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Simulation studies on the role of templating organic molecules in the synthesis of microporous materials: 2. Modelling the electronic interaction between the templating molecules and ZSM-5

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Abstract

Several templating organic molecules lead to the synthesis of ZSM-5. In the previous part of this series, we attempted to bring out the common features and amplify the qualities of tetrapropyl ammonium compounds (TPA) which make it best among the lot. Here, we report the interaction of various organic molecules with a suitable cluster model of ZSM-5 framework studied by MNDO calculations. The influence of the nature of the functional group and the alkyl group on the electronic interaction is studied systematically. The orientation of the template and the actual conformation of the 'template-framework' complex are decided based on the X-ray crystal structure reports and the MNDO energetics. It has been shown that quantum chemical calculations could be successfully utilized for the generalised description of the importance of several complex interactions which are mutually present.

Keywords: ZSM-5; Templating organic molecules; Quantum chemical calculations; Porous material synthesis; Electronic interactions

1. Introduction

In the hydrothermal synthesis of porous materials, the templating organic molecules (TOM) play the central role of nucleating and crystallizing a specific structure. Hence, there are several attempts to characterise the nature of interaction between the TOM and framework of the porous materials [1–3]. For zeolite ZSM-5, the number of TOM present in the unit cell and their location are fairly well established from the thermal analysis [4,5] and XRD studies [6,7] of as-synthesised zeolite. However, it is not clear if the nature of interaction between the TOM and synthesis gel are same during nucleation and in the final product.

Multitechnique studies utilising XRD, DTA/TGA, IR, SEM/TEM, NMR and light scattering methods have been utilized and the findings are briefly summarized below. Particles having the size of the unit cells of ZSM-5 have been identified by Scholle et al. [8], Nastro and Aiello [9] have identified the presence of secondary building units (SBU) and claim that TOM assemble the SBUs into ZSM-5 lattice.

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Song and Xu [10] have claimed that the TOM play the role of combining the sheets of *bc* planes of ZSM-5 lattice along the *a* direction from the XRD studies. Recently, light scattering techniques [11] have been applied to study the appearance, growth and size distribution of zeolite particles in gel phase formed from clear solution. By the studies on nuclear growth it is argued that the agglomeration of $Si(OH)_4$ units with the release of a water molecule for each Si–O–Si linkage will be the closest description of reality in the first few hours of crystallization. Although IZA synthesis commission [12] recommends monitoring the synthesis solution during the crystallization, it notes that the synthesis will have interference due to monitoring leading to low yield. Thus the 'in situ' or 'intermediate stage' characterization of precursors have not led to a definite conclusion due to the complexity of gel chemistry and the analytical problems.

There have been attempts to calculate the electronic properties of templates and model their templating role [13,14]. There are also simulation studies using model compounds [15] or modelling the as-synthesised structures where the template molecules are incorporated in the pores [16]. There are reports in the recent International Zeolite Association Conference dealing with the simulation of template molecules in various zeolites by energy minimisation approaches [17–19]. However, there are no reports which deal with the electronic interaction between the TOM with different functional groups with the framework of a porous material. Many templates utilized in the synthesis of ZSM-5 are unstable under the synthesis conditions and hence are converted to secondary products [20]. Therefore, it is difficult to determine whether the organic additives or its decomposed products are influencing the course of crystallization of ZSM-5. Thus the role played by organic additives in the synthesis of ZSM-5 is a complicated one and we adopted a systematic quantum chemical approach to gain further information on this important subject matter. In the present study, we have utilized suitable cluster models of ZSM-5 framework and studied the interaction of various organic molecules.

2. Method and model

The MNDO calculations have been performed on a typical cluster model of ZSM-5 framework and adsorption complexes formed between framework cluster and the organic molecule. The calculations were carried out using AMPAC (QCPE Program No. 506) and the calculation procedure is as described by Dewar and Thiel [21]. The computational advantages in using this semi-empirical procedure for performing multitude of calculations on large cluster models of zeolite framework [22] as well as the reliability of these results for description of electronic interactions [15] are reported in the literature.

