Alumina-Supported SAPO-34 Membranes for CO_2/CH_4 Separation

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Supporting Information

I.- Experimental Methods

SAPO-34 seeds synthesis

In a typical synthesis, $Al(i\text{-}C_3H_7O)_3$ (> 99.99%, Aldrich), H_3PO_4 (85 wt% aqueous solution, Aldrich) and deionized H_2O were stirred for 3 h to form an homogeneous solution, and then Ludox AS-40 colloidal silica (40 wt % suspension in water, Sigma-Aldrich) or tetraethyl orthosilicate, 98%, (Aldrich) was added and the resulting solution was stirred for another 3 h. The templates were then added, and the solution stirred for 4 days at 318-323 K. Tetraethylammonium hydroxide, 35 wt% solution in water (Sigma-Aldrich), dipropylamine, 99% (Aldrich), and cyclohexylamine, 99% (Sigma-Aldrich), morpholine, >99% (Sigma-Aldrich), N,N-dimethylbutylamine, 99% (Aldrich), N,N-dimethylethanolamine, 99.5% (Aldrich) and tetraethylammonium chloride, >98% (Sigma) were used as templates. The solution was then placed in an autoclave and held at 493 K for 24 h. After the solution was cooled to room temperature, it was centrifuged at 2700 rpm for 20 min to separate the seeds, which were then washed with water. This procedure was repeated three times. The resulting precipitate was dried overnight and calcined at 823 K for 8 h. The calcination heating and cooling rates were 1 and 10 K/min, respectively. The molar ratios for the various seeds are detailed in the supporting section.

SAPO-34 membranes synthesis

The membranes were prepared by rubbing the inside surface of a porous α-Al_2O_3 supports (0.2 µm pores, US Filter) with dry, calcined SAPO-34 seeds. Prior to membrane preparation, about 1 cm on each end of the ceramic supports was glazed (Duncan IN 1001 envison glaze, Duncan ceramics) to prevent membrane bypass and to provide a sealing surface for *O*-rings. The permeate area for the ceramic supports was approximately 5.3 cm^2. The rubbed porous supports, with their outside wrapped with Teflon tape, were then placed in an autoclave and filled with synthesis gel. The hydrothermal treatment was carried out at 493 K for 24 h. One or two synthesis layers were applied. After the hydrothermal step, the membranes were washed with deionized water and dried for ~2 h at 338 K. The membranes were calcined in air at 673 K for 8 h to remove the template(s). The calcination heating and cooling rates were 0.7 and 0.9 K/min, respectively. The synthesis gel molar ratio was 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.3 SiO_2 : 1.0 TEAOH : x DPA: 77 H_2O (where x = 1.6 or 3.2)

Characterization

Scanning electron microscopy images were obtained with a JEOL JSM-6400 SEM with an acceleration voltage of 25 kV. The XRD patterns were obtained with an Inel CPS 120 diffraction system employing CuKα radiation. The ICP analysis was carried out on an Applied Research Laboratories ARL3410+ ICP-OES. The CO_2/CH_4 separation system is described elsewhere [7]. The compositions of the feed, retentate, and permeate streams were measured using a Hewlett-Packard 5890/series II gas chromatograph equipped with a thermal conductivity detector and HAYESEP-D column (Alltech). The oven, injector, and detector temperatures were all kept at 423 K.

II.- Synthesis conditions of Membranes A1-A5

Table S1. Synthesis properties for SAPO 34 membranes

Membrane	Seed composition	Gel composition	Number of layers
A1	0.8 DPA: 0.8 CHA: 52 H_2O	1.6 DPA: 77 H_2O	1
A2	0.8 DPA: 0.8 CHA: 52 H_2O	1.6 DPA: 77 H_2O	1
A3	1.6 DPA: 77 H_2O	1.6 DPA: 77 H_2O	1
A4	1.6 DPA: 77 H_2O	3.2 DPA: 77 H_2O	1
A5	1.6 DPA: 77 H_2O	1.6 DPA: 77 H_2O	2

The seed and gel molar compositions were 1.0 Al_2O_3: 1.0 P_2O_5: 0.3 SiO_2 :1.0 TEAOH

For DPA/TEAOH = 1.6, the ICP composition was Si/Al=0.17, and P/Al=1.07.

For DPA/TEAOH = 3.2, the ICP composition was Si/Al=0.17, and P/Al=1.04.

