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Amidoximes: promising candidates for CO_2 capture†

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Monoethanolamine (MEA) dominates power plant carbon dioxide (CO_2) scrubbing processes, though with major disadvantages such as a 8–35% energy penalty. Here we report that structurally comparable amidoximes are promising CO_2 capture agents based on RIMP2 electronic structure calculations. This was experimentally verified by the synthesis and testing of representative amidoximes for capture efficiencies at pressures as high as 180 bar. Acetamidoxime, which has the highest percent amidoxime functionality showed the highest CO_2 capacity (2.71 mmol g^{-1}) when compared to terephthalamidoxime (two amidoximes per molecule) and tetraquinoamidoxime (four amidoximes per molecule). Polyamidoxime surpassed activated charcoal Norit RB3 for CO_2 capture per unit surface area. Adsorption isotherms exhibit Type IV behavior and acetamidoxime found to increase CO_2 capture with temperature, a less observed anomaly. Porous amidoximes are proposed as valuable alternatives to MEA.

The ever increasing atmospheric carbon dioxide (CO_2) concentration (currently at 393 ppm)[1] is undeniably an alarming environmental issue.[2] Effective carbon sequestration demands reduction of CO_2 emissions by capturing it prior to emission, depositing in a suitable repository and then its utilization.[3–6] Though ample technologies exist (*i.e.* chemical solvent absorption, physical adsorption, cryogenic fractionation, membrane separation, biological fixation as well as the O_2/CO_2 combustion process),[7–13] solvent absorption is still the most extensively used technique for reducing CO_2 emissions and the materials currently known in this respect typically involve amine functional groups.[14–16] Among them, monoethanolamine (MEA) is widely accepted to be the industrial standard, although it possesses many limitations such as toxicity, degradability, high regeneration energy requirements and corrosive behavior.[17,18] A solid, recyclable sorbent, therefore, is highly desirable.[7,19]

Amines show selective binding to CO_2 (*i.e.* forming carbamates), therefore, it is essential to incorporate the molecular specifics of their CO_2–sorbent interactions in order to fabricate superior carbon-capture systems.[20] Extensive attempts were made with solid adsorbents on silica, activated carbons, zeolites, metal oxides, metal–organic frameworks, alkali metal carbonates, metal nitrides, hydrotalcites, calcium and alkali ceramic based adsorbents and amine-rich carbonaceous materials,[7,21,22] however the quest for superior performing amine sorbents is far from being over.

Amidoximes are an important class of organic compounds featuring a fused amide and oxime functionality (Scheme 1).[23] Their use as starting materials for the synthesis of valuable heterocyclics and related intermediates[23,24] has enabled a wide range of applications in novel pharmaceuticals, antitumor agents,[25] antimalarial agents,[26] nitric oxide synthase (NOS) substrates,[27,28] enhanced textile materials, synthetic polymers and chelating resins.[29] Amidoximes are also known to bind selectively to UO_2^{2+},[30] enabling uranium harvesting as part of the direct desalination of seawater.[31–33]

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Broader context

Carbon dioxide (CO_2) is a major greenhouse gas and believed to be a significant contributor to global warming and climate change. In order to lessen its impact, CO_2 emissions need to be cut dramatically. Accounting for more than 40% of all CO_2 emissions, fossil fuel based power plants as well as cement and steel factories are expected to employ CO_2 scrubbing operations, at the cost of significant losses in profit. So far, no scrubber other than monoethanolamine (MEA) has been chosen for large scale applications, mostly because of the extensive expertise on MEA processes. Although many solid sorbents have been reported to surpass MEA in capacity, regenerability and cost, none made into market. In this study, our goal is to learn from MEA (thus importing its chemical expertise) to construct solid alternatives based on amidoxime functionality, which features a different configuration of the amine and hydoxyl terminal components than MEA. This report is the first step in branding a new CO_2 adsorbent family of compounds and the first ever study of CO_2 sorbents under extreme pressures (up to 180 bars).

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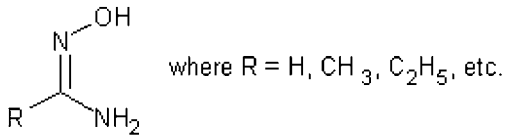


Scheme 1 Amidoxime functionality.

