Synthesis and Gas Permeation Properties of AEI Zeolite Membranes by DIPEA as a Template

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AEI-type AlPO-18 zeolite membranes were prepared on macroporous mullite and two-layer α -Al₂O₃ tubes with less expensive N, N-diisopropylethylamine (DIPEA) as a single template. The obtained membranes by single DIPEA template showed both high CO₂/CH₄ and N₂/CH₄ perm-selectivities and fluxes. The membrane prepared on two-layer α -Al₂O₃ support showed a CO₂ single gas permeance as high as 4.2×10^{-6} mol m⁻² s⁻¹ Pa⁻¹ with the perm-selectivity of 90 for CO₂/CH₄ at 298 K and 0.11 MPa. Besides, a compatible N₂/CH₄ perm-selectivity of 8.1 with N₂ single gas permeance of 1.5×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ at 298 K and 0.11 MPa was obtained from the membrane prepared on macroporous mullite support. Although a few of AFI type AlPO-5 impurities were formed on the surface of those AlPO-18 zeolite membranes, the AFI impurities didn't lower the gas permeation performance.

Keywords : AEI type AlPO-18 zeolite membrane / single DIPEA template / gas permeation

1. Introduction

The separation of CO₂ and N₂ from other components, such as CH₄, typically present in natural gas wells is of importance since both decrease the energy content of the gas, and meanwhile CO₂ is corrosive in the presence of moisture. Carbon dioxide can be removed with amine scrubbers or polymer membranes. The amine scrubbers require high pressure and thus they are relatively expensive, and the selectivity of polymer membranes decreases at high pressure due to the plasticization from dissolved CO₂. Cryogenic distillation allows the separation of N₂ but energy costs are high ¹⁾. Membrane separation with inorganic membranes that have molecular-sized pore and good thermal, hydrothermal stabilities is thus of interest for natural gas separation, as energy requirements are low and they are not susceptible to plasticization. Several types of zeolite membranes such as T ²⁾, DDR ³⁾, SAPO-34 ^{4, 5)}, Si-CHA ⁶⁾, SSZ-13 ^{5, 6)}, SAPO-17 as well

as AlPO-17 ⁷⁾, AlPO-18 ^{8, 9)} and the MOF material ZIF-8 ¹⁰⁾ have been investigated for CO₂ separation. The SAPO-34 ^{1, 5, 11 ~ 13)}, SSZ-13 ⁵⁾, and AlPO-18 ¹⁴⁾ zeolite membranes also have N₂/CH₄ selectivity that are above to the upper bound of the Robeson plot ¹⁵⁾ that is commonly used to compare polymers membranes.

AlPO-18 is an aluminophosphate zeolite with the AEI-type framework that is formed from equimolar AlO₄⁻ and PO₄⁺ tetrahedral units. It has three-dimensional, electrically neutral pores with a diameter of 3.8 Å, indicating the potential for separating CO₂ (3.3 Å) and N₂ (3.64 Å) from CH₄ (3.8 Å) by molecular sieving. The Carreon group ^{14, 16)} showed that AlPO-18 zeolite membranes can separate both CO₂/CH₄ and N₂/CH₄ mixtures. The CO₂/CH₄ separation was further improved by Wang *et al.* ⁸⁾ with a CO₂ permeance of 6.5×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (~ 1940 GPU). This permeance was still lower than the highest permeances reported for SAPO-34 membranes ⁴⁾ but the N₂ fluxes ¹⁴⁾ for N₂/CH₄ separation were higher than those previously reported for SAPO-34 membranes, while, the N₂/CH₄ selectivity was lower than that of the SAPO-34 membranes ¹²⁾. Furthermore, the AlPO-18 zeolite membranes were conventional prepared

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through the high cost tetraethylammonium hydroxide template (TEAOH). In the view of low cost to industrial application, less expensive DIPEA template is cost-saving towards preparing the AlPO-18 zeolite membranes. Hasegawa *et al.*¹⁷⁾ successfully fabricated the AEI type AlPO-18 zeolite membranes by single DIPEA for H₂O/EtOH separation, while the gas permeations have not been discussed.

