Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The adsorption and decomposition of cyanogen chloride by modified inorganic molecular sieves

Jessica L. Pickett[a]; Majid Naderi[b]; Matt J. Chinn[a]; David R. Brown[b]
[a] Chemical and Biological Protection, Salisbury, Wiltshire, UK [b] Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield, UK

To cite this Article Pickett, Jessica L. , Naderi, Majid , Chinn, Matt J. and Brown, David R.(2002) 'The adsorption and decomposition of cyanogen chloride by modified inorganic molecular sieves', Separation Science and Technology, 37: 5, 1079 — 1093

To link to this Article: DOI: 10.1081/SS-120002242

URL: http://dx.doi.org/10.1081/SS-120002242

SEPARATION SCIENCE AND TECHNOLOGY, 37(5), 1079–1093 (2002)

THE ADSORPTION AND DECOMPOSITION OF CYANOGEN CHLORIDE BY MODIFIED INORGANIC MOLECULAR SIEVES

Jessica L. Pickett,[1] Majid Naderi,[2] Matt J. Chinn,[1] and David R. Brown[2,*]

[1]Chemical and Biological Protection, Dstl, Porton Down,
Salisbury, Wiltshire SP4 0JQ, UK
[2]Centre for Applied Catalysis, Department of Chemical and
Biological Sciences, University of Huddersfield,
Huddersfield HD1 3DH, UK

ABSTRACT

Aluminosilicate and silicate porous solids have been evaluated as supports for triethylenediamine (TEDA) for the adsorption and decomposition of cyanogen chloride. A series of silica-gel supports has been used to study the effect of varying pore size. A series of faujasitic zeolites has been used to examine the effect of the cation exchange capacity of the support and the type of exchangeable cation. Results show that the activity of adsorbed TEDA towards cyanogen chloride appears to increase with increasing support pore diameter, and TEDA seems to be activated by basic adsorption sites on the support. Cesium-exchanged zeolite supports are particularly active. In general, zeolite supports appear to confer significantly higher activity to TEDA than traditional activated carbon supports. A series of mesoporous MCM-41 and AlMCM-41 supports has also

---

*Corresponding author. Fax: (441) 484-472182; E-mail: d.r.brown@hud.ac.uk

been studied, but the activities of adsorbed TEDA are lower than expected. Significantly, the specific surface area of the inorganic supports does not seem to be a primary factor in controlling adsorbed TEDA activity.

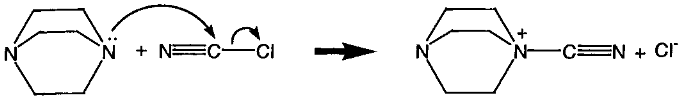
Key Words: Adsorbents; Activated carbon; Triethylenediamine; Cyanogen chloride; Zeolite; Silica; MCM-41

INTRODUCTION

Activated carbons have been used for many years as adsorbents for the removal of toxic gases in both civilian and military applications. The vapor-protection spectrum offered by activated carbon is often widened to include highly volatile gases by the incorporation of reactive impregnants. For example, triethylenediamine (TEDA) has been found to facilitate the removal of radioactive methyl iodide and cyanogen chloride (CNCl) (1). However, whilst improving protection against specific gases, impregnation incurs the penalty of reducing the capacity of carbon to physisorb more volatile vapors. Furthermore, the reactive nature of the carbon surface is thought to promote the degradation of impregnants with storage at high temperature and/or humidity (1). In the present study, we have begun to evaluate a series of inorganic porous solids as alternative supports for TEDA.

The use of zeolites, silicas, and other molecular sieve materials for adsorption and catalytic degradation of toxic gases such as hydrogen cyanide (HCN) (2) and other organic pollutants (3–7) is well established. Factors such as the nature of the exchangeable cation (2), relative hydrophobicity (8), and surface acidity (9–11) can all influence the activity of the adsorbent towards specific gases and vapors. The adsorption characteristics of the recently discovered MCM-type mesoporous molecular sieves have also been the subject of research (12,13). Furthermore, and of significance to this work, it is well known that zeolitic aluminosilicates permit very effective dispersion of alkylamines similar to TEDA over the surfaces of these supports (14).

In this work, a series of microporous zeolites, mesoporous molecular sieves, and silica gel materials have been evaluated as supports for TEDA, in terms of the subsequent activity of adsorbed TEDA toward the decomposition of CNCl. Triethylenediamine reacts with cyanogen chloride as shown in reaction 1.



Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

It seems reasonable that the control of surface properties available with aluminosilicate and silicate supports, which is largely unavailable with carbon supports, should allow us to optimize the surface for TEDA adsorption and effective dispersion, and to design adsorption sites that activate TEDA towards reaction with CNCl.

The objective has been to identify the structural features of inorganic porous support materials that are important in conferring activity to TEDA in this reaction. Silicate and aluminosilicate supports have been chosen for the study to illustrate the effects of pore size and pore structure, crystal structure, hydrophilicity/hydrophobicity (through varying Si/Al ratios), and the nature of exchangeable cations present (in the case of aluminosilicates).

EXPERIMENTAL

Siliceous MCM-41 was prepared using the procedure of Cheng et al. (15), and Al-MCM-41 ($Si/Al = 40$) was synthesized following the procedure of Luan et al. (16) using 25% tetramethylammonium hydroxide, 25% cetyltrimethylammonium chloride, and aluminum sulphate. Zeolite X was prepared according to the procedure of Hathaway and Davis (17). Zeolite Y was obtained from Aldrich (Gillingham, UK). De-aluminated zeolite Y was provided kindly by Ineos Ltd, Warrington, UK ($Si/Al = 30$) and Degussa (Dusseldorf, Germany) ($Si/Al \geq 200$).

The procedures followed for zeolite and AlMCM-41 metal ion exchange were adapted from Hathaway and Davis (17). A sample of BPL coal-based, granular, activated carbon was supplied by Chemviron Ltd (Oldham, UK) and used for comparison purposes. The series of silica gels were provided by Ineos Ltd.

Noncarbonaceous samples were characterized by powder x-ray diffraction (XRD) using a Philips (Cambridge, UK) diffractometer (Cu Kα radiation) and, where appropriate, elemental chemical analysis (Butterworth Laboratories, Teddington, UK). The surface areas and pore size distributions were determined by nitrogen adsorption/desorption (Coulter Omnisorb, High Wycombe, UK) at 77K. Solid State ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were recorded at the Engineering and Physical Sciences Research Council (EPSRC) facility at the University of Durham.

Adsorbents were prepared by deposition of 2% (w/w) TEDA on each of the support materials, using the standard method developed for activated carbons. Samples of support were dried at 100°C for 24 hr in an oven and then held under vacuum in a glass system (designed with the minimum glass surface area) at room temperature for 5 hr. The appropriate weight of TEDA was introduced to the closed system at the same temperature and left for two days, after which all the TEDA had sublimed and been adsorbed by the support in all cases.

The interaction between TEDA and CNCl on each support was monitored using a Setaram (Lyon, France) continuous combined thermogravimetric analyzer/differential scanning calorimeter (model TG/DSC111). Samples of the adsorbent and a non-adsorptive reference material (2.5 mg) were placed in the instrument under a helium flow ($50\,\mathrm{mL\,min^{-1}}$) at 30°C until they had stabilized. Cyanogen chloride ($250\,\mu\mathrm{L}$) was injected into the helium. The sample weight and the heat output of the differential calorimeter were monitored, relative to the reference, until no further changes occurred. Adsorption was an exothermic process and the total heat output was recorded in joules. The overall irreversible sample weight increase was converted to moles of CNCl and the molar enthalpy of CNCl adsorption calculated. Measurements were made for each support and support/TEDA system.

The interaction between TEDA and support was studied using temperature programmed desorption (TPD) on adsorbents with 2% (w/w) TEDA loadings. Samples (5 mg) were heated from 25 to 600°C at a rate of $10^{\circ}\mathrm{C\,min^{-1}}$, using a solid insertion probe fitted with a home-built temperature programmer described elsewhere (18) positioned in the high vacuum source of a VG Micromass (Manchester, UK) 70–70 double focusing mass spectrometer. Mass spectral data were recorded over the relevant mass range for each experiment and compared with the library mass spectrum of TEDA. In this way, it was established that TEDA was desorbed largely intact in all cases. Experiments were performed in duplicate to ensure reproducibility of recorded temperatures of maximum TEDA desorption.

RESULTS

The inorganic supports and the reference BPL carbon used in this study are listed in Table 1. The BPL-activated carbon was chosen for this comparison, as it is a carbon that is currently in widespread use as an adsorbent for toxic gases and as a support for impregnants such as TEDA. Furthermore, recent studies aimed at identifying optimum carbon supports for TEDA have found BPL carbon to be a good support for this impregnant (19).

