substrates by ultrasonication–electrostatic adsorption method. 0.1 g of TS-1 zeolite seeds was dispersed into 49.9 g TPAOH aqueous solution with pH = 8 under stirring. The seed solution with concentration equal to 0.2 wt.% and pH equal to 8 was obtained. Then, 0.5 ml, 0.75 ml and 1.0 ml of the seed solution were added dropwise on $\alpha\text{-Al}_2\text{O}_3$ substrates under ultrasonication, respectively. The oscillation frequency, power and temperature of the ultrasonication were 40 kHz, 100 W and 40 $^\circ\text{C}$, respectively. Thus, the b-oriented seed layers were formed. In this method, the substrates do not need to be modified as with the other literature reports [11,12].

For the purpose of comparison, 0.1 g of TS-1 zeolite seeds was dispersed into 49.9 g of TPAOH aqueous solution with pH = 12.5 and the seed solution with concentration equal to 0.2 wt.% and pH equal to 12.5 was prepared, then with the same procedure as mentioned above, 0.75 ml of the seed solution was added dropwise on $\alpha\text{-Al}_2\text{O}_3$ substrate and another seed layer was obtained.

The secondary growth solution was prepared by similar procedure with the TS-1 seeds. The molar ratio of the final solution was TEOS:TBOT:TPAOH: H_2O = 1:0.008:0.13:77. The secondary growth solution and the seeded substrate was transferred into a 50 ml Teflon-lined stainless steel autoclave, in which the substrate was put horizontally by a home-made Teflon holder with the seed layer facing the bottom. Then the hydrothermal reaction was carried out at 453 K for 24 h. After cooling down, the samples were washed several times with deionized water until neutrality and dried at room temperature. After that, the samples were calcined in a temperature-programmed furnace at a heating rate of 1 K min^{-1} . After heating to 823 K and maintaining this temperature for 2 h, the furnace was allowed to cool down to room temperature.

2.2. Materials characterization

The morphology of TS-1 seed layers and membranes was investigated by scanning electron microscope (SEM, Philips XL30ESEM) operated at 20 kV. The crystalline structure and orientation of seed layers and membranes were analyzed by using an X-ray diffractometer (XRD, Rigaku D/max 2500) operated at 40 kV and 100 mA, with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in a θ – 2θ configuration using a graphite monochromator. An angular range (2θ) from 5 to 26.5 $^\circ$, and a scanning rate of 8 $^\circ/\text{min}$ were applied. The UV–Vis spectrum was obtained on an asco VARIA17 UV/Vis Spectrometer with the wavelength from 190 nm to 440 nm. The Ti content in the membrane

was measured by a Philips XL30ESEM equipped with an Oxford-Isis 300 energy dispersive X-ray spectrometer and operated at 20 kV.

2.3. Catalytic activity measurements

The catalytic activity of the TS-1 membrane was measured using an atmospheric water-jacketed glass reactor with two compartments separated by the TS-1 membranes. The experimental results were reported as the average reaction rate based on unit membrane volume ($\text{mol m}^{-3} \text{h}^{-1}$). The product distribution is represented as

$$\frac{\text{alcohol}}{\text{ketone}} = \frac{2 - \text{hexanol} + 3 - \text{hexanol}}{2 - \text{hexanone} + 3 - \text{hexanone}} \quad (1)$$

The membrane area exposed in the reactor was about 1.0 cm^2 . The reaction was performed at 328 K for 5 h, as was reported in literature [16]. 1 g of n-hexane and 3 g of H_2O_2 solution were used in the experiment. The reaction rate and product distribution were measured by collecting aliquots of both the aqueous and organic phase at the end of each run. n-Hexane and oxygenates were analyzed using a gas chromatograph (GC-950, Shanghai Haixin Chromatography Instrument Co., Ltd.) equipped with a capillary column (DB wax, the length of 30 m and the inner diameter of 0.32 mm) and a flame ionization detector.

3. Results and discussion

Fig. 1 shows the SEM images of the seed layers. It can be seen that the seeds are flat and thinner in the b-axis. With the seed solution of pH = 8, most seeds in the seed layer are b-oriented and the seed layer is thin with monolayer seed, but the seed layer is discontinuous, when the amount of seed solution is 0.5 ml (Fig. 1A and B). When the amount of seed solution is increased to 0.75 ml, most seeds in the seed layer lie on the substrate with their b-axes perpendicular to the substrate surface. The seed layer is uniform with satisfactory coverage, and with 1.8 μm thickness (Fig. 1C and D). When the amount of seed solution is further increased to 1.0 ml, the seed layer is also b-oriented and continuous, but becomes thicker with 5 μm thickness (Fig. 1E and F). While with the seed solution of pH = 12.5 and 0.75 ml, the seed layer is misoriented (Fig. 1G). When pH of seed solution is equal to 8, the surface of the $\alpha\text{-Al}_2\text{O}_3$ substrate possesses a positive charge and the surface of the seeds possesses a negative charge. The seed layer is formed under the ultrasonication and electrostatic adsorption. When pH of seed solution is equal to 12.5, both $\alpha\text{-Al}_2\text{O}_3$ substrate and seeds possess a negative charge. The seed layer is formed under the ultrasonication and electrostatic repulsion. So we can draw the conclusion that only under the combined action of ultrasonication and electrostatic adsorption, the b-oriented seed layer can be formed.

Fig. 2 exhibits the X-ray diffraction (XRD) patterns of the seed layers, which reveals that the crystals have the MFI zeolite structure. With the seed solution of pH = 8, the XRD patterns of all the three seed layers (Fig. 2A, curves a, b and c) show the diffraction peaks at 8.8 $^\circ$, and 17.7 $^\circ$ in the 2θ region between 5 $^\circ$ and 26.5 $^\circ$, respectively, which correspond to the reflections arising from (020) and (040) planes. There is only one peak at the (020) position according to the enlarged XRD pattern. The detection of dominant (0k0) peaks by XRD together with SEM observations in Fig. 1 leads to the conclusion that the crystal grains are preferentially b-oriented. Fig. 1 also indicates the presence of some misoriented grains and twin grains. They contribute to the weak (101) and (501) peaks in the XRD patterns at $2\theta = 7.8^\circ$ and 23.2 $^\circ$, respectively. With the seed solution of pH = 12.5, the XRD pattern of the seed layer (Fig. 2A, curve d) shows the strong diffraction peaks at $2\theta = 7.8^\circ$, 8.8 $^\circ$, 23.2 $^\circ$, corresponding to the reflections that arise from (010), (020), and (501) planes, and weak peaks at $2\theta = 23.9^\circ$, 24.5 $^\circ$, corresponding to the reflections that arise from (511) and (313)

Download English Version:

<https://daneshyari.com/en/article/1666242>

Download Persian Version:

<https://daneshyari.com/article/1666242>

[Daneshyari.com](https://daneshyari.com)