In this work, we prepared the AEI zeolite membranes with single and less expensive DIPEA template. The effects of temperature ranges from 298 K to 473 K and pressure from 0.11 to 0.40 MPa on the permeation of AEI membranes were also investigated.

2. Experimental

2.1 Preparation of AEI type AlPO-18 zeolite membranes

The AEI membranes were prepared by secondary growth on the outside of porous mullite tubes (12 mm OD, 9 mm ID and 1.3 μm average pore size, Nikkato Co.) and two-layer porous α -Al₂O₃ supports (12 mm OD, 9 mm ID, 100 nm/2.1 μm average pore size, Nikkato Co.) with the gel composition of 1.0 Al₂O₃ : 1.0 P₂O₅ : (1.0 ~ 1.8) DIPEA : 120 H₂O, where the DIPEA is N, N-diisopropylethylamine. The gel solution was prepared by mixing Al(i-C₃H₇O)₃ (98%, Sigma-Aldrich), H₃PO₄ (85 wt.% aqueous solution, Wako) and deionized water and stirred for 3 h at room temperature to form a homogeneous solution. Then the DIPEA (99 wt.%, TCI.Co) was added drop-wise. The resulting solution was then stirred for 12 h. The rub-coating seeded supports were placed vertically into an autoclave and the synthesis gel was slowly added. Zeolite growth was carried out under hydrothermal conditions at 478 K for 48 h. Here, the AEI-type AlPO-18 crystals prepared as described previously⁹⁾ were used as the seed and rubbed onto the outer surface of porous tubes. After synthesis, the AEI membranes were washed under running tap water, then rinsed and soaked until the soaking solution was clear. The membranes were dried in an oven at 353 K and then calcined in air at 753 K for 6 h with heating and cooling rates of 0.5 K/min.

2.2 Characterization

The morphologies of as-synthesized AEI membranes were determined by a field emission scanning electron

Fig. 1 XRD patterns of the as-synthesized AEI membranes and the standard AEI after calcination.

microscope (FE-SEM, JEOL JSM 6335 F) at an acceleration voltage of 5 KV. The crystallinity of the AEI membranes was identified by X-ray diffraction (XRD) using a RIGAKU Smart Lab 9/SWXD diffractometer with Cu-K α radiation at a scanning range of $2\theta = 5 \sim 45^\circ$ and a scanning rate of $4^\circ/\text{min}$.

2.3 Single gas permeation measurements

Single gas permeation of He, H₂, CO₂, O₂, N₂, CH₄, CF₄ and SF₆ was measured between 298 K and 473 K under vacuum using the time-lag method with fixed-volume apparatus as described previously¹⁸⁾. The membranes were mounted in a stainless-steel cell and sealed with 4 rubber o-rings and 2 stainless steel rings on both ends. The area of the membranes was 18.9 cm². Before the permeation measurements, the membrane was degassed at 473 K for 20 h. For the permeation measurements, the test gas was introduced to the feed side with a back-pressure regulator. The pressure increase on the fixed-volume permeate side due to the gas permeation was monitored with a pressure transducer after closing the vacuum line to the permeate volume. The permeance (P) was then calculated from the pressure increase and the known cell volume on the permeate side. Ideal selectivity (α) for different gas pairs was calculated as the ratio of the single gas permeances.

3. Results and discussion

3.1 Characterization

AEI membranes prepared with n(DIPEA) of 1.0 ~

Table 1 AEI membranes prepared with different synthesis conditions and gas permeation properties at 308 K and 0.11 MPa

