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Modified mesoporous silicates for the adsorption and decomposition of toxic gases†

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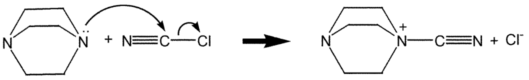
New adsorbents based on MCM-41 have been developed for the adsorption and decomposition of HCN and CNCl. Adsorption of CNCl is provided by diaminoalkylsilane tethers bound to the surface. Reactivity towards HCN is provided by Cu^{2+} ions complexed by the diamines. Overall reactivity towards the two gases depends on the balance between free amine and Cu^{2+} concentrations. The performance of these adsorbents is superior to that of carbon-based adsorbents in which alkylamine and copper(II) salt are physisorbed on the carbon surface.

I Introduction

The traditional adsorbent used in military respirators for the adsorption of toxic gases is activated carbon.[1] Although effective for physisorption of relatively high boiling point materials, adsorption of low boiling point compounds such as cyanogen chloride (CNCl) and hydrogen cyanide (HCN) requires that the carbon be treated with suitable reactive impregnants.[2,3] An alkylamine, triethylenediamine (TEDA), is used widely as an effective impregnant for CNCl adsorption, reacting with and trapping CNCl as follows (Scheme 1).



Scheme 1

Copper(II) salts facilitate adsorption of HCN through formation of $Cu(CN)_2$ on the support. However, this can be followed by reduction of Cu^{2+}, forming CuCN and the toxic gas cyanogen [$(CN)_2$] which can then desorb. In practice, carbon-based adsorbents are usually treated with a chromium(VI) salt to promote hydration of $(CN)_2$ to oxamide.

Unfortunately, this impregnation reduces the available surface area and consequently compromises the physisorption performance.[4] Further problems are associated with relatively facile reduction of Cu^{2+} to inactive Cu^+ and Cu(0) on carbon supports, and a tendency for impregnated salt to aggregate into larger crystals of lower activity on exposure to humid air.[5–7] It is partly because of these shortcomings, together with the desirability of eliminating chromium on health grounds, that inorganic adsorbents are being reviewed as alternatives to carbon.[8] In principle, it should be possible to chemically bind both metal and amine to the surface of an inorganic support to provide well-defined and tailored active sites and, in this way, overcome some of the problems associated with carbon-based adsorbents.

We have studied a number of porous inorganic solids in this respect. In this paper we report on a comparison of the methods by which copper(II) ions and organic amines can be incorporated into inorganic adsorbents, using as a support the mesoporous silicate molecular sieve SiMCM-41. In the first method, the Cu^{2+} ions have been complexed with aminoalkylsilane tethers chemically bound to the SiMCM-41 silicate surface. In the second, the metal ion has been ion-exchanged into a SiAlMCM-41 support and the amine (TEDA) sublimed onto the surface. In neither case have chromium salts been used. The reactivities of the adsorbents towards HCN and CNCl have been compared with those of an activated carbon with physisorbed amine, and copper(II) and chromium(IV) salts, a material that is representative of carbon-based adsorbents in current use.

II Experimental

(a) Cu^{2+}-complexed ethylenediamine-functionalised SiMCM-41 (SiMCM-41-en-Cu^{2+})

The siliceous mesoporous molecular sieve SiMCM-41 was prepared according to the method of Cheng *et al.*[9] and calcined at 550 °C for 8 h under air. The product was characterised by powder X-ray diffraction and by nitrogen adsorption at 77 K following outgassing at 200 °C. To bind the ethylenediamine (en) tethers to the silica surface, the calcined SiMCM-41 (1.5 g) was refluxed for 12 h with a dry toluene solution (50 cm^3) of trimethoxysilylpropylethylenediamine (0.02 mol) under nitrogen.[10] The solid was then separated, washed in toluene and methanol, and dried at 50 °C for 12 h. The functionalised product was characterised again by XRD and nitrogen adsorption at 77 K (following outgassing at 130 °C), and elemental analysis† (Butterworths) was performed for carbon and nitrogen.

