The Interaction of Methanol with Brønsted Acid Sites in ZSM-5

Julian D. Gale,*[a,b] C. Richard A. Catlow[b] and Anthony K. Cheetham[a,b]

[a] *Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, UK*
[b] *Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK*

Semi-empirical cluster calculations (CNDO/BW) of the interaction between methanol and a Brønsted acid site in the zeolite ZSM-5 reveal hydrogen bond formation and a concomitant activation of the electrophilic nature of the methyl group, in contrast to an earlier *ab initio* treatment which suggested an elongation of a C–H bond.

ZSM-5 is known to be a highly effective and shape-selective Brønsted acid catalyst,[1] not least for the conversion of methanol to gasoline,[2] and there is good experimental evidence from both IR and NMR spectroscopy[3,4] that water and methanol are readily protonated in the pores of the zeolite. We have attempted to simulate the protonation reactions by performing calculations on embedded clusters of various sizes, representing the Brønsted acid site and its surroundings in ZSM-5. The calculations were undertaken using the Boyd–Whitehead modification[5] of the CNDO method (CNDO/BW) with the electrostatic lattice potential, evaluated by an Ewald summation, included in the diagonal elements of the core Hamiltonian.[6]

Initially we investigated the embedded cluster that had already been studied at the *ab initio* level by Vetrivel *et al.*[7] This fragment consisted of three tetrahedral TO_4 units, including one aluminium on the T2 site with a proton on an adjacent bridging oxygen. In order to parallel the previous work, half charges (Si^{2+}, O^-) were assigned to the lattice ions surrounding the cluster. Geometry optimization resulted in complete abstraction of a hydrogen from the methyl group by the framework, in agreement with the results found at the *ab initio* level. However, these embedding conditions may be misleading as they correspond to the interaction of methanol with a quadruply negatively charged defect owing to an imbalance between the lattice and cluster charges.

Half charges: $CH_3OH \cdots\cdots HAlSi_2O_{10}{}^{8-}(\text{lattice}^{4+})$

Full charges: $CH_3OH \cdots\cdots HAlSi_2O_{10}{}^{8-}(\text{lattice}^{8+})$

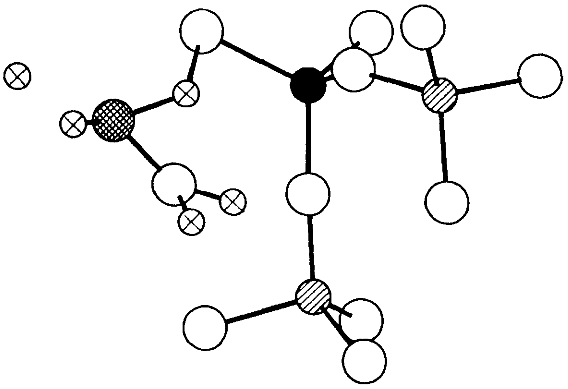

Fig. 1 Methanol bound to an embedded trimer cluster, illustrating the configuration **1** in which the framework has abstracted a proton

Repeating the optimization with full lattice charges again leads to removal of a proton from the methyl group **1**, but now the basic site is a point-charge oxygen ion of the surrounding lattice and the energy of the system tends towards minus infinity. This is clearly an artifact of cluster size.

We next examined a much larger cluster containing 20 tetrahedral atoms representing the double ten-ring unit of the straight channel. Although energy minimisation at the *ab initio* level would be prohibitively expensive for such a cluster, treatment at the semi-empirical level is practicable. Methanol is now found to be hydrogen bonded to the framework proton **2** with the carbon atom acquiring a significantly increased positive charge (Δq_C +0.25), thus enhancing its electrophilicity. This state would be one of several possible intermediates (depending on the aluminium substitution site) formed immediately prior to protonation and could be a direct precursor to the formation of dimethyl ether by nucleophilic attack at the methyl group, leaving water coordinated to the framework defect site.

How are we to explain the contrast between the large cluster results and those on smaller fragments? With small clusters it is difficult to achieve entirely satisfactory consistency between the quantum mechanical region and the surrounding point charge array, and Sauer[8] has argued that use of negatively charged clusters will exaggerate the proton affinity of the cluster unless the two regions are carefully matched. It is clear that the field within the zeolite pore has a major influence on the nature of the reactions for sorbed molecules and that it is easier to simulate this field accurately when larger clusters are used. At the present time, this can only be done by semi-empirical methods.

The present calculations are broadly consistent with the widely held view[9] that the methanol to gasoline reaction proceeds *via* a carbenium ion intermediate, although a bimolecular process involving two methanol molecules, one of which is bound to the active site, is also in accordance with our findings. Nevertheless, we believe that it is quite possible that C–H bond weakening could play an important role in the vicnity of defects carrying a high local negative charge density. In general, however, the dominant initial process is a strong association of the methanol with protonated framework sites, with subsequent protonation, though the possibility is suggested that formation of dimethyl ether proceeds by the reaction of two methanol molecules, one of which is coordinated to the framework, enhancing its electrophilicity.

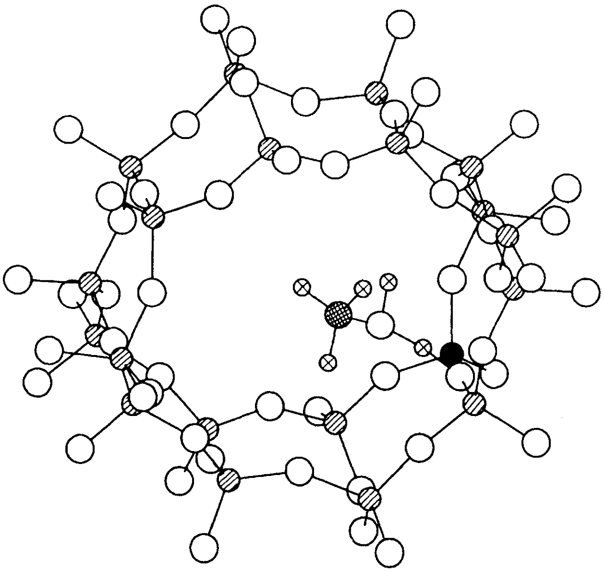

Fig. 2 Straight-channel binding arrangement **2** of methanol in ZSM-5

Received, 1st November 1990; Com. 0/04921B

References

1 G. T. Kokotailo and W. M. Meier, in *Properties and Applications of Zeolites*, ed. R. P. Townsend, The Chemical Society, 1980, p. 133.
2 S. L. Meisel, J. P. McCullogh, C. H. Lechthaler and P. B. Weisz, *Chemtech*, 1976, **6**, 86.
3 T. J. Gricus-Kofke, R. J. Gorte and W. E. Farneth, *J. Catal.*, 1988, **114**, 34.
4 G. Mirth, J. A. Lercher, M. W. Anderson and J. Klinowskí, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3039.
5 R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1972, 73.
6 M. R. Hayns and L. Dissado, *Theoret. Chim. Acta*, 1975, **37**, 147.
7 R. Vetrivel, C. R. A. Catlow and E. A. Colbourn, *J. Phys. Chem.*, 1989, **93**, 4594.
8 J. Sauer, in *Theory and Modelling of Zeolites*, ed. C. R. A. Catlow, Academic Press, to be published.
9 C. D. Chang, *Catal. Rev. Sci. Eng.*, 1983, **25**, 1.