III.- Synthesis conditions, SEM images and XRD of SAPO-34 seeds

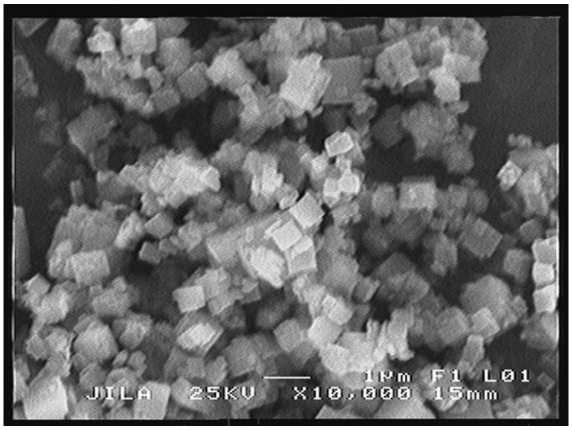
Table S2. Synthesis conditions for SAPO-34 seeds with different crystal size

Average seeds crystal size	Template (s) [a]	Silica source	Molar composition (Al_2O_3 and P_2O_5 = 1.0)
0.7 ± 0.1	TEAOH, DPA	Ludox	0.3 SiO_2: 1.0 TEAOH: 1.6 DPA: 77 H_2O
0.8 ± 0.1	TEAOH, DPA CHA	Ludox	0.3 SiO_2: 1.0 TEAOH: 0.8 DPA: 0.8 CHA: 52 H_2O
1.2 ± 0.2	TEAOH, CHA	Ludox	0.3 SiO_2: 1.0 TEAOH: 1.6 CHA: 60 H_2O
1.8 ± 0.3	DMBA, DPA	TEOS	0.3 SiO_2: 2 DMBA: 1.6 DPA: 77 H_2O
2.5 ± 0.5	DMBA	TEOS	0.3 SiO_2: 3DMBA: 77 H_2O
4.0 ± 1.0	DMEA, TEACl	Ludox	0.2 SiO_2: 2 DMEA: 1.0 TEACl: 77 H_2O [b]
8.5 ±1.2	MOR	TEOS	0.6 SiO_2: 3 MOR: 60 H_2O

[a] TEAOH= tetraethyl ammonium hydroxide, DPA=dipropylamine, CHA= cyclohexylamine, DMAB=N,N-dimethylbutylamine DMEA=N,N-dimethylethanolamine, TEACl=tetraethylammonium chloride, MOR=morpholine

[b] P_2O_5 molar ratio =1.15

Figures S1-S7 show the SEM images and XRD patterns of SAPO-34 seeds synthesized with the templates described in Table S1. Unidentified peaks correspond to AlPO-18 impurities.



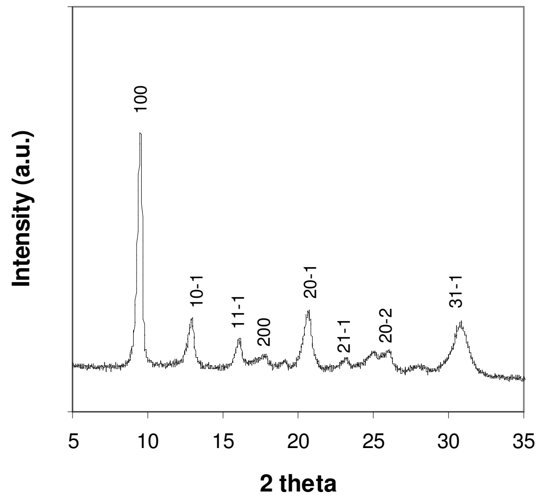
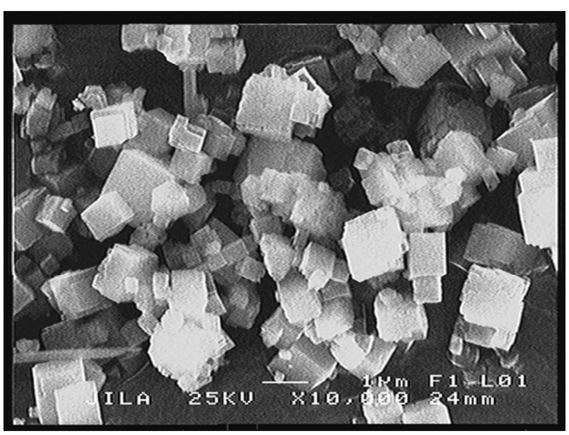


Figure S1. SEM image and XRD pattern of SAPO-34 seeds synthesized with **TEAOH-DPA**