Membrane	Support	n (DIPEA)	Syn. Conditions	Phase	Permeance [10^{-7} mol m $^{-2}$ s $^{-1}$ Pa $^{-1}$]			Ideal selectivity α [-]	
					CO $_2$	N $_2$	CH $_4$	CO $_2$ /CH $_4$	N $_2$ /CH $_4$
AEI-1	Mullite	1.0	478K, 36h	AEI			Leak		
AEI-2	Mullite	1.0	478K, 36h	AEI			Leak		
AEI-3	Mullite	1.0	478K, 48h	AEI+AFI	13.8	1.22	0.17	79.9	7.05
AEI-4	Mullite	1.0	478K, 48h	AEI+AFI	20.4	1.90	0.30	67.8	6.32
AEI-5	α -Al $_2$ O $_3$	1.0	478K, 36h	AEI	53.4	7.62	3.06	17.5	2.49
AEI-6	α -Al $_2$ O $_3$	1.0	478K, 48h	AEI+AFI	50.2	8.12	3.97	12.6	2.04
AEI-7	α -Al $_2$ O $_3$	1.0	478K, 48h	AEI+AFI	23.3	4.42	3.91	5.95	1.13
AEI-8	α -Al $_2$ O $_3$	1.2	478K, 36h	AEI	29.8	3.07	0.66	45.0	4.64
AEI-9	α -Al $_2$ O $_3$	1.2	478K, 48h	AEI+AFI	34.8	2.52	0.45	76.2	5.52
AEI-10	α -Al $_2$ O $_3$	1.2	478K, 48h	AEI+AFI	35.1	2.55	0.46	75.9	5.52
AEI-11	α -Al $_2$ O $_3$	1.2	478K, 48h	AEI+AFI	52.1	4.37	0.95	55.1	4.62
AEI-12	α -Al $_2$ O $_3$	1.2	478K, 48h	AEI+AFI	34.2	2.94	1.35	25.4	2.18
AEI-13	α -Al $_2$ O $_3$	1.8	478K, 48h	AEI	28.2	2.03	0.52	53.8	3.87
AEI-14	α -Al $_2$ O $_3$	1.8	478K, 48h	AEI	23.2	3.14	2.74	8.49	1.15
AEI-15	α -Al $_2$ O $_3$	1.8	478K, 48h	AEI			Leak		
AEI-16	α -Al $_2$ O $_3$	1.8	478K, 48h	AEI			Leak		

Membrane	Support	n (TEAOH)	Syn. Conditions	Phase	Permeance [10^{-7} mol m $^{-2}$ s $^{-1}$ Pa $^{-1}$]			Ideal selectivity α [-]	
					CO $_2$	N $_2$	CH $_4$	CO $_2$ /CH $_4$	N $_2$ /CH $_4$
M-1	Mullite	1.8	488K, 12h	AEI	7.05	0.59	0.09	80.1	6.71
M-2	Mullite	1.8	488K, 12h	AEI	7.42	0.61	0.10	71.2	5.85

Gel composition: 1.0Al $_2$ O $_3$: 1.0P $_2$ O $_5$: n (DIPEA or TEOH): 120H $_2$ O

Fig. 2 Surface (a) and cross section (b) of membrane AEI-3, cross section (c) of membrane AEI-9.

1.8 under 478 K for 48 h were summarized in Table 1. In comparison, two AEI type AlPO-18 zeolite membranes (M-1 and M-2) were prepared by TEOH template with the similar procedures as our previous reported⁹⁾. The corresponding synthesis conditions and gas permeation results are also displayed in Table 1. XRD patterns of as-synthesized membranes M-1, AEI-3 on mullite support by 1.0 DIPEA and membrane AEI-9 on α -Al $_2$ O $_3$ support by 1.2 DIPEA after calcination are shown in Fig. 1. All three membranes show the characteristic peaks of the AEI zeolite, while AFI type AlPO-5 impurity with the characteristic peak at $\sim 7.4^\circ$ is formed on those membranes prepared by single

DIPEA template. AlPO-5, with the AFI type framework, is another microporous aluminophosphate with one dimensional, cylindrical pores, owns a diameter of 7.3 Å that was much bigger than the kinetic diameter of CO $_2$, N $_2$ and CH $_4$. Thus permeances of AlPO-5 membranes¹⁹⁾ are much higher but selectivities are low. It has been reported that the competing phase of AFI formed at $n(\text{DIPEA}/\text{P}_2\text{O}_5) < 1.2$ when preparing AEI type SAPO-18 zeolite with DIPEA template²⁰⁾. Although Hasegawa *et al.*¹⁷⁾ claimed that high temperature favors to form AFI impurity on AEI membranes when using single DIPEA template, pure AEI membranes can be obtained by shortening synthesis time to

Fig. 3 Single gas permeances as a function of the kinetic diameter of gases for AEI membranes performed at 308 K, 0.11 MPa.

