A Novel and Less-expensive Preparation of Titanium Silicalite-1 Membrane

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A novel method was developed for the preparation of titanium silicalite-1 (TS-1) zeolite membrane with low cost through tetrapropylammonium bromide (TPABr)/weak organic base synthesis system, in which TS-1 crystals grew on an unseeded support from a synthesis gel containing seeds. This membrane reactor showed relatively high catalytic activity for the oxidation of 2-propanol.

Titanium silicalite-1 (TS-1) zeolite has attracted increasing attention in the catalytic field owing to its excellent catalytic activity.[1,2] However, there are two disadvantages for TS-1 zeolite as catalyst. One is its high cost and the other is the difficulty in recovering it from the catalytic reaction solution because of the small size. In order to reduce the cost, some efforts have been done by replacing the expensive template of tetrapropylammonium hydroxide (TPAOH) with a less-expensive one of tetrapropylammonium bromide (TPABr).[3,4] When TPABr was used as template, the nucleation and crystallization was not easy, and as a result the seed crystals and the severe synthesis conditions of higher temperature (170–185 °C) and longer time (3–10 days) were required. Furthermore, the thus-obtained TS-1 zeolite exhibited lower catalytic activity because of the larger crystal size[3] and the inactive octahedral extra-framework titanium.[4] On the other hand, in order to resolve the recovery problem of TS-1 zeolite powder, TS-1 zeolite membranes on porous supports were prepared,[5] which could combine the catalytic reaction and membrane separation in a unit operation. The growth of TS-1 crystals on porous supports involves many factors such as the synthesis gel composition, silica source, hydrothermal synthesis conditions, and so on. Compared with TS-1 zeolite powder, the preparation of TS-1 membranes is much more complicated.[6] To date, TS-1 membranes have been prepared by an in situ crystallization method using a large amount of TPAOH as a template and displayed high catalytic activity for some oxidation reactions.[5,7] To reduce the cost of TS-1 membranes, we tried to use TPABr as template. TS-1 membranes could not be prepared by an in situ crystallization method, but by a preseeding method on supports. However, the thus-obtained TS-1 membranes exhibited the lower catalytic activity, probably because of unfavorable orientation of TS-1 crystals on the supports. In this work, a novel method is presented for the preparation of TS-1 membranes, in which TPABr is used as template and the TS-1 seed crystals are added into the synthesis gel instead of on the support. By this method, TS-1 membrane can be prepared under mild synthesis conditions of 150 °C and 3 days and has relatively high catalytic activity for the oxidation reaction of 2-propanol (IPA). Furthermore, the cost of TS-1 membrane is remarkably reduced because the cost of reagents is only about 4% of that for the method using TPAOH as template.

TS-1 membrane with an effective area of 37.6 cm^2 was formed on the outside surface of tubular mullite support with a porosity of 45% and an average pore size of 1.3 µm. A gel solution for the synthesis of the membrane was prepared as follows. First, the mixture containing 10.8 g of diethylamine (Et_2NH, Wako, 99%), 1.6 g of titanium tetrabutoxide (TBOT, Aldrich, 97%), and deionized water was stirred at room temperature for 0.5 h. And then, 23.3 g of colloidal silica solution (AS-40, Aldrich, 40%) was introduced into the mixture solution. The mixture was stirred for 0.5 h followed by the sequential addition of 4.2 g of TPABr (Wako, 98%) and 1.0 g of H_3PO_4 (Wako, 85%). The addition of H_3PO_4 was to shorten the crystallization time because $PO_4{}^{3-}$ ion can significantly accelerate the nucleation and crystallization of TS-1 zeolite.[8] The resultant mixture had a molar composition of SiO_2:$0.03TiO_2$:$0.1TPABr$:$0.9Et_2NH$:$80H_2O$:$0.06H_3PO_4$. TS-1 seed (0.5 g) prepared according to the patent[1] was introduced into the above solution, and then the mixture was transferred into a stainless still autoclave with Teflon liner. The support was vertically immersed in the synthesis solution. The autoclave was placed in a convection oven, and the crystallization was carried out at 150 °C for 3 days. The as-prepared membranes were washed in hot deionized water, and then dried at 80 °C for 12 h. In order to remove the template they were calcined at 500 °C for 30 h with heating and cooling rates of 0.3 and 0.4 °C/min, respectively.

The calcined TS-1 membrane was characterized by X-ray diffraction (Shimadzu XRD-6100) with Cu Kα radiation and scanning electron microscopy (JEOL 6335F). The powder collected from the bottom of the autoclave was characterized by Fourier transformed infrared spectroscopy (JASCO FT/IR-610) using KBr pellet technique and UV–vis spectroscopy (JASCO, V-500).

Figure 1 shows the XRD patterns of TS-1 membrane, powder and mullite support. The typical peaks of MFI structure are observed from the XRD patterns of TS-1 membrane and powder,

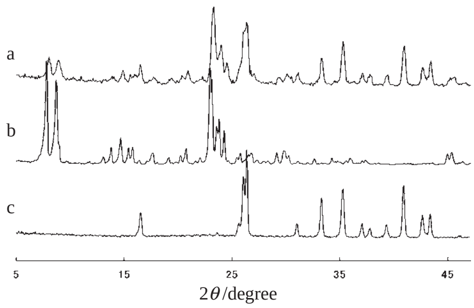

Figure 1. XRD patterns of (a) TS-1 membrane, (b) TS-1 powder, and (c) mullite support.

