Simultaneous and cooperative gas storage and gas production using bifunctional zeolites†

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Nitric oxide can be stored in and produced from zeolites in a simultaneous and cooperative process

The interaction of nitrogen oxides with zeolites is of great interest in catalytic and adsorption technologies for environmental remediation[1–3] and for medical gas-storage applications.[4,5] There is a wide range of knowledge about this interaction from thousands of publications. However, the research has almost exclusively concentrated on the destruction of nitric oxide (NO) using zeolites, particularly in relation to selective catalytic reduction deNO$_x$ processes.[6–8] There are no examples of zeolites being used to produce NO. Here we demonstrate that copper-containing zeolites with the X (FAU) and ZSM-5 (MFI) framework structures can be used both to store NO and to produce NO from nitrite ions (NO_2^-), facilitating the delivery of the gas for extended periods of time that are significantly longer than possible with gas storage alone and increasing the deliverable capacity by an order of magnitude. That zeolites can be used to produce NO goes completely against their traditional uses as deNO$_x$ catalysts. Furthermore, we also show that these two mechanisms, the release of stored gas and the chemical production of gas, occur simultaneously and, most surprisingly, that there is a cooperative effect in that the amount and lifetime of gas produced from NO_2^- is considerably enhanced if the zeolite is pre-adsorbed with stored NO. Such cooperative effects between gas storage and gas production are unprecedented.

Gas-delivery technologies[9] are of increasing importance in many areas of science, with emerging applications that include the storage of hydrogen[10] and methane[11] as energy carriers and the delivery of nitric oxide (NO) for medical therapies.[12] A common method of achieving such delivery is to store the gas inside a storage material.[9,13] One of the drawbacks of this approach is that the reservoir of stored gas in a material is finite and is inevitably depleted as it is released for use. An alternative method of delivering an active gas is to produce the gas chemically from a suitable substrate.[14,15] Combining these two methods has the potential to significantly increase the capacity and lifetime of a gas-delivery material beyond what is possible with gas storage alone.

Copper-containing zeolites make some of the most active deNO$_x$ catalysts known, and have been extensively studied over many years.[6–8] However, Cu(I) species are also active for the transformation of NO_2^- to NO. This occurs in bacterial nitrite reductase enzymes,[16] and in solution state[17,18] and polymer-bound models for this reaction.[15] However, the NO_2^- to NO reaction has never been demonstrated in zeolites. Extra-framework copper(II) ions are easily incorporated into zeolites, such as those with the zeolite-X (FAU) or ZSM-5 (MFI) framework types (Fig. 1), by standard ion-exchange procedures (See ESI†). The as-synthesised Cu(II)-containing materials (*i.e.* directly after ion exchange) are not active for the production of NO from NO_2^-. This control experiment proves that the environment (*e.g.* the buffer) does not reduce the copper ions in the zeolite. In addition, the addition of nitrites to a solution containing only aqueous cupric cations did not induce any NO release, which illustrates the critical role of cuprous cations. However, thermal activation of copper-containing zeolites leads to the formation of Cu(I) species in the zeolites—the so called 'self reduction' reaction[19] (see ESI†). Self-reduction involves several different steps as the zeolites are heated, including a complex reorganization of the copper over the cation sites as the water of hydration is eliminated, followed by reduction from Cu(II) to Cu(I) at higher temperatures and structural rearrangement to maintain neutrality.[19]

Addition of NO_2^- solution to activated (dehydrated) copper-exchanged zeolite-X (framework Si/Al ratio = 1, copper exchange = 43%, 10.3 wt% copper determined by ICP) or to copper-exchanged zeolite-X (framework Si/Al ratio = 60, copper exchange = 92%, 3.2 wt% of copper) leads to a significant production of NO (Fig. 2a). The amount of NO

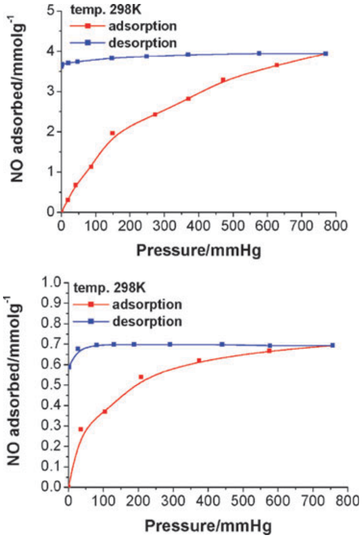

Fig. 1 The adsorption/desorption isotherms for NO on the Cu-zeolite-X (top) and Cu-ZSM-5 (bottom) samples used in this study.

