Supporting information

Stepwise synthesis of sandwich-structured composite zeolite membranes with enhanced separation selectivity

Aisheng Huang, Nanyi Wang, and Jürgen Caro

Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover,
Callinstraße 3-3A, D-30167 Hannover, Germany

Experimental methods

1. Materials

Chemicals were used as received: LUDOX AS-40 colloidal silica (40% SiO_2 in water, Aldrich) as Si source; aluminum foil (Fisher Scientific); sodium hydroxide (>99%, Merck); 3-aminopropyltriethoxysilane (98%, Abcr); toluene (Acros); doubly distilled water. Porous α-Al_2O_3 disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer) were used as supports.

2.2. Preparation of LTA bottom layers on APTES functionalized Al_2O_3 supports

The LTA bottom layers were prepared on covalently functionalized α-Al_2O_3 supports by using APTES as covalent linker, as schematically shown in Figure 1. Porous α-Al_2O_3 disks were treated with APTES (0.2 mM in 10 mL toluene) at 110 °C for 0.5 h under argon, leading to APTES monolayer deposited on the α-Al_2O_3 support surface [1, 2]. For synthesis of the LTA bottom layer, a clear synthesis solution with the molar ratio of $50\ Na_2O : 1Al_2O_3 : 5SiO_2 : 1000H_2O$, was prepared according to the procedure reported elsewhere [3]. The aluminate solution was prepared by dissolving 22.22 g sodium hydroxide in 50 g deionized water, then adding 0.3 g aluminum foil to the solution at room temperature. The silicate solution was prepared by mixing 4.17 g LUDOX AS-40 colloidal silica and 47.5 g deionized water at 333 K with vigorous stirring. The prepared aluminum solution was added into the silicate solution with stirring for 20 h to produce a clear, homogenous solution. The APTES-treated α-Al_2O_3 supports were horizontally placed face down in a Teflon-lined stainless steel autoclave and the synthesis solution was poured in. After in-situ growth for 24 h at 60 °C, the solution was decanted off and the membrane was washed with deionized water several times, and then dried in air at 110 °C over night for next step, characterization and permeation measurement.

2.3. Preparation of sandwich-structured LTA-FAU composite membranes on Al_2O_3 supports

The as-made LTA bottom layer was treated with APTES (0.2 mM in 10 mL toluene) at 110 °C for 0.5 h under argon, leading to APTES deposited on the surface of the LTA bottom layer. For synthesis of the FAU top layer on the APTES functionalized LTA bottom layer, a clear synthesis solution with the molar ratio of 70 Na_2O: $1Al_2O_3$: $20SiO_2$: $2000H_2O$ [4, 5], was prepared by mixing sodium hydroxide, aluminum foil and LUDOX AS-40 colloidal silica in deionized water at 333 K. The prepared final synthesis solution was stirred overnight to produce a clear, homogenous solution. The APTES-treated LTA bottom layer on α-Al_2O_3 supports were horizontally placed face down in a Teflon-lined stainless steel autoclave and the synthesis solution was poured into. After in-situ growth for 24 h at 75 °C, the solution was decanted off and the LTA-FAU composite membrane was washed with deionized water several times, and then dried in air at 110 °C over night for characterization and permeation measurement.

2.4. Characterization of zeolite membranes

The SEM micrographs were taken on a JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10 μA. The chemical composition of the zeolite membranes were characterized by energy-dispersive X-ray spectroscopy (EDXS) using the same SEM microscope at 5 kV and 20 μA. Phase purity and crystallinity of the zeolite membranes were confirmed by X-ray diffraction (XRD). The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with CuKa radiation at 40 kV and 40 mA.

