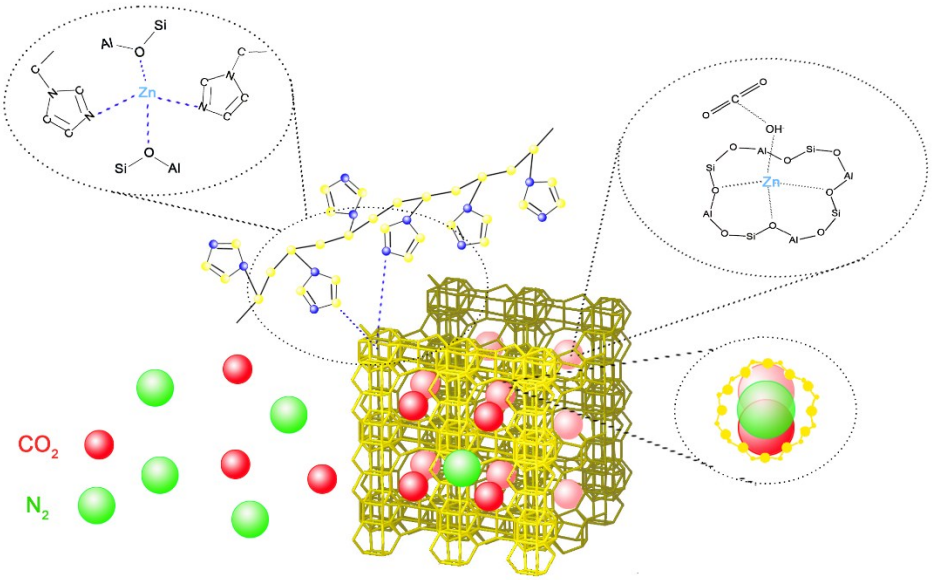

Fig. S1 Schematic illustration of PVI/Zn-*β* material

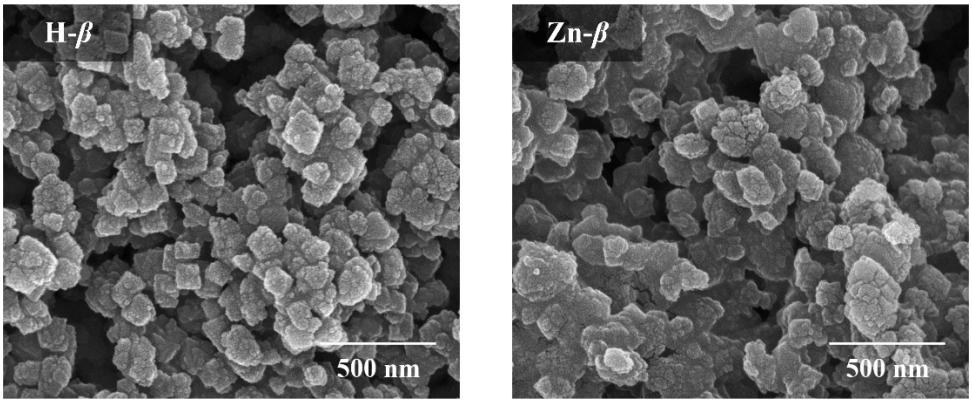

Fig. S2 SEM images of zeolite *β* before and after ion-exchange.

