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## COMMUNICATION

## Composite 5A Zeolite with Ultrathin Porous TiO<sub>2</sub> Coating for Selective Gas Adsorption

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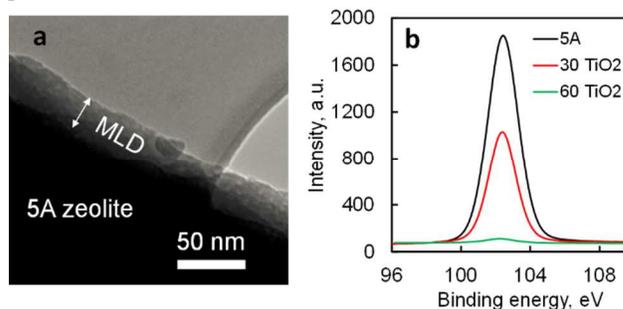
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**A composite zeolite adsorbent was prepared by conformally depositing an ultrathin porous TiO<sub>2</sub> coating on the external surface of the 5A zeolite by molecular layer deposition (MLD) and subsequent calcination. The composite adsorbent showed significantly improved ideal adsorption selectivity for CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub> and propylene/propane.**

Adsorptive separation is an important technology for gas separation in industry<sup>1-4</sup>. Porous adsorbents with desirable adsorption and/or diffusion properties are essential for designing energy-efficient, adsorption-based separation processes. Zeolites/molecular sieves, a class of crystalline microporous oxides, are one of the most widely used adsorbents in adsorptive processes, because of their uniform, molecular-sized pores and high chemical, thermal, and mechanical stabilities<sup>5</sup>. Despite there are more than 200 types of zeolites, not all the desired pore sizes can be found. This makes it a great challenge to achieve size-selective separation for some industrially important mixtures composed of molecules with very small size differences, such as O<sub>2</sub>/N<sub>2</sub>, N<sub>2</sub>/CH<sub>4</sub>, ethylene/ethane, propylene/propane. Therefore, it would be highly favorable if the pore sizes of the zeolites/molecular sieves can be fine-tuned to achieve adsorption separation based on very small size differences, typically ~0.01 nm.

Pores of zeolites/molecular sieves have been adjusted by methods such as dehydration and ion exchanges<sup>6-9</sup>. For example, the effective pore size of titanium silicate ETS-4 was gradually contracted through dehydration at elevated temperature to achieve difficult size-based separations<sup>8</sup>; 5A zeolite pore opening was narrowed by silver exchange to successfully distinguish ethylene from ethane by molecular sieving<sup>9</sup>. These methods, however, are valid only for some specific zeolites and/or may not be used to continuously tune zeolite pore sizes. More effective techniques, therefore, are still needed to further fine-tune zeolite pore sizes.

Molecular layer deposition (MLD) is a technique to deposit hybrid coatings by conducting a series of sequential, self-limiting surface reactions on a substrate<sup>10, 11</sup>. The self-limiting nature of the surface reactions leads to several characteristic advantages of MLD coating growth, such as exquisite control over coating thickness at sub-nanometer level and continuous, conformal pinhole-free coatings on high aspect ratio structures<sup>12-14</sup>. Here, we report an innovative use of MLD to prepare ultrathin, conformal microporous TiO<sub>2</sub> coatings on 5A zeolite to modify the zeolite pore opening. Porous TiO<sub>2</sub> coatings were formed by removing the organic compound in the dense titanium alkoxide coatings, deposited by MLD, upon calcination in air at elevated temperature (see Supporting Information for experimental details).