2.5. Evaluation of single gas permeation and mixture gas separation

For the single gas permeation and mixture gas separation, the Al_2O_3 supported LTA membrane, FAU membrane and LTA-FAU composite membranes were sealed in a permeation module with silicone O-rings. Before measurements, the membrane was in-situ heated at 110°C for 24 h under sweep gas to remove the pre-adsorbed water and CO_2. The sweep gas N_2 (except for the N_2 permeation measurement where CH_4 was used as sweep gas) was fed on the permeate side to keep the concentration of permeating gas as low as possible thus providing a driving force for permeation. The total pressure on each side of the membrane was atmospheric. The fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromotograph (HP6890) was used to measure the gas concentrations. The separation factor $\alpha_{i,j}$ of a binary mixture permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i,j) in the retentate, as show in Eq. 1.

$$\alpha_{i/j} = \frac{y_{i,Perm} / y_{j,Perm}}{y_{i,\mathrm{Ret}} / y_{j,\mathrm{Ret}}} \tag{1}$$

Reference

[1] A. Huang, F. Liang, F. Steinbach and J. Caro, *J. Membr. Sci.*, 2010, **350**, 5.

[2] A. Huang and J. Caro, *Chem. Mater.*, 2010, **22**, 4353.

[3] A. Kulak, Y. Lee, Y. S. Park, K. B. Yoon, *Angew. Chem. Int. Ed.* 2000, **39**, 950.

[4] G. Zhu, Y. Li, H. Zhou, J. Liu and W. Yang, *J. Membr. Sci.*, 2009, **337**, 47.

[5] A. Huang, N. Wang and J. Caro, *J. Membr. Sci.,* , 2012, **389**, 272.

Figure S1

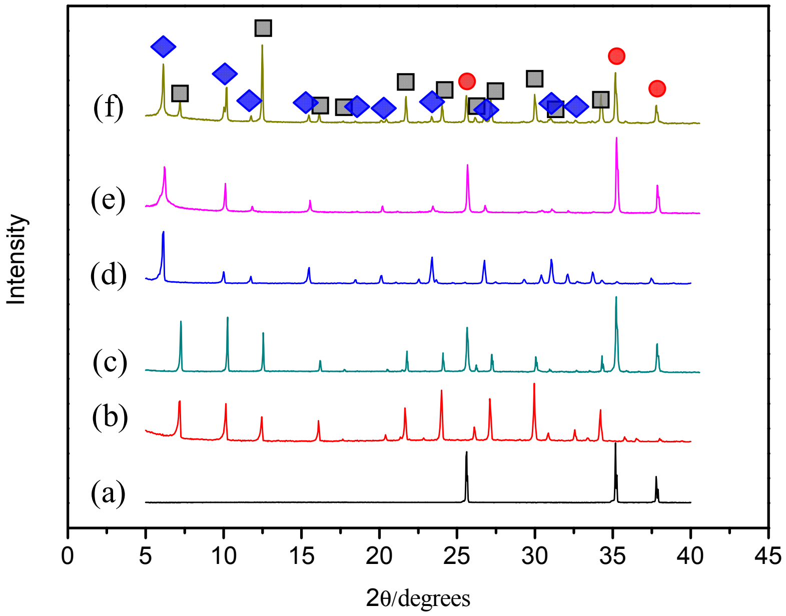

Fig. S1. XRD patterns of the Al_2O_3 support, LTA powder (b), LTA membrane on Al_2O_3 supports (c), FAU powder (d), FAU membrane on Al_2O_3 supports (e), and LTA-FAU composite membrane on Al_2O_3 support (f). (■): zeolite LTA, (♦): zeolite FAU, (●): Al_2O_3 support.