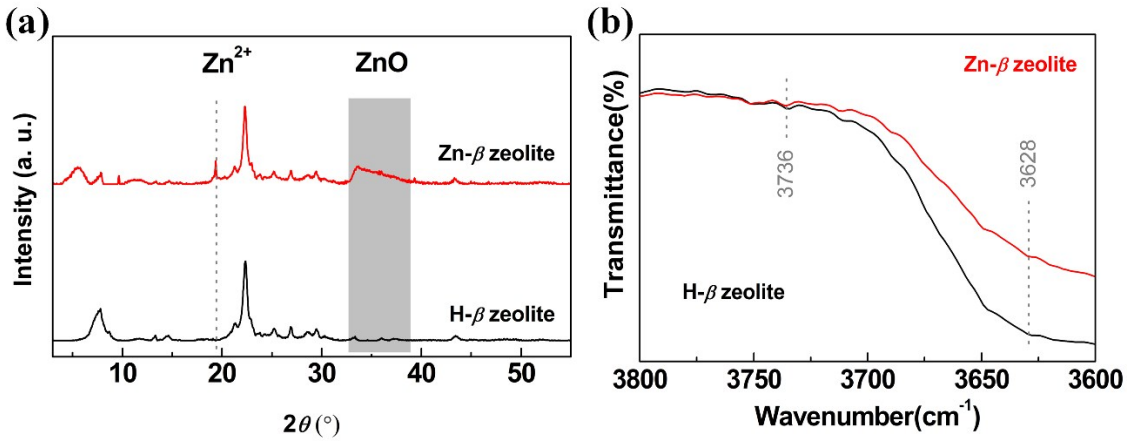

Fig. S3 (a) XRD patterns of zeolite Zn-β and zeolite H-β. (b) FTIR spectra of zeolite β before and after ion-exchange

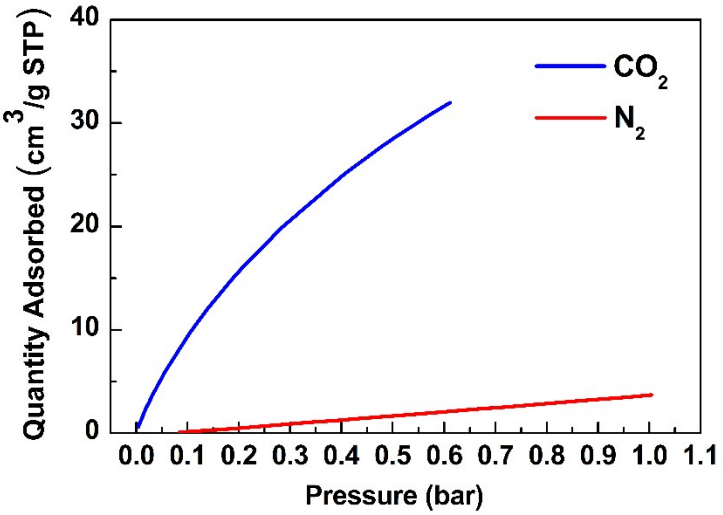

Fig. S4 Adsorption isothermal plot of zeolite Zn-β (25°C)

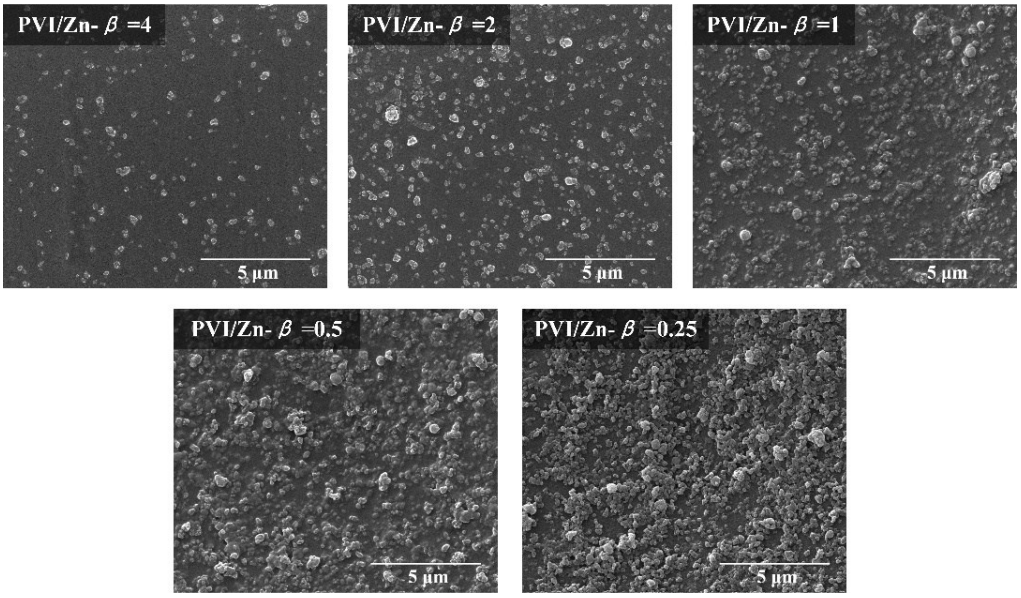

Fig. S5 Surface SEM images of membranes prepared by PVI/Zn-β with different mass ratio.

