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ARTICLE TYPE

Effect of pyridine modification of Ni/DOBDC on CO₂ capture under humid conditions

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The metal-organic framework Ni/DOBDC was modified with pyridine molecules to make the normally hydrophilic internal surface more hydrophobic. Experiments and molecular simulations show that the pyridine modification reduces H₂O adsorption while retaining substantial CO₂ capacity at the conditions of interest for carbon capture from flue gas.

Carbon dioxide (CO₂) is considered the primary anthropogenic greenhouse gas and the major contributor to global warming. Among the options for capturing CO₂ produced during energy generation from fossil fuels, post-combustion capture is perhaps the most feasible on a short time scale, since many of the proposed capture technologies can be retrofitted to existing power plants, which are major sources of greenhouse gas.¹ Although absorption by aqueous amine solutions is currently the leading technology for post-combustion CO₂ capture, the use of adsorption processes with appropriate porous materials may reduce the costs associated with capture and sequestration because of the relatively milder conditions.²

Metal-organic frameworks (MOFs),³⁻⁵ a rapidly growing class of porous adsorbents, have received considerable attention due to their tunable structures as well as their potential in CO₂ separation and capture. Recently, Bae and Snurr⁶ evaluated over 40 MOFs for their potential in CO₂ separation processes using five adsorbent evaluation criteria. The comparison with three commercially available adsorbents including zeolites showed that several MOFs are promising for CO₂ separations. It should be noted that a difficulty in using traditional zeolites for CO₂ capture from flue gases is the adsorption of water, which is contained in the flue gases and is strongly adsorbed in the zeolite pores.⁷ Therefore, it is important to take water into account when considering CO₂ separation and capture in MOF materials. Previously, the effect of water on the CO₂ capacity has been investigated for the MOF HKUST-1 and for the M/DOBDC MOF series (where M = Zn, Mg, Co, and Ni; DOBDC = 2,5-dihydroxybenzenedicarboxylic acid). The MOF M/DOBDC⁸ is also denoted CPO-27-M⁹ or M-MOF-74¹⁰ in the literature. These MOFs are considered promising for CO₂ capture from flue gas. Low et al.¹¹ confirmed that HKUST-1 and Zn/DOBDC show reasonable hydrothermal stabilities from

steaming tests. In a combined experimental and simulation study, Yazaydin et al.¹² showed that the CO₂ capacity for HKUST-1 can be mildly enhanced by preadsorbing water molecules on the open metal sites. Liu et al.⁷ experimentally measured the adsorption equilibrium of CO₂, H₂O vapor, and their mixtures in two MOFs (HKUST-1 and Ni/DOBDC) and two zeolites (5A and NaX) and showed that water does not inhibit CO₂ adsorption for the two MOFs as much as it does for the two zeolites. Ni/DOBDC retained considerable CO₂ capacity under moderate water loadings. On the other hand, Kizzie et al.¹³ showed recently that the other MOFs in the series, Mg/DOBDC and Zn/DOBDC, suffer significant reductions in their CO₂ capacities after hydration and regeneration. In addition, Liu et al.¹⁴ compared the hydrothermal stabilities of Ni/DOBDC and Mg/DOBDC. Their results showed that Ni/DOBDC can maintain its CO₂ capacity after steam conditioning and long-term storage, whereas Mg/DOBDC cannot. These studies suggest that Ni/DOBDC may be a promising material for CO₂ capture from flue gases, which typically contain considerable water content.

Despite outperforming other adsorbents, Ni/DOBDC showed suppressed CO₂ capacities under conditions of 40% relative humidity (RH) due to the hydrophilic nature of the open metal sites.⁷ Here, we modified Ni/DOBDC with pyridine molecules in a post-synthesis treatment to create a more hydrophobic surface within the pores. We reasoned that covering some of the hydrophilic open metal sites with hydrophobic pyridine molecules would reduce H₂O adsorption while retaining substantial CO₂ capacity at the industrially relevant conditions. In order to compare CO₂ capacities under humid conditions between the unmodified and modified Ni/DOBDC material, we measured experimental adsorption isotherms for CO₂, H₂O vapor, as well as mixtures of both. In addition, these experimental isotherms were compared with grand canonical Monte Carlo (GCMC) simulations performed on the unmodified Ni/DOBDC structure as well as on several pyridine-modified structures to understand and interpret the experimental results.

