Sorption of nitrogen oxides in a nonporous crystal

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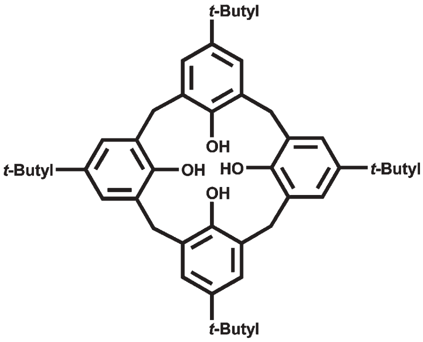
The uptake of various nitrogen oxides was studied with the well known nonporous *p-tert*-butylcalix[4]arene under ambient conditions.

Emissions of nitrogen oxides (NOx) are a significant problem for many chemical processers and electric utility operators. Federal regulations in the USA, such as the Clean Air Act Amendments and various state and local regulations, require industry to control and reduce NOx emissions for both new and existing sources. Nitrogen oxides are released from internal combustion engines (50%), power plants (20%), and other point sources (30%). There is growing recognition of a need to stabilize global NOx atmospheric concentration to avoid climate change,[1] similar to what is now acknowledged for CO_2. NOx's as a class are the third most important gases that contribute to global warming, to the formation of ground level ozone, and to acid aerosols. The widespread use of nitrogen-containing fertilizers and the burning of fossil fuels are the main contributors to NOx emission. The most common method employed in automobiles to capture NOx's involves passing the exhaust through a catalytic converter. This is an expensive and rather ineffective solution to the problem. Methods for gas sorption based on chemisorption on oxide surfaces and physical adsorption on porous carbons, zeolites, metal–organic frameworks, and nonporous materials are focused mainly on hydrogen and carbon dioxide capture.[2] Capture of NOx's has not been reported. Herein we describe the sorption of NOx gases on a well-known low density polymorph of nonporous *p-tert*-butylcalix[4]arene, **1** (Scheme 1).[3]



Scheme 1

In the present context, calix[4]arenes have attracted considerable interest and exhibit unexpected behavior in solution and in the solid state.[4] For example, Kochi and co-workers[5] have demonstrated that the exposure of a dichloromethane solution of 1,3-alternate *tert*-butyl-tetramethoxycalix[4]arene to gaseous nitric oxide results in a dark purple solution, indicating the encapsulation of nitric oxide (NO). Initially, the *tert*-butyl-tetramethoxycalix[4]-arene was oxidized and complexed with nitric oxide, leading to the formation of a calixarene–nitrosonium species, which in turn was stabilised by strong charge transfer interactions between the NO^+ and the π face of the calixarene (the $NO^+\cdots\pi$ face distance of 2.4 Å is less than the van der Waals contact, 3.2 Å). Similarly, Rudkevich *et al.*[6] have shown that the addition of *tert*-butyl nitrite to the solution of tetra-*O*-alkylated calix[4]arenes or calix nanotubes in the presence of $SnCl_4$ leads to the formation of calixarene–NO^+ and calixarene–NO_2^+ complexes. The formation of these adducts can be achieved by dissolving the host (calixarene) and guest (NOx) in the presence of a Lewis acid. From a storage and separation point of view, the host has to retain its void space in the solid state and the gas uptake and release have to be fully reversible under ambient conditions.

In order to obtain the guest-free form of *p-tert*-butylcalix[4]arene, we sublimed sample **1** under reduced pressure at 280 °C. As previously described, the single crystal X-ray structure shows that the calixarene molecules in this polymorph of **1** are arranged in a bilayer fashion, resulting in the formation of skewed capsules with an estimated free volume of 235 $Å^3$ (Fig. 1). The nonporous, low density form of **1** absorbs N_2, O_2, CO, CO_2, and CH_4 under ambient conditions.[7] The same polymorph can also be used to separate hydrogen from a mixture with CO_2.[8] Very recently we have shown that the low density polymorph of **1** stores acetylene at 90 times the compression limit for the safe storage of pure acetylene (the density of the absorbed acetylene at STP is 0.18 g cm^{-3}).[9] It is also known that low density **1** undergoes a single-crystal-to-single-crystal phase transformation upon immersion of crystals in liquid vinyl bromide.[3] In this study, we extended our sorption studies on low density **1** to the storage of various forms of NOx at STP.