The functionalised SiMCM-41-en was then treated with aqueous $Cu(NO_3)_2$ solutions of varying concentrations to allow complexation of Cu^{2+} and formation of SiMCM-41-en-Cu^{2+}. The solid was thoroughly washed, and dried at 50 °C for 12 h. Copper content was measured for this and all copper-containing materials described below using atomic absorption spectroscopy following acid digestion.

The environment of the Cu^{2+} ion in this adsorbent was studied with electron paramagnetic resonance (EPR) spectroscopy. Spectra were recorded at room temperature and at 77 K on a Varian E106 X-band spectrometer, using data collection software written in-house and a DPPH spectral marker.

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†Electronic supplementary information (ESI) available: elemental analyses for the MCM-41 and carbon-based adsorbents. See http://www.rsc.org/suppdata/jm/b1/b110111k/

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(b) Cu^{2+} ion-exchanged SiAlMCM-41/physisorbed amine (Cu^{2+}-SiAlMCM-41-TEDA)

The aluminosilicate SiAlMCM-41 (Si : Al = 40) was prepared using the method of Luan *et al.*[11] and calcined for 8 h at 550 °C in air. It was characterised by powder X-ray diffraction and nitrogen adsorption at 77 K following outgassing at 200 °C (BET surface area 660 $m^2\ g^{-1}$). Incorporation of Al in tetrahedral lattice sites was verified using ^{27}Al MAS-NMR. The solid (5 g) was ion-exchanged with Cu^{2+} by stirring overnight with 500 cm^3 of 0.05 mol dm^{-3} $Cu(NO_3)_2$ solution. Triethylenediamine (TEDA) was sublimed onto the Cu^{2+}-exchanged SiAlMCM-41 in an evacuated vessel at room temperature.[3,12] Sufficient TEDA was used to produce a 2% w/w loading. The disappearance of visible traces of TEDA after 4 h sublimation suggested that essentially all the TEDA was transferred to the adsorbent. This was verified by a combination of thermogravimetric analysis and temperature programmed desorption/mass spectrometric measurements on selected samples.[12]

(c) Activated carbon/physisorbed Cu^{2+} and Cr(VI) salts, and amine (carbon-Cu-Cr-TEDA)

Copper and chromium were impregnated on a coal-based activated carbon (surface area 1140 $m^2\ g^{-1}$) from an ammoniacal solution of $CuCO_3$ and CrO_3, using the Whetlerite procedure.[2] This ensures that copper is deposited as a Cu(II) salt and chromium as a chromate(VI) salt. Following drying at 220 °C for 2 h, TEDA was sublimed onto the carbon as above at a loading of 2%.[3,12] Chromium contents were measured at the same time as copper with atomic absorption spectroscopy on acid digests.

(d) Adsorption capacities

The adsorption capacities of these materials for HCN and CNCl were measured using standardised flow experiments designed to mimic realistic conditions associated with the use of this material in filtration applications. Each gas, at a concentration of 8.0 g m^{-3} in air and a relative humidity of 80%, was separately passed through fresh 0.15 g beds of adsorbent at 22 °C and at a flow rate of 50 $cm^3\ min^{-1}$. The gas was analysed by GC downstream of the adsorbent bed. In all cases, the concentrations of HCN, CNCl and $(CN)_2$ remained very low or undetectable up to well-defined times at which the concentrations rose to the levels detected in the absence of adsorbent. These breakthrough times for the three gases were recorded for each adsorbent.

III Results and discussion

(a) Cu^{2+}-complexed ethylenediamine-functionalised SiMCM-41 (SiMCM-41-en-Cu^{2+})

Elemental analyses for C and N gave a C : N molar ratio of 3.2 (±0.3), indicative of, on average, binding to the silica through condensation of two of the three methoxy groups, as shown in Fig. 1(a). From the N and C analyses it has also been possible to calculate that 1.3 (±0.3) mmol of ethylenediamine groups were anchored per 1 g of SiMCM-41. Assuming that 30% of silicon atoms in calcined SiMCM-41 have silanol groups available for reaction,[13] this means that about 50% of the available silanols were bound to organosilane groups.

