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Synthesis of nanoporous 1,2,4-oxadiazole networks with high CO_2 capture capacity†

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Developing an adsorbent to mitigate carbon dioxide without large energy penalty is highly desired. Here, we present a silylation synthetic route to form a processable and otherwise impossible porous 1,2,4-oxadiazole network, which achieves 2 mmol g^{-1} of CO_2 capacity owing to a nitrogen-rich structure. This network shows high CO_2–N_2 selectivity, thermal stability up to 450 °C, and low heat of adsorption (26.4 kJ mol^{-1}), facilitating easy regeneration.

The immediate crisis of climate change and greenhouse effect is evident and the major contributing reason is the rising CO_2 levels in the atmosphere. CO_2 has the lowest global warming potential compared to other greenhouse gases (GHGs); however, the volume of the emissions makes it the GHG with the most impact.[1] Naturally, CO_2 is captured by oceans or when used as a carbon source in photosynthesis by plants. However, anthropogenic CO_2 emissions are too large to be contained by nature. Since gases are spread globally by circulation, mitigation of CO_2 has become a global task. Hence, research groups around the world are working to capture CO_2 by various ways such as liquid absorbents, solid adsorbents, and membranes. Among those, solid adsorbents are the most popular thanks to their easy handling and regeneration. Metal–organic frameworks (MOFs),[2] covalent organic frameworks (COFs),[3] covalent triazine-based frameworks (CTFs),[4] porous polymer frameworks (PPFs),[5] Schiff base networks (SNWs),[6] porous aromatic frameworks (PAFs),[7] ordered mesoporous carbons (OMCs)[8] and others have been shown to have sufficient surface area and capacity for CO_2. In order to increase uptake capacities, researchers are also using post-functionalization of the original adsorbent.[9] However, gas uptake ability has to be coupled with high selectivity to provide a sorbent good enough to replace monoethanolamine (MEA), which has been used for more than 60 years despite its shortcomings. Among the solid adsorbents, amorphous porous polymers are especially promising because of their robust structure from covalent bonding and their ability to adsorb by both chemical and physical mechanisms. Recently, using triazine group, we have shown that covalent organic polymers (COPs) have enhanced gas uptake abilities,[10] and with azo-linkers achieve high CO_2–N_2 selectivity.[11] Learning from our previous research we could now design high-performance adsorbents by using the basic nitrogen atoms in a porous polymer[12] and enhanced CO_2 binding from heterocycles. Here, we designed a new COP with an oxadiazole heterocycle, which contains two nitrogen atoms and one oxygen atom, as a solid adsorbent. Oxadiazoles are well known with their high electron affinity and have been studied for 80 years for medical[13] and pesticide uses.[14] The major synthetic method to form a molecular oxadiazole heterocycle is heating reagents using toxic Lewis acid catalysts.[15] To the best of our knowledge, there are no reports of porous and network polymers of 1,2,4-oxadiazoles. We believe this is mainly because of the competition of reaction sites during polymerization and ring closure (Scheme 1). This led us to an alternative synthetic method to form oxadiazoles without any rotational freedom, where silylation directs the coupling to the more reactive –N terminal. The stable intermediate also permits film making because of its solubility in solvents. The resulting oxadiazole covalent organic polymer (Oz-COP) has many heteroatoms, polarizability, and basicity for enhanced CO_2 uptake with high selectivity[16] in addition to high thermal stability.[17,18]

When developing an adsorbent for carbon dioxide capture, one has to consider not only uptake capacity but also selectivity for CO_2. For example, activated carbons, which are commonly used in the gas processing industry for having high surface areas, cannot be used for CO_2 capture because of their low selectivity. Their pores get filled with mixed gas, leading to no advantage over direct compression of the flue gas. In order to achieve both capacity and selectivity, we chose oxadiazole structures, since they present both porosity and chemistry.

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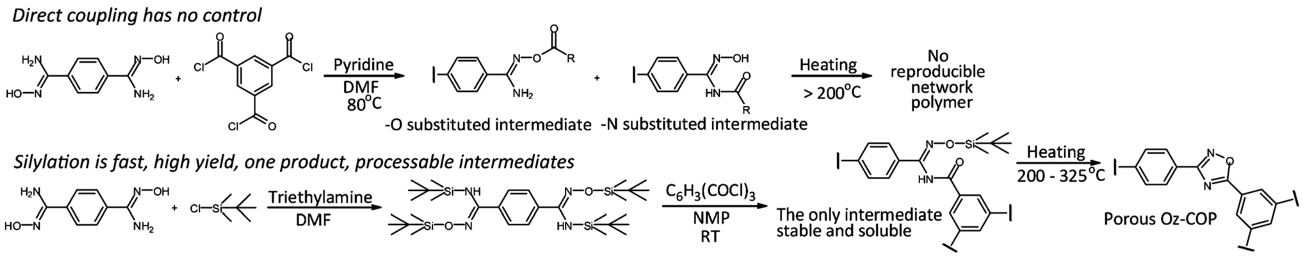

Scheme 1 (top) Failed synthesis of oxadiazole-COP (Oz-COP) by a conventional route, without silylation. (bottom) Synthesis of Oz-COP in three steps: (i) silylation of the monomer, (ii) pre-oxadiazole polymer formation with protected hydroxyl group, and (iii) ring closure by annealing.