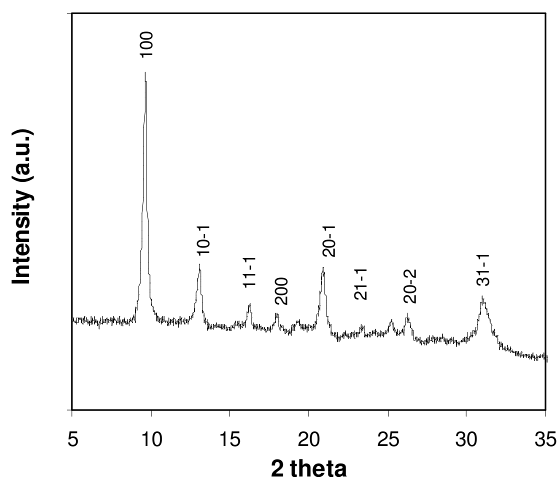


Figure S2. SEM image and XRD pattern of SAPO-34 seeds synthesized with **TEAOH-DPA-CHA**

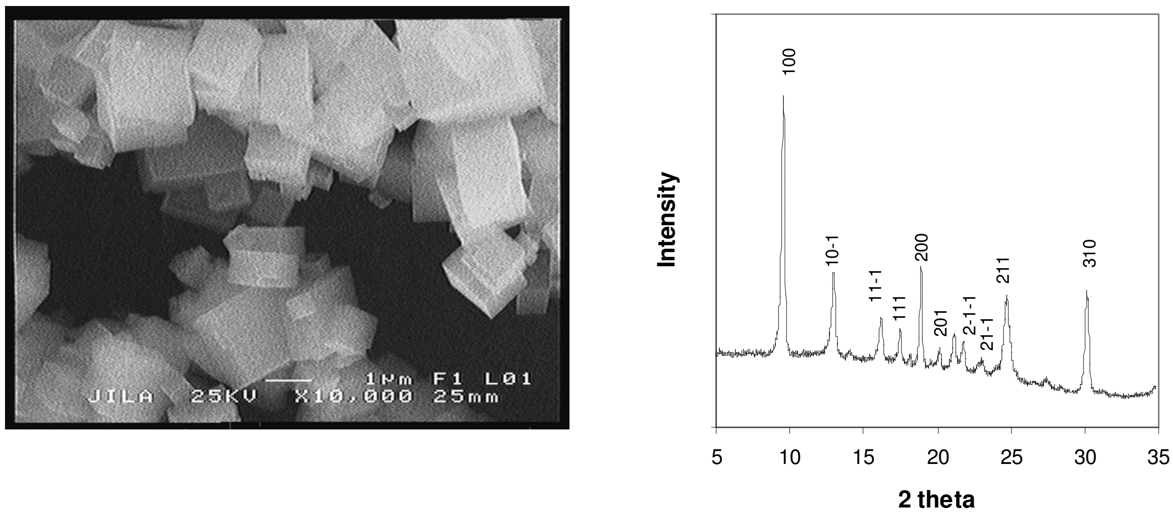


Figure S3. SEM image and XRD pattern of SAPO-34 seeds synthesized with **TEAOH-CHA**