The atomic positions in the cluster model representing ZSM-5 framework are derived from the X-ray crystal structure report by van Koningsveld et al. [6]. We have adopted a localized cluster model approach to represent the zeolite framework as introduced by Derouane et al. [23,24], in their pioneering work. In our earlier study [25], we compared the electronic properties of clusters with varying sizes to study the electronic properties of all the 12 crystallographically distinct T-sites in ZSM-5. It was found that a pentameric cluster model, where a TO_4 group is linked to another TO_4 group rather than hydrogen is a better representation to study the electronic properties. Accordingly, a pentameric cluster model (containing five TO_4 groups) where the valency of the peripheral oxygens are saturated by adding hydrogen atoms are chosen. The position of these hydrogen atoms are same as the adjacent T sites. The actual geometry and the topology of this cluster model is described in a later section. The geometry of the organic molecules are as reported by the XRD studies [6]. The position of hydrogens for the organic molecules are not available in

the XRD studies, further the increase and decrease in the alkyl chain length was studied by replacing the terminal hydrogen by methyl group or vice versa, respectively. For fixing the position of hydrogen atoms and building an optimized cluster models without Van der Waals contact, molecular graphics and force-field calculations were made use. These calculations were performed using the Quanta/CharmM software packages distributed by Polygen Corporation, USA. All the calculations were carried out in a Silicon Graphics IRIS workstation.

3. Results and discussion

3.1. Description of the cluster model

A schematic illustration of the sinusoidal channel as viewed along the *b*-axis of the unit cell of ZSM-5 is shown in Fig. 1. The straight channels run parallel to the *b*-axis. Among the 12 crystallographically distinct T-sites, T_4 and T_{10} sites are never present in the 10-m rings which form the sinusoidal channel. Similarly T_8 and T_{11} sites are never present in the 10-m rings which form the sinusoidal channel. Thus there

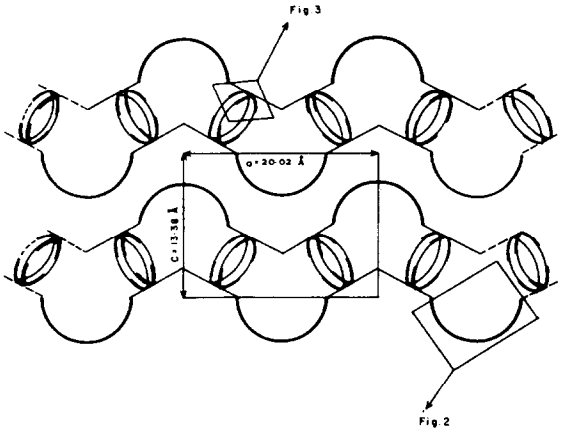

Fig. 1. A schematic view of the pore architecture in the *ac* plane of ZSM-5. The cross section of the sinusoidal channel is shown. The darkly shaded lines represent the T sites, which are common to both straight and sinusoidal channels. The detailed conformation and connectivity of these common T sites, highlighted here are exemplified in Figs. 2 and 3.

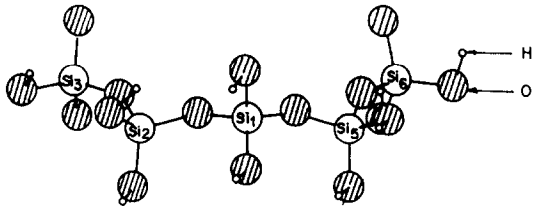

Fig. 2. The conformation of a pentameric cluster in the straight channel of ZSM-5. The topography of this cluster in the structure of ZSM-5 is highlighted in Fig. 1.

are 8 T-sites which are common to both straight and sinusoidal channels. We have identified a pentameric cluster, containing five continuously connected T sites, namely T_3, T_2, T_1, T_5 and T_6 This pentameric cluster forms the top-half and bottom-half of the 10-m rings of the straight channel in consecutive layers. This regular alternate occurrence of the pentameric cluster at the top and bottom halves of the straight channels occur along both *a* and *b* axes.