36 h or increasing $n(\text{DIPEA})$ to 1.8 at 478 K as shown in Table 1.

The as-synthesized membrane AEI-3 on mullite support has a compact and continuous layer covering the support surface with the thickness of $\sim 12 \mu\text{m}$ as shown in SEM (Fig. 2b). Plate-shaped AEI crystals morphologies with the size of $\sim 1 \mu\text{m}$ were covered on the top of the surface as shown in Fig. 2a, which is smaller than the pore size of the mullite support. The AFI type crystals with hexagonal morphology were stuck into the membrane layer. On the contrary, the membrane AEI-9 prepared on two-layer $\alpha\text{-Al}_2\text{O}_3$ support displayed the continuous zeolite layer with the thickness of $\sim 4.5 \mu\text{m}$ as shown in Fig. 2c, which is less than half of the membrane prepared on mullite support. The difference of the membrane thickness on alumina and mullite supports may due to the structural properties of these supports. The $0.1 \mu\text{m}$ average pore size layer of alumina support may provide a smoother surface than that of $1.3 \mu\text{m}$ mullite support⁴⁾, which results in a thinner seeded layer after seeding the supports. It may improve the gas permeance compared with thicker zeolite separation layer on mullite support (Fig. 2b and Table 1). At the same time, some voids were formed within the membrane layers on both mullite and $\alpha\text{-Al}_2\text{O}_3$ supports, it may also improve the permeances.

3.2 Single-gas permeation

Fig. 3 shows single gas permeances of the membranes AEI-3 and AEI-9 at 308 K and 0.11 MPa as a function of kinetic diameter of gases. The single gas

permeances of membrane M-1 are also shown in Fig. 3. The variations in permeances for three membranes are similar to each other with the order of $\text{CO}_2 > \text{H}_2 > \text{He} > \text{O}_2 > \text{N}_2$ as described in our previous study⁹⁾. These gases seem to permeate into the AEI zeolite pores. CO_2 shows the highest permeances although its molecular weight is higher than those four gases, which suggests adsorption selectivity. On the other hand, the permeance of CH_4 with relatively low molecular weight is lower than the permeances of those five gases. This is due to the molecular sieving effect. The AEI zeolite membrane, therefore, is quite suitable for CO_2/CH_4 and N_2/CH_4 separations.

CF_4 (4.7 Å) and SF_6 (5.5 Å), which were much larger than the AEI zeolite pores, are also permeated a little through those prepared membranes. This seems due to the presence of a few defects, which may be at crystal grain boundaries. However, as the permeances are 1/5 or 1/10 of that to CH_4 , it can be concluded the membranes AEI-3 and AEI-9 have few defects. These membranes prepared with DIPEA display higher gas permeability than the membranes prepared with TEAOH, which may be attributed to the AFI type crystals. The presence of impurity AFI crystals in membrane AEI-3 and AEI-9 may reduce the effective thickness of zeolite layer. The AEI membranes on the two-layer alumina tubes exhibit higher gas permeability than that on mullite tubes. It may due to thinner zeolite layer as shown in Fig. 2.

3.3 Temperature dependence of permeation

Temperature dependence ranges from 298 K to 473 K on the single gas permeances through membranes AEI-3 and AEI-9 at 0.11 MPa is shown in Fig. 4. The effect of temperature on single gas permeances for both two membranes are similar although membrane AEI-9 shows much higher gas permeance than AEI-3. The permeances of CO_2 , O_2 and N_2 are strongly affected by temperature. These permeances continuously decreased, while the permeances of He, H_2 and CH_4 were almost independent to the temperature. The permeance of SF_6 slightly increased with increasing the temperature. The activation energy of SF_6 calculated from Arrhenius equation for membrane AEI-3 was +4.7 kJ/mol, indicates the activated diffusion of the SF_6 through the membrane. Since the AEI pore size (0.38 nm) is smaller than the SF_6 (0.55 nm), the permeance may due to the non-zeolite pores in the membrane.