Figure S2

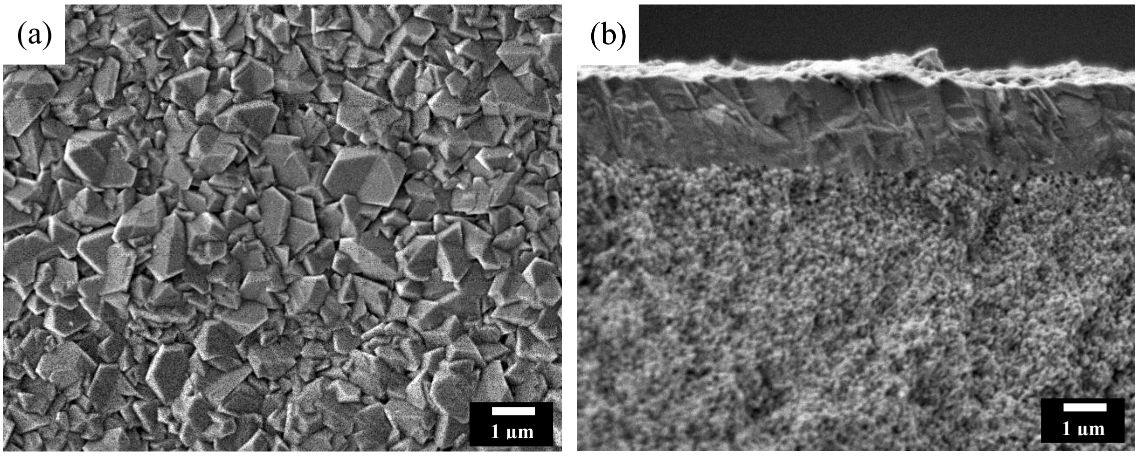

Fig. S2. Top view (a) and cross section (b) SEM images of the FAU membrane prepared on APTES functionalized Al_2O_3 support.

Figure S3

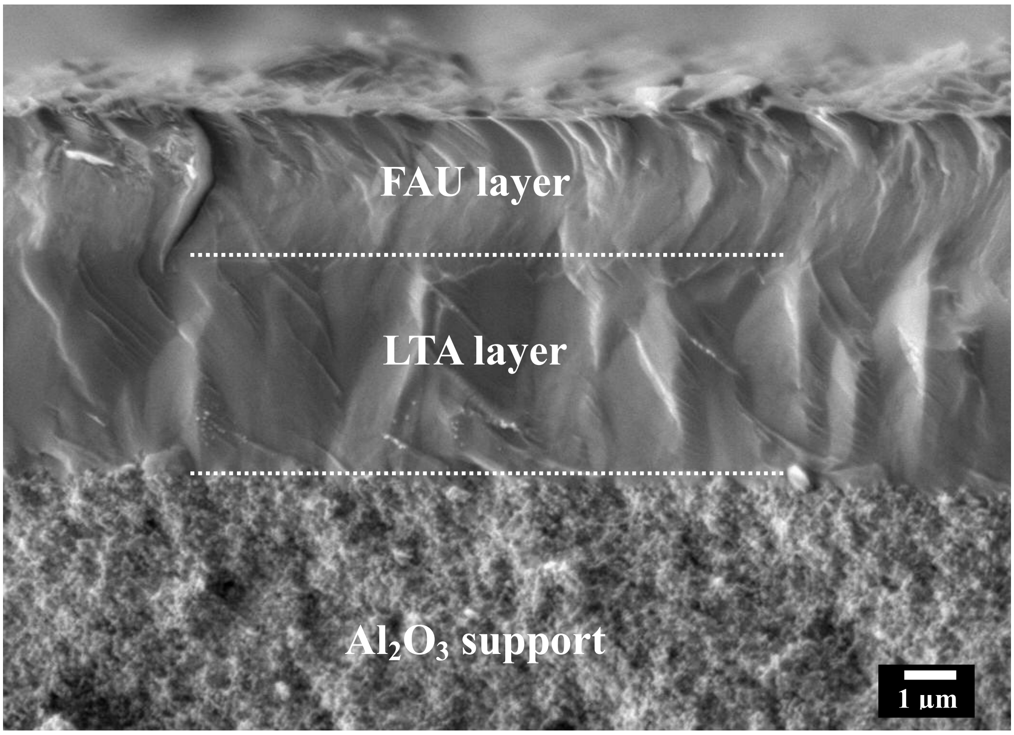

Fig. S3. High magnifications cross-section SEM of the LTA-FAU composites membrane. For the low magnifications cross-section SEM see Fig. 2d in text.

