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BENZENE DISPLACEMENT ON IMOGOLITE

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Abstract—The adsorption of ^{13}C-labeled benzene on imogolite has been studied on samples which had been evacuated and then heated to remove water below their decomposition point. After adsorption of labeled benzene, the samples were studied by nuclear magnetic resonance using non-spinning techniques. The results show that benzene can occupy more than one pore type and that water does not displace benzene from the intra-tube pores at atmospheric pressure. A further finding is that there are at least two types of adsorbed benzene in so called inter-tube pores, one of which is more rigidly held than that in intra-tube pores. The presence of disordered materials at the edge of pores could also play a role in altering the pore mouth thereby creating new types of pores. Moreover, where two tubes do not pack properly, space might be created where an adsorbed molecule may bind more tightly than expected in a conventional pore.

Key Words—Benzene, Imogolite, Solid-state Nuclear Magnetic Resonance, Pores.

INTRODUCTION

Imogolite is a microporous hydrated aluminosilicate with a well-defined structure. It is believed to have between 10 and 14 gibbsite units (20 and 28 Al atoms) per tube, with circumference depending on origin. Its structure can be described as a tube whose wall consists of a curved single sheet of modified gibbsite (Cradwick *et al.*, 1972). Whereas gibbsite consists of a flat sheet of octahedral alumina, in imogolite the hydrogens on the hydroxyls on one side of the gibbsite octahedral sheets are replaced by silica tetrahedra such that the silanol groups are facing towards the inside of the tube. As the Si–O bonds are shorter than Al–O bonds, this substitution causes the gibbsite sheet to curve. The chemical composition of this mineral is $(OH)_3Al_2O_3SiOH$, illustrating the layers of atoms as one passes from the exterior to interior of the tube.

The external tube diameter has been shown to be ~2.5 nm by TEM and SAXS (Ackerman *et al.*, 1994; Barrett *et al.*, 1991; Bursill *et al.*, 2000; Kajiwara *et al.*, 1985, 1986) and the lengths of the tubes are of the order of several μm. Electron micrographs have shown that the tubes exist in a high degree of order as self-aligned bundles. The consequence of this packing is that the imogolite structure consists of three types of pores (Figure 1). These are: (1) intra-tube pores (Type A, Figure 1); (2) inter-tube spaces (Type B, Figure 1), which are the spaces between three aligned tubes in a regular packing; and (3) meso-pores (Type C, Figure 1), which are the empty spaces which exist between bundles of tubes. Simple inspection of models shows that the pore-size relationship is C>A> B. B pores are so small (0.3–0.4 nm) that they can be ignored in any discussion of adsorption (Ackerman *et al.*, 1993).

A large number of studies have been performed on the adsorption of neutral molecules on imogolite (Ackerman *et al.*, 1993, 1994; Huling *et al.,* 1992; Imamaru *et al.*, 1993, 1996; Adams, 1980; He and Horikawa, 1997; Karube *et al.*, 1992) including benzene (Adams, 1980) and water (Karube and Abe, 1998; Earl *et al.*, 1994; Ozeki *et al.*, 1994). The faster-relaxing water was ascribed to that immobilized on the inner surface of the tubes, *i.e.* in A pores and the other water as being present in C type pores. Little is known of how benzene adsorbs.

Here we used ^{13}C-labeled benzene to investigate adsorbed benzene. The objectives of the study were to determine the location and mobility of adsorbed benzene molecules on imogolite and to determine the ability of water vapor or air to displace benzene from A- and C-type pores of imogolite.