The terminal groups of the amidoximes resemble those of MEA (where $-NH_2$ and $-OH$ coexist in a *syn* fashion albeit through a double bond), which led us to consider their performance as CO_2 scavengers. Amidoxime ($pK_a \leq 6$) and MEA ($pK_a = 10$) have very different pK_as[34] and hence potentially different chemical reactivity toward CO_2 depending on solvent properties. Also, the increased nucleophilicity of the amidoxime hydroxyl group due to lone pair electrons on adjacent nitrogen atoms (alpha effect)[34] may make amidoxime more reactive than MEA in certain solvent conditions. However, since CO_2 scrubbing processes that utilize amidoximes will mainly operate differently than MEA (*i.e.* aqueous solution *vs.* solid phase), we began investigating their capacity by calculating the CO_2 binding energy of a model compound acetamidoxime (AAO) in comparison to that of a matching methyl-MEA.

Although MEA removes CO_2 mainly *via* the formation of carbamate in aqueous solution while AAO, as we show below, captures CO_2 *via* the physical adsorption in solid, the CO_2 adsorptivity of AAO judging from a simple measure of binding energy appears at least comparable to that of methyl-MEA. In fact, due to the planar backbone structure of amidoxime, CO_2 can bind to both hydroxyl and amine functional groups simultaneously whereas, in MEA, CO_2 preferentially interacts with the hydroxyl group alone in the lowest energy structure (Fig. 1). Thus, theoretical assessments (Fig. S1 in the ESI†) seem to suggest that amidoximes should have a strong affinity towards carbon dioxide.

Using our theoretical analysis as a basis, we carried out synthesis, characterization and CO_2 adsorption experiments for select amidoximes in an attempt to produce high performance solid sorbents for CO_2. To the best of our knowledge, this study contains the first data with extreme pressures (as high as 180 bar) applied for CO_2 storage on conventional solids. Supercritical carbon dioxide adsorption at pressures as high as 180 bar at different isotherms (43 °C and 70 °C) is quite essential from a practical engineering point of view, since such conditions are frequently used in acid gas removal units of the chemical industries. Such processes are known to operate at pressures as high as 150 bar and temperatures up to 50 °C.

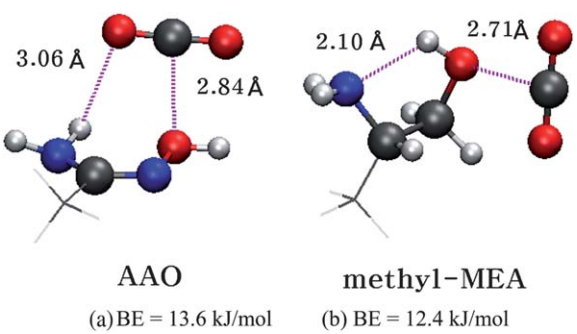
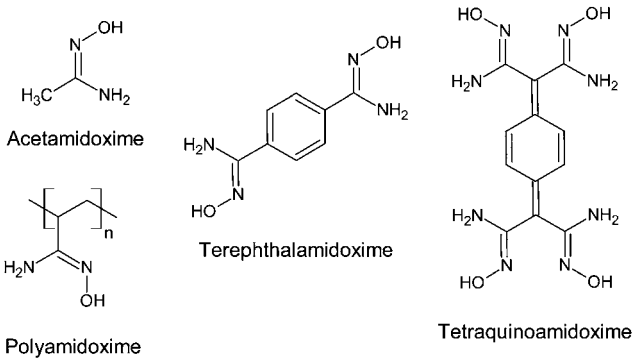


Fig. 1 The lowest energy structures of the (a) CO_2–AAO and (b) CO_2–methyl-MEA complexes with comparable binding energies (BE).



Scheme 2 Chemical structures of the amidoximes studied in this work.