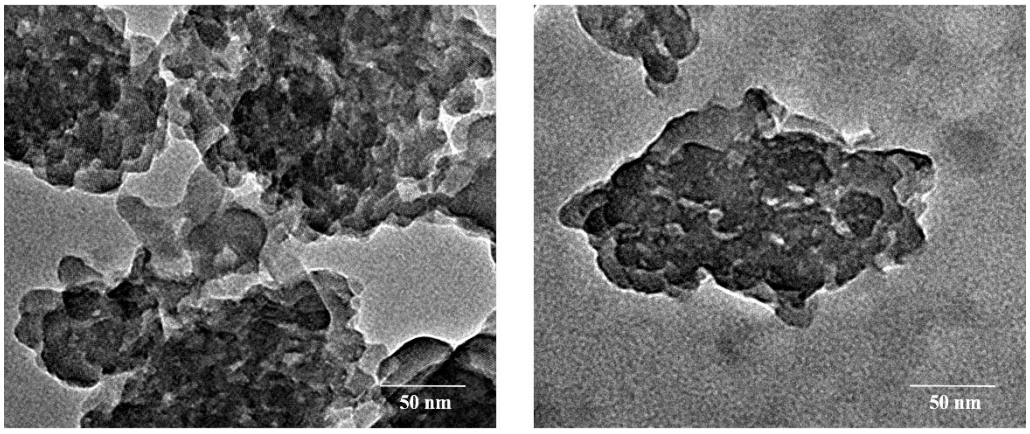

Fig. S6 TEM images of PVI/Zn-β = 1 (mass ratio).

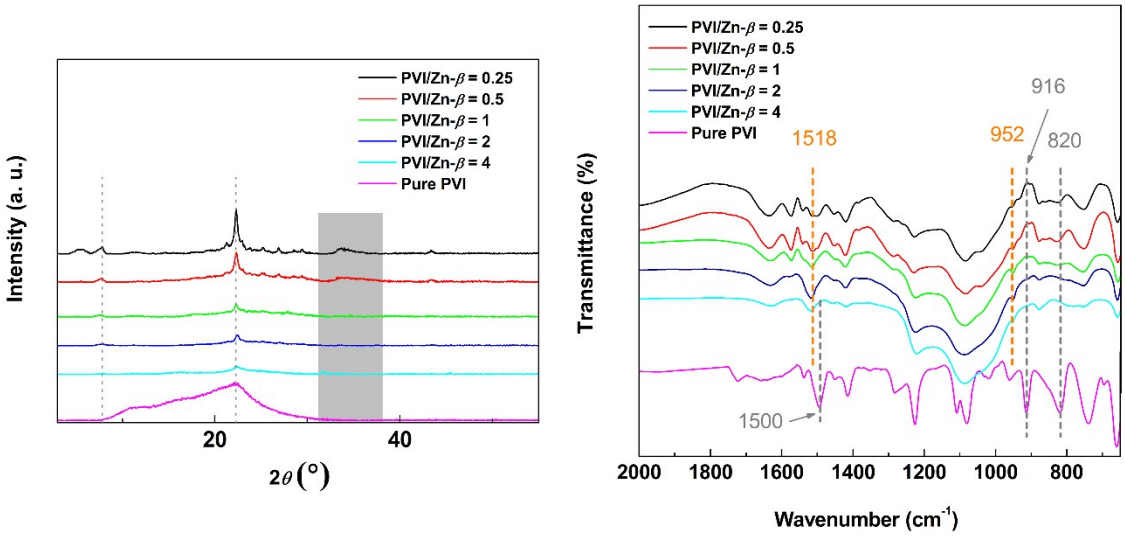

Fig. S7 (a) XRD patterns of PVI/Zn-β with different mass ratio. (b) FTIR spectra of PVI/Zn-β with different mass ratio.