Fig. 4 Temperature dependence of gas permeance on membrane AEI-3 (a) and AEI-9 (b). Pressure drop was 0.11 MPa.

The calculated H_2/CH_4 , CO_2/CH_4 , CO_2/N_2 and N_2/CH_4 ideal selectivities of membranes AEI-3 and AEI-9 are shown in Fig. 5 as a function of temperature. The perm-selectivity of CO_2/CH_4 , CO_2/N_2 and N_2/CH_4 for both two membranes decreased dramatically with increasing temperature from 298 K to 473 K. The CO_2 single gas permeance decreased by 86% from $1.58 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 298 K to $2.20 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 473 K with the CO_2/CH_4 ideal selectivity decreased from 87.4 to 13.4 for membrane AEI-3, and the CO_2 permeance decreased by 88% from $(4.17 \text{ to } 0.52) \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for AEI-9 with the CO_2/CH_4 ideal selectivity decreased from 89.6 to 12.3.

At 298 K, the N_2/CH_4 ideal selectivity was 8.1 (Fig. 5a) with a N_2 single gas permeance of $1.46 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for AEI-3 and 6.1 with N_2 single gas permeance of $2.82 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for AEI-9. Even though AIPO-18 preferentially adsorbs CH_4 over

Fig. 5 The effect of temperature on membrane AEI-3 (a) and AEI-9 (b) for ideal selectivity. Pressure drop was 0.11 MPa.

N_2 ¹⁴, molecular sieving affect may result in preferentially permeation of N_2 over CH_4 . The N_2 single gas permeance decreased to $0.46 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for AEI-3 and $0.98 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for AEI-9 at 473 K with the N_2/CH_4 ideal selectivity of 2.8 for AEI-3 and 2.3 for AEI-9.

3.4 Pressure dependence of permeation

Fig. 6 shows the changes in gas permeance for CO_2 , N_2 and CH_4 as well as the corresponding perm-selectivity for CO_2/CH_4 and N_2/CH_4 through membrane AEI-3 and AEI-9 as a function of feed pressure at 308 K. But for membrane AEI-9, it is difficult to measure permeance of CO_2 due to the permeance that beyond the limit of equipment. For membrane AEI-3, the CO_2 permeance decreased when increasing pressure from 0.11 MPa to 0.4 MPa, whereas both the N_2 and CH_4 permeance increases slightly with pressure,

Fig. 6 The effect of pressure on membrane AEI-3 (a) for CO₂/CH₄ and N₂/CH₄ separations and AEI-9 (b) for N₂/CH₄ separation. Temperature was 308 K.

therefore, the CO₂/CH₄ and N₂/CH₄ perm-selectivity dropped to 62.8 and 6.76 at 0.4 MPa, respectively.

3.5 Comparison

Fig. 7 shows plots of P_{CO_2} vs α (CO₂/CH₄) and P_{N_2} vs α (N₂/CH₄) of the AEI membranes prepared with single TEOH and DIPEA template at 0.11 MPa and 298 K. Compared with the reported CO₂/CH₄ separation membranes, highest CO₂ single gas permeance of $4.17 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ was obtained by using less expensive DIPEA template with the ideal selectivity of 89.6 for AEI-9 on two-layer α -Al₂O₃ support. However, for the N₂/CH₄ separation, the separation performance is still lower than the reported data, although membrane AEI-3 prepared on mullite support showed a compatible N₂/CH₄ selectivity of 8.08 with the N₂ permeance of $1.46 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. More studies should be performed to optimize

Fig. 7 P_{CO_2} vs α (CO₂/CH₄) (a) and P_{N_2} vs α (N₂/CH₄) of AEI membranes under single TEOH and DIPEA template. (*: single gas permeations)

the synthesis conditions in order to obtain high-performance AEI membranes.

