Electrical Supporting Information

For

Composite 5A Zeolite with Ultrathin Porous TiO_2 Coating for Selective Gas Adsorption

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Experimental details

Molecular layer deposition (MLD) on 5A zeolite

We used 5A zeolite from W.R.Grace & Co.-Conn. Zeolite samples were firstly outgassed at 200°C for 4 hours. The titanium alkoxide MLD films were prepared by using titanium tetrachloride ($TiCl_4$; 99.9%, Sigma Aldrich) and ethylene glycol ($HO(CH_2)_2OH$; 99%, Alfa Aesar). Each MLD cycle started with 240 second vacuum, then ethylene glycol was diffused into the reactor with a partial pressure of 50 mTorr and then settled for 120 second, 240 second vacuum was followed to evacuate extra unreacted ethylene glycol. Ultrahigh purity N_2 (Airgas) was used as the purge at 20 sccm for 30 second. Then 240 second vacuum was applied to evacuate N_2. After that, $TiCl_4$ was diffused into the reactor with a partial pressure of 150 mTorr and then settled for 120 second, followed by 240 second vacuum to evacuate extra unreacted $TiCl_4$. Ultrahigh purity N_2 (Airgas) was used as the purge at 20 sccm for 30 second. Then 240 second vacuum was applied to evacuate N_2. This whole process is one titanium alkoxide MLD cycle. Each cycle MLD was deposited on the zeolite sample at 100 °C. Then the coated samples were heated in air from room temperature to 250°C at a rate of 1°C/min^{-1}, kept at 250°C for 4 hours, and then cooled to room temperature at the same rate.

Adsorption equilibrium and kinetics measurement

Ultra-high purity CO_2 (99.999%), N_2 (99.999%), CH_4 (99.999%), chemically pure 2.0 grade propane and n-butane were purchased from Airgas. Propylene (>99%) was purchased from Sigma-Aldrich. Gas adsorption isotherms were measured by a volumetric method using a home-built adsorption system. Sorbent (~0.20 g) was firstly outgassed at 200 ℃ for 2 h. Helium was then used to calibrate the volume of adsorption cell with sorbent at 20℃. After vacuum to remove residue gasses in the adsorption system, interested gases were introduced at 20℃. The pressure change was collected in real time using a Swagelok E model transducer and LabVIEW 2012 software. CO_2, N_2 and CH_4 adsorption isotherms on 5A zeolite and 5A zeolite with different TiO_2 MLD cycles are shown in Figure S3. Butane adsorption isotherm on 5A zeolite and 5A zeolite with different TiO_2 MLD cycles is shown in Figure S4. CH_4 adsorption isotherms on 15 cycles of TiO_2 coated 5A zeolite before calcination and 30 cycles of TiO_2 coated 5A zeolite before calcination are shown in Figure S5.

Characterization

X-ray diffraction (XRD)

X-ray powder diffraction (XRD) was carried out using a Rigaku MiniFlex II diffractometer with Cu Kα radiation (λ = 0.15418 nm). The diffraction data was recorded for 2θ angles between 5° and 50°. The scanning rate is 2°/min. XRD pattern of 5A zeolite and 5A zeolite with different TiO_2 MLD coating were shown in Figure S2.

X-ray photoelectron spectroscopy (XPS) analysis

The surface chemical compositions of 5A zeolite and TiO_2 MLD coated 5A zeolite were analyzed by XPS (Kratos Axis Ultra DLD instrument equipped with a monochromated Al Ka x-ray source and hemispherical analyzer capable of an energy resolution of 0.5 eV). Table S1 shows the MLD coatings after calcination are TiO_2. As the MLD coating thickness increased, much smaller amount underlying silicon can be seen (Figure 1b).

Field emission scanning electron microscopy (FE-SEM)

The FE-SEM (Zeiss Ultraplus Thermal Field Emission Scanning Electron Microscope) images of 5A zeolite crystals were shown in Figure S1. 5A zeolite pellet were firstly crushed into powder. Then a proper concentration of 5A zeolite sample was loaded on the conductive carbon tape.

Transmission electron microscopy (TEM)

The TEM (Hitachi H8000 Scanning Transmission Electron Microscope) images of 60 cycles of MLD coated 5A zeolite were shown in Figure1b. 5A zeolite pellet were firstly crushed into powder. A proper concentration of 5A zeolite was dispersed in DI water and sonicated for 30 minute and then dripped on the TEM carbon grids.