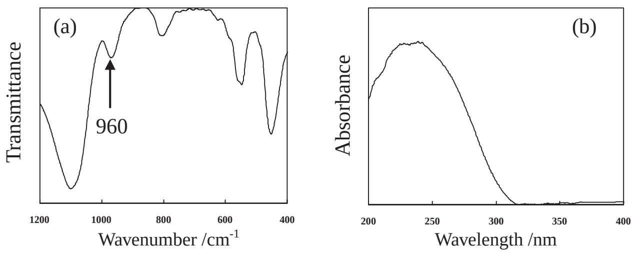

Figure 2. IR spectrum (a) and diffuse-reflectance UV–vis spectrum (b) of TS-1 powder.

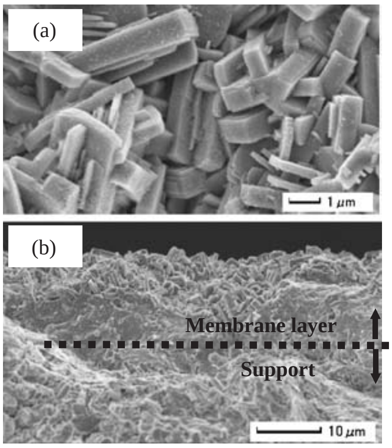

Figure 3. SEM photographs of TS-1 membrane surface (a) and cross section (b) views.

and the peak at $2\theta = 24.4^\circ$ indicates the typical orthorhombic symmetry of TS-1 zeolite.[9] It can be clearly concluded that TS-1 membrane was formed on the support. IR spectrum (Figure 2a) shows a characteristic absorption peak of the transition-metal-substituted zeolites at 960 cm^{-1},[9] indicating the incorporation of titanium into the lattice framework. The absence of any other hetero-phase of titanium oxide is proved by the UV–vis spectrum (Figure 2b). The dominant peak at 220–240 nm indicates the presence of the tetrahedral titanium in the zeolite framework.[10] A well-defined absorption band around 330 nm that is attributed to anatase[11] was not observed. We can thus conclude that the zeolites do not contain anatase-like oxide species inside the channels.

Figure 3 shows the SEM micrographs of the surface and cross section of TS-1 membrane. It can be observed that the outer surface of the unseeded support is covered fully by the well-intergrown crystals with an average size of $4 \times 1.5 \times 0.5\,\mu m^3$, and the crystals randomly grow on the support. The cross sectional view supports a random orientation of crystals in the top of compact crystal layer, and it is also found that TS-1 crystals are scattered on the inner surface of support. The thickness of the compact membrane layer is about 10 μm.

The catalytic activity of the obtained TS-1 membrane was tested by the oxidation reaction of IPA under perevaporation (PV) condition at 60 °C. The PV-aided catalysis apparatus shown in the literature was used.[12] An aqueous solution with IPA and H_2O_2 concentrations of 0.167 mol/L, of which the pH was adjusted at about 4 by adding 2–3 drops of HCl solution, was used as feed. The catalytic oxidation reaction took place in the TS-1 membrane layer during the permeation of IPA from the feed side to the permeate side. The flux was determined by weighing the permeate sample mass then divided by the permeation time and the membrane area. The conversion of the reaction was given by the following equation: $C_{IPA} = (M_{acetone})_{Permeate}/(M_{acetone} + M_{IPA})_{Permeate} \times 100$, C and M refer to the conversion and molar fraction, respectively. The compositions of the feed and the permeate were measured by a gas chromatograph (Shimadzu GC-8A).

Table 1. The oxidation of IPA over TS-1 membrane[a]

Run No.	$W_{IPA,f}$ /wt %	Flux /kg m^{-2} h^{-1}	$W_{IPA,p}$ /wt %	$W_{Acetone,p}$ /wt %	C_{IPA} /%
1st	9.60	0.65	3.48	10.66	76
2nd	9.73	0.94	2.61	9.59	79
3rd	9.07	1.15	3.66	10.62	75

[a] $W_{IPA,f}$ and $W_{IPA,p}$ are the mass concentration of IPA in the feed and permeate, respectively; $W_{Acetone,p}$ refers to the mass concentration of acetone in the permeate; Flux represents the total flux.

The catalytic reaction results of TS-1 membrane reactor are listed in Table 1. In the first run, the fresh TS-1 membrane gave 76% of IPA conversion after achieving the steady state. The catalytic activity was measured again after the membrane was regenerated at 500 °C for 30 h. There was no decrease in the catalytic activity of TS-1 membrane with IPA conversions of 79 and 75% in the second and third runs. Although the total fluxes in the three runs were slightly varied because of slight changes in the feed composition, the conversions and the permeate composition were almost the same, suggesting that the catalytic activity of TS-1 membrane could be recovered by the calcination. These results indicate that the TS-1 membrane prepared using TPABr as template has high catalytic activity and high potential as membrane reactor. The slightly lower conversion of IPA than the previous result (92%)[5] was probably attributed to the larger crystal size ($4 \times 1.5 \times 0.5\,\mu m^3$) than that ($1.2 \times 0.7 \times 0.3\,\mu m^3$) of TS-1 membrane prepared using TPAOH as template.[7] However, it is possible to improve the catalytic activity of TS-1 membrane by further optimising the synthesis parameters.

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