The X-ray diffraction patterns for SiMCM-41 before and after functionalisation with aminoalkylsilane tethers are shown in Fig. 2. They are relatively well resolved and are typical of MCM-41 materials.[13] Prominent d_{100} reflections, corresponding to approximately 4.3 nm in both cases, show that the lattice spacings are not significantly altered by functionalisation.

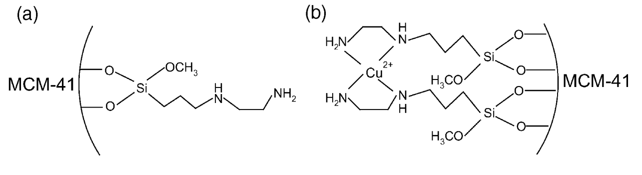


Fig. 1 Functionalised surface of SiMCM-41 using trimethoxysilylpropylethylenediamine, showing (a) uncomplexed, and (b) Cu^{2+}-complexed, ethylenediamine groups.

The pore size distributions, calculated using the Barrett, Joyner and Halenda (BJH) method from the nitrogen desorption isotherm, appear in the same figure. The pore diameters are reduced on functionalisation from about 3.6 to 2.6 nm. Based on the size of the peaks at these diameters, the overall mesopore volume is dramatically reduced on functionalisation. In theory, the volume of a cylindrical pore would be reduced to 52% of its value if its diameter were reduced by this amount. The actual reduction in pore volume is clearly much greater than this, so the tethered alkylamine groups must be causing some pore blockage as well as simply narrowing the pores.

The surface area (BET) of the SiMCM-41 support was found to be 970 $m^2\ g^{-1}$ which decreased to 470 $m^2\ g^{-1}$ following functionalisation. This is consistent with the evident fall in pore volume described above. Based on both these results and those of others who have used a range of alkylamines to functionalise supports of this type,[14] we are certain that a higher surface area and greater pore volume could be retained by judicious choice of support and functionalising group.

(b) The Cu^{2+} environment

In Fig. 3 the EPR spectrum of Cu^{2+} in cation-exchange sites on the adsorbent, Cu^{2+}-SiAlMCM-41-TEDA is compared

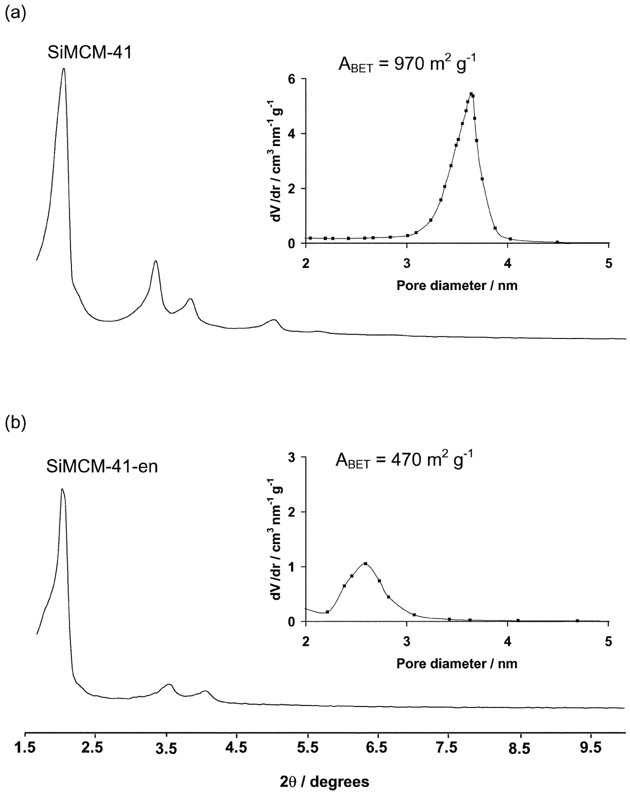


Fig. 2 Powder X-ray diffraction (Cu Kα radiation) patterns for (a) calcined SiMCM-41, and (b) calcined SiMCM-41 following ethylenediamine functionalisation. The specific surface areas (BET) together with pore size distributions (BJH) are also shown.