Figure S4

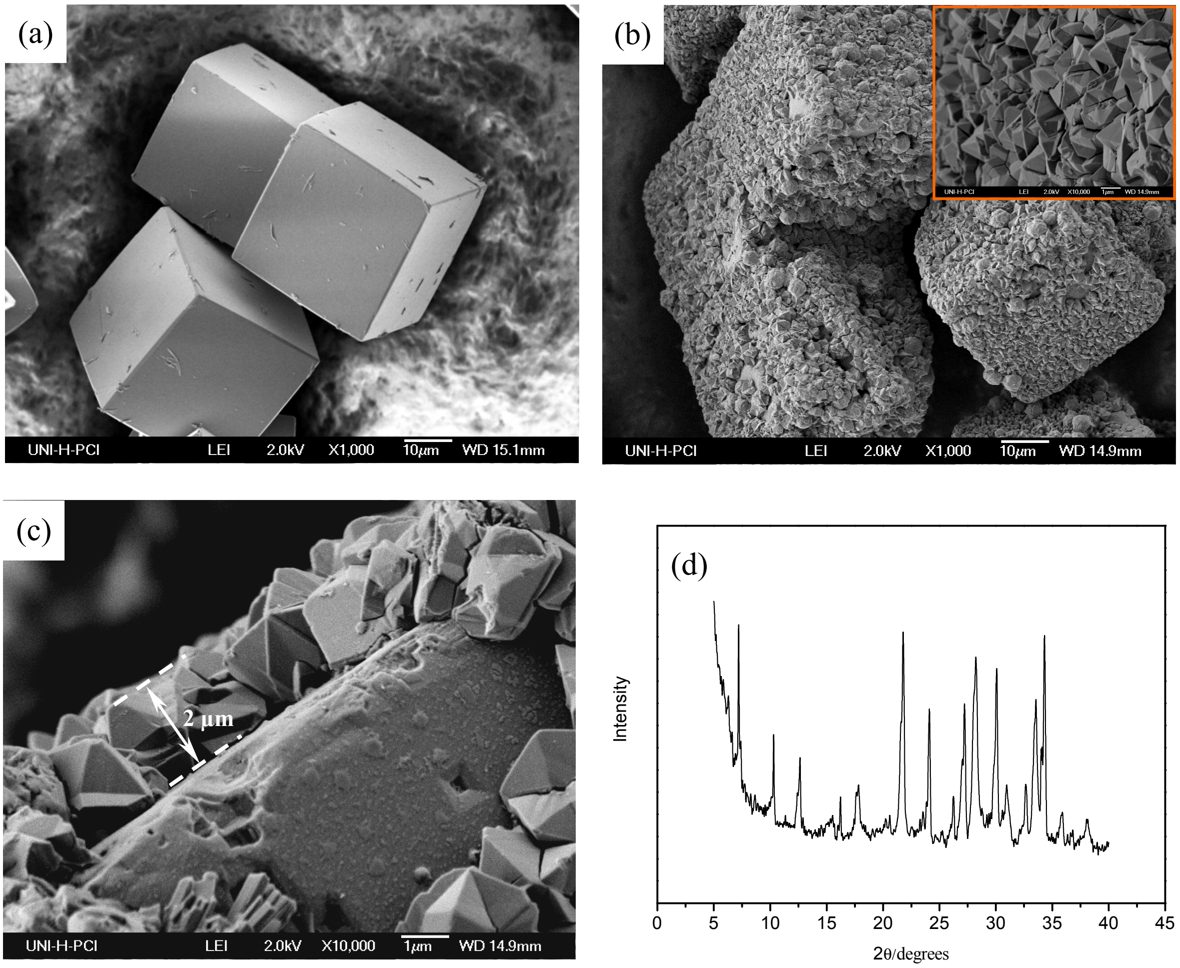

Fig. S4. SEM images of LTA single crystals (a), core (LTA)-shell (FAU) composite (b), and cross section (c) of the core (LTA)-shell (FAU) composite prepared by using APTES as an interlayer. XRD pattern of the core (LTA)-shell (FAU) composite (d).