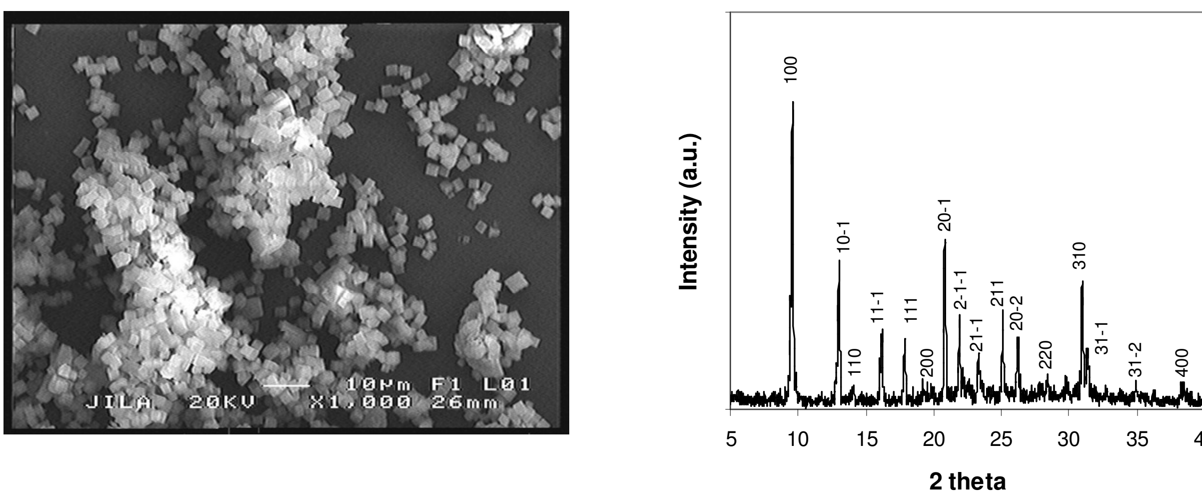


Figure S4. SEM image and XRD pattern of SAPO-34 seeds synthesized with **DMBA-DPA**

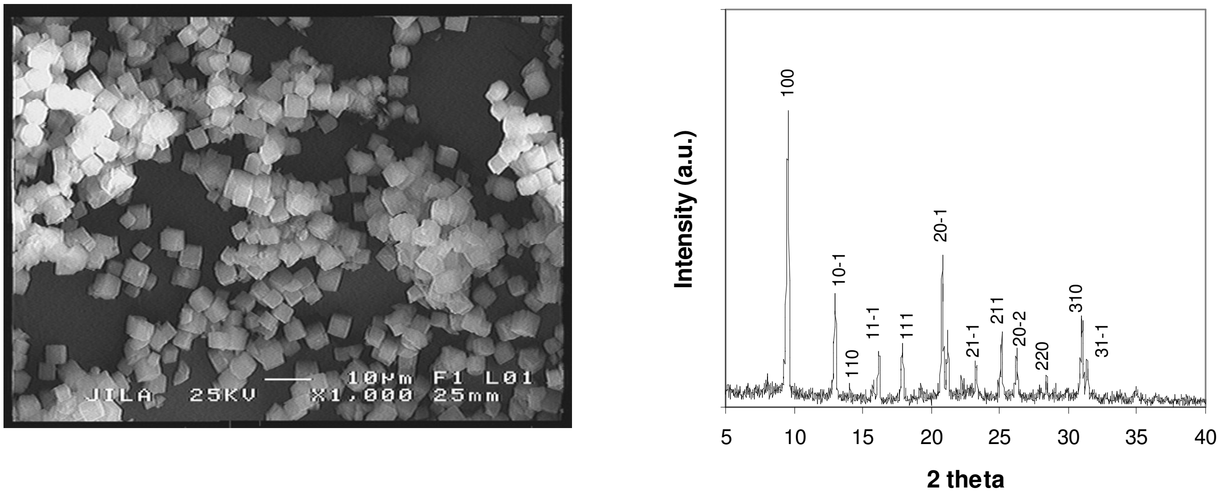


Figure S5. SEM image and XRD pattern of SAPO-34 seeds synthesized with **DMBA**

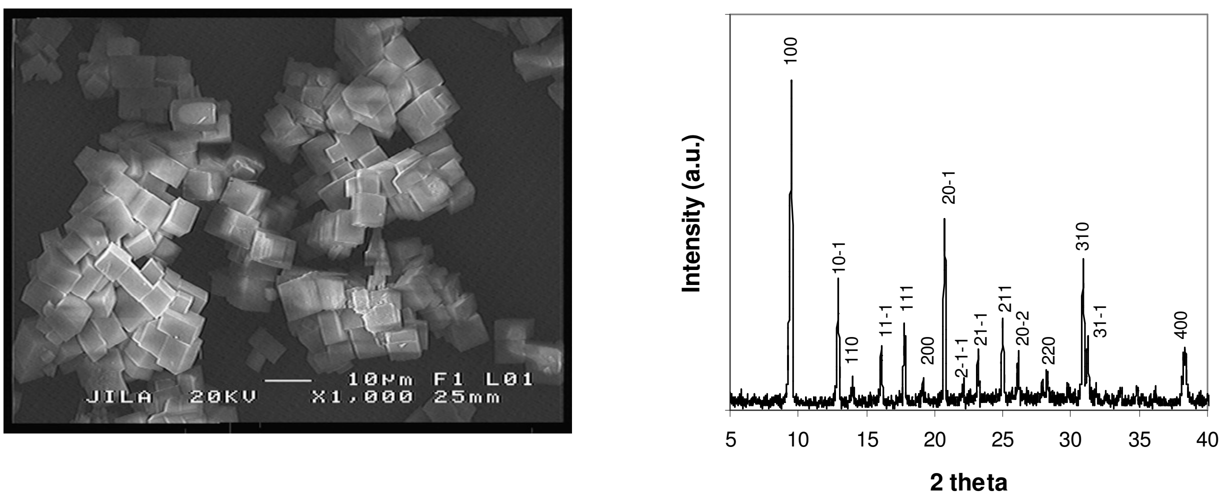


Figure S6. SEM image and XRD pattern of SAPO-34 seeds synthesized with **DMEA-TEACl**