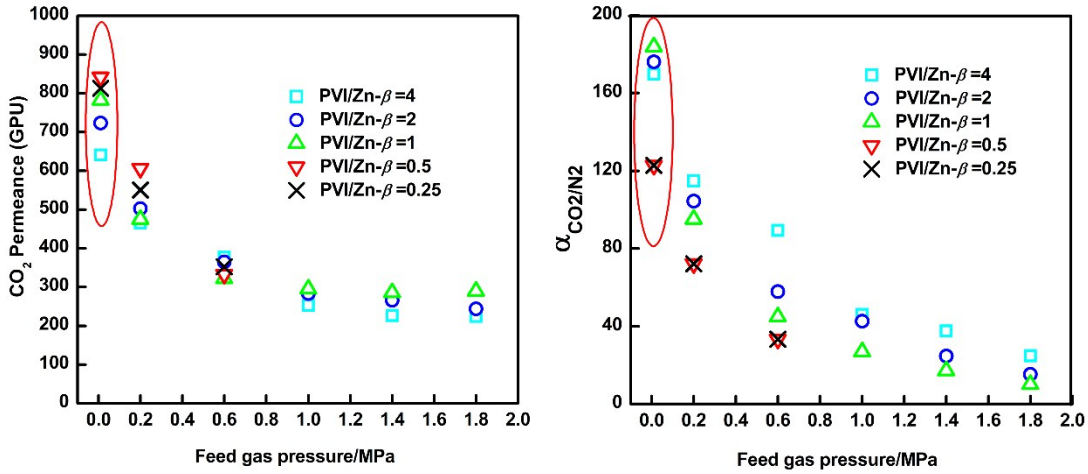

Fig. S8 CO_2 permeance and CO_2/N_2 (15/85 vol%) selectivity of PVI/Zn-β/PSf composite membranes with different PVI/Zn-β ratio as a function of feed gas pressure; wet membrane coating thickness: 100 μm

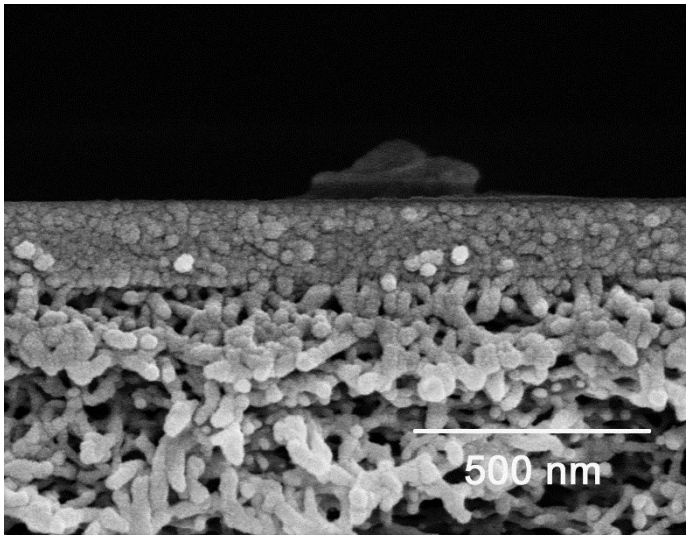

Fig. S9 SEM image of membrane (PVI/Zn-β = 0.25) cross-section

Table S1. Gas permeance and selectivity of membranes reported in references

Membrane	$p_{(CO2)}$/MPa	Temperature/°C	P_{CO2}/GPU	$\alpha_{CO2/N2}$	$\alpha_{CO2/CH4}$	Ref.
PVI-Zn	0.017	25	1120	83	-	[1]
PVI-Zn	0.2	25	970	77	-	[1]
PEO-*b*-PES	0.0068	20	2160	2.02	-	[2]
DAmPEG-TMC	0.075	22	1310	33	-	[3]
PVAm-PIP	0.02	25	6500	277	-	[4]
PVAm-PIP	0.25	25	6097	200	-	[4]
PVI/Zn-β	0.01	25	4620	224	-	this work
PVI/Zn-β	0.2	25	1978	91	-	this work
Zn-PVI@CNT	0.2	30	75[a]	-	70	[5]
Cellulose acetate@ β-CD-MWCNTs	0.38	25	742	40	-	[6]
Pebax®1657@ZIF-7	0.38	20	291	68	23	[7]

[a] Estimated by CO_2 permeability data in the reference with a membrane thickness of 160 nm.