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produced scales well with the amount of copper in the samples (4.71×10^{-5} mol NO g^{-1} in 300 min for Cu-X *versus* 1.28×10^{-5} mol NO g^{-1} in 300 min for Cu-ZSM-5). That the dehydrated zeolites are active is further evidence that the mechanism requires Cu(I). However, the NO production from thermally activated samples decreases quickly so that the flux of NO is reduced to zero after only a few hours (Fig. 2a). There is no added reductant in the reaction and so no way of re-reducing Cu(II) to Cu(I), therefore this reaction is stoichiometric.

Water is known to be important in the deactivation of copper zeolite-based deNO$_x$ catalysts by favouring the re-oxidation of Cu(I) species to Cu(II)[19] and explains why the activity of the dehydrated sample is reduced so quickly. Activated copper zeolites are therefore of limited value for the production of NO in the presence of water.

In some ways, the fact that zeolites can be used to produce NO at all is a surprise, given their extensive deNO$_x$ chemistry. However, even more surprising is the effect of pre-adsorbing and storing NO on the gas production reaction. Zeolites, including copper-exchanged ones, can also be used as NO storing materials that release NO on exposure to moisture. Such materials have been used to remove NO from gas streams in pressure swing adsorption applications[20] and as a source of NO in biologically relevant amounts.[5] Exposure of activated copper-exchanged zeolite-X to gaseous NO leads to a material that 'irreversibly' adsorbs ~3.6 mmol of NO per g of zeolite (the term irreversibly stems from pressure swing adsorption terminology and means that NO is not released on reduction of the gas pressure). Cu-ZSM-5 only irreversibly adsorbs ~0.6 mmol NO per g of zeolite because it has a much higher framework Si/Al ratio (60) and therefore considerably fewer copper ions are needed to balance the framework charge. Adsorption/desorption isotherms for NO on both copper-exchanged zeolites are shown in Fig. 1.

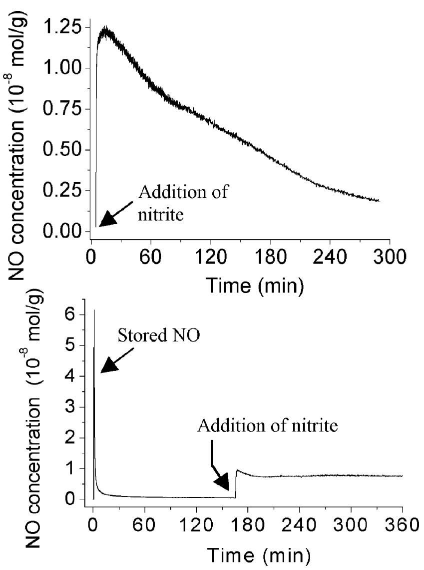

Fig. 2 The nitrite to NO reaction over zeolites. The top panel shows the NO production, on addition of nitrite (total volume 2.6 mL, pH 7.4, $[NO_2^-]$ = 470 μM, 1.60×10^{-3} g of Cu FAU X *i.e.* 1.65×10^{-4} g of Cu), to an activated sample of Cu-exchanged zeolite X (no pre-loaded NO). The bottom panel illustrates the effect of pre-adsorbing the same zeolite with NO. On exposure of the NO-loaded zeolite to water some of the NO is released while on addition of nitrite solution (total volume 2.6 mL, pH 7.4, $[NO_2^-]$ = 470 μM, 2×10^{-3} g of Cu FAU X *i.e.* 2.06×10^{-4} g of Cu) the lifetime of the NO production is extended significantly when compared to the experiment depicted in the top panel.

Release of the stored gas is triggered by contact with water[4] (Fig. 2) with a relatively short-lived burst, followed by a steadily decreasing release of a small amount of NO that lasts for about 100 minutes. For both Cu-ZSM-5 and Cu-X only a small proportion of the stored NO is releasable on contact with water at ambient temperature meaning that there is significant gas inside the zeolites that is irreversibly adsorbed even in the presence of water. A similar situation is also seen on NO adsorption on some metal organic framework materials.[21,22]

Addition of NO_2^- to the solution in contact with the NO-loaded zeolites immediately produces a large amount of NO. For example, adding 25 μL of 0.05 M NO_2^- to a simulated physiological solution (total volume 2.6 mL, pH 7.4, $[NO_2^-]$ = 470 μM) in contact with NO-loaded Cu-X leads to an average NO flux during the experiment time scale of ~0.2 nmol per min per mg of zeolite that lasts ten times longer than the release of any stored NO. Importantly, unlike the activated samples containing no stored gas, the NO production does not decrease quickly but is relatively constant for about 10 hours, lasting well beyond the time when the production from NO-free zeolites has reduced to zero. In our batch experiments, after 10 hours the NO production slowly decreases until it reaches near zero levels after approximately 20 hours. As well as increasing the lifetime by an order of magnitude, the NO delivery capacity of the material is also increased approximately ten-fold. Cu-ZSM-5 shows similar properties. The effect is not due to copper leaching from the zeolites, as removal of the solid by centrifugation completely inhibits the NO production, even when a reducing agent is added to the solution to reform Cu(I) from any copper that has been oxidised to Cu(II).