4. Conclusion

The AEI membranes were prepared with DIPEA as single and less expensive template using a gel composition of 1 Al₂O₃ : 1 P₂O₅ : (1.0 ~ 1.8) DIPEA : 120 H₂O. Minority AFI impurity was formed on the surface of AEI membranes, however, it didn't affect CO₂/CH₄ and N₂/CH₄ separations. These membranes displayed a much higher gas property than the membranes prepared by single and expensive TEOH template.

Membrane prepared on two-layer α -Al₂O₃ support showed CO₂ single gas permeance as high as $4.2 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with the perm-selectivity up to 90 for CO₂/CH₄. Membrane prepared on mullite support

displayed a compatible N₂/CH₄ selectivity of 8.1 with the N₂ gas permeance of 1.5×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ and at 298 K and 0.11 MPa.

CO₂ and N₂ single gas permeances were strongly affected by temperature and pressure, while CH₄ was almost independent for these AEI membranes.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 15H04174.

References

- 1) Li S, Zong Z, Zhou SJ, Huang Y, Song Z, Feng X, Zhou RF, Meyer HS, Yu M, Carreon MA : *J. Membr. Sci.*, **487**, 141-151 (2015)
- 2) Cui Y, Kita H, Okamoto K : *Chem. Commun.*, 2154-2155 (2003)
- 3) Himeno S, Tomita T, Suzuki K, Nakayama K, Yajima K, Yoshida S : *Ind. Eng. Chem. Res.*, **46**, 6989-6997 (2007)
- 4) Carreon MA, Li S, Falconer JL, Noble RD : *J. Am. Chem. Soc.*, **130**, 5412-5413 (2008)
- 5) Wu T, Diaz MC, Zheng YH, Zhou RF, Funke HH, Falconer JL, Noble RD : *J. Membr. Sci.*, **473**, 201-209 (2015)
- 6) Kida K, Maeta Y, Yogo K : *J. Membr. Sci.*, **522**, 363-370 (2017)
- 7) Zhong S, Bu N, Zhou RF, Jin WQ, Yu M, Li S : *J. Membr. Sci.*, **520**, 507-514 (2016)
- 8) Wang B, Hu N, Wang HM, Zheng YH, Zhou RF : *J. Mater. Chem. A.*, **3**, 12205-12212 (2015)
- 9) Wu T, Wang B, Lu ZH, Zhou RF, Chen XS : *J. Membr. Sci.*, **471**, 338-346 (2014)
- 10) Venna SR, Carreon MA : *J. Am. Chem. Soc.*, **132**, 76-78 (2010)
- 11) Huang Y, Wang L, Song Z, Li S, Yu M : *Angew. Chem. Int. Ed.*, **54**, 10843-10847 (2015)
- 12) Zong Z, Carreon MA : *J. Membr. Sci.*, **524**, 117-123 (2017)
- 13) Zong Z, Feng X, Huang Y, Song Z, Zhou RF, Zhou SJ, Carreon MA, Yu M, Li S : *Microporous Mesoporous Mater.*, **224**, 36-42 (2016)
- 14) Zong Z, Elsaidi SK, Thallapally PK, Carreon MA : *Ind. Eng. Chem. Res.*, **56**, 4113-4118 (2017)
- 15) Robeson LM : *J. Membr. Sci.*, **320**, 390-400 (2008)
- 16) Carreon ML, Li S, Carreon MA : *Chem. Commun.*, **48**, 2310-2312 (2012)
- 17) Hasegawa Y, Abe C, Ikeda T, Sato K : *J. Membr. Sci.*, **499**, 538-543 (2016)
- 18) Cui Y, Kita H, Okamoto K : *J. Mater. Chem.*, **14**, 924-932 (2004)
- 19) Li S, Falconer JL, Noble RD : *Adv. Mater.*, **18**, 2601-2603 (2006)
- 20) Robson H, Lillerud KP : “*Verified Syntheses of Zeolitic Materials*”, 81-83 (2001)

(Received 4 December 2017 ;

Accepted 23 February 2018)