Specific surface areas (Brunauer, Emmett, and Teller method) of the support materials are shown in Table 1. Temperature-programmed desorption data are shown as the temperature at which the rate of TEDA desorption is a maximum. A typical mass spectrometer, traces from TPD experiments on TEDA-impregnated Na^+-zeolites X and Y appear in Fig. 1. Note that the difference in intensities of the two mass spectral signals are not significant but simply a consequence of small variations in sample mass in the solid insertion probe attachment for the mass spectrometer. It was established that such variations did not affect the temperature of maximum desorption.

The molar heats of adsorption/interaction of CNCl on both the untreated support materials and the TEDA-impregnated supports are given in the last two

Table 1. Inorganic Supports: Physical Characteristics, Adsorbed Triethylenediamine (TEDA) Temperature Programmed Desorption (TPD) Data, and Cyanogen Chloride (CNCl) Molar Adsorption Enthalpies

Support	Surface Area ($m^2\,g^{-1}$)	TPD: Temperature of Maximum TEDA Desorption (°C)	ΔH^0_{ads} CNCl (No TEDA) ($kJ\,mol^{-1}$)	ΔH^0_{ads} CNCl (2% TEDA) ($kJ\,mol^{-1}$)
BPL carbon	1140	170	58	180
Silica 1 (4.0 nm)	697	260	84	149
Silica 2 (6.5 nm)	426	230	84	211
Silica 3 (10.0 nm)	376	200	64	271
Silica 4 (25.0 nm)	297	210	43	297
Na 13 X (Si/Al = 1.3)	750	495	60	344
Na Y (Si/Al = 2.6)	770	390	49	273
De-Al Na Y (Si/Al = 30)	867	395	51	267
De-Al Na Y (Si/Al = 200)	661	240	32	135
Na 13 X (Si/Al = 1.3)	750	495	60	344
Cs 13 X	541	360	59	440
Na Y (Si/Al = 2.6)	770	390	49	273
Cs Y	571	400	53	340
MCM-41	868	200	40	72
Na-AlMCM-41 (Si/Al = 40)	659	320	63	83
Cs-AlMCM-41	250	130	124	278

columns of Table 1. These values are being used as indicators of effectiveness for irreversibly adsorbing CNCl.

CYANOGEN CHLORIDE ADSORPTION

Figure 2 shows TG/DSC traces for CNCl on Na^+-zeolite X, with and without TEDA. Note that CNCl adsorption in the absence of TEDA is fully and rapidly reversible. With TEDA present, the adsorption is largely irreversible and desorption of the fraction of CNCl which is only reversibly adsorbed, is relatively slow. Irreversible adsorption is presumably associated with the reaction between CNCl and TEDA (reaction 1).

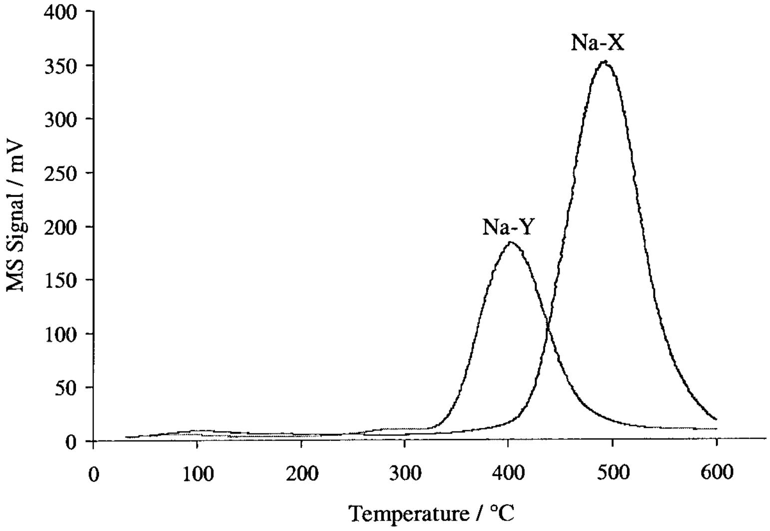


Figure 1. Temperature-programmed TEDA desorption profile ($m/e = 42$), for TEDA-Impregnated Na^+-Zeolite X and Na^+-Zeolite Y. (Note that the difference in signal intensities between the two samples is associated with instrumental conditions and is not significant.)