In order to verify their CO_2 sorbent potential, four different amidoximes were chosen based on their amidoxime valency: acetamidoxime (AAO—monovalent), terephthalamidoxime (TPAO—divalent), tetraquinoamidoxime (TQAO—tetravalent) and polyamidoxime (PAO—polyvalent) (Scheme 2). These structures were prepared using a facile synthetic methodology of treating the corresponding nitriles with hydroxylamine[35] (Fig. S2, ESI†). A typical synthesis of AAO involved the reaction of acetonitrile (0.02 mol) with hydroxylamine solution (50 wt% in H_2O) (0.022 mol) in ethanol at 70 °C for 7 h. The reaction mixture was highly transparent and colorless. Hexane was added to this mixture in order to isolate the product which was then dried under vacuum (see the ESI† for detailed syntheses).

Gravimetric CO_2 uptake studies of various amidoximes were studied at two different temperatures (43 °C and 70 °C) within a pressure range of 0 to 180 bar using a high-pressure magnetic suspension balance (MSB) sorption device. MSB measures the change in weight of a sorbent sample in the gravity field due to adsorption of molecules from a surrounding gas phase through a contactless force transmission by using magnetic suspension coupling from a closed and pressure-proof metal container to an external microbalance. The cell temperature is measured with a platinum resistance thermometer, Jumo DMM 5017 Pt100, that operates within ±0.6 °C accuracy and pressure is monitored *via* Paroscientific® Digiquartz 745-3K with an accuracy of 0.01% in pressure in full scale. Adsorption data are calculated by using eqn (1) below:

$$W + W_{\text{buoy,sample}} + W_{\text{buoy,sink}} = m_{\text{ads}} + m_{\text{sample}} + m_{\text{sink}} \quad (1)$$

where W = signal read by the instrument, $W_{\text{buoy,sample}} = V_{\text{sample}} \times d_{\text{gas}}$ = buoyancy correction due to the sample, V_{sample} = volume of the sample, d_{gas} = density of the gas, $W_{\text{buoy,sink}} = V_{\text{sinker}} \times d_{\text{gas}}$ = buoyancy correction due to the sinker, V_{sinker} = volume of the sinker, m_{ads} = adsorption amount, m_{sample} = mass of the sample, and m_{sink} = mass of the sinker.

D_{gas} is measured *in situ* by means of the second measurement position (Fig. S3†) and crosschecked with REFPROP 9.0[36] for quality assurance purposes since it is essential for accurate measurements. The mass of the empty sinker was measured at several pressures of helium to determine the buoyancy due to the sinker ($W_{\text{buoy,sink}}$). The volume of the sinker (V_{sinker}) is calculated from the slope of weight *vs.* density plot obtained from this measurement. A blank measurement at vacuum was performed to determine the mass of the sinker (m_{sink}). The buoyancy correction due to the sample ($W_{\text{buoy,sample}}$) was performed by calculating the volume of the sample (V_{sample}), which is