The topography of this pentameric cluster and its regular alternate occurrence along *a*-axis is shown in Fig. 1 as darkly shaded semicircles. The exact T-sites, their connectivity and the termination of peripheral oxygen by attaching hydrogen atoms in this pentameric cluster model is given in Fig. 2. A part of this cluster, namely T_1, T_2 and T_3 sites are common to the sinusoidal channel on the left, while the rest of this cluster, namely T_5 and T_6 sites are common to the sinusoidal channel on the right. The picture

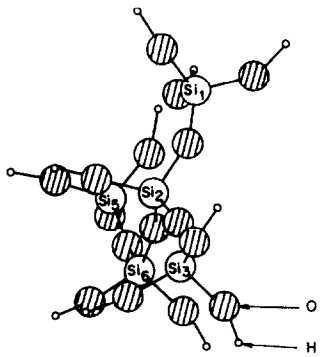

Fig. 3. The conformation of a pentameric cluster in the sinusoidal channel of ZSM-5. The topography of this cluster in the structure of ZSM-5 is highlighted in Fig. 1.

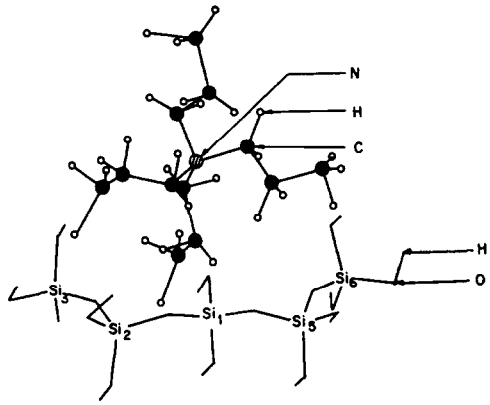

Fig. 4. The conformation of the TPA cation at the channel intersection of ZSM-5 framework. Only the pentameric cluster model of the framework is shown for easy visualization of the proximity of TPA cation to these specific framework atoms. The positions of nitrogen and carbon atoms are as reported by the XRD studies [6], while the position of hydrogen atoms are as derived from force field calculations.

where both the straight and sinusoidal channels are commonly sharing these T sites could not be schematically shown in the 2-dimensional figure as is the case in Fig. 1. Hence, the connectivity of these T-sites in two layers of *a*-axis as viewed from the sinusoidal channel is given in Fig. 3. Thus the local geometry of the individual TO_4 groups in the cluster models shown in Figs. 2 and 3 are same, while their connectivities are different. Due to such a topographically important location the cluster model shown in Fig. 2 is considered in our present study to understand the interaction of organic molecules with the framework.

Table 1
The electronic properties of the pentameric cluster model shown in Fig. 2

Property	Value
Total energy (eV)	−5779.785
HOMO (eV)	−10.61
Net charges on silicon at site 1	
Si_1	1.97
Net charge on bridging oxygens:	
O_1	−0.95
O_2	−0.93
Net charges on terminal oxygens:	
O_3	−0.84
O_4	−0.76

Additionally, in the X-ray crystal report analysis of as-synthesised TPA–ZSM-5 has been reported [6,7], it was found that the TPA cation is at the channel intersection. The location of the TPA cation with respect to the pentameric cluster (Fig. 2) as derived from the reported crystal structure is shown in Fig. 4. Although, it would be ideal to consider the interaction of the organic molecule with the whole ZSM-5 framework cage, the calculations have to be restricted to a cluster model for computational feasibility. By comparing the X-ray crystal structure reports and molecular graphics methods we derive that the pentameric cluster shown in Fig. 2 is the most likely site of interaction for templates. The electronic properties calculated for this framework cluster is given in Table 1. The positive charge on the silicon at the centre (Si_1) is minimum among the five silicon atoms and the

Table 2
The interaction of tetralkyl and dialkyl ammonium cations with the framework cluster. The alkyl groups are either 'propyl' (TPA and DPA) or 'butyl' (TBA and DBA)