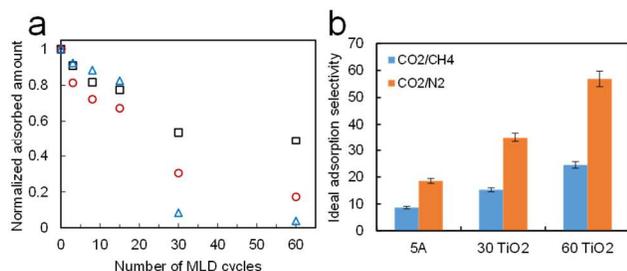


**Figure 1.** (a) Transmission electron microscopy (TEM) image of 60 cycles of TiO<sub>2</sub> MLD coating (after calcination) on 5A zeolite. (b) X-ray photoelectron spectroscopy (XPS) spectra of Si 2P of 5A zeolite with (30 and 60 cycles) and without MLD coatings.

Field emission scanning electron microscopy (FE-SEM) shows that 5A zeolite crystals are cubic and have an average size of approximately 2  $\mu\text{m}$  (Figure S1 in the Supporting Information). After depositing 60 cycles of MLD and calcination, an approximately 25 nm thick porous TiO<sub>2</sub> coating was formed on the 5A zeolite surface (Figure 1a), corresponding to a nominal microporous TiO<sub>2</sub> growth rate of 0.42 nm/cycle. X-ray diffraction

(XRD) confirmed that all the peaks of 5A zeolite match those reported by Gramlich<sup>15</sup> before and after MLD, indicating TiO<sub>2</sub> MLD coatings had negligible effects on the 5A zeolite crystal structure (Figure S2). X-ray photoelectron spectroscopy (XPS) shows the MLD coatings after calcination are TiO<sub>2</sub> (Table S1). Also, as the MLD coating cycles or coating thickness increased, the detectable amount of the underlying silicon decreased, and after 60 cycles of MLD, silicon can hardly be seen (Figure 1b), suggesting a continuous and uniform TiO<sub>2</sub> coating on the 5A zeolite surface, which effectively blocked electron penetration.

We measured the adsorption isotherms of gas molecules with different kinetic diameters (CO<sub>2</sub>: 0.33 nm<sup>16</sup>, N<sub>2</sub>: 0.364 nm<sup>16</sup>, CH<sub>4</sub>: 0.38 nm<sup>16</sup>, and n-C<sub>4</sub>H<sub>10</sub>: 0.46 nm<sup>17</sup>) to explore the effective pore sizes of the composite sorbent (Figure S3 and S4). Figure 2a shows the relative adsorbed amount changes of CO<sub>2</sub>, CH<sub>4</sub> and n-butane on 5A zeolite and those with different cycles of MLD coatings. For the initial 15 cycles, adsorbed amounts of both CO<sub>2</sub> and CH<sub>4</sub> decreased approximately linearly, with higher decreasing rate of CH<sub>4</sub> than CO<sub>2</sub>. This leads to an almost constant ideal adsorption selectivity of CO<sub>2</sub> over CH<sub>4</sub>. From 15 to 30 cycles, adsorbed amount of CO<sub>2</sub> decreased following the same trend, but that of CH<sub>4</sub> decreased even faster, resulting in an increased selectivity from 8.7 to 15.2. From 30 to 60 cycles, adsorbed amount of CO<sub>2</sub> kept almost constant, while that of CH<sub>4</sub> decreased about another 50%. Although butane showed a similar linear decrease below 15 cycles, a sharp decrease was seen between 15 and 30 cycles; from 30 to 60 cycles, its adsorbed amount decreased to half of that at 30 cycles. As a result, the ideal adsorption selectivity of CO<sub>2</sub> over butane increased drastically from 1.9 (bare 5A) to 24.9 (5A with 60 MLD cycles). This suggests with a microporous TiO<sub>2</sub> coating, formed from 60 cycles of MLD, the composite 5A sorbent should have an effective pore size smaller than butane (0.46 nm). Figure 2b shows that compared with bare 5A, ideal adsorption selectivity of CO<sub>2</sub> over N<sub>2</sub> and over CH<sub>4</sub> increased 2 and 1.8 times for 30 MLD cycles and 3.1 and 2.9 times for 60 MLD cycles, respectively. This seems to suggest that the average pore size may become smaller than N<sub>2</sub> and CH<sub>4</sub> after 60 cycles of MLD, although there may be a pore size distribution of the composite 5A adsorbent so both N<sub>2</sub> and CH<sub>4</sub> can still be adsorbed. These results demonstrate the 5A zeolite composite adsorbent with ultrathin (~25 nm) microporous TiO<sub>2</sub> coating may be a promising candidate for CO<sub>2</sub> capture in post combustion or CO<sub>2</sub> separation in nature gas purification. The high CO<sub>2</sub> selectivity and capacity of the 60 cycles of TiO<sub>2</sub> coated 5A zeolite composite adsorbent are comparable to other recent works<sup>18-20</sup>.