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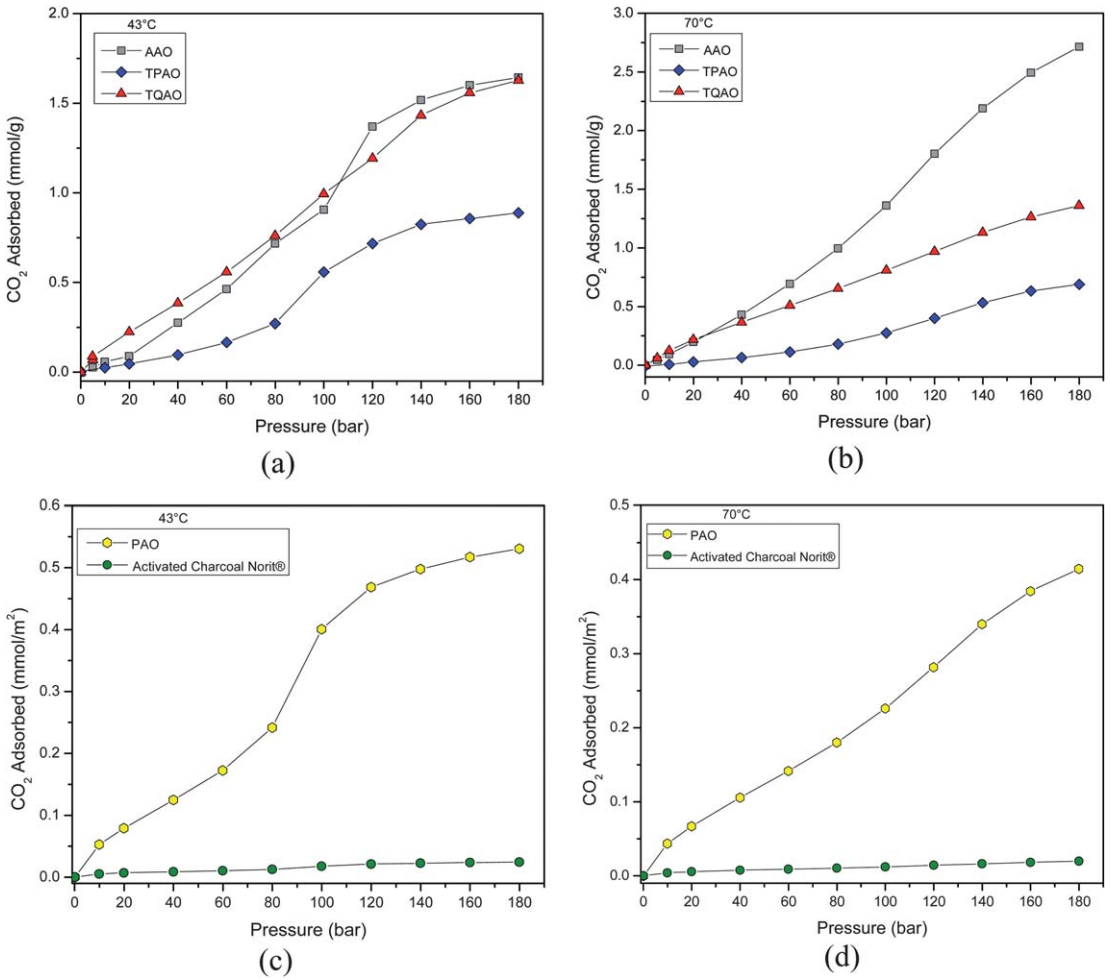

Fig. 2 (a and b) CO_2 adsorption isotherms (mmol g^{-1}) for acetamidoxime (AAO) (■), terephthalamidoxime (TPAO) (◆) and tetraquinoamidoxime (TQAO) (▲) at 43 °C and 70 °C; (c and d) CO_2 adsorption isotherms (mmol m^{-2}) for polyamidoxime (PAO) (⬢) and activated charcoal Norit RB3 (●) at 43 °C and 70 °C.

obtained by the slope of weight *vs.* density plot obtained by a similar helium measurement of the sinker with the sample.

The CO_2 adsorption data of AAO, TPAO and TQAO were found to be dependent on the percent amidoxime functionality present in each molecule (Fig. 2a and b). AAO has the highest amidoxime functionality per molecule (79.7% w/w) and showed the largest CO_2 adsorption values of 1.64 and 2.71 mmol (CO_2) g^{-1} at 43 °C and 70 °C respectively at 180 bar pressure. TPAO, with the lowest amidoxime functionality per molecule (60.8% w/w), exhibited a minimum adsorption uptake at 180 bar corresponding to the values of 0.88 and 0.69 mmol (CO_2) g^{-1} at 43 °C and 70 °C, in good agreement with the calculated percent amidoxime functionality data (see the ESI†).

In order to assess the chemical affinity of polymeric amidoxime to CO_2, adsorption per unit surface area is chosen to be a better fit since interaction of a guest gas molecule with the high molecular weight solid sorbent is predominantly related to heterogeneous interfaces.[37] Thus, per weight arguments fall short of explaining the chemistry of sorptivity in macromolecules. PAO gave adsorptions 0.53 and 0.41 mmol (CO_2) m^{-2} at 43 °C and 70 °C indicating a significant chemical interaction between the gas molecules and the sorbent, as opposed to the adsorptions obtained for highly porous, inert Norit RB3 (0.020 and 0.024 mmol(CO2) m^{-2}).