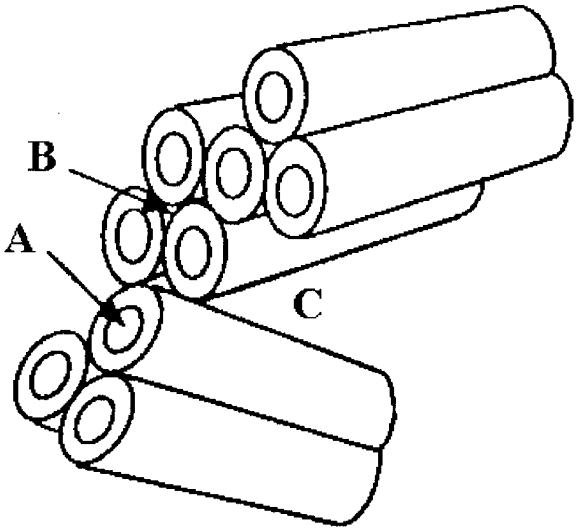


Figure 1. Three types of cavities (A,B,C) formed in the imogolite bulk (modified from Ackerman *et al.*, 1993)

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EXPERIMENTAL

Preparation of imogolite

Imogolite was prepared essentially using the method of Wada *et al.* (1979). To a stirred solution of aluminum chloride (4 mM) was slowly added an aqueous solution of tetraethylorthosilicate (2 mM) so that the final concentrations were 2 mM with respect to Al and 1 mM with respect to Si. Aqueous NaOH (16 mL, 0.1 M) was then added at the rate of 0.5 mL/min until the Al:Si:OH ratio was 2:1:4 (Wilson *et al.*, 2001). The solution was stirred for 2 h and then heated at 371 K for 5 days. A white gel was obtained by flocculation with NaCl and collected by centrifuge. The white gel was purified by dialysis in 12,000 MWCO tubes (Sigma-Aldrich) for 4 days. A white feathery solid was collected by freeze drying. The purity of the sample was checked by TEM, ^{29}Si and ^{27}Al NMR and infrared (IR) spectroscopy (Barron *et al.*, 1982; Bursill *et al.*, 2000; Farmer *et al.*, 1983; Kajiwara *et al.*, 1985, 1986; McKenzie *et al.*, 1989; Wilson, 1987; Wilson *et al.*, 1988).

Preparation of imogolite incorporating ^{13}C-labeled benzene

Three separate experiments were carried out to determine the extent of adsorption of ^{13}C-labeled benzene in the type-A pores. In procedure 1, methods were used which for zeolites have been used to trap only intra-cavity (tubes in this case) benzene (Breck, 1974; Barrer, 1978). Procedures 2 and 3 were variants to see the amount of bound benzene in C pores. All preparative steps were carried out on a home-built vacuum line and care was taken to exclude all water. Imogolite (7.5 mg) and ^{13}C-labeled benzene (Sigma-Aldrich) (0.4 mg) were degassed under vacuum (10^{-4} kPa) at room temperature before the ^{13}C-labeled benzene was isolated from the system. Removal of water from the imogolite was achieved by stepwise heating the sample (~1 K/min) under vacuum to a temperature of 573 K (Farmer *et al.,* 1983; Wilson *et al.,* 1988). The slow increase in temperature was to avoid dissociation of the imogolite structure which was checked by solid-state ^{29}Si NMR. In procedure 1, the measured quantity (0.4 mg) of ^{13}C-labeled benzene was then condensed into the water-free imogolite from a side arm and sealed in 4 mm o.d. tubes. A loading of 12 ^{13}C-labeled benzene molecules per imogolite tube cross-section was used (corresponding to one molecule per empirical formulae of imogolite-12 ($(HO)_3Al_2O_3SiOH$). In procedure 2, a similar loading was used on the water-free imogolite sample but the sample was opened to moist air after annealing so water could be captured in pores from which benzene could be displaced. In principle, benzene should only be in the intra-tube A pores bearing in mind the literature on zeolites (Breck, 1974; Barrer, 1978). In procedure 3, the imogolite was not freed of intrinsic water or dehydrated. The ^{13}C-labeled benzene was added after the imogolite was degassed at 1.3×10^{-5} kPa for 2 h. The sample was then exposed to moist air. This experiment ensures that the porewater is retained.