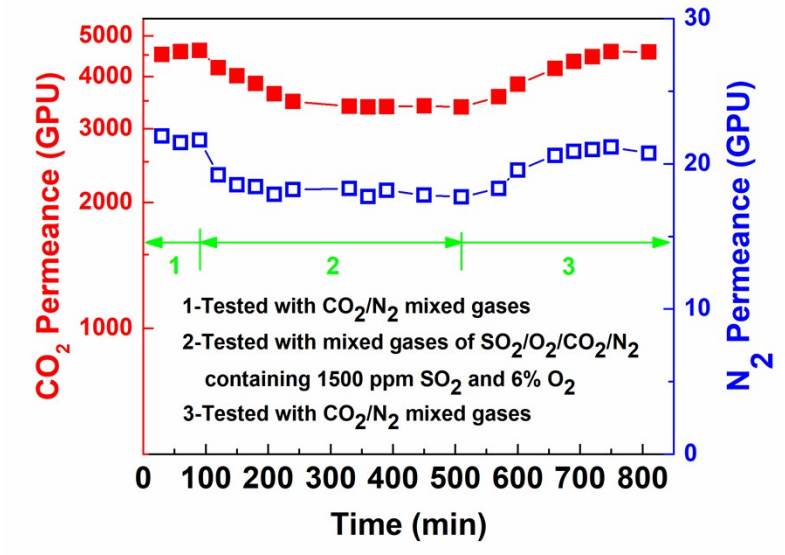

Fig. S10 Changes in gas permeance of PVI/Zn-*β*/PSf composite membranes with time. Wet membrane coating thickness: 30 μm. Feed gas pressure: 0.01 MPa.

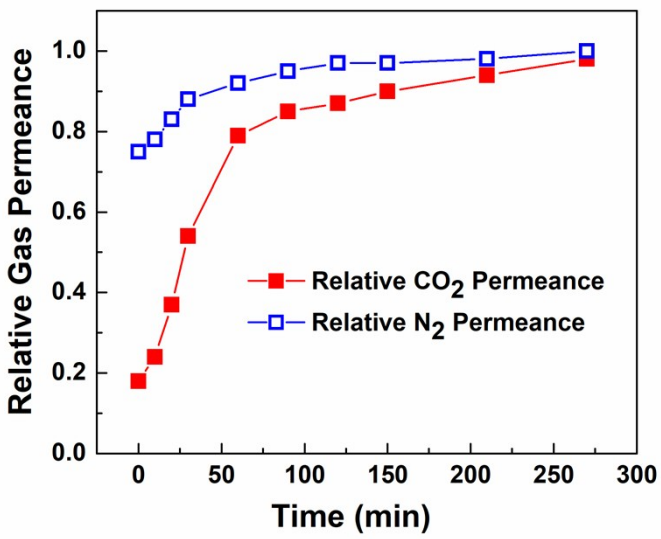

Fig. S11 Changes in relative gas permeance with time performed with CO_2/N_2 mixed gases at 0.01 MPa. The relative gas permeance is the ratio of gas permeance after exposure to steady gas permeance before exposure. The membrane is exposed to water saturated SO_2 (5000ppm)/CO_2 (15 vol%)/N_2 mixed gas for 12 hours. The product of SO_2 concentration and the treating time was defined as treatment intensity.

The treatment intensity here was 6×10^4 ppm·h, which is equivalent to 4000 h treatment in desulfurized flue gas (SO_2 concentration =15 ppm).

Experimental

Materials

1-Vinylimidazole (purity 99%) and Zinc chloride ($ZnCl_2$, purity 99%) were purchased from Aladdin (China), and 1-vinylimidazole was distilled under vacuum before use while $ZnCl_2$ was used without further purification. Azobisisobutyronitrile (AIBN, purity 99%) and benzene (purity 99.5%) were purchased from J&K Chemical (China), and both chemicals were directly used with no purification. Hydrochloric acid (HCl, Analytical reagent) and acetone (Analytical reagent) were purchased from Jiangtian Chemical Reagent Co. Ltd. (China). Zeolite β was purchased from Catalyst Plant of Nankai University (China), and SiO_2/Al_2O_3 = 25. The average particle size was 70 nm. PSf flat ultrafiltration membranes (average cut-off molecular weight = 6000 Dalton) were purchased from Vontron Technology Co. Ltd. (China). The PSf membrane was composed of PSf layer (about 50 μm thick) and polyester backing fabric (about 90 μm thick).

