Synthesis of Membranes of Zeolites ZSM-5 and ZSM-35 by the Vapour Phase Method

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Membranes of zeolites ZSM-5 and ZSM-35 are synthesized and characterized by employing X-ray powder diffraction, scanning electron microscopy and chemical analysis.

It is well known that zeolites can be used as absorbents and catalysts. Zeolitic membranes with molecular sieving properties can be manufactured by several methods, for example, from the zeolitic crystals themselves after hydrothermal synthesis;[1] by embedding microcrystals of zeolites in a glassy silica matrix;[2] and by growing zeolites on metal or alloy surfaces.[3,4] Except for the first method, other methods for the preparation of zeolitic membranes can only produce products containing less of the zeolitic crystals. In this paper, we report the first synthesis of membranes of zeolites ZSM-5 and ZSM-35 by the vapour phase method.[5]

In our experiments, aluminosilicate gels are prepared

Table 1 Typical reaction conditions and products

Run	Reaction composition/molar ratio		Membranes		Gels	
	Amorphous gels	Liquid phase	Phase	SiO_2/Al_2O_3	Phase	SiO_2/Al_2O_3
1	2.3 Na_2O: 1.8 B_2O_3: Al_2O_3: 44.8 SiO_2: 230 H_2O	1.0 $PrNH_2$: 2.0 H_2O	ZSM-35	38.4	ZSM-5+ ZSM-35	43.8
2	0.7 NaF: 1.7 Na_2O: Al_2O_3: 44.3 SiO_2: 215 H_2O	1.0 Et_2NH: 1.5 H_2O	ZSM-5	32.8	ZSM-5+ 10% T[a]	44.0
3	1.7 Na_2O: Al_2O_3: 86.4 SiO_2: 410 H_2O	1.0 EDA: 3.8 Et_3N: 7.5 H_2O[b]	ZSM-5	49.3	ZSM-5	86.2

[a] T = tridymite. [b] EDA = ethylenediamine.

Table 2 Permeation of nitrogen[a]

	ZSM-35		ZSM-5 in run 2		ZSM-5 in run 3	
	Cal.	Non-cal.	Cal.	Non-cal.	Cal.	Non-cal.
Pressure difference/atm	0.3	0.8	0.3	0.8	0.3	0.8
Flow rate 1[b]/ml min^{-1}	12.6	19.8	12.6	19.8	12.6	19.8
Flow rate 2[b]/ml min^{-1}	9.2	0.0	7.6	0.0	8.7	0.0

[a] Cal. = calcinated; Non-cal. = non-calcinated. [b] Flow rate 1 is that in front of the membrane; Flow rate 2 is that behind the membrane.

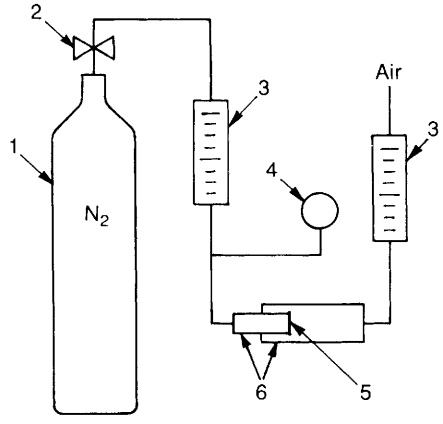

Fig. 1 Diagram of the detection apparatus 1 nitrogen cylinder; 2 pressure reduction valve; 3 flowmeter; 4 pressure gauge; 5 membrane; 6 glassy pipe

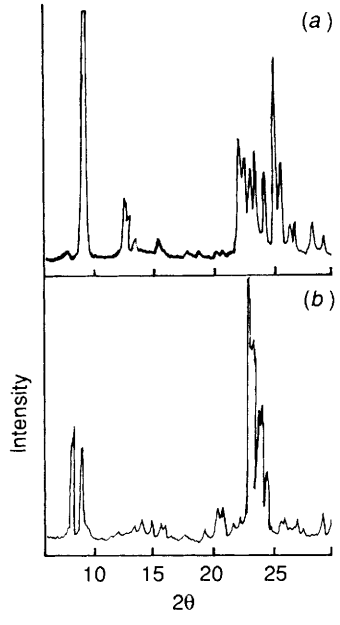

Fig. 2 Typical patterns of X-ray powder diffraction. (*a*) Membrane of zeolite ZSM-35; (*b*) membrane of zeolite ZSM-5.

according to previous reports.[5,6] The method of preparing the membranes of zeolites ZSM-5 and ZSM-35 is similar to that in ref. 5. The only difference is that glass plates or pipes are put on the surface of aluminosilicate gels or embedded in the gels. The reaction is carried out at 473 ± 2 K for 3–7 days. After crystallization, the glassy plates or pipes are dipped for about 30 min in distilled water. Then they are dried at 373 ± 2 K. The membranes of about 2 × 2 cm can be removed from the plate surface. A powder of the membranes is characterized by X-ray powder diffraction, scanning electron microscopy and chemical analysis. The permeation of nitrogen on the membranes has been determined by a simple apparatus (see Fig. 1).