N_2 adsorption isotherm measurements and pore size distribution analysis

N_2 adsorption isotherms at 77 K were measured on a Micromeritcs ASAP 2020 unit. Prior to analysis, the materials were degassed in situ for 10 h at 250 °C. Pore size distribution was then calculated using N_2 adsorption isotherms. N_2 adsorption isotherms at 77 K were shown in Figure S8 and pore size distribution was shown in Figure S9.

Table S1. Surface atomic concentrations of Al, Si, O and Ti of 5A zeolite and 5A zeolite with different cycles of MLD coatings (after calcination), measured from XPS spectra of Al 2P, Si 2P, O 1S and Ti 2P.

Cycles of MLD on 5A zeolite	**Atomic concentration (%)**			
	Al	**Si**	**O**	**Ti**
0	15.3	15.0	69.7	0.0
30	4.8	6.8	67.0	21.4
60	1.9	1.7	72.9	23.5

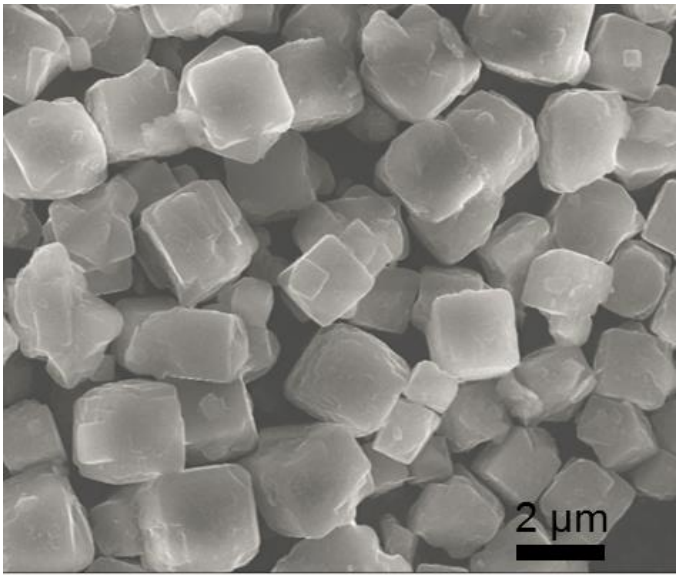

Figure S1. FE-SEM image of 5A zeolite.

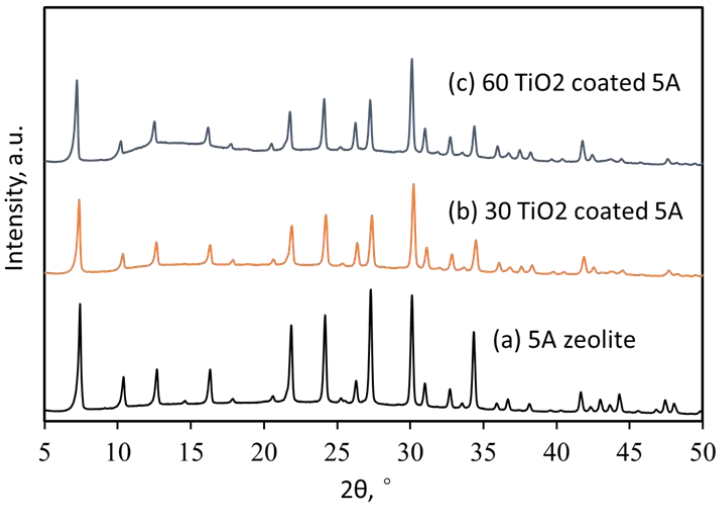

Figure S2. XRD patterns. (a) 5A zeolite, (b) 30 cycles of TiO_2 coated 5A zeolite, (c) 60 cycles of TiO_2 coated 5A zeolite.