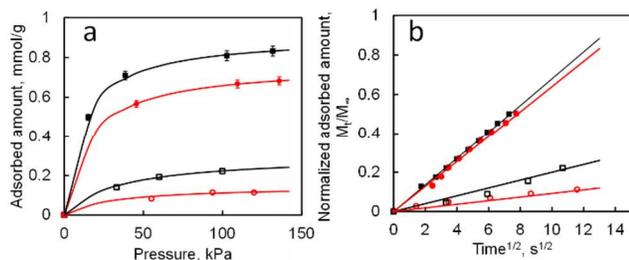
**Figure 2.** (a) Normalized sorption capacity change with the number of MLD coating cycles on 5A: CO<sub>2</sub> (□), CH<sub>4</sub> (○), and n-butane (Δ). (b) Ideal adsorption selectivity of CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> on 5A and 5A with 30 and 60 cycles of MLD. All the sorption capacity is at 50 kPa and 20 °C. As a reference, sorption capacities of CO<sub>2</sub>, CH<sub>4</sub> and n-butane on 5A are 1.86, 0.22 and 0.97 mmol/g, respectively.

To understand the adsorption selectivity increase when MLD cycle numbers were  $\geq 30$ , we firstly studied the coating quality by

measuring CH<sub>4</sub> adsorption on 5A zeolite with MLD coatings that were not calcined and thus expected to be dense. Indeed, after 30 cycles of MLD, no measurable CH<sub>4</sub> uptake was seen (Figure S5). This is consistent with the dense MLD coating assumption. However, after 15 cycles of MLD, approximately 20% of CH<sub>4</sub> can still be adsorbed, compared with the bare 5A. Apparently, 15 cycles of MLD did not form a continuous coating on the 5A zeolite surface, and thus the underneath zeolite pores may still be exposed. Therefore, a dense initial MLD coating is essential for reducing the effective pore size of the 5A composite sorbent. Since one precursor for the MLD, TiCl<sub>4</sub> (0.64 nm<sup>21</sup>), is much larger than the 5A zeolite pore size, MLD coatings are expected to be on the external surface of the 5A zeolite only. Therefore, the narrowest pores may locate at the interface between the porous TiO<sub>2</sub> coating and 5A zeolite or in the porous TiO<sub>2</sub> coating. We speculate the bottleneck is located at the interface, as supported by the diffusion rate measurements and MLD coating pore size calculation using N<sub>2</sub> adsorption isotherms at 77 K discussed below. Besides, it is likely that some zeolite pores have been blocked by the microporous TiO<sub>2</sub> coating on the 5A zeolite surface and thus not available for gas uptake. This may explain why the adsorbed amount for all the molecules decreased.