Preparation of the core (LTA)-shell (FAU) composite

The core (LTA)-shell (FAU) composite was prepared according to the similar process of the preparation of the LTA-FAU composite membrane besides the FAU top layer was grew on the surface of the single zeolite LTA crystals

Figure S5

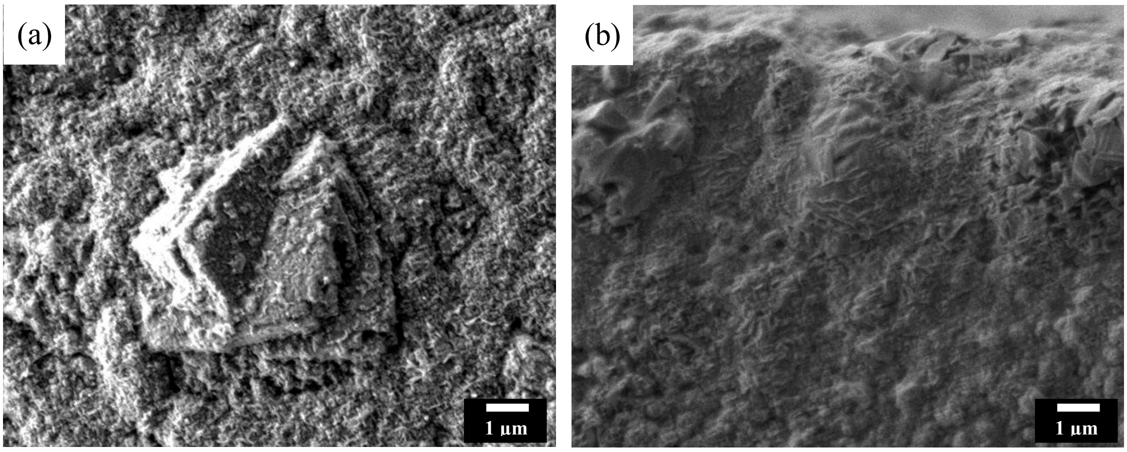

Fig. S5. Top view (a) and cross section (b) SEM images of the LTA-FAU layer prepared without APTES treatment of the as-made LTA bottom layer.