The adsorption isotherms of amidoximes exhibit "Type IV" behavior, in which multilayer adsorption is observed after the completion of the first layer. Among the amidoximes studied, the adsorption isotherm of PAO possesses a clear distinction between the first layer (0–60 bar region) and multilayer (60–180 bar region) adsorptions indicating that the adsorbate–adsorbent interactions present in this amidoxime are the strongest.

The amount of CO_2 adsorbed on all amidoximes decreased with temperature except for AAO. Adsorption of a gas is normally greater

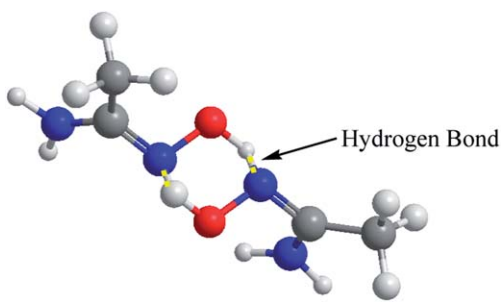

Fig. 3 Hydrogen bonding mediated dimerization in acetamidoxime.

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at low temperatures because of the exothermic nature of the binding.[38] The anomaly in AAO could be, however, because of the enhanced accessibility of the amine functionality at elevated temperatures. Amidic $-NH_2$ would only be hindered if there was a preferred dimerization in AAO (Fig. 3). Indeed, it is widely known that dimer formation is prevalent in acetic acids[39] as well as the lower molecular weight solid amidoximes where intermolecular hydrogen bonding assists stacking.[35] This behavior also explains the crossing of AAO adsorption isotherm over the TQAO at lower temperature, 43 °C (Fig. 2a). When the temperature reaches 70 °C, the dimers already are disconnected, which could explain the abnormal adsorption performance.

Conclusions

The amidoxime functionality dependent CO_2 adsorption presented in this study showed that the amidoxime groups offer new chemical approach for selective CO_2 binding. Their previously unknown behavior puts this well-known class of organic building blocks into the spotlight for the pursuit of commercial scale CO_2 capture and storage. In an attempt to quantify their performance, four representative amidoximes with varying amidoxime contents were screened. The highest percent amidoxime functionality present in acetamidoxime (AAO) was found to show the highest capacity (2.71 mmol g^{-1}). AAO also featured a dimerization which leads to an enhanced adsorption with an increase in temperature. Polymeric amidoxime showed superior adsorption per surface area when compared to a well-known activated carbon. An immediate task would be to produce highly porous, amidoxime rich solids using the ample knowledge learnt from clays, mesoporous materials and metal–organic frameworks.