Both the BET surface area and pore volume decreased when Ni/DOBDC was modified with pyridines (see **Table S1**). These are expected results because bulky pyridine

groups

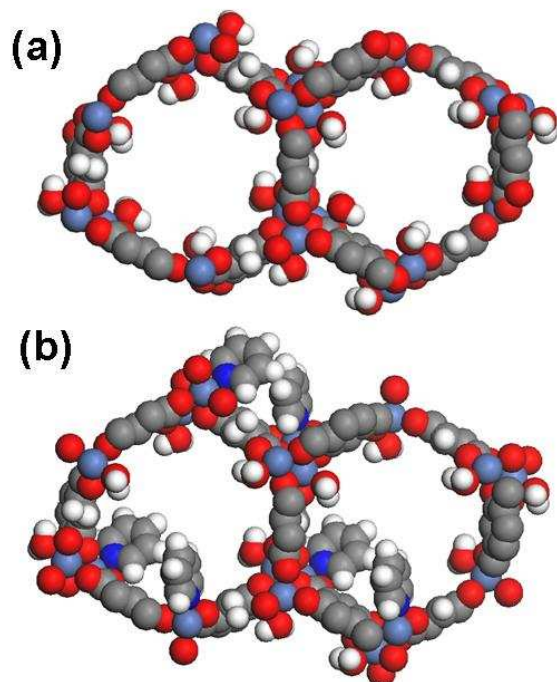


Fig. 1. Structures of (a) hy-Ni/DOBDC and (b) 33%Py-c-hy-Ni/DOBDC, where the letter c indicates the arrangement of the pyridine molecules. See Figure S1.

were added into the pores. The surface area and total pore volume of experimental Ni/DOBDC are rather smaller than those calculated for the perfect crystal structure of Ni/DOBDC (see Table S2). This discrepancy may come from partial collapse after the evacuation and/or some remaining guest solvents, such as water. However, the experimental surface area (798 m²/g) is almost the same as the value (784 m²/g) reported by Liu et al.¹⁴ Interestingly, the experimental surface area and total pore volume match very closely with the calculated values (796 m²/g) for the hydrated Ni/DOBDC (hy-Ni/DOBDC) in which H₂O molecules occupy all of the open metal sites (Fig. 1a).

Since it was not possible to obtain a crystal structure of Py-Ni/DOBDC, we computationally constructed hypothetical structures. To make the construction faster and more reproducible, we wrote a piece of software called FunctionalizeThis, which alters repeating motifs in large molecules or periodic systems in an automated way. See the Supporting Information. There was sufficient space for all the open metal sites in Ni/DOBDC to be substituted by pyridines (100%Py-Ni/DOBDC). However, when we calculated the accessible surface area of this 100%Py-Ni/DOBDC structure using a nitrogen probe, there was no accessible pore space in the structure. Since the experimental Py-Ni/DOBDC structure showed a large BET surface area (409 m²/g), we infer that only a portion of open metal sites were actually substituted by pyridines. In order to estimate the content of pyridines in Py-Ni/DOBDC, we created several hypothetical pyridine-modified structures (x%Py-hy-Ni/DOBDC; x = 16, 33, or 50) by replacing x % of coordinated water molecules in hy-

Ni/DOBDC with pyridines in several plausible arrangements (see Fig. S1). Then, we calculated the surface areas and pore