Nuclear magnetic resonance (NMR) spectroscopy

Solid-state ^{13}C NMR spectra were obtained on a Bruker DRX 200 MHz Avance instrument operating at 50.33 MHz with proton decoupling during acquisition. Static spectra were obtained at the magic angle (MA) but without spinning. The glass samples were inserted directly into the probe. The spectra were normally acquired using single-pulse experiments with a 90° pulse length of 4 μs and a 20 s recycle time. Some cross-polarization (CP) experiments were carried out with a 90° pulse length of 4 μs, a 2 s recycle time and a contact time of 1–2 ms. All spectra were collected in 1 K points, zero filled to 4 K, and Fourier transformed with a line-broadening factor of 5–30 Hz to obtain the frequency domain spectra. An external reference of TMS (0 ppm) was used. The low-field peak of adamantane was employed as a secondary reference (38.3 ppm). An internal standard for spin counting was not used but differences in tuning were small between samples and the changes observed were large so this was not necessary for semi-quantitative comparisons. A number of experiments was carried out with different numbers of scans. Line widths at half-height measurements were made at high attenuation to maximize accuracy.

The ^{29}Si and ^{27}Al solid-state NMR spectra were obtained using established procedures on the same instrument to check for purity of imogolite (Barron *et al.*, 1982; McKenzie *et al.*, 1989; Wilson, 1987; Wilson *et al.*, 1988).

RESULTS AND DISCUSSION

Table 1 shows data on spectra obtained under different conditions. They are static spectra so chemical shift anisotropy has not been removed. Although samples are at the magic angle, without spinning, all benzene molecules are not so orientated. The samples are static but the molecules are mobile although not liquids. Thus a powder pattern spectrum is not obtained and line broadness reflects mobility.

Table 1 shows that for the static ^{13}C spectrum of pure ^{13}C-labeled benzene in the absence of imogolite, the line width at half height $W_{1/2}$ is 61 Hz. In contrast, the line width at half height is 667 Hz for the static spectrum of the benzene in imogolite that had been prepared without prior heating and exposed to air (procedure 3). A ^{1}H NMR study confirmed the presence of water which could be present before the benzene was adsorbed or introduced after exposure to air. Water would still fill the A pores of this imogolite and any benzene is probably surface bound to C pores. The benzene is tightly bound to the surface since it does not evaporate. This is also shown by the large line width.

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Table 1. Spectroscopic parameters for NMR experiments with ^{13}C-labeled benzene and imogolite.

Experiment	Details of sample	Relative signal intensity on an equal number of scans basis	Line width at half height ($W_{1/2}$, Hz)
Bloch decay spectrum, imogolite absent	Free benzene	n.d.	61
Procedure 3. Bloch decay spectrum, imogolite present	Degassed, opened	1	667
Procedure 1. Bloch decay spectrum, imogolite present	Vacuum, no exposure to air	55	152
Procedure 1. Cross polarization spectrum, imogolite present	Vacuum, no exposure to air	20	265
Procedure 2. Bloch decay spectrum, imogolite present	Vacuum, opened	2	364

n.d.: not determined and irrelevant

In the Bloch decay static spectrum of benzene loaded in imogolite freed of intrinsic water (procedure 1) the spectrum shows 55 times more benzene for the same number of scans than obtained using procedure 3. Thus benzene is adsorbed into sites not otherwise available. The line width is 152 Hz, which is much smaller than the sample prepared by procedure 3 (667 Hz). Thus the extra adsorbed benzene is more mobile. The CP spectrum has a width at half height ($W_{1/2}$) of 265 Hz, a little larger than that seen in the Bloch decay spectrum. The reason for this is that at the contact time used in the experiment, the slower moving benzene is observed in greater intensity. This is confirmed since the Bloch decay spectrum gave a better signal to noise ratio for the same number of scans than the CP spectrum. At 1–2 ms contact time, cross polarization kinetics do not give optimum signal intensity when the dipolar interaction is severely weakened by molecular motion (Wilson, 1987; Gizachew *et al.*, 1994; Hanna and Wilson, 1992). The molecules are not rotating quickly enough, however, to reduce the C-H dipole interaction to zero, as is the case for liquid benzene. This benzene is adsorbed and not free as in a liquid. Therefore the extra benzene is adsorbed but in different types of pores to those described above.