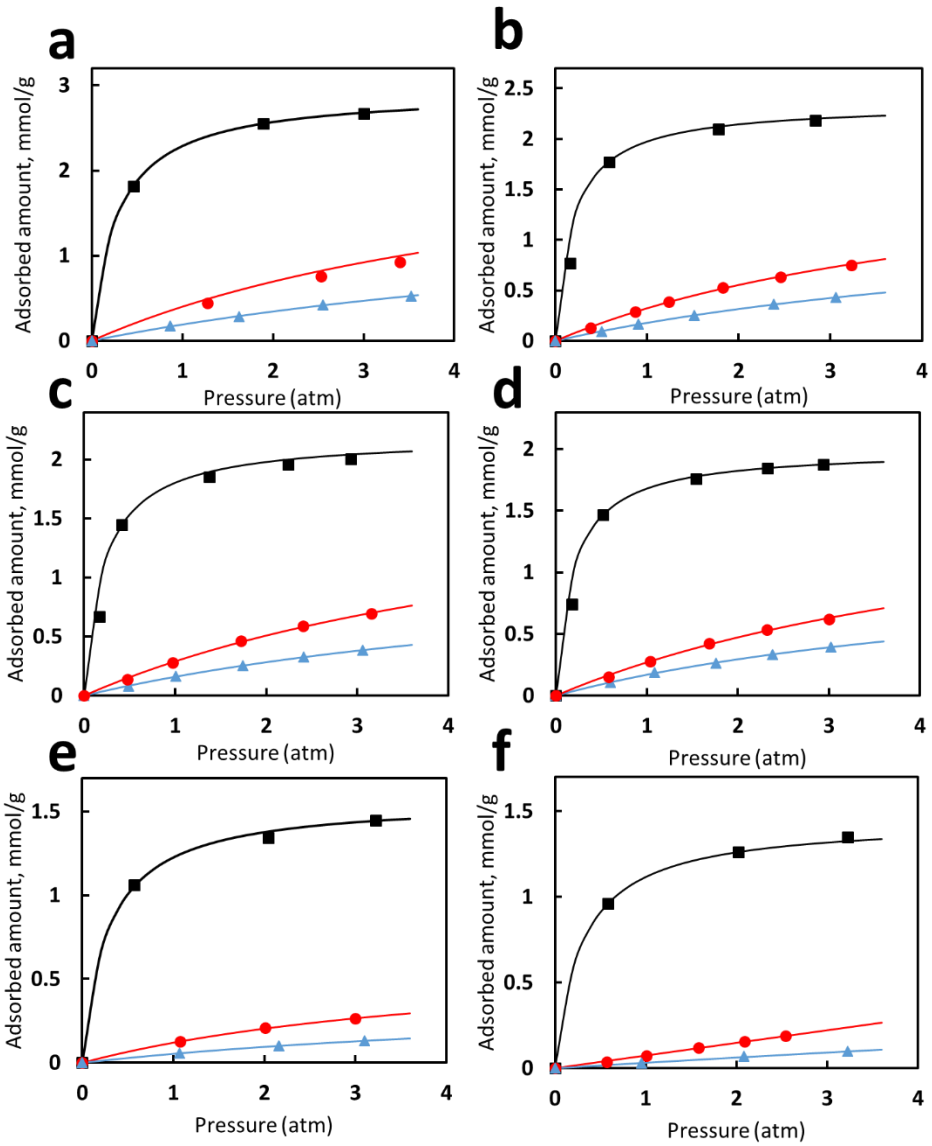

Figure S3. CO_2, N_2 and CH_4 adsorption isotherms at 20℃ on (a) 5A zeolite, (b) 3 cycles of TiO_2 coated 5A zeolite, (c) 8 cycles of TiO_2 coated 5A zeolite, (d) 15 cycles of TiO_2 coated 5A zeolite, (e) 30 cycles of TiO_2 coated 5A zeolite, and (f) 60 cycles of TiO_2 coated 5A zeolite. Solid lines indicate fits from Langmuir equation. CO_2 (■), CH_4 (●), and N_2 (▲).

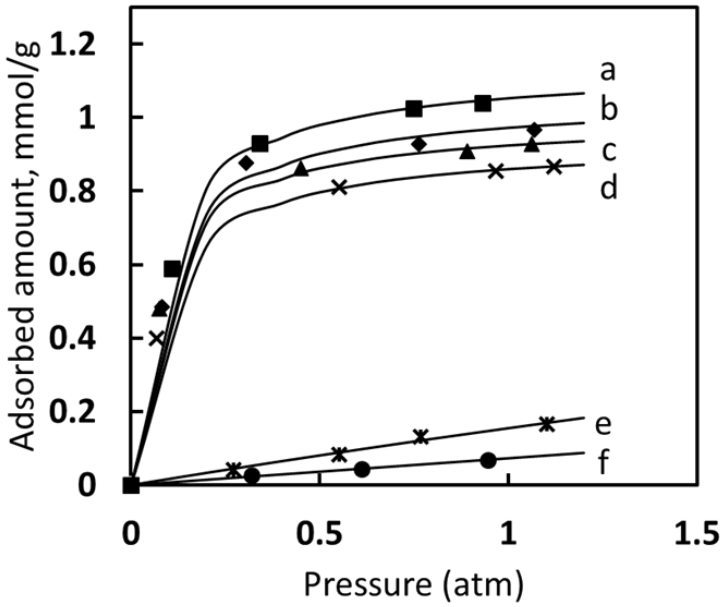

Figure S4. C_4H_{10} isotherms at 20℃ on (a) 5A zeolite, (b) 3 cycles of TiO_2 coated 5A zeolite, (c) 8 cycles of TiO_2 coated 5A zeolite, (d) 15 cycles of TiO_2 coated 5A zeolite, (e) 30 cycles of TiO_2 coated 5A zeolite, and (f) 60 cycles of TiO_2 coated 5A zeolite. Solid lines indicate fits from Langmuir equation.