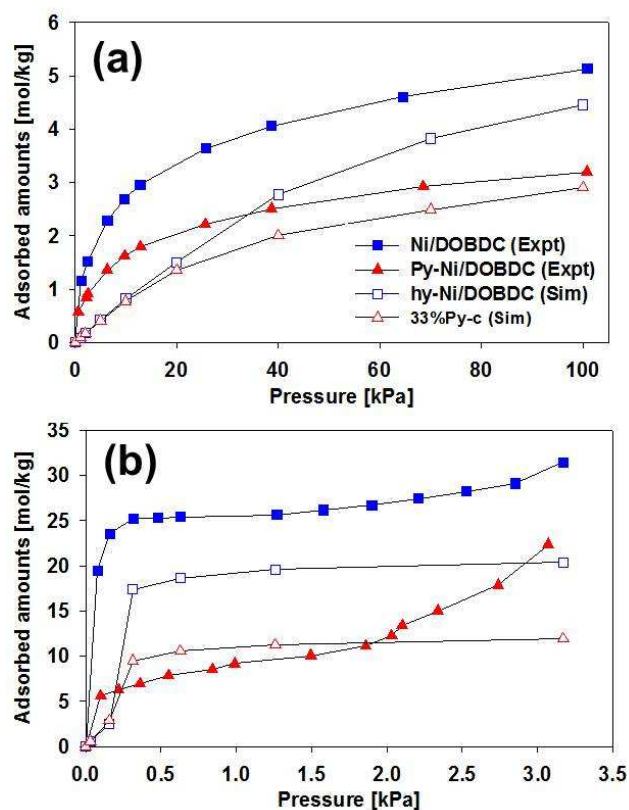


Fig. 2. Experimental and simulated isotherms in unmodified and pyridine-modified Ni/DOBDC at 298 K: (a) CO₂ and (b) H₂O.

volumes of these hypothetical pyridine-modified structures (see Table S2). We found that the experimental surface area (409 m²/g) and total pore volume (0.18 cm³/g) for Py-Ni/DOBDC match reasonably with those calculated for 33%Py-c-hy-Ni/DOBDC (433 m²/g and 0.23 cm³/g). From this, we reason that around 33% of the open metal sites in Py-Ni/DOBDC are coordinated by pyridines, possibly in a configuration resembling that of 33%Py-c-hy-Ni/DOBDC (Fig. 1b). For comparison, this corresponds to a loading of pyridine on the Ni/DOBDC after activation of 14.0 wt%, which is in reasonable agreement with the estimate of 12 ± 2 wt% obtained from experimental results (Fig. S10).

Experimental CO₂ and H₂O adsorption isotherms at 298 K are shown in Figs. 2a and 2b, respectively, for Ni/DOBDC and Py-Ni/DOBDC. As expected, the pyridine modification decreases both CO₂ and H₂O uptake due to the decreases in surface area and pore volume. Since the partial pressure of CO₂ in flue gas is typically around 10 kPa, we selected 10 kPa as the point of interest (POI) for CO₂ capture. In a previous study, Liu et al.⁷ found that Ni/DOBDC has an even higher CO₂ capacity than 5A and NaX zeolites at the POI due to very strong interactions between CO₂ and the open metal sites. In this work, the CO₂ capacity at the POI for Py-Ni/DOBDC is about 1.64 mol/kg, which is 40% less than that for Ni/DOBDC. Nevertheless, Py-Ni/DOBDC shows much less H₂O adsorption than Ni/DOBDC. Such a dramatic decrease in

H₂O uptake cannot be solely explained by the decreases in surface area and pore volume. A contributing factor is the increased hydrophobicity of Py-Ni/DOBDC due to the