Preparation of PVI-Zn-β composite membranes

The poly(N-vinylimidazole) was synthesized via radical polymerization. 10 g 1-Vinylimidazole was dissolved in 30 ml benzene, and 0.035 g AIBN was used as the initiator. The reaction was promoted at 70°C in a nitrogen atmosphere. The products were filtered and washed three times with acetone. Finally, the white powdery products were drained in a vacuum oven at 60°C.

The zeolite *β* was ion-exchanged by a microwave irradiation method. The purchased zeolite *β* was suspended in an aqueous solution of zinc chloride (1M). The suspension was microwave irradiated in a household microwave oven (maximum power of 1200 W) for 2 min. The solid was separated by centrifugation, and repeated the above steps for 5 times. The final product was washed three times with distilled water after centrifugation. Then the solid was drained at 80°C in a vacuum oven for 24 h and zeolite Zn-*β* was obtained.

The PVI solid was dissolved in deionized water to prepare a 5wt% aqueous solution. The zeolite Zn-*β* was ultrasonically dispersed in deionized water to prepare a 5wt% dispersion. The PVI/Zn-*β* solution was obtained by gradually dropping the Zn-*β* dispersion into the PVI solution under agitation. The pH value of the PVI/Zn-*β* solution was adjusted 7 by 1M hydrochloric acid. The proportion of PVI aqueous solution, Zn-*β* dispersion, and deionized water is listed in Table 1. The PVI/Zn-*β* casting solution was stirred for 12 h and then ultrasonic dispersed for 1 h, and stood 12 h before use.

Table S2. Constitutions of PVI/Zn-*β* solutions with different mass ratio

PVI/Zn-*β*(wt/wt)	5%wt PVI solution (g)	5%wt Zn-*β* dispersion (g)	Deionized water (g)
Pure PVI	1.2	0	6.8
4	1.2	0.3	6.5
2	1.2	0.6	6.2
1	1.2	1.2	5.6
0.5	1.2	2.4	4.4
0.25	1.2	4.8	2

Composite membranes were prepared by casting PVI/Zn-*β* solutions on polysulfone ultrafiltration membranes by a coating applicator. The wet coating thickness was pre-settled. Then the membranes were dried at 30°C and 40% relative humidity for 24 h. The pre-settled wet coating thickness was 100 μm for membranes with different mass ratios. Then membranes with PVI concentration of 1.5wt% and PVI/Zn-*β*=1 were prepared for CO_2/N_2 and CO_2/CH_4 mixed gas tests, and the pre-settled wet coating thickness was 30 μm.

Characterization of zeolite *β and membranes*

The chemical characterization of zeolite *β* before and after ion-exchanged, as well as the composite membranes were performed by attenuated total reflectance infrared (ATR-FTIR) spectroscopy (VERTEX 70/70v, Bruker, Germany). The crystalline structure of the zeolite *β* and PVI/Zn-*β*/PSf membranes were explored by X-ray diffraction (XRD) spectra, and an X-ray diffractometer (D/MAX-2500) was used in reflection mode under 8kW power. The surface morphology of the PVI/Zn-*β*/PSf composite membranes were obtained by scanning electron microscopy (SEM, Nova NanoSEM430, Philips, USA). The membrane fragments were covered with gold by a sputter applicator. The images of Zn-*β* particles in PVI were examined by transmission electron microscopy (TEM, TECNAL G2 F20, FEI, USA). CO_2 and N_2 adsorption behavior of zeolite Zn-*β* particles at 25°C was measured by surface area pore size analyzer (3H-2000PM2, BeiShiDe, China).

Gas permeation measurements

The gas perm-selectivity of the PVI/Zn-*β*/PSf membranes was measured by a home-made apparatus using CO_2/N_2 (15/85 vol%) and CO_2/CH_4 (10/90 vol%) mixed gas. The details of our home-made apparatus are listed below. The schematic diagram of the permeation apparatus is shown in **Fig. S12**.