Consistent with this are the much greater molar enthalpies of CNCl adsorption in the presence of TEDA than in its absence, and this largely confirms that TEDA plays a similar role on inorganic supports to that on carbon. In fact, most of the measured enthalpies of adsorption are very much higher for the inorganic supports than for BPL-activated carbon.

Silica Gel Supports

This series illustrates the effect of support pore size on TEDA activity. The molar enthalpies of adsorption for CNCl on TEDA/silica rise steadily as the pore size increases up to 25 nm diameter (even though surface area is decreasing).

The TPD experiments show that the TEDA desorption temperatures fall as the pore size increases. However, this trend would be predicted anyway, based on the desorption of a physisorbed adsorbate from pores of increasing diameter and, in itself, tells us little about any relationship which might exist between the strength of TEDA/surface bonding and enthalpies of reaction with CNCl.

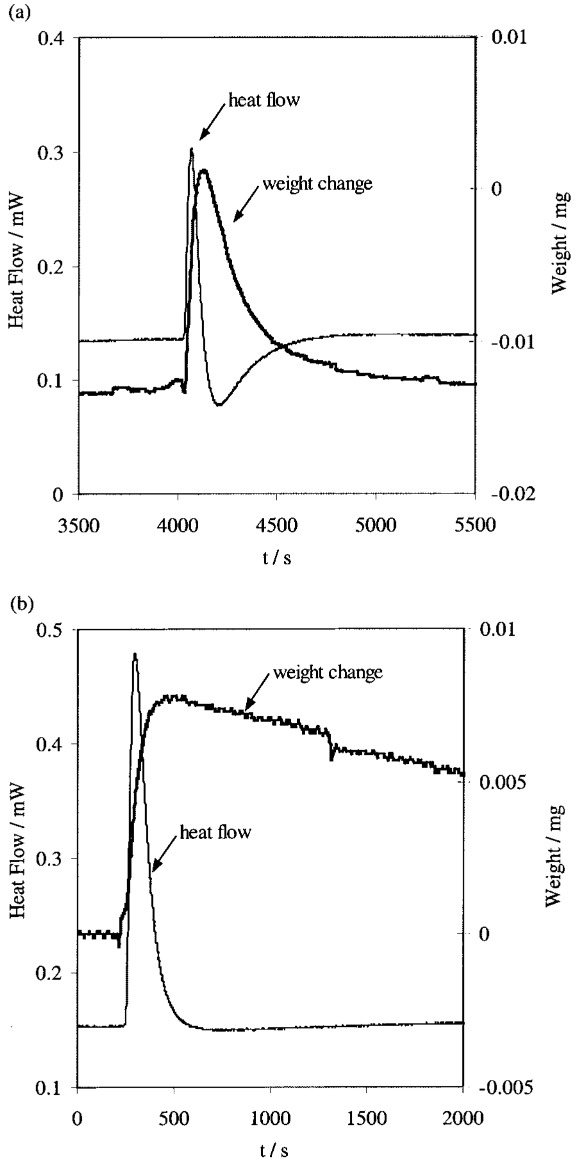


Figure 2. Thermogravimetric analyzer/differential scanning calorimeter traces for the interaction of Na^+-exchanged Zeolite X with CNCl, (a) in the absence of TEDA and (b) with 2% (w/w) adsorbed TEDA.

Zeolite Supports

The faujasitic zeolites, X and Y, have been used to evaluate the effect of varying both the Si/Al ratio and the nature of the exchangeable cation. Comparing the Na^+ forms of zeolite X, Y and the two de-aluminated Y zeolites, it seems that the enthalpy of reaction/adsorption increases with Al content, suggesting that the presence of exchangeable cations is important for imparting activity to adsorbed TEDA. It is worth noting that the enthalpies of adsorption for the zeolite with the highest exchange capacity, zeolite X, is higher than any measured for the silica gel supports, even though the zeolite pores are considerably smaller than those of any of the silicas. This implies that the presence of exchange capacity in the support might be an equally, if not more, important factor than pore size for TEDA activity.