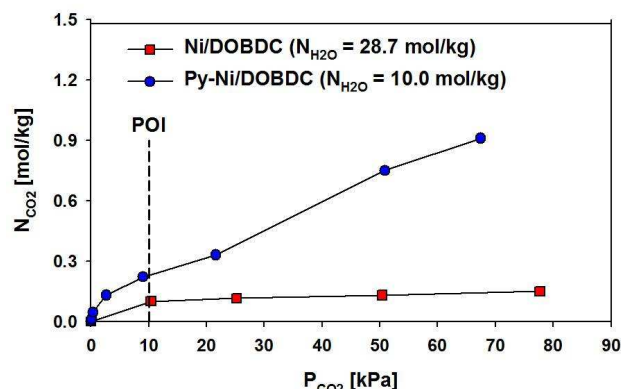


Fig. 3. Experimental CO₂ isotherms at 298 K for Ni/DOBDC and Py-Ni/DOBDC after preloading H₂O at about 45% RH.

presence of pyridine groups. Therefore, although Py-Ni/DOBDC shows lower CO₂ uptake than Ni/DOBDC, it is less negatively impacted by water.

To explain these experimental results, we performed GCMC simulations for hy-Ni/DOBDC and 33%Py-c-hy-Ni/DOBDC. Interestingly, the calculated isotherms for CO₂ and H₂O adsorption in hy-Ni/DOBDC and 33%Py-c-hy-Ni/DOBDC reasonably predict the experimental isotherms for Ni/DOBDC and Py-Ni/DOBDC, although they underestimate them at low pressures (Figs. 2a and 2b). The underestimation at low pressures may come from the presence of some open metal sites in the experimental samples.

We also calculated the isosteric heat (Q_{st}) for CO₂ and H₂O adsorption in hy-Ni/DOBDC, 16%Py-hy-Ni/DOBDC, and 33% Py-c-hy-Ni/DOBDC from GCMC simulations. The Q_{st} values at low loadings clearly show correlations with the amount of pyridine in the structure (see Fig. S7). As the pyridine content increases, the CO₂ Q_{st} at low loadings increases but the H₂O Q_{st} at low loadings decreases. Also, snapshots of H₂O adsorption in pyridine-modified structures clearly show that H₂O molecules initially adsorb near the coordinated water located away from pyridines (see Fig. S8). These results support the hypothesis that the dramatic decrease in H₂O uptake for the Py-Ni/DOBDC sample is a result of the increased hydrophobicity of Py-Ni/DOBDC due to the pyridine molecules in the pores.

In order to understand whether pyridine modification can further reduce the water effect on CO₂ adsorption in Ni/DOBDC, we measured the CO₂ isotherms for Py-Ni/DOBDC with different H₂O loadings using the experimental technique previously reported.⁷ The CO₂ capacity at the POI decreases with increasing H₂O loading (see Fig. S9), which is similar to the previous results for Ni/DOBDC.⁷ Nevertheless, the Py-Ni/DOBDC sample retained a considerable CO₂ capacity (1.2 mol/kg) at the POI, even with a 1.0 mol/kg H₂O loading at 298 K. To see the effect of water on CO₂ adsorption more clearly, we measured CO₂ isotherms at 298 K for Ni/DOBDC and Py-Ni/DOBDC after preloading H₂O at about 45% RH conditions. Fig. 3

clearly shows that pyridine modification improves the CO₂ uptakes at 45% RH. We also calculated the selectivity of H₂O over CO₂ at 10 kPa (POI) and 298 K for Ni/DOBDC and Py-Ni/DOBDC using the experimental CO₂ isotherms obtained after preloading H₂O at 45% RH (see Table S3). The calculated H₂O/CO₂ selectivities for Ni/DOBDC and Py-Ni/DOBDC are 1844 and 308, respectively. This indicates that pyridine modification brought a dramatic decrease in H₂O/CO₂ selectivity due to the suppression of H₂O adsorption from the presence of hydrophobic pyridine groups.

From a combined experimental and simulation study, we found that pyridine modification of a MOF can reduce H₂O adsorption while retaining considerable CO₂ capacity at conditions of interest for flue gas separation. This indicates that post-synthesis modification of MOFs by coordinating hydrophobic ligands to unsaturated metal sites may be a powerful method to generate new sorbents for gas separation under humid conditions.

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5