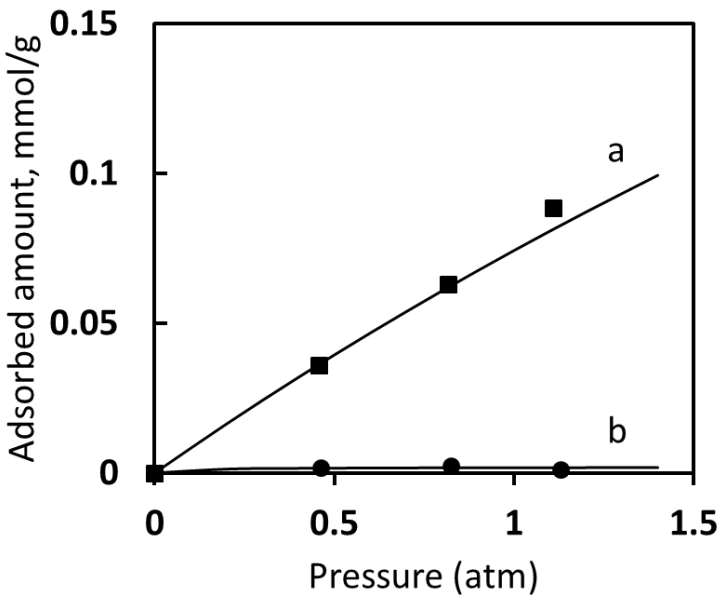

Figure S5. CH_4 isotherms at 20℃ on (a) 15 cycles of TiO_2 coated 5A zeolite before calcination, (b) 30 cycles of TiO_2 coated 5A zeolite before calcination. Solid lines indicate fits from Langmuir equation.

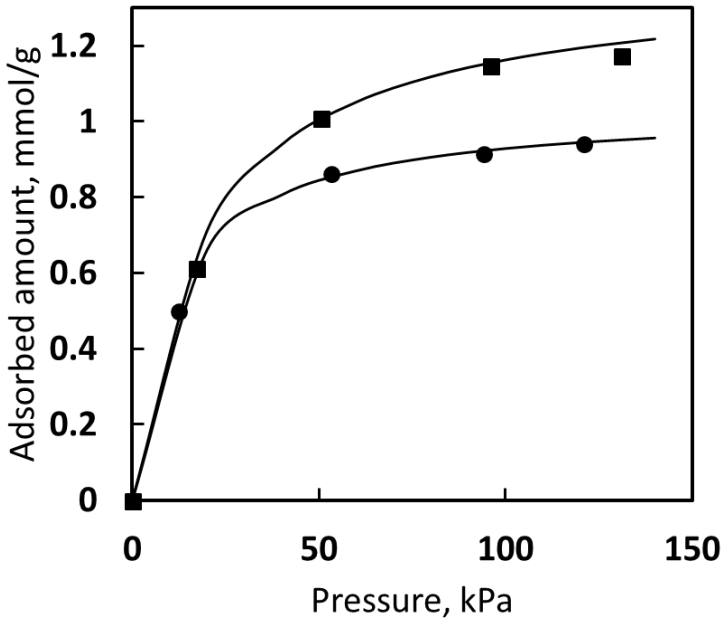

Figure S6. Adsorption isotherms of propylene (■) and propane (●) on 5A zeolite at 20 ℃. Solid lines are from Langmuir model fitting.

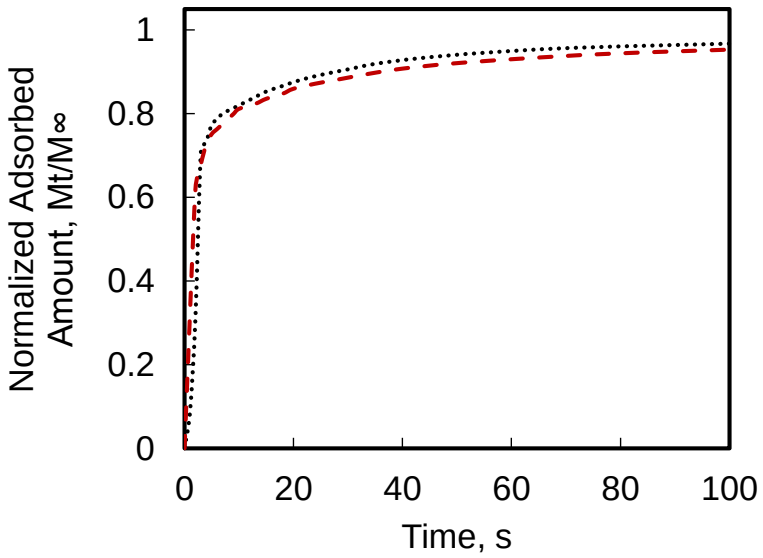

Figure S7. Adsorption uptake curves of propylene (red dash line) and propane (black dot line) on 5A zeolite at 20 ℃. M_t is the adsorbed amount at time t, and M_∞ is the adsorbed amount at equilibrium.