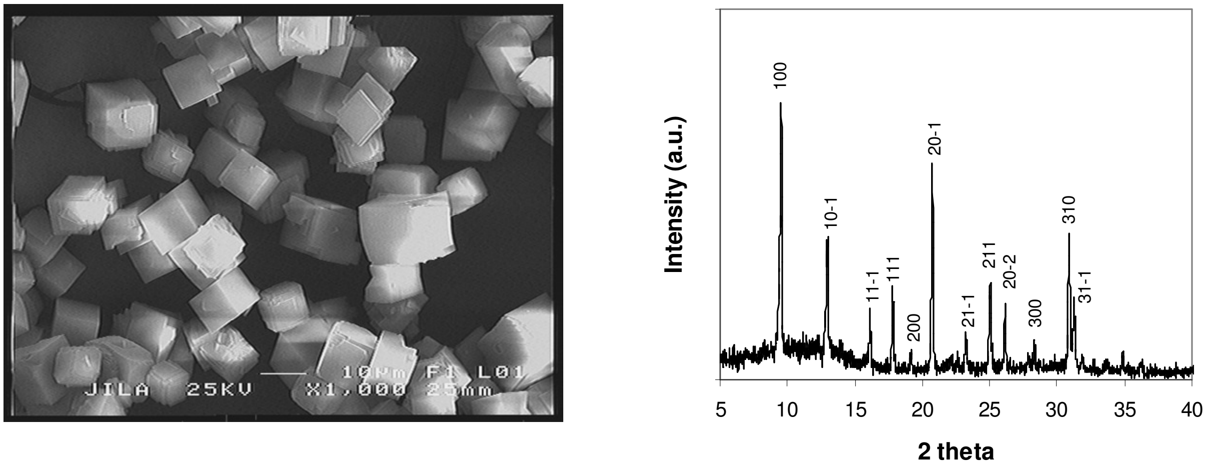


Figure S7. SEM image and XRD pattern of SAPO-34 seeds synthesized with **MOR**

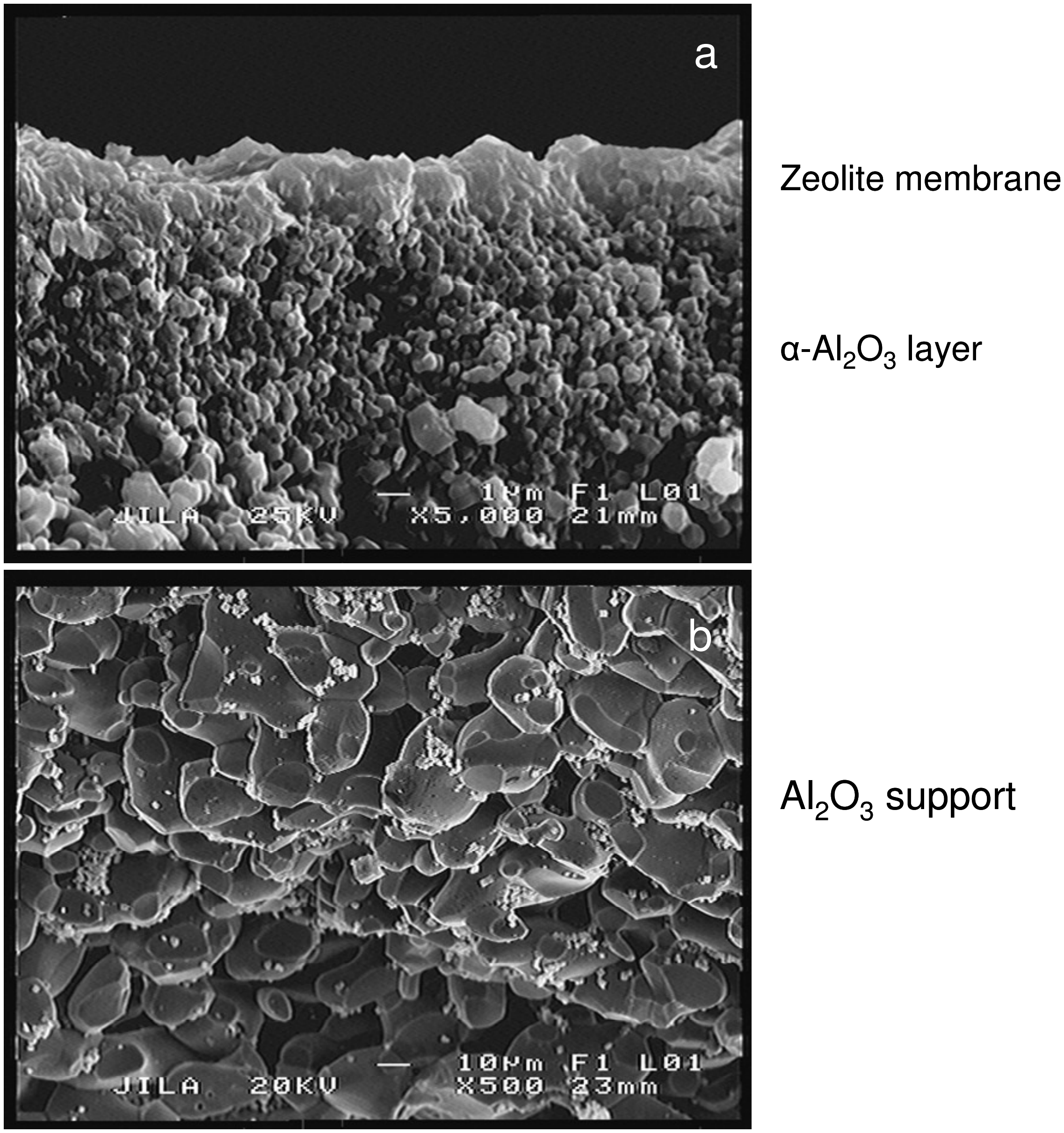


Figure S8. Cross sectional view of SAPO-34 membrane prepared on α-Al_2O_3 support. Few SAPO-34 crystals are attached on a) the α-Al_2O_3 layer. More SAPO-34 crystals are attached