Property	$[TPA]^+$	$[TBA]^+$	$[DPA]^+$	$[DBA]^+$
Total energy of the molecule (eV)	−2099.109	−2707.239	−1182.271	−1489.859
Total energy of framework cluster [a] with interacting molecule (eV)	−7879.473	−8485.639	−6910.256	−7216.819
Interaction energy (eV)	−0.579	1.385	51.80	52.825
Net charge on N in:				
(i) free molecule	−0.13	−0.13	−0.11	−0.09
(ii) interacting molecule	−0.13	−0.13	−0.10	−0.09
Net charge on single alkyl chain in:				
(i) free molecule	0.26	0.26	0.33	0.36
(ii) interacting molecule	0.38	0.36	0.38	0.40

[a] Total energy of the framework cluster model = −5779.785 eV.

positive charges on the two silicons at the terminal positions (Si_3 and Si_6) are maximum, according to the Mulliken population analysis. The oxygen atoms bridging the silicons posses higher negative charge compared to the terminal oxygen atoms.

3.2. Interaction of organic molecules with framework cluster models

There are several detailed reviews at periodical intervals where there are arguments supporting and contradicting the structure directing role of templating organic molecules (TOM) [26–30]. According to the recent evidences provided by Gies and Marler [30], the answer is "NO" to the question — "provided the right gel chemistry is achieved, can all the molecular sieves by synthesised in the absence of TOM?", which was raised by Lok et al. [27] nearly ten years before. Although the answer may be "YES" for ZSM-5, we take it up as model system due to the wealth of information available on 'template-ZSM-5' interactions. The selection of a suitable template has not evolved to a 'rule-based' situation even for the well studied ZSM-5 system. We attempt to compare and contrast the electronic interaction of various organic molecules in order to derive guidelines for the selection of a suitable template.

3.2.1. Influence of the alkyl groups

The results of the calculations to study the influence of propyl and butyl groups in the ammonium cation are given in Table 2. The tetrapropyl ammonium (TPA) and tetrabutyl ammonium (TBA) cations have a relatively favourable interaction energy with the framework cluster models than the dipropyl ammonium (DPA) and dibutyl ammonium (DBA) cations. When the propyl group is replaced by a butyl group, the distance between the framework atoms and nitrogen is further increased. This situation also leads to unfavourable interaction, although relatively smaller in magnitude. In these calculations, the absolute values of energy do not have any chemical meaning due to the semi-empirical parameterisation involved in the MNDO method and due to cluster model approximation used for the ZSM-5 framework. Further, it is assumed that the interaction from the rest of the framework qualitatively will be the same for all the molecules for a uniform Si/Al ratio, which is infinity in our case. This is a valid assumption since the alkyl chains are known to be pointing into either the straight or sinusoidal channels.

The electronic properties of various tetralkyl ammonium (TAA) cations are given in Table 3. The total energy values are a function of the number of atoms, as expected. The values of highest occupied molecular orbital (HOMO) for these molecules are strongly dependent on the nature of alkyl group. Since the molecules have a charge compensating role, the LUMO of the molecules are expected to accept the electronic charge. The electron transfer is expected to occur from the HOMO of the zeolite, which are contributed by the framework oxygen atoms [25]. The electron accepting capabilities are higher for TAA cations with smaller alkyl groups. It is also seen that the net charge on the nitrogen of these molecules are close to zero, while the positive charge is equally distributed

Table 3
The electronic properties of ammonium and tetralkyl ammonium cations

Property	$[NH_4]^+$	$[TMA]^+$	$[TEA]^+$	$[TPA]^+$	$[TBA]^+$
Total energy of the molecule (eV)	−256.991	−880.843	−1515.099	−2099.109	−2707.239
HOMO (eV)	−25.811	−19.019	−17.132	−13.771	−13.285
Net charge on N	0.06	−0.09	−0.05	−0.13	−0.13
Net charge on single alkyl chain	0.23	0.27	0.24	0.26	0.26

Table 4
The interaction of various C_4 alcohols and amines with the framework cluster