The spectrum for the sample obtained on the imogolite freed of intrinsic water but exposed to air (procedure 2) is different. In this instance, only benzene that has replaced water under vacuum but now cannot be removed at atmospheric pressure is present, *i.e.* it is possibly in the intra-tube A pores. The signal intensity is greater than that for the unheated sample exposed to air which shows imogolite has taken up more benzene because the water has been displaced. It has less signal intensity compared with the equivalent spectrum of the heated sample which was not exposed to air (Table 1) showing that exposure to air removes loosely-bound benzene. The signal intensity is better than that of the sample prepared by procedure 3 showing that some extra benzene is captured by thermally removing water prior to benzene adsorption, and this is not lost on exposure to air. It is also more mobile since the line width is less. Thus, benzene is adsorbed which cannot evaporate and it is not benzene in the C pores observed in procedure C. This supports the concept that it is in intra-tube A pores. This benzene is unlikely to be as mobile as the benzene observed in procedure 2 since it is confined inside a pore only approximately twice its size. The diameter, from H across to H, of benzene is 0.4956 nm; the kinetic diameter is 0.62 nm (Adams, 1980).

It also now clear that benzene can occupy more than one pore type and that water or air does not displace benzene from the intra-tube pores (A pores) at atmospheric pressure.

A further finding is that there are at least two types of adsorbed benzene in so-called C pores. One type of C-pore benzene is tightly bound and one type loosely bound. The latter is not free as in a liquid. While it is rash to speculate where these benzene molecules adsorbed, molecular modeling can predict different pore-sizes depending on whether the structure is considered as covalent or ionic (Pohl *et al.*, 1996), and silyating OH groups considerably alters adsorption behavior (Ackerman *et al.*, 1994). The presence of disordered materials at the edge of pores could also play a role in altering the pore mouth thereby creating new types of pores. Moreover where two tubes do not pack properly, space might be created where an adsorbed molecule may bind more tightly than expected in a conventional C pore.

REFERENCES

Ackerman, W.C., Hua, D.W., Kim, Y.W. Huling, J.C. and Smith, D.M. (1994) Adsorption studies of pure and modified imogolite as a potential pore size standard. (In *Characterisation of Porous Soilds* III, J. Rouquel, F. Rodriguez-Reinoso, K.S.W. Sing and K.K. Uger, editors). *Studies in Surface Science and Catalysis*, **87**, 735–744.

Ackerman, W.C., Smith, D.M., Huling, J.C., Kim, Y.-H., Bailey, J.K. and Brinker, C.J. (1993) Gas/vapor adsorption in imogolite: A microporous tubular aluminosilicate. *Langmuir*, **9,** 1051–1057.

Adams, M.J. (1980) Gas chromatographic adsorption studies on synthetic imogolite. *Journal of Chromatography*, **188**, 97–106.

Barrett, S.M., Budd, P.M and Price, C. (1991) The synthesis and characterisation of Imogolite. *International Polymer*

https://doi.org/10.1346/00098600260358111 Published online by Cambridge University Press

Journal, **27**, 609–612

Barron, P.F., Wilson, M.A., Campbell, A.S. and Frost, R.L. (1982) Detection of imogolite in soils using solid state ^{29}Si NMR. *Nature*, **299**, 616–618.

Breck, D.W. (1974) *Zeolite Molecular Sieves*. John Wiley, London, UK.

Barrer, R.M. (1978) *Zeolite and Clay Minerals as Sorbents and Molecular Sieves*. Academic Press, London, UK.

Bursill, L.A., Peng, J.L. and Bourgeois, L.N. (2000) Imogolite: An aluminosilicate nanotube material. *Philosophical Magazine A*, **80**, 105–117.

Cradwick, C.P.G., Farmer, V.C., Russell, J.D., Masson, C.R., Wada, K. and Yoshinaga, N. (1972) Imogolite, a hydrated aluminium silicate of tubular structure. *Nature: Physical Science*, **240**, 187–189.

Earl, W.L., Kim, Y.-W. and Smith, D.M. (1994) NMR measurement of pore structure. *Studies in Surface Science and Catalysis,* **87**, 301–309.

Farmer, V.C., Adams, M.J., Fraser, A.R. and Palmieri, F. (1983) Synthetic imogolite: Properties, synthesis and possible applications. *Clay Minerals*, **18**, 459–472.