Figure S6

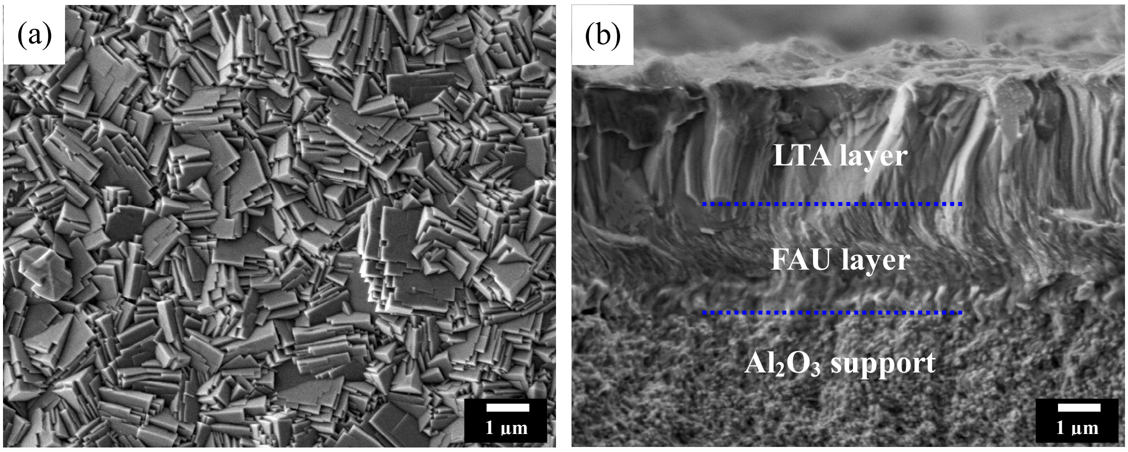

Fig. S6. Top view (a) and cross section (b) SEM images of FAU-LTA composite membrane prepared on APTES functionalized Al_2O_3 supports.

Preparation of the FAU-LTA composite membrane

The FAU-LTA composite membrane was prepared according to the similar process of the preparation of the LTA-FAU composite membrane besides the first growth of FAU layer and then secondary growth of LTA layer.

Figure S7

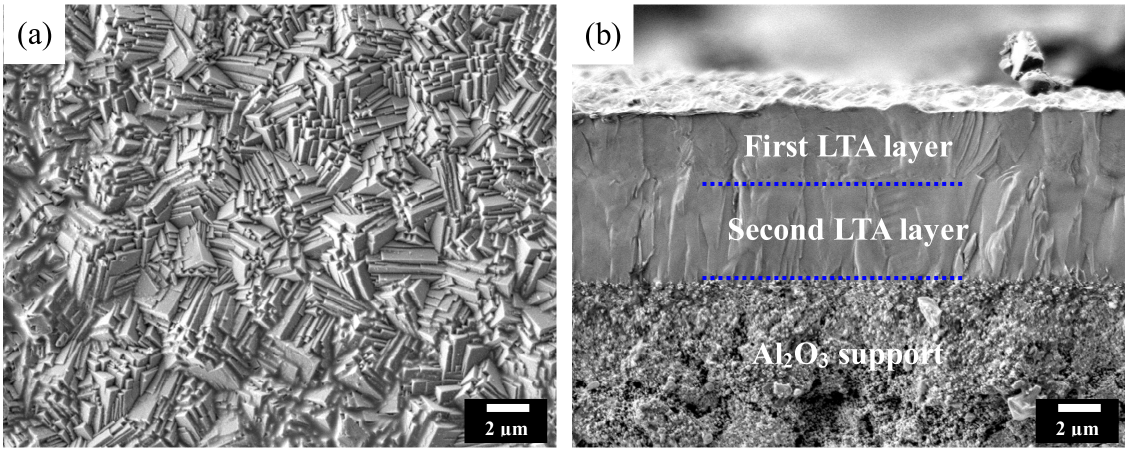

Fig. S7. Top view (a) and cross section (b) SEM images of the LTA-LTA composite membrane prepared on APTES functionalized Al_2O_3 supports.

Preparation of the LTA-LTA composite membrane

The FAU-LTA composite membrane was prepared according to the similar process of the preparation of the LTA-FAU composite membrane besides the first growth of LTA layer and then secondary growth of LTA layer.