Property	Butylamine	Butanol	Isobutylamine	Isobutanol	Neobutylamine	Neobutanol
Total energy of the molecule (eV)	−871.997	−973.856	−871.501	−973.367	−862.686	−964.558
HOMO (eV)	−8.982	−10.541	−8.911	−10.451	−8.931	−10.065
Total energy of the framework cluster [a] with interacting molecule (eV)	−6610.736	−6713.314	−6621.706	−6724.989	−6614.581	−6717.843
Interaction energy (eV)	41.046	40.327	29.581	28.163	27.891	26.502
Net charge on $-NH_2$ [b]						
(i)	−0.06		−0.07		−0.07	
(ii)	−0.07		−0.29		−0.29	
Net charge on −OH [b]						
(i)		−0.07		−0.08		−0.08
(ii)		0.01		0.08		0.08

[a] Total energy of the framework cluster model = −5779.785 eV.
[b] (i) Free molecule and (ii) interacting molecule.

among the four alkyl groups. However, due to smaller size of the TMA and TEA than the diameter of the cage formed by the channel intersections, they cannot have favourable interaction with the framework compared to larger TPA and TBA cations. The following facts could be derived from the above results:

1. The interaction between the TOM and the framework is favoured by the increasing number of alkyl groups in the ammonium cation.
2. The interaction is most favourable for TPA cation.
3. The chemical interaction is between the alkyl group and the framework oxygen atoms.

3.2.2. *Influence of the functional groups*

Among the various functional groups, alcoholic and amino group containing molecules have enjoyed wide success as templates. In Table 4, we present the results of the calculations on the interaction of primary, secondary and tertiary alcohols or amines with the framework cluster. The stability of these compounds as predicted by the total energy are

primary ~ secondary > tertiary

The frontier molecular orbitals of amines have larger energy than the alcohols but they are invariant to the position of the functional groups. Thus the alcohols may be better electron withdrawing compounds than the amines. The same trend is depicted in the interaction energy values also; the values for alcohols are invariably favorable than those of amines. The net charges on the functional groups indicate that the interaction in these molecules are through both the alkyl group and functional group. This is in contrast to the observation in the case of TAA cations where the interactions are solely through the alkyl groups.

However, it should be noted that in the amines and alcohols, the tetrahedral symmetry present in the tetraalkyl ammonium cation, is absent. It is observed that the electronic requirements are satisfied by several group of compounds, while the geometric requirement is specifically fulfilled by the TAA cations. Thus the approximate tetrahedral void space generated by the intersection of the straight and sinusoidal channels in ZSM-5 can be expected to nucleate more easily around the TAA cations.

4. Summary

A suitable cluster model of the framework has been chosen to study the nature of interaction of TOM with ZSM-5. The selection was based on the topography of various T-sites in the ZSM-5 framework and from the X-ray crystal structure of as-synthesised TPA–ZSM-5 sys-

tem. The interaction energy and the electron distribution of several organic molecules with ZSM-5 are reported. The gel chemistry variation during the synthesis is complicated and the structure of precursor species are not yet known. We have considered a pentameric cluster model which form the alternate concentric 10-member rings in a straight channel of ZSM-5 and which is also common to sinusoidal channel. By calculating the interaction of TOM with such regularly repeating framework section, we have attempted to work out the suitability of a organic molecule as the template for the synthesis of ZSM-5.

Among all the organic molecules studied TAA cations have the most favourable interaction energy with the framework cluster model. There is no linear correlation between the interaction energy and the nature of the alkyl group in TAA cation. Hence, TAA cations with mixed alkyl groups such as diethyl, dipropyl ammonium or dimethyl, dibutyl ammonium cations can be expected to have more favourable interaction than TPA cation. It has been shown that quantum chemical calculations could lead to certain general description of the complex interactions involved in templating theory. However, further studies on the influence of the size and geometry of the framework cluster model and the influence of presence of trivalent framework cations such as Al^{3+} are needed to improve our understanding. Such studies using various framework cluster models having regular geometry, as well as of those derived from X-ray crystal structure reports are in progress.

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References

[1