As concluded above, with a microporous TiO<sub>2</sub> coating formed from 60 cycles of MLD the effective pore size is expected to be smaller than butane (0.46 nm) but may have a pore size distribution that covers the sizes of CO<sub>2</sub> and CH<sub>4</sub>. To test the potential of the composite sorbent for separating other gas mixtures, we selected two important molecules, propane and propylene. Separation of propane/propylene mixtures is one of the most important and energy-consuming operation in the petrochemical industrial<sup>22, 23</sup>. Adsorption-based processes may work as an energy-efficient alternative for propane/propylene separation<sup>9</sup>. The critical diameters of propane and propylene are 0.446 and 0.431 nm, respectively<sup>24</sup>. Therefore, increased adsorption selectivity of the propylene over propane, after 60 cycles of MLD coating, is expected. Adsorption isotherms of propane and propylene on bare 5A zeolite (Figure S6), 5A with 30 and 60 cycles of MLD are shown in Figure 3a. The ideal adsorption selectivity of propylene over propane at 100 kPa increased from 1.2 for bare 5A to 3.7 and 6.0 for the composite sorbent with 30 and 60 cycles of MLD coatings. Consistent with the other gas adsorption results above, adsorbed amount of propylene decreased approximately 44%. We also measured uptake kinetics of propylene and propane on 5A zeolite (Figure S7) and 5A composite adsorbent with 30 and 60 cycles of MLD (Figure 3b). When the microporous TiO<sub>2</sub> coating thickness was doubled assuming a constant coating deposition rate, propylene adsorption kinetics was hardly affected. This suggests the major transport resistance is not in the MLD coating. Reitmeier *et al.*<sup>25</sup> found that with a microporous SiO<sub>2</sub> coating on HZSM-5, the sticking probability of several molecules changed, which changed uptake rates of these molecules. Therefore, microporous TiO<sub>2</sub> coating may influence sticking probability of propylene and propane and thus their uptake rates. However, since the ideal adsorption selectivity of propylene over propane at equilibrium increased from 1.2 to 6.0 after coating 5A with 60 cycles of MLD, we believe effective pore size reduction may play a more important role on the uptake kinetics change. The pore size of the microporous TiO<sub>2</sub> MLD coating was estimated to be ~1 nm from the N<sub>2</sub> adsorption isotherms on 5A and 5A with 60 cycles of MLD (Figure S9). Therefore, the narrowest pores may locate at the interface between the microporous TiO<sub>2</sub> coating and the 5A zeolite pores. The effective diffusivity ratio of propylene to propane for 5A zeolite and MLD coated 5A zeolite was calculated using an equation given by Kaerger and Ruthven for short time<sup>26</sup>. The effective diffusivity ratio,  $D(\text{propylene})/D(\text{propane})$ , increased drastically from ~1 for 5A, based on our measurement and the

literature result<sup>26</sup>, to ~12 and ~44 for coated 5A zeolite with 30 and 60 cycles of MLD coatings. 5A composite sorbent, therefore, shows great potential of achieving effective propylene/propane separation based on both equilibrium uptake and diffusivity differences.



**Figure 3.** (a) Adsorption isotherms of propylene (■ and ●) and propane (□ and ○) on 30 cycles (squares) and 60 cycles (circles) of TiO<sub>2</sub> MLD coated 5A zeolite at 20 °C. Solid lines are from Langmuir model fitting. (b) Adsorption uptake curves of propylene (■ and ●) and propane (□ and ○) on 30 cycles (squares) and 60 cycles (circles) of TiO<sub>2</sub> MLD coated 5A zeolite at 20 °C.  $M_t$  is the adsorbed amount at time  $t$ , and  $M_\infty$  is the adsorbed amount at equilibrium. Lines are from linear fitting.

In summary, the work reported here represents the first attempt of depositing ultrathin porous TiO<sub>2</sub> coatings by MLD on the 5A zeolite surface to modify zeolite pore sizes. The pore sizes were effectively reduced by a ~25-nm thick, microporous TiO<sub>2</sub> coating on the 5A zeolite surface. As a result, adsorption selectivities for CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> and propylene/propane were significantly increased. In addition, due to the narrowed pores, diffusivity ratio of propylene to propane increased up to 44 times. We expect this approach can be applied, in principle, to other zeolite/molecular sieves, or zeolite membranes to fine tune the pore size and increase separation selectivity.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, Fig. S1-S7. See DOI: 10.1039/c000000x/See DOI: 10.1039/c000000x/

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