on b) the granules surface of the alumina support. However, crystal inclusion inside the pores is minimum.

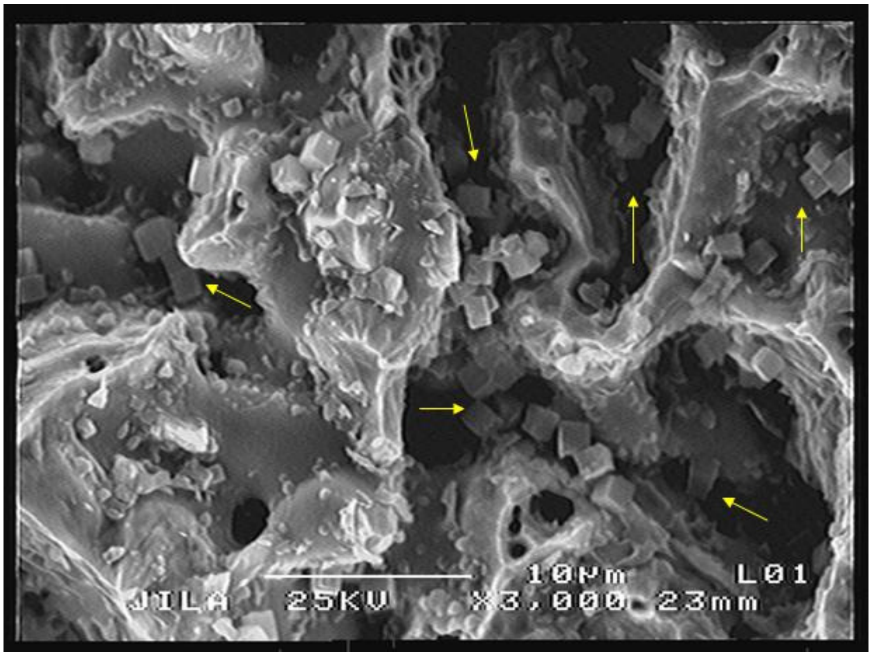


Figure S9. Cross sectional view of of SAPO-34 membrane prepared on stainless steel support. Crystal inclusion inside the pores (indicated by arrows) is greater as compared to the ceramic support.