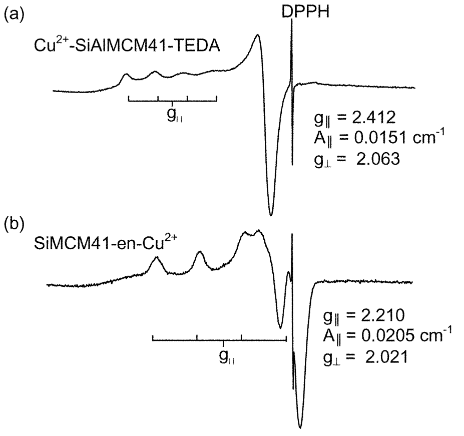


Fig. 3 EPR spectra recorded at 77 K of Cu^{2+} in (a) air-dried SiAlMCM-41 ion-exchanged with Cu^{2+}, following adsorption of 2% TEDA (Cu^{2+}-SiAlMCM-41-TEDA), and (b) air-dried SiMCM-41 functionalised with ethylenediamine (SiMCM-41-en-Cu^{2+}).

with the spectrum of chelated Cu^{2+} in amine-functionalised SiMCM-41-en-Cu^{2+}. These spectra were recorded at 77 K.

The EPR parameters for the ion-exchanged Cu^{2+} [Fig. 3(a)] are typical of Cu^{2+} fully coordinated by six oxygen ligands.[15–17] The room temperature spectrum of this Cu^{2+} centre (not shown) is isotropic, indicative of a freely rotating hydrated Cu^{2+} ion in the pore of the SiAlMCM-41. This strongly suggests that the Cu^{2+} ion in this adsorbent is not associated with the adsorbed TEDA. A very different EPR spectrum is seen for SiMCM-41-en-Cu^{2+} [Fig. 3(b)]. In this case the room temperature spectrum largely retains the anisotropy seen at 77 K, suggesting that the motion of this Cu^{2+} centre is restricted. The very much lower $g_{\parallel}$ and increased $A_{\parallel}$ compared with the ion-exchanged material are strong evidence for the presence of a discrete Cu(II)–amine complex. They are very similar to those found for the $[Cu(H_2NCH_2CH_2NH_2)_2]^{2+}$ complex in homogeneous solution[18] ($g_{\parallel}$ = 2.200, $A_{\parallel}$ = 0.0200 cm^{-1}, and $g_{\perp}$ = 2.045), and Cu^{2+} co-ordinated by tethered ethylene diamine ligands as a CuN_4 complex in the interlayer region of α-zirconium phosphate[17] ($g_{\parallel}$ = 2.210, $A_{\parallel}$ = 0.0201 cm^{-1}, and $g_{\perp}$ = 2.029). This is strong evidence for the proposed complex in the adsorbent shown in Fig. 1(b), probably with oxygen ligands in the fifth and sixth co-ordination sites.

(c) The activity of SiMCM-41-en-Cu^{2+} towards HCN, CNCl and $(CN)_2$

The breakthrough times for the three gases were measured for the organosilane-functionalised SiMCM-41-en-Cu^{2+} adsorbent with varying Cu^{2+} contents. These are shown in Fig. 4. Calculation shows that approximately 4% w/w Cu^{2+} would be sufficient to react with all the amine present to form the four co-ordinate CuN_4 complex shown in Fig. 1(b). In practice we found that concentrations of Cu^{2+} higher than 4% were achievable, most likely due to cation-exchange directly on the siliceous MCM-41 surface through hydroxy proton exchange. The presence of some cation exchange capacity on purely siliceous MCM-41 has been reported by Kevan and coworkers who also reported the EPR spectra of Cu^{2+} ions occupying these exchange sites.[19] In this work, systems in which the Cu^{2+} content exceeded 4% w/w showed broad, poorly-resolved EPR spectra, almost certainly due to a combination of CuN_4 species and Cu^{2+} ions co-ordinated by oxygen ligands in exchange sites. It is significant that, at lower Cu^{2+} loadings, no EPR evidence for Cu^{2+} in ion-exchange sites was found, suggesting a strong preference by the ion for CuN_4 sites.