The TPD data show that TEDA desorption occurs at higher temperatures generally from these zeolites than from the silicas. This may, in part, be a consequence of the "fit" of TEDA in the zeolite micropores, resulting in stronger binding to the surface than in larger pores where TEDA binds to only one part of the pore wall. Indeed, this may also be a factor in explaining the high molar enthalpies of adsorption of TEDA on zeolites described above. In addition to this overall difference between desorption temperatures for silicas and zeolites, there is also a trend toward higher TEDA desorption temperatures as the exchangeable cation concentration in the zeolite is increased. This suggests that TEDA is bound more strongly to cation exchange sites in the zeolites than to other sites.

Data are also shown for the Cs^+-exchanged zeolites. Two initial points should be made. The first is that the surface areas for the Cs^+ forms are lower than that for the Na^+ forms. This phenomenon is well known, and Cs^+ is thought to partially block some of the pores in zeolite lattices (17,20,21). The second point is that bulk elemental analyses performed on the X and Y zeolites show that, with Cs^+ exchange, a maximum of 50% Cs^+ exchange could be achieved. So the nominal Cs^+ zeolites are, in fact, Na^+/Cs^+ zeolites. Neither of these points significantly affect the conclusions drawn below.

Table 1 shows that the enthalpies of adsorption of CNCl are consistently higher for the Cs^+ than the Na^+ forms of the zeolites (and the same trend is seen for AlMCM-41 described below), suggesting that the Cs^+ forms are the more effective adsorbents for CNCl. However, the TPD data for the two ion-exchanged forms of zeolite X and Y do not show consistent patterns, with the higher TEDA desorption temperatures corresponding to the Na^+ form of zeolite X but the Cs^+ form of zeolite Y. Consequently, no attempt is made to interpret these differences in TPD results in terms of the relative reactivities of Na^+ and Cs^+ exchange ions toward CNCl.

Mesoporous Molecular Sieve Supports

The MCM-41 supports were prepared in both siliceous form and as aluminosilicate AlMCM-41 ($Si/Al = 40$). The powder x-ray diffraction pattern and ^{27}Al MAS NMR spectrum of calcined Na^+-AlMCM-41 are shown in Fig. 3. The NMR spectrum demonstrates that virtually all lattice Al are tetrahedrally coordinated. The XRD pattern is consistent with the structure of AlMCM-41 (16). Both materials exhibit pore diameters of about 2.5 nm (estimated from N_2 desorption) in their as-prepared form. The Si/Al ratio of AlMCM-41 was verified by elemental analysis.

The surface areas are less for the AlMCM-41 supports than for the siliceous MCM-41, consistent with the reduced structural integrity and long range order which is inevitably observed in these materials on incorporation of lattice heteroatoms (16). In addition, Table 1 shows that the surface areas fall on exchange with Cs^+, as in zeolites, presumably also due to pore blocking by the larger cation (20,21).

On the basis of the results for silica gels and for zeolitic supports, we initially predicted that the relatively large pore size of the AlMCM-41, combined with its cation exchange capacity, especially in the presence of Cs^+ ions, would make it a very effective support for TEDA. Surprisingly, this does not seem to be the case and the enthalpies of CNCl adsorption are no higher, and in many cases lower, than those for equivalent zeolite supports.

However, despite the relatively low enthalpies of adsorption overall, there are some consistent trends in the behavior of the MCM-41 supports. The very low enthalpy for siliceous MCM-41 compared to AlMCM-41 supports the idea that cation exchange capacity is important in activating TEDA, and the higher CNCl adsorption enthalpy for the Cs^+ over the Na^+ form is consistent with the zeolite data.

The TPD results show that TEDA is desorbed at significantly lower temperatures from both MCM-41 and AlMCM-41 than from zeolites X and Y. This possibly suggests that there may be fundamental differences between the nature of TEDA adsorption on zeolites and on MCM-41 supports, and these differences could, in principle, be linked to the relatively low activities of TEDA on these supports.