Figure S8

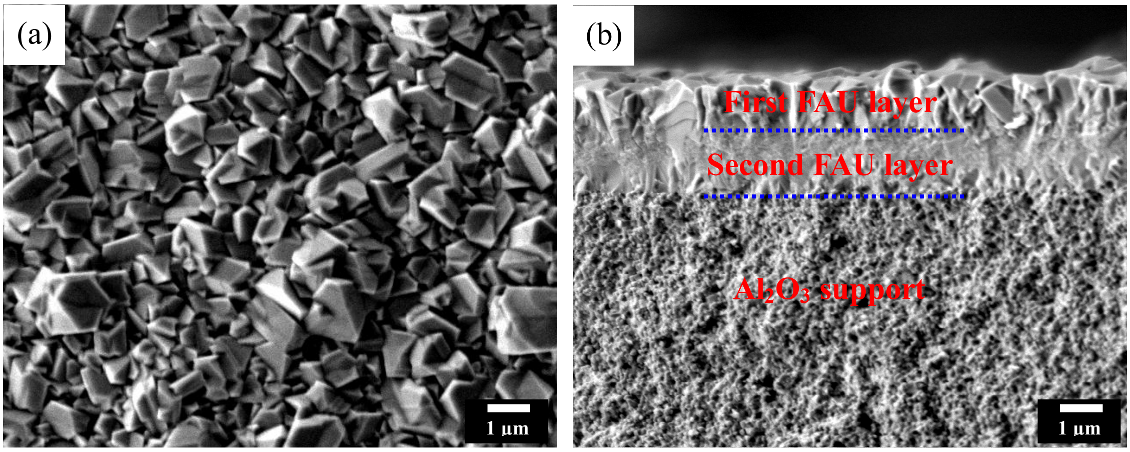

Fig. S8. Top view (a) and cross section (b) SEM images of the FAU-FAU composite membrane prepared on APTES functionalized Al_2O_3 supports.

Preparation of the FAU-FAU composite membrane

The FAU-LTA composite membrane was prepared according to the similar process of the preparation of the LTA-FAU composite membrane besides the first growth of FAU layer and then secondary growth of FAU layer.

Figure S9

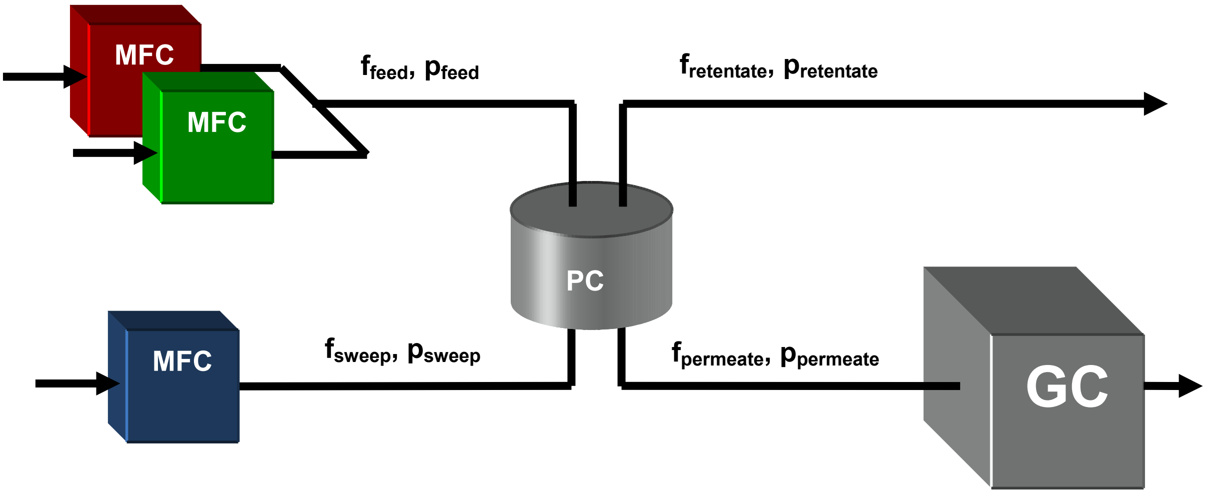

Figure S9. Measurement equipment for both single and mixed gas permeation.