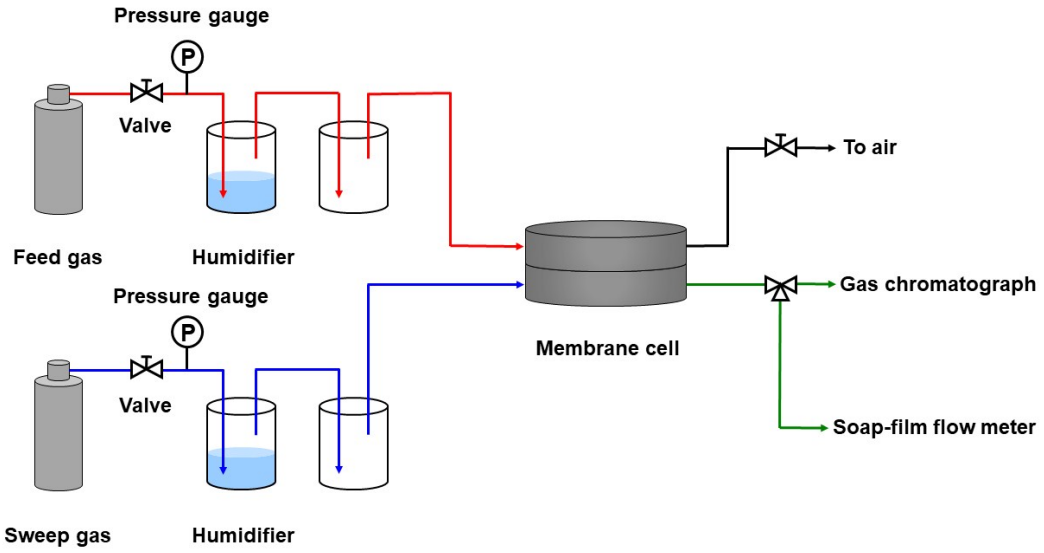

Fig. S12 Schematic diagram of the home-made gas permeation apparatus

The operation conditions were consistent with our previous work[8-10]. The membrane was emplaced in a membrane cell made of stainless steel. The effective membrane area tested was 19.26 cm^2. The feed gas was saturated with water vapor by entering and bubbling in a humidifier, and the outgoing gas went into the membrane cell. The permeate side of the membrane was maintained at atmospheric pressure by sweeping. H_2 saturated with water vapor was used as the sweep gas and the flow rate of the sweep gas was measured by a soap-film flow meter. The composition of the outgoing sweep gas was analyzed by a gas chromatograph (HP 7890A) equipped with

a thermal conductivity detector. The fluxes of both binary gas mixtures could be calculated from the flow rate and composition of the outgoing sweep gas. The permeance is defined as the quotient of the flux divided by the partial pressure difference between the upstream and downstream side of the membrane. The selectivity of the membrane is defined as the ratio of CO_2 permeance over permeance of the other gas.

The impacts of PVI/Zn-β mass ratio on composite membrane performance were evaluated by using CO_2/N_2 mixed gas. Then, CO_2/N_2 and CO_2/CH_4 mixed gases were used to measure separation performance of composite membranes with a thinner thickness of 30 μm. All reported CO_2 permeance and CO_2/N_2 or CO_2/CH_4 selectivity were the average values of three membranes prepared under the consistent condition, and the error bars represented the standard errors.

Changes in gas permeance with time were tested by alternately using CO_2/N_2 (15/85 vol%) and SO_2 (1500 ppm)/O_2 (6 vol%)/CO_2 (15 vol%)/N_2 mixed gases, and the tests remained 810 min. Changes in relative gas permeance with time were tested by placing the membrane in a water-saturated SO_2 (5000 ppm)/CO_2 (15 vol%)/N_2 mixed gas atmosphere for 12 hours. The relative gas permeance is the ratio of gas permeance after exposure to steady gas permeance before exposure. The product of SO_2 concentration and the treating time was defined as treatment intensity. The treatment intensity here was 6×10^4 ppm·h, which is equivalent to 4000 hours treatment in desulfurized flue gas (SO_2 concentration=15 ppm). The gas permeation performance of the treated membrane was tested with CO_2/N_2 mixed gas and the feed

pressure was 0.01 MPa.

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