DISCUSSION

There are a number of factors that might be expected to influence the activity of adsorbed TEDA toward reaction with CNCl. The first is the specific surface area of the support and, with activated carbon supports, surface area has been traditionally used as a likely indicator of effectiveness. A significant surface

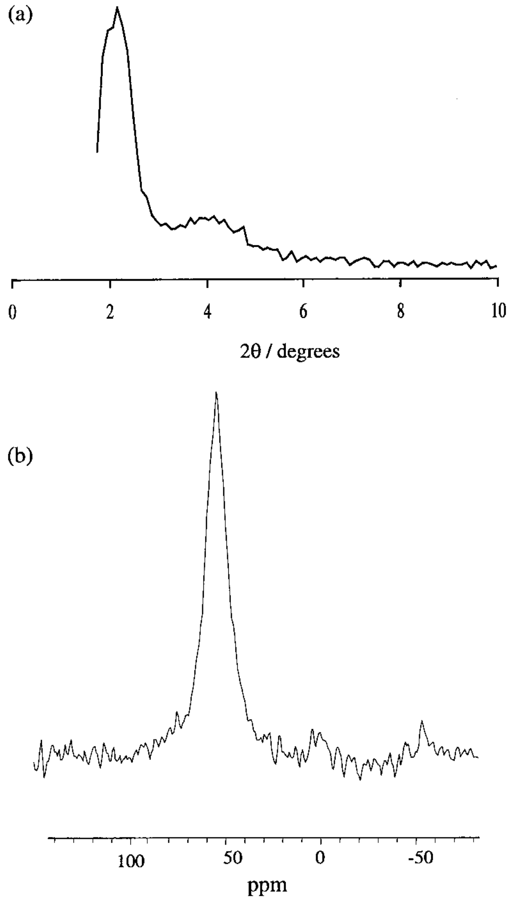


Figure 3. (a) Powder X-ray diffraction pattern, using Cu Kα radiation, and (b) ^{27}Al MAS NMR Spectrum [with respect to $Al(H_2O)_6^{3+}$ at 0 ppm], of calcined Na^+-AlMCM-41.

area is obviously required of any support material, but the results here for inorganic supports show that specific surface area is not a *primary* factor in controlling the ability of these supports to activate adsorbed TEDA.

This is not surprising since the surface area measured by N_2 adsorption would not be necessarily expected to represent the area accessible to TEDA. In the case of microporous zeolites for example, a proportion of the surface would be inaccessible to TEDA because the relatively low temperature used to activate the zeolite for TEDA adsorption would not fully dehydrate the lattice beforehand. Furthermore, TEDA would be too large to enter all but the α-cage in the zeolite structure. Recent similar studies on activated carbons are now suggesting that the same may be true for these adsorbents and surface area alone may not be a good guide to effectiveness as a support for TEDA (19).

Another possible factor is the hydrophilicity of the support surface. It seems likely that a hydrophilic surface would promote hydrogen bonding and stable adsorption, as well as effective dispersion of TEDA, and therefore the exposure of a large surface area for reaction. A hydrophobic surface, which interacts with TEDA less strongly, might be expected to promote pore filling instead, and a much lower resultant available surface area. The traditional support, carbon, is relatively hydrophobic. Indeed a comparatively low TEDA desorption temperature of 170°C was recorded in TPD experiments, supporting the view that TEDA is held only weakly to the carbon surface. On this basis, siliceous inorganic supports should offer advantages, particularly if higher loadings of TEDA are required.

Amongst the inorganic supports studied here, the silica gels exhibit abundant surface silanol groups making them very hydrophilic. The zeolites contain lattice aluminum enhancing surface polarity but they lack the pendant hydroxyl groups of the silicas. The MCM-41 supports are probably closer to the silicas in this respect, although they are probably less hydrophilic as a result of the calcination step in their synthesis, which inevitably condenses some of the surface silanol groups.

Another factor is the accessibility of adsorbed TEDA to CNCl. The data for silica supports show that activity increases with pore size (up to 25 nm at least), and this probably reflects the accessibility of TEDA within the support pores. The larger pores would then be less likely to block with TEDA and hence more likely to allow co-adsorption of CNCl.

A further question is how the surface interaction between TEDA and the lattice is likely to influence the reaction with CNCl. The first step in the reaction between CNCl and TEDA involves nucleophilic attack by the TEDA amine nitrogen on the carbon atom in CNCl. If this is rate determining, the base strength of the amine is crucial. It follows, therefore, that TEDA adsorbed on an acid site might be relatively inactive, whereas adsorption on a more basic site should enhance the basicity, and hence the activity of the amine towards reaction with CNCl.

This is consistent with the results for zeolites. Triethylenediamine activity increases with ion exchange capacity and it is highest for the Cs^+ forms in all cases. Alkali metal exchanged zeolites are known to be basic solids, with base strength increasing with the ionic radius of the metal cation (22).