Fig. 3 shows that the release of stored NO and the production of NO occur simultaneously. Exposure of the NO loaded Cu zeolite-X to a buffered solution leads to delivery of NO from the zeolite as indicated. Addition of an aliquot of NO_2^- (100 μl, 2.5×10^{-4} M; final concentration, 9.6 μM) to the solution in contact with the zeolite produces measurable NO over and above that already being delivered from the stored reservoir of NO. Subsequent addition of similar quantities of the same nitrite solution produces broadly the same increases in NO flux at each addition, taking into account the change in overall concentration caused by adding new liquid to the buffer. Further additions of more concentrated nitrite solution (100 μl, 5×10^{-4} M; final NO_2^- concentration, 19.2 μM) induce approximately twice the response in the NO analyzer, indicating that the concentration-response is broadly proportional at these concentrations of substrate. The first aliquot addition, highlighted in Fig. 3, shows that the stored NO is being delivered at the same time as it is being produced from nitrite. Such simultaneous stored-gas release and gas production is previously unknown as far as we are aware.

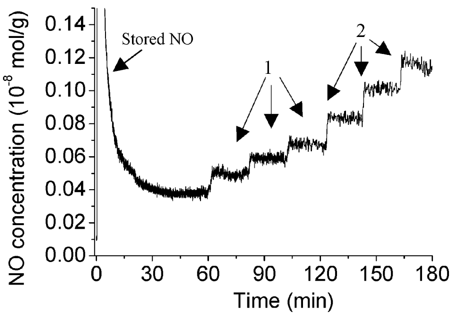

Fig. 3 The dose–response curve for addition of nitrite to NO-loaded Cu zeolite-X (2.2×10^{-3} g of Cu FAU X *i.e.* 2.27×10^{-4} g of Cu). Addition of an aliquot of nitrite (100 μl, 2.5×10^{-4} M) to the 2.6 mL buffer solution in contact with the zeolite produces measurable NO over and above that already being delivered from the stored reservoir of NO. Further additions of the same amount of nitrite (marked 1 in the figure) produce similar increases in NO production. Subsequent consecutive additions of aliquots of twice the concentration of nitrite (marked 2, 100 μL, 5×10^{-4} M) lead to approximately double the increase in NO production.

The redox behaviour of copper when contained in zeolites is extremely complex. Diffraction,[23] IR,[19] Exafs[19] and many other techniques[7,8] reveal large changes in extra-framework siting and coordination and even changes to the framework to accommodate charge-balance issues on alteration of the copper oxidation state. The rapid deactivation of the non-NO loaded zeolites is undoubtedly due to fast reoxidation of Cu(I) to inactive Cu(II). Fast reoxidation of this kind requires the presence of both water and dioxygen. Dioxygen on its own is not sufficient.[19] For the lifetime of the nitrite to NO reaction to be extended by such a long time must mean that oxidation of Cu(I) to Cu(II) in the NO-loaded zeolite is inhibited by the presence of the pre-loaded NO (*i.e.* in NO-pre-loaded samples it is clear that this reoxidation is much slower). It is likely that the irreversibly stored NO (*i.e.* that which is not released on contact with water) slows oxidation of the Cu(I) by limiting the interaction with water, enhancing the lifetime of the Cu(I) species and, by extension, the lifetime of the NO delivery.

The cooperative effect of the stored NO on the NO generation process is an exciting example of how gas delivery can be increased and extended well beyond that possible with gas-storage materials alone. This may be particularly important in cases where it is difficult to recharge or replace a storage material, for example when the NO-delivery material is part of a coating on medical devices that remain in contact with blood for extended periods (*e.g.* in dwelling catheters, stents, combined glucose monitors/insulin pumps) and are hence prone to both infection and thrombosis.[24] A further exciting possibility is the use of naturally occurring reservoirs of substrate (nitrite) to recharge NO-releasing materials so that the anti-bacterial, anti-thrombosis and anti-mitogenic properties of NO are extended at least an order of magnitude beyond those possible with gas-storage materials alone. The very slow leaching of copper from zeolites means that, at least for applications that only require the device to be in the body for several hours the toxicology of copper may not be disadvantageous, as is likely for the bare metal. There are also potential *in vitro* applications (*e.g.* anti-bacterial materials) where any potential toxicity of copper is much less of an issue.

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