Prepared membranes are powdered and the zeolites structures are determined by X-ray powder diffraction (Rigaku 2034). Fig. 2 illustrates the typical patterns. They are compared with those in refs. 7 and 8. The results indicate that the samples are zeolite ZSM-35 [see Fig. 2(*a*)] and zeolite ZSM-5 [see Fig. 2(*b*)], respectively.

In run 1, the crystallization time is 7 days. The result shows an interesting phenomenon that n-propylamine ($PrNH_2$) may be used as a templating agent for forming a membrane of zeolite ZSM-35. But it is not a templating agent in the preparation of zeolite ZSM-35 by the current method.[8] The crystallization times are 3.5 and 5 days in runs 2 and 3, respectively. The membranes of zeolite ZSM-5 can be obtained from the vapour of diethylamine (Et_2NH)–H_2O and ethylenediamine (EDA)–triethylamine (Et_3N)–H_2O. If the crystallization conditions are suitable the membrane and powder of zeolite ZSM-5 may be synthesized simultaneously (see Table 1, run 3). The compositions of the membranes are different from those of zeolite powders. These differences could be caused by reaction of both gels and glass, although this hypothesis still needs to be demonstrated (Table 1).

The thicknesses of the membranes are measured by employing a scanning electron microscope (KYKY 1000B). Figs. 3(*a*), (*b*) and (*c*) are the photos for runs 1, 2 and 3, respectively. The δ values in Fig. 3 are the thicknesses of the membranes. The membrane of zeolite ZSM-35 is about 89 μm; the membranes of zeolite ZSM-5 are about 46 and 39 μm. The data are similar to the result of Sano and coworkers.[1]

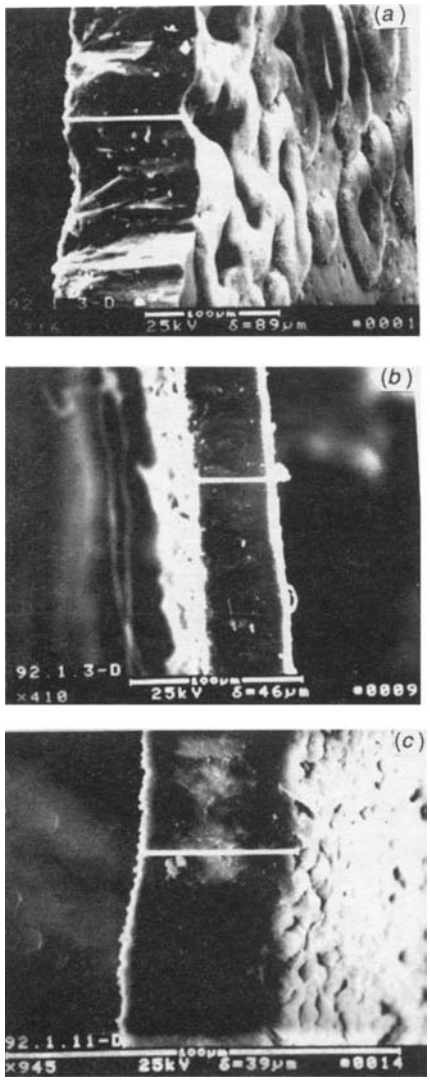

Fig. 3 Scanning electron microscope images. (*a*) ZSM-35 in run 1; (*b*) ZSM-5 in run 2; (*c*) ZSM-5 in run 3.

However, the membranes of zeolites ZSM-35 and ZSM-5 can be synthesized by employing the vapour phase method.

The membranes are calcined at 773 ± 5 K for 6 h. The calcined and non-calcined membranes are sealed to the end of a glass pipe and joined into the detection system (see Fig. 1). The results are listed in Table 2. When the pressure difference between two sides of the non-calcined membranes is 0.8 atm, there is no flow of nitrogen which shows that there is no crack in the membranes. When the calcined membranes are determined, the pressure difference between two sides of the membranes is 0.3 atm and the flow rate of nitrogen through the membranes is 12.6 ml min^{-1}. The different samples show unequal flow rate differences. They are 3.4 ml min^{-1} (ZSM-35), 3.9 ml min^{-1} (ZSM-5 in run 3) and 5.1 ml min^{-1} (ZSM-5 in run 2), respectively.

In summary, this paper reports the first synthesis of membranes made up of zeolite crystals alone. The technique exploits a new route for the preparation zeolite membranes and expands the range of use of the vapour phase method. Many problems, such as controlling the size and thickness of membranes, and their properties of adsorption and catalysis, are still to be studied.

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