The sorption isotherms were monitored volumetrically on low density **1** using the same amount of sample (650 mg) for each guest. A sample of **1** was placed in the sample chamber (10.5 cm^3) and evacuated for 2 h to remove any trace amount of gas trapped in the host lattice. Fig. 2 and Fig. 3 represent the absorption isotherms of low density **1** in which nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2) were introduced in separate experiments at initial pressures of 1 atm. Equilibrium was established after 3 h for N_2O and NO, whereas for NO_2 equilibrium was attained after only 20 min. Under these conditions, low density **1** appears to discriminate among the

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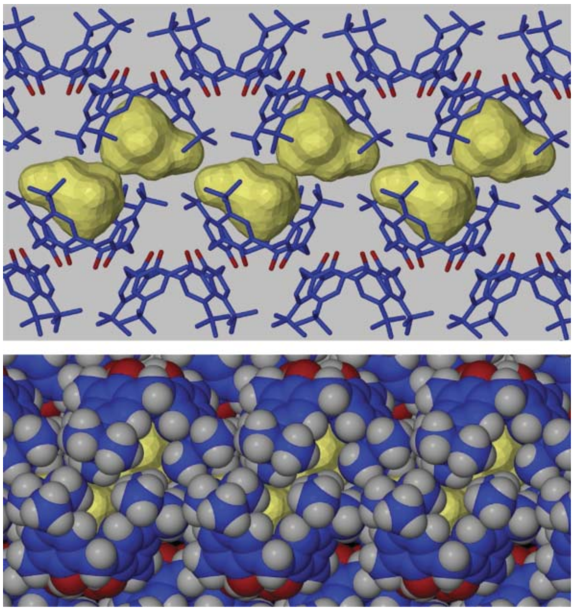

Fig. 1 Bilayer packing of *p-tert*-butylcalix[4]arene molecules in **1**.[11] Stick model (top, hydrogen atoms are removed for clarity) and space filling model (bottom). The 235 Å^3 of void space are depicted (in yellow) as Connolly molecular surfaces.[12]

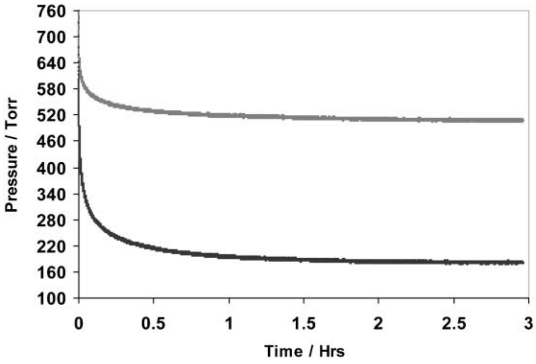

Fig. 2 Isotherms of nitrous oxide (black) and nitric oxide (gray) at STP.

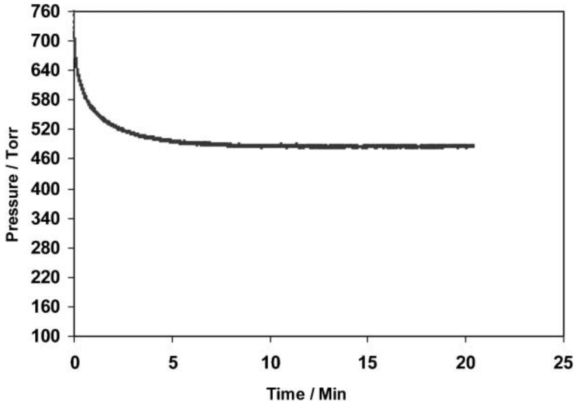

Fig. 3 Sorption curve for nitrogen dioxide at room temperature.