In a typical run (Scheme 1), terephthalamidoxime was silylated with *tert*-butyldimethylsilyl chloride in DMF before reacting with trimesoyl chloride into a soluble pre-polymer. When the pre-polymer intermediate is calcined (Scheme 1), solid state NMR peaks for amide groups, 175.1 (C═O) and 157.8, 157.2 (C═N), were shifted to the oxadiazole locations (Fig. 1) and those at 31.7 (CH_3, Si-methyl) disappeared. Similarly, from the FT-IR spectra, the peak at 1635 (C═O) shifted to 900 and 1510 (oxadiazole) and methyl band at 1217 disappeared when the heating reaction completed (Fig. S2, ESI†).

Surface area of the Oz-COP was measured by using the BET theory after the formation of the oxadiazole (Fig. S4, ESI†). Due to the low uptake of the N_2 probe (Fig. S7, ESI†) we used the CO_2 isotherm at 273 K at low pressure below 0.15 bar. A BET surface area of 107.2 m^2 g^{-1} was found. The pore size distribution that is calculated by density functional theory shows distributions around 5 to 8.5 Å, and 7 to 8.5 Å, all within the micropore range. N_2 probe, on the other hand, is unable to penetrate through micropores, conveniently showing mesoporous and macroporous morphology (Fig. S7, ESI†), an observation that can also be noted from the SEM images in Fig. S8 of ESI.†

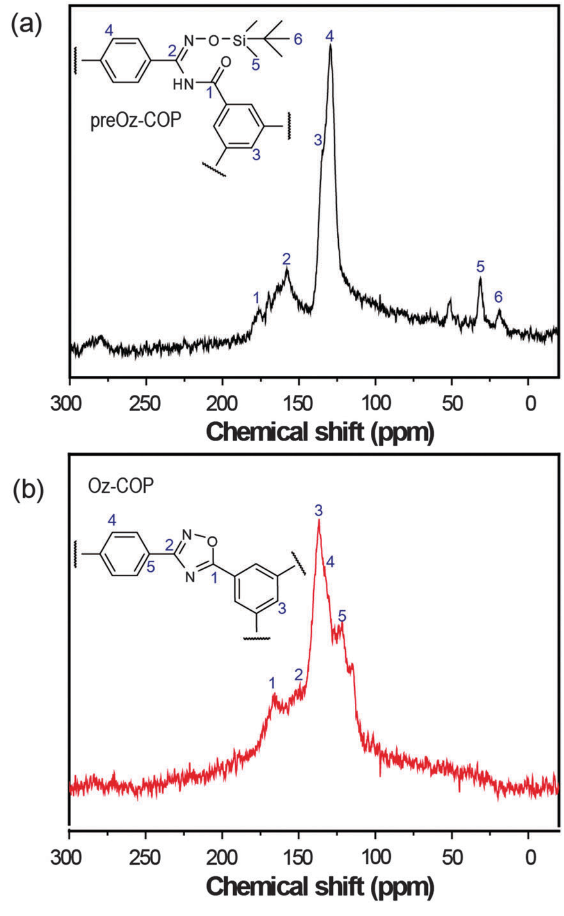

Fig. 1 Solid state CP/MAS ^{13}C NMR of (a) pre-polymer and (b) oxadiazole-COP. Amide group signals at 175.1 (C═O), 157.8, 157.2 (C═N) were transformed to oxadiazole peaks: 164.9 (oxadiazole ring), 151.2 (C═N, oxadiazole ring), and methyl signal from pre-polymer at 31.7 (CH_3, Si-methyl) completely disappeared.