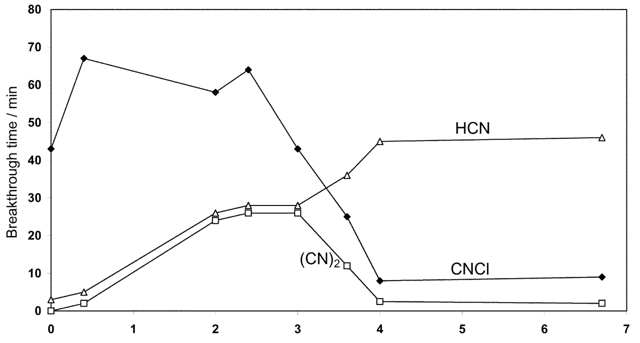


Fig. 4 Breakthrough times for HCN, CNCl and $(CN)_2$ for SiMCM-41 functionalised with ethylenediamine and complexed with Cu^{2+} (SiMCM-41-en-Cu^{2+}): dependence on Cu^{2+} concentration.

Fig. 4 shows that the adsorption capacity for CNCl falls as the Cu^{2+} content increases, suggesting that only free amine is active towards this adsorbate. This is not unreasonable since coordination to Cu^{2+} would reduce the nucleophilicity of the amine and therefore its reactivity towards CNCl (Scheme 1). The adsorption capacity for HCN increases with increasing Cu^{2+} content, as expected. It is worth noting that Cu^{2+} is evidently reactive towards HCN even when chelated by surface-functionalised ethylenediamine ligands. From the trends seen in the figure, an optimum Cu^{2+} content of 2.4% has been identified in terms of both HCN and CNCl breakthrough times. It is worth noting that this is very much lower than the typical copper loading used in carbon-based adsorbents (see Table 1).

The breakthrough times for $(CN)_2$ are similar to those for HCN at low Cu^{2+} contents. At higher Cu^{2+} loadings, particularly above 4% where there is sufficient Cu^{2+} to complex all the amine, the breakthrough times for $(CN)_2$ become progressively shorter.

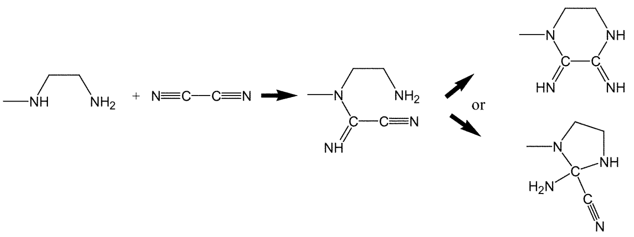
It is significant that measurable amounts of $(CN)_2$ are formed even when the Cu^{2+} concentration is zero. This suggests that $(CN)_2$ can be formed by air oxidation of HCN, as well as by Cu^{2+} oxidation when the metal ion is present. The results in Fig. 4 have led us to propose the following possible model to explain the adsorption profiles of HCN and $(CN)_2$.

Under all conditions, a proportion of the HCN passing over the adsorbent is converted to $(CN)_2$, by either air or Cu^{2+} oxidation. We suggest that this proportion is small in the early stages because: (1) relatively little of the Cu^{2+} is in the form of $Cu(CN)_2$, which is the precursor for $(CN)_2$; and (2) air oxidation is suppressed while the adsorption of HCN on the surface is relatively efficient. The small concentration of $(CN)_2$ produced under these conditions can be adsorbed by reaction with free amine as shown in Scheme 2 below, provided the Cu^{2+} content on the adsorbent is low enough to leave a sufficient concentration of free, uncomplexed amine for this reaction.

In the later stages of exposure to HCN, when all Cu^{2+} in the adsorbent has been converted to the cyanide, the HCN concentration above the adsorbent rises. The $(CN)_2$ concentration also increases, as a result of both air oxidation of HCN in the gas phase and Cu^{2+} oxidation of CN^-. This elevated concentration of $(CN)_2$ is now too high for trapping by the amine, so breakthrough of $(CN)_2$ occurs.