The results from silica and zeolite supports are consistent and seem to give clear guidance on desirable support properties. In particular, the basicity of the support seems to confer activity to adsorbed TEDA. This result alone represents a potentially significant advantage of zeolitic over carbon supports.

However, the mesoporous molecular sieve supports, which initially seem to offer similar surface properties to zeolites but in a meso- rather than microporous structures, show disappointingly low activities for adsorbed TEDA. It is difficult to explain this, but one possible reason is that the low concentration of lattice aluminum, together with fewer pendant hydroxyl groups, makes the surface relatively hydrophobic and incompatible with adsorption of TEDA, so the amine may be poorly dispersed over the support surface.

Despite the overall poor performance of MCM supports, it is clear that presence of exchangeable cations enhances TEDA activity. This leads to another possible explanation for the observed activities, that the alkali metal cations are less basic in AlMCM-41 lattices than in zeolitic lattices. It is certainly true that acidic cations are weaker in AlMCM-41 than in zeolites, due in part to the presence of much of the isomorphously substituted lattice aluminum being *within*, rather than *on the outsides of*, the pore walls (23). The same structural features would certainly reduce the basicity of Na^+ and Cs^+ cations compared to the same exchangeable cations in zeolites.

Finally, one aspect of the results with AlMCM-41 supports not so far discussed may prove to be very significant. The molar enthalpies of CNCl adsorption on Cs^+ exchanged AlMCM-41 in the absence of TEDA are surprisingly high, and suggest that AlMCM-41 in this ion-exchanged form may be as active for CNCl adsorption as many of the other supports with adsorbed TEDA. The reason for this is unclear. It is possible that the relatively large Cs^+ ion is much more accessible in an AlMCM-41 mesopore than in a zeolite. This, combined with the relatively hydrophilic nature of the AlMCM-41 surface, may allow it to act as an effective base in binding CNCl. Further study is being carried out with these adsorbents to identify the products of any surface reaction of CNCl at the cation site, and to characterize any properties of the adsorbent which impart reactivity toward CNCl without the need for impregnants.

Studies of the ageing properties, and susceptibilities to storage temperature and humidity of these inorganic adsorbents are underway. Preliminary results suggest that deterioration in the reactivity of adsorbed TEDA is comparable with, and no worse than, that seen with carbon-based adsorbents.

CONCLUSION

It seems clear that inorganic supports, particularly zeolitic materials, can impart significantly higher activities to TEDA toward CNCl decomposition than conventional activated carbon supports. We believe that this demonstrates the possibility of “tuning” zeolitic supports to activate the adsorbed TEDA for reaction.

On the basis of this work, it seems likely that this activation can be achieved through basic sites on the surface of the support, and the presence of such sites would seem to be a desirable feature for an effective support material. Beyond this, pore size is also important, with large pores allowing access of CNCl to adsorbed TEDA. There may well be further factors, however, particularly related to the hydrophilicity of the aluminosilicate surface, which are important in conferring activity toward adsorbed TEDA, and the importance of these has not yet been established fully.

ACKNOWLEDGMENTS

Thanks are due to Chemical and Biological Protection, Dstl, Porton Down, for funding the work at both Porton Down and Huddersfield under contract 2258/002/CBD, and for giving permission to publish. The EPSRC MAS NMR facility at the University of Durham is acknowledged for providing spectra on synthesized zeolites and molecular sieves.

REFERENCES

1. Hall, C.R.; Sing, K.S. Protection—The Black Art. Chem. Br. **1988**, *24*, 670–676.
2. Blower, C.J.; Smith, T.D. FTIR Spectroscopic Study of the Zeolitic Adsorption of Hydrogen Cyanide on Acidic Sites. J. Chem. Soc. Faraday Trans. **1994**, *90*, 919–929.
3. Garforth, A.; Lin, Y.H.; Sharratt, P.; Dwyer, J. Catalytic Polymer Degradation for Producing Hydrocarbons over Zeolites. Stud. Surf. Sci. Catal. **1999**, *121*, 197–202.
4. Blocki, S.W. Hydrophobic Zeolite Adsorbent—A Proven Advancement in Solvent Separation Technology. Environ. Prog. **1993**, *12*, 226–230.
5. Dahl, I.M.; Myhrvold, E.; Slagtern, Å.; Stöcker, M. Adsorption of Lower Alcohols from Water Solutions on High Silica Zeolites, Mesoporous MCM-41 and AlPO4-5. Ads. Sci. Technol. **1997**, *15*, 289–299.
6. Denayer, J.F.; Souverijns, W.; Jacobs, P.A.; Martens, J.A.; Baron, G.V. High Temperature Low Pressure Adsorption of Branched C_5–C_8 Alkanes on Zeolite Beta, ZSM-5, ZSM-22, Zeolite Y, and Mordenite. J. Phys. Chem. B **1998**, *102*, 4588–4597.
7. Nguyen, C.; Do, D.D. Adsorption of Benzene and Ethanol on Activated Carbon, MCM-41 and Zeolite Y. Ads. Sci. Technol. **1998**, *16*, 439–452.