Gizachew, D., Vangorkom, L.C.M., Dance, I.G., Hanna J.V. and Wilson M.A. (1994) Cross-polarization dynamics in 2,6-dimethylbicyclo[3.3.1]nonane-exo-2-exo-6-diol inclusion compounds as studied by C-13-magic-angle spinning nuclear magnetic resonance spectroscopy. *Solid State NMR*, **3**, 67–78.

Hanna, J.V and Wilson, M.A. (1992) Cross polarisation of C60 and C70 in the presence of organic impurities. *Journal of Physical Chemistry*, **96**, 6518–6523.

He, M. and Horikawa, Y. (1997) Electrokinetic properties of variable charge clays in the presence of an anionic xanthan polysaccharide and inorganic electrolytes. *Soil Science and Plant Nutrition*, **43**, 307–315.

Huling, J.C., Bailey, J.K., Smith, D.M and Brinker, C.J. (1992) Synthetic imogolite paracrystals. *Material Research Society (Pittsburg, Pennsylvania) Symposium Proceedings*, **271**, 511–516.

Imamura, S., Hayashi, Y., Kajiwara, K., Hoshino, H and Kiato, C. (1993) Imogolite: A possible new type of shape selective catalyst. *Industrial Engineering Chemistry Research*, **32**, 600–603.

Imamura, S., Kokuba, T., Yamashita, T., Okamotao, K., Kajiwara, K. and Kanai, H. (1996) Shape selective copper loaded imogolite catalyst. *Journal of Catalysis*, **160**, 137–139.

Kajiwara, K., Donkai, N., Fujiyoshi, Y., Hiraki, Y., Urakawa, H. and Inagaki, H. (1985) Some remarks on imogolite mesophase. *Bulletin of the Institute of Chemical Research, Kyoto University,* **63**, 320–331.

Kajiwara, K., Donkai, N., Fujiyoshi, Y. and Inagaki, H. (1986) Mesophase of imogolite 2. Microscopic observation of imogolite mesophase. *Macromolecular Chemistry*, **187**, 2895–2907.

Karube, J. and Abe, Y. (1998) Water retention by colloidal allophane and imogolite with different charges. *Clays and Clay Minerals*, **46**, 322–329.

Karube, J., Nakaishi, K., Sugimoto, H. and Fujihira, M. (1992) Electrophoretic behaviour of imogolite under alkaline conditions. *Clays and Clay Minerals*, **40**, 625–628.

MacKenzie, K.J.D., Bowden, M.E., Brown, I.W.M. and Meinhold, R.H. (1989) Structure and thermal transformations of imogolite studied by ^{29}Si and ^{27}Al high resolution solid state NMR. *Clays and Clay Minerals*, **37**, 317–324.

Ozeki, S., Masuda, Y., Nishimoto, Y. and Henmi, T. (1994) Water in spherical, cylindrical and slit-like pores. (In: *Characterisation of Porous Solids* III, J. Rouquel, F. Rodriguez-Reinoso, K.S.W. Sing and K.K. Uger, editors). *Studies in Surface Science and Catalysis,* **87**, 179–186.

Pohl, P.I., Faulon, J.-L. and Smith, D.M. (1996) Pore structure of imogolite computer models. *Langmuir*, **12**, 4463–4468.

Wada, S.-I., Eto, A. and Wada, K. (1979) Synthetic allophane and imogolite. *Journal of Soil Science*, **30**, 347–355.

Wilson, M.A. (1987) *NMR Techniques and Applications in Geochemistry and Soil Chemistry.* Pergamon Press, Oxford, UK.

Wilson, M.A., Wada, K. and Wada, S.I. (1988) Thermal transformations of poorly ordered aluminosilicates. *Clay Minerals*, **23**, 175–190.

Wilson, M.A., Lee, G.S.H. and Taylor, R.C. (2001) Tetrahedral rehydration during imogolite formation. *Journal of Non-crystalline Solids*, **296**, 172–181.

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https://doi.org/10.1346/00098600260358111 Published online by Cambridge University Press