This model explains why the breakthrough times for HCN and $(CN)_2$ are almost coincident at Cu^{2+} loadings significantly below 4%. Above this level of Cu^{2+} there is very little free, unreacted amine, insuffient to trap even the relatively low levels of $(CN)_2$ produced in the early stages of exposure. The breakthrough time for $(CN)_2$ for these high copper content adsorbents falls as the amount of free amine falls. When there is no free amine at all (above 4% Cu^{2+}) both $(CN)_2$ and CNCl break through very quickly.

This model highlights the importance of the alkylamine for adsorption of $(CN)_2$ *as well* as CNCl. We believe that the ethylenediamine moiety is a good choice in this respect because, in principle, $(CN)_2$ can react with both amine groups sequentially, to form either a six-membered or a five-membered ring structure, as shown in Scheme 2. Both might be expected to be stable or lead to further stable products. It is worth pointing out that the equivalent reaction of $(CN)_2$ with the tertiary diamine TEDA, as used on the other adsorbents, would not be expected to form stable ring structures in this way. The importance of this is that, by using an amine which can react with both CNCl *and* $(CN)_2$, the requirement for an additional impregnant to specifically adsorb $(CN)_2$ can be avoided.



Scheme 2

(d) Inorganic and carbon adsorbents compared

The adsorption capacities of the Cu^{2+}-complexed alkylamine-functionalised SiMCM-41(2.4% Cu) are compared with those for ion-exchanged Cu^{2+}/SiAlMCM-41/physisorbed TEDA (Cu^{2+}-SiAlMCM-41-TEDA) and the carbon-based adsorbent, Carbon-Cu-Cr-TEDA, in Table 1. The breakthrough times for the three gases are compared.

Table 1 Breakthrough times for HCN, CNCl and $(CN)_2$ for the MCM-41 and carbon-based adsorbents

Adsorbent	Cu^{2+} content/% w/w	HCN/min	$(CN)_2$/min	CNCl/min
SiMCM-41-en-Cu^{2+} (2.4% Cu^{2+})	2.4	28	26	64
Cu^{2+}-SiAlMCM-41-TEDA	0.6	7	3	4
Carbon-Cu-Cr-TEDA (Cr content = 3.0% w/w)	7.0	24	22	29

The performance of Cu^{2+}-SiAlMCM-41-TEDA is inferior to the carbon-based material with respect to all three gases. This is partly explained by the relatively low copper content, but it also appears that TEDA, which is at the same level on the SiAlMCM-41 as on the carbon adsorbent, shows very poor activity towards CNCl. It is not clear why this is so, but it is possible that physisorbed TEDA is not as well dispersed on a siliceous support as on a carbon support, meaning a smaller proportion of the TEDA is accessible for reaction. Another feature of the Cu^{2+}-SiAlMCM-41-TEDA adsorbent is that $(CN)_2$ breaks through very early, suggesting that this material, like activated carbon, would not offer protection against $(CN)_2$ without adsorbed chromium(VI).

By far the most effective of the three adsorbents is the functionalised SiMCM-41-en-Cu^{2+}, discussed above. Even though the copper content is very much lower than that of the carbon adsorbent and, significantly, the adsorbent contains no chromium, it shows superior adsorption capacities for HCN, CNCl and $(CN)_2$ than the carbon-based adsorbent. We believe that the explanation for this lies in the combination of a high surface area support, well-dispersed Cu^{2+} sites, discrete and accessible amine centres chemically bound to the support, and a carefully chosen alkyldiamine able to deactivate not only CNCl but also $(CN)_2$.

These results illustrate the potential of inorganic adsorbents for the adsorption of HCN, CNCl and $(CN)_2$. The ability to form discrete chemically bound metal and amine centres on the surface of the support imparts advantages over carbon, for which there is little control over the chemical nature of the adsorbed impregnants. Further work is continuing to optimise the performance of these materials. In addition, other important practical properties of these materials, such as susceptibility to ageing and capacity for regeneration, are also under investigation.

Acknowledgements

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