8. Weitkamp, J.; Ernst, S.; Grunzel, B.; Deckwer, W.D. Separation of Gaseous Water Ethanol Mixtures by Adsorption on Hydrophobic Zeolites. Zeolites **1991**, *11*, 314–317.
9. Grady, M.C.; Gorte, R.J. Adsorption of 2-Propanol and Propene on H-ZSM-5—Evidence for Stable Carbenium Ion Formation. J. Phys. Chem. **1985**, *89*, 1305–1308.
10. Biaglow, A.I.; Adamo, A.T.; KoKotailo, G.T.; Gorte, R.J. An Examination of the Acid Sites in SAPO-5. J. Catal. **1991**, *131*, 252–259.
11. Tittensor, J.G.; Gorte, R.J.; Chapman, D.M. Isopropylamine Adsorption for the Characterisation of Acid Sites in Silica–Alumina Catalysts. J. Catal. **1992**, *138*, 714–720.
12. Kim, J.Y.; Yu, J.; Kevan, L. Location of Cupric Ion and Its Adsorbate Interactions in Cu(II)-Exchanged Mesoporous AlMCM-41 Determined by Electron Spin Echo Modulation. Mol. Phys. **1998**, *95*, 989–997.
13. Corma, A. From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. Chem. Rev. **1997**, *97*, 2373–2419.
14. Li, H.X.; Santiesteban, J.G.; Armor, J.N. Triethylendiamine Synthesis with Base-Treated Zeolites as Catalysts. US Patent 5,731,449, Sept 23, 1996.
15. Cheng, C.F.; Park, D.H.; Klinowski, J. Optimal Parameters for the Synthesis of the Mesoporous Molecular Sieve [Si]-MCM-41. J. Chem. Soc. Faraday Trans. **1997**, *93*, 193–197.
16. Luan, Z.H.; Cheng, C.F.; Zhou, W.Z.; Klinowski, J. Mesopore Molecular Sieve MCM-41 Containing Framework Aluminum. J. Phys. Chem. **1995**, *99*, 1018–1024.
17. Hathaway, P.E.; Davis, M.E. Base Catalysis by Alkali Modified Zeolites. 1. Catalytic Activity. J. Catal. **1989**, *116*, 263–278.
18. Fesenko, E.A.; Barnes, P.A.; Parkes, G.M.B.; Brown, D.R.; Naderi, M. A New Approach to the Study of the Reactivity of Solid-Acid Catalysts: The Application of Constant Rate Thermal Analysis to the Desorption and Surface Reaction of Isopropylamine from NaY and HY Zeolites. J. Phys. Chem. B **2001**, *105*, 6178–6185.
19. Dawson, E.A.; Parkes, G.M.B.; Barnes, P.A.; Chinn, M.J.; Norman, P.R. A Study of the Activation of Carbon Using Sample Controlled Thermal Analysis. J. Thermal Anal. Calorim. **1999**, *56*, 267–273.
20. Barrer, R.M. Zeolite Frameworks, Cations and Water Molecules. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; 1st Ed.; Academic Press: London, 1978; 71–76.
21. Dyer, A. Zeolites as Ion Exchangers. In *An Introduction to Zeolite Molecular Sieves*; 1st Ed.; Wiley: New York, 1988; 63–76.
22. Barthomeuf, D. Basic Zeolites: Characterisation and Uses in Adsorption and Catalysis. Catal. Rev. Sci. Eng. **1996**, *38*, 521–612.

23. Brown, D.R.; Yiu, H. Lewis and Bronsted Acid Catalysis with AlMCM-41 and AlMMS: Dependence on Exchange Cation. Catal. Lett. **1998**, *56*, 57–64.

Received April 2001
Revised July 2001

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:35 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS120002242