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Notes and references

1 U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA), *Trends in Atmospheric Carbon Dioxide*, http://www.esrl.noaa.gov/gmd/ccgg/trends/, accessed July 2011.
2 R. A. Kerr, *Science*, 2007, **316**, 188–190.
3 U.S. Department of Energy, *Innovative Concepts for Beneficial Reuse of Carbon Dioxide*, http://fossil.energy.gov/recovery/projects/beneficial_reuse.html, accessed Aug 2011.
4 R. Van Noorden, *Nature*, 2010, **463**, 871–873.
5 K. S. Lackner, *Science*, 2003, **300**, 1677–1678.
6 J. M. Matter and P. B. Kelemen, *Nat. Geosci.*, 2009, **2**, 837–841.
7 Q. A. Wang, J. Z. Luo, Z. Y. Zhong and A. Borgna, *Energy Environ. Sci.*, 2011, **4**, 42–55.
8 O. Aschenbrenner and P. Styring, *Energy Environ. Sci.*, 2010, **3**, 1106–1113.
9 D. M. Munoz, A. F. Portugal, A. E. Lozano, J. G. de la Campa and J. de Abajo, *Energy Environ. Sci.*, 2009, **2**, 883–891.
10 M. T. Ho, G. W. Allinson and D. E. Wiley, *Ind. Eng. Chem. Res.*, 2008, **47**, 4883–4890.
11 M. B. Hagg and A. Lindbrathen, *Ind. Eng. Chem. Res.*, 2005, **44**, 7668–7675.
12 B. J. P. Buhre, L. K. Elliott, C. D. Sheng, R. P. Gupta and T. F. Wall, *Prog. Energy Combust. Sci.*, 2005, **31**, 283–307.
13 D. Aaron and C. Tsouris, *Sep. Sci. Technol.*, 2005, **40**, 321–348.
14 G. T. Rochelle, *Science*, 2009, **325**, 1652–1654.
15 A. B. Rao and E. S. Rubin, *Ind. Eng. Chem. Res.*, 2006, **45**, 2421–2429.
16 C. Lastoskie, *Science*, 2010, **330**, 595–596.
17 S. Lee, T. P. Filburn, M. Gray, J. W. Park and H. J. Song, *Ind. Eng. Chem. Res.*, 2008, **47**, 7419–7423.
18 J. C. Abanades, E. S. Rubin and E. J. Anthony, *Ind. Eng. Chem. Res.*, 2004, **43**, 3462–3466.
19 C. T. Yavuz, B. D. Shinall, A. V. Iretskii, M. G. White, T. Golden, M. Atilhan, P. C. Ford and G. D. Stucky, *Chem. Mater.*, 2009, **21**, 3473–3475.
20 R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650–653.
21 L. Zhao, Z. Bacsik, N. Hedin, W. Wei, Y. H. Sun, M. Antonietti and M. M. Titirici, *ChemSusChem*, 2010, **3**, 840–845.
22 P. Galhotra, J. G. Navea, S. C. Larsen and V. H. Grassian, *Energy Environ. Sci.*, 2009, **2**, 401–409.
23 F. Eloy and R. Lenaers, *Chem. Rev.*, 1962, **62**, 155–183.
24 B. Mlakar, B. Stefane, M. Kocevar and S. Polanc, *Tetrahedron*, 1998, **54**, 4387–4396.
25 K. P. Flora, B. Vantriet and G. L. Wampler, *Cancer Res.*, 1978, **38**, 1291–1295.
26 J. B. Hynes and L. G. Hack, *J. Med. Chem.*, 1972, **15**, 1194.
27 K. Rehse and F. Brehme, *Arch. Pharm.*, 1998, **331**, 375–379.
28 A. Jousserandot, J. L. Boucher, Y. Henry, B. Niklaus, B. Clement and D. Mansuy, *Biochemistry*, 1998, **37**, 17179–17191.
29 B. L. Rivas, H. A. Maturana and S. Villegas, *J. Appl. Polym. Sci.*, 2000, **77**, 1994–1999.
30 S. Das, A. K. Pandey, A. Athawale, V. Kumar, Y. Bhardwaj, S. Sabharwal and V. K. Manchanda, *Desalination*, 2008, **232**, 243–253.
31 K. Saito, T. Hori, S. Furusaki, T. Sugo and J. Okamoto, *Ind. Eng. Chem. Res.*, 1987, **26**, 1977–1981.
32 L. Astheimer, H. J. Schenk, E. G. Witte and K. Schwochau, *Sep. Sci. Technol.*, 1983, **18**, 307–339.
33 H. Omichi, A. Katakai, T. Sugo and J. Okamoto, *Sep. Sci. Technol.*, 1985, **20**, 163–178.
34 Y. S. Simanenko, T. M. Prokop'eva, I. A. Belousova, A. F. Popov and E. A. Karpichev, *Theor. Exp. Chem.*, 2001, **37**, 288–295.
35 E. A. Bruton, L. Brammer, F. C. Pigge, C. B. Aakeroy and D. S. Leinen, *New J. Chem.*, 2003, **27**, 1084–1094.
36 U.S. Department of Commerce, *NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)*, http://www.nist.gov/srd/nist23.cfm, accessed July 2011.
37 H. A. Al-Abadleh and V. H. Grassian, *Surf. Sci. Rep.*, 2003, **52**, 63–161.
38 D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, Inc, New York, 1984.
39 J. Chocholousova, J. Vacek and P. Hobza, *J. Phys. Chem. A*, 2003, **107**, 3086–3092.