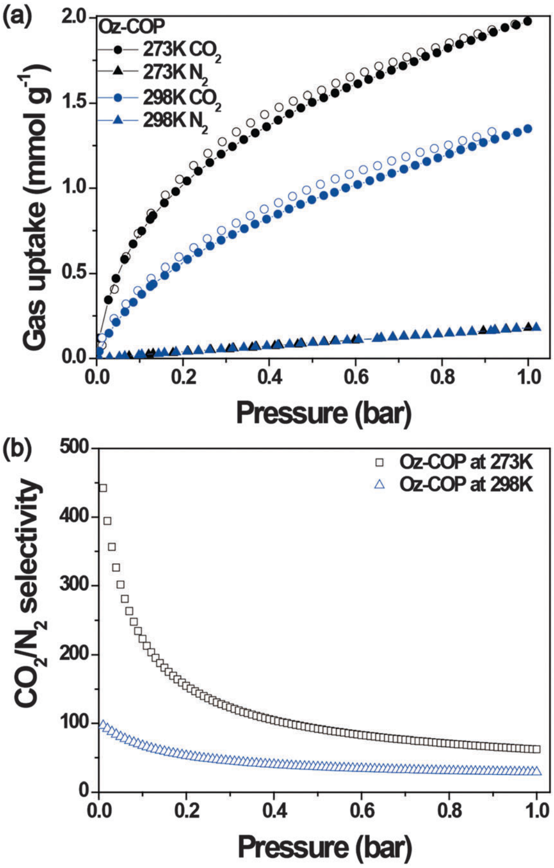

Fig. 2 (a) Oxadiazole-COP CO_2 and N_2 adsorption–desorption isotherms at 273 K and 298 K. Filled and empty symbols represent adsorption and desorption. (b) Selectivity in nitrogen and carbon dioxide mixture gas. The mixture ratio is $N_2 : CO_2 = 0.85 : 0.15$ and it was calculated by IAST.

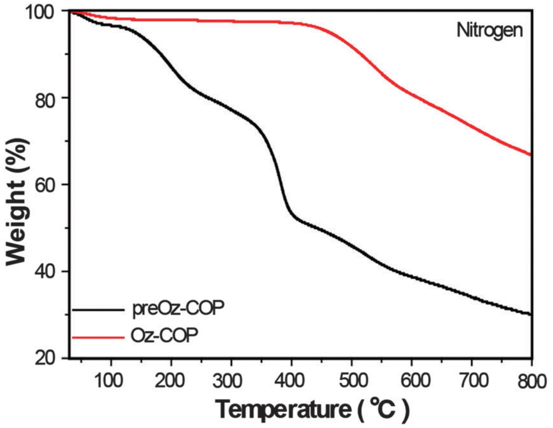

Fig. 3 Thermogravimetric analysis of preOz-COP and Oz-COP. Temperature was increased from 30 °C to 800 °C in N_2 atmosphere. Temperature increasing rate was 10 °C min^{-1}.

We believe that Oz-COP adsorbs CO_2 efficiently with a synergetic effect from its pores so that it captures about 2 mmol g^{-1} of CO_2 (Fig. 2a), even though its surface area is smaller than that of other crystalline counterparts. Also, Oz-COP selectively captures 61 times more CO_2 than N_2 in a mixed gas ($N_2 : CO_2 = 0.85 : 0.15$) (Fig. 2b) due to the interactions between CO_2 and the heteroatoms (two N and one O) in oxadiazole.[19]

We looked, next, at the isosteric heat (Q_{st}) of CO_2 adsorption as a parameter for the affinity between our porous polymer and CO_2. As is well known, Q_{st} can be used as an indicator of favourable binding and as a minimum value for the energy required to release CO_2 in a regeneration step. We calculated Q_{st} by the Van't Hoff equation and found it to be in the range of 26.4–31.7 kJ mol^{-1} (Fig. S5 in ESI†). These values are similar to those of many physisorptive solids.[11]

Oz-COP is thermally very stable after forming the oxadiazole network structure. PreOz-COP decomposes below 150 °C, whereas Oz-COP was stable until 450 °C (Fig. 3), far above the accepted minimum of thermal stability (at least 200 °C) for a CO_2 cyclic operation.[20] The pre-polymer preOz-COP can be cast to form a thin and transparent red-brown film (Fig. S6 in ESI†).[21,22]

In summary, we used silylated intermediates to make the first network structure of 1,2,4-oxadiazoles. The method prevented rotational dislocations, yielding a reproducible procedure that afforded a nanoporous oxadiazole-based covalent organic polymer (Oz-COP). The heteroatom-rich Oz-COP captured 2 mmol g^{-1} (273 K and 1 bar) of CO_2 and had a CO_2–N_2 selectivity of 61 with low regeneration requirements. Oz-COP showed enhanced thermal stability up to 450 °C. The pre-polymer was found to have an unprecedented solubility that allows it to be used to form a porous polymer film. The synthetic methodology we developed as reported here can be applied to make new porous polymers of other heterocycles, with the prospect of using them in the CO_2-capture industry for replacing the standard amine (MEA) solutions or using them as membranes to separate CO_2 from feed gas mixtures.

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