various NOx's both in rate of uptake and in amount absorbed. It is clear from a comparision of Fig. 2 and Fig. 3 that N_2O is absorbed to a significantly greater extent than NO and NO_2, but NO_2 is absorbed far more rapidly than the other two guests. The calculated molar ratios of NOx to calixarene at the equilibrium pressure are 0.32 : 1 (P_{equi} = 0.24 atm of N_2O), 0.13 : 1 (P_{equi} = 0.67 atm of NO) and 0.15 : 1 (P_{equi} = 0.64 atm of NO_2). This means that 64% of the dimeric capsules are filled with N_2O at 0.76 atm, 26% are filled for NO at 0.24 atm, and 30% are filled for NO_2 at 0.35 atm. An occupancy study of N_2O at STP demonstrates that the uptake of nitrous oxide is approximately 3.6% by weight. The seemingly nonporous crystals of low density **1** absorb 0.45 mol of N_2O per mol of host, indicating nearly complete filling of the available cavities in the crystal structure. The absorption and desorption isotherms for N_2O show a type I relationship between the equilibrium pressure and percentage of calixarene lattice voids occupied by the gas. The occupancy of nitrous oxide is close to 100% at 1.4 atm pressure. As shown in Fig. 4, the absorption and desorption processes for N_2O are fast, and no hysteresis is observed. This behavior is very similar to that of CO_2, as previously reported.[7]

Thus far, it has not been possible to obtain single crystal X-ray diffraction data on crystals of **1** loaded with one of the NOx guests. However, the crystals of low density **1** become pink (N_2O) and pale yellow (NO and NO_2) after the absorption experiments. This color change indicates that a charge transfer complex has formed between the host **1** and the guest NOx. It therefore seems likely that the NOx gases may be detected in the presence of other gases by using low density **1** as a sorbent.

Unlike known porous materials that absorb and desorb gas molecules, no channels may be observed in the single crystal X-ray structure of the low density polymorph of **1**. However, as we reveal in this communication, and as we have noted previously, gas molecules diffuse through the seemingly nonporous lattice of low density **1** without a structural transformation. The upper rim *tert*-butyl groups of the calixarenes appear to play a critical role in the absorption/desorption process. In the solid-state crystal structure of low density **1** at room temperature, the upper rim *tert*-butyl groups are disordered over at least two positions. At 120 K, only one of the *tert*-butyl groups is disordered. We propose that the mechanism by which gases diffuse into the seemingly nonporous lattice of low density **1** involves the cooperative rotation of the *tert*-butyl groups to provide a turnstile for the admission of gases into the cavities of low density **1**. We have now measured the surface

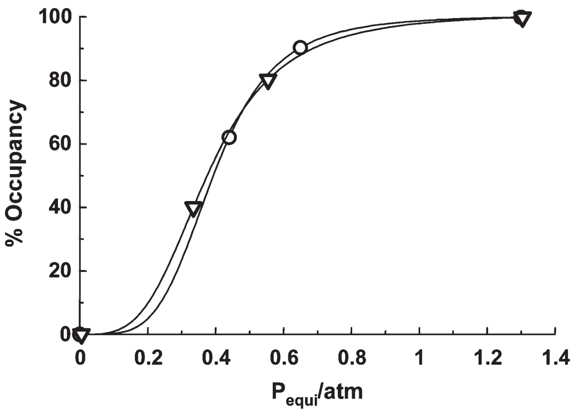

Fig. 4 Occupancy study of nitrous oxide at 298 K shows complete filling of pores at 1.4 atm. Circles indicate sorption and triangles indicate desorption. No hysteresis was observed.

area of low density **1** using the BET method at liquid nitrogen temperature and 1 atm pressure. The observed surface area is 15 m^2 g^{-1}. Thus, the low density polymorph of **1** is nonporous and the cavities are not accessible to N_2 at 77 K.[10]

In conclusion, we have observed sorptive behavior of low density **1** for NOx's. This sorption is quite different for the NOx gases, both in level of sorption and time for establishment of equilibrium. These measurements indicate potential for this family of organic solid-state materials to be used for both entrapment and detection of NOx compounds. Important unresolved issues are the selectivity for NOx at ppm levels and color center development in multicomponent gas mixtures as would be present in industrial sources. We are continuing to explore the properties of these crystalline organic materials to guide practical applications for NOx control technology.

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