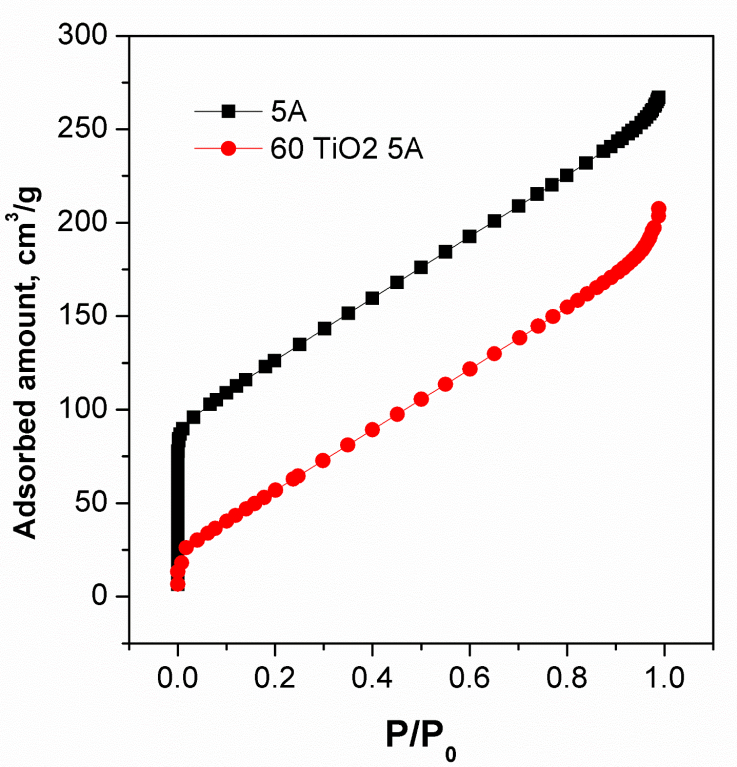

Figure S8. N_2 adsorption isotherms at 77 K on 5A and 5A with 60 cycles of MLD.

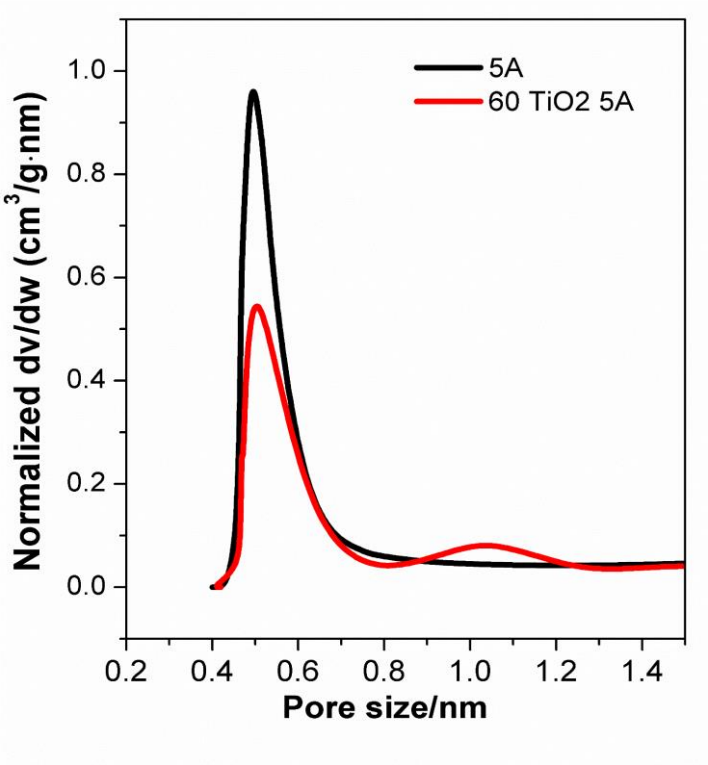

Figure S9. Pore size distribution of 5A and 5A with 60 cycles of MLD.