Legend:

MFC: Mass flow controller

PC: Permeation cell with mounted membrane

GC: Gas chromatograph

f: Volumetric flow rate

p: Pressure

Figure S10

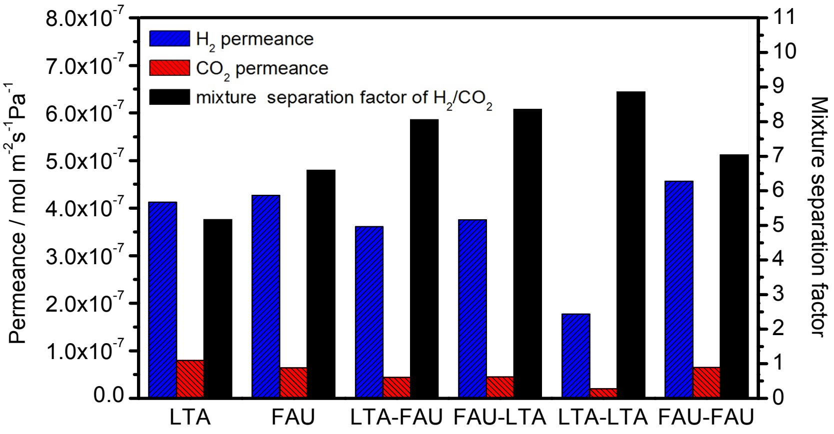

Fig. S10. Comparison of separation performances of single phase zeolite membranes and composite zeolite membranes for H_2-CO_2 mixtures at 100 ºC and 1 bar.

Figure S11

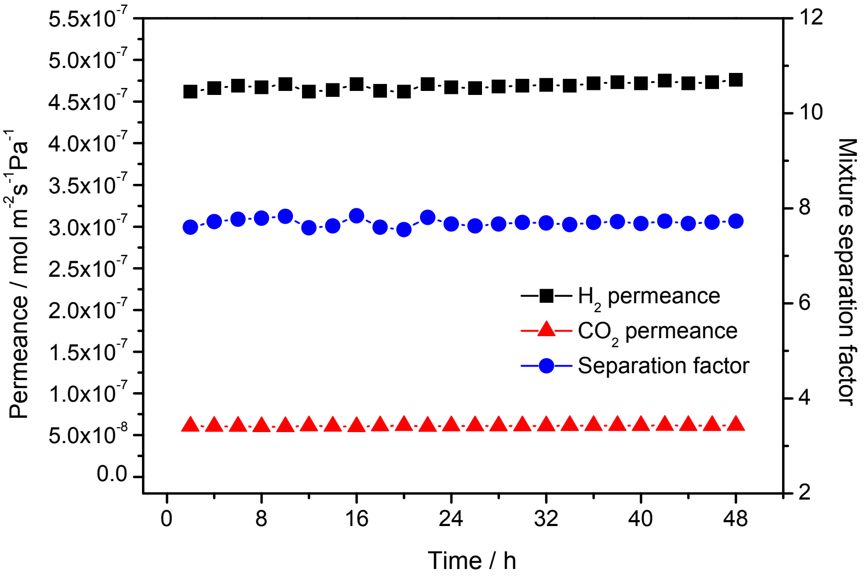

Fig. S11. H_2/CO_2 selectivity and permeances of the LTA-FAU composite membrane as function of the operating time at 150 ºC and 1 bar.

Table S1

Table S1. Separation performances of single phase zeolite membranes and composite zeolite membranes for H_2-CO_2 mixtures at 100 ºC and 1 bar.

Membranes	Membrane thickness [a] (μm)	H_2 permeance ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	H_2 permeability [b] (Barrers)	H_2/CO_2 mixture selectivity
Single zeolite LTA membrane	3.5	4.12×10^{-7}	4370	5.2
Single zeolite FAU membrane	2.8	4.37×10^{-7}	3654	6.6
LTA-FAU composite membrane	5.5	3.61×10^{-7}	5951	8.2
FAU-LTA composite membrane	5.3	3.75×10^{-7}	5936	8.3
LTA-LTA composite membrane	7.6	1.77×10^{-7}	4018	8.8
FAU-FAU composite membrane	2.6	4.56×10^{-7}	3541	7.0

[a] After subtracting the interface thickness.

[b] Permeability is calculated as the membrane permeance multiplied by the membrane thickness.
1 Barrer = 3.348×10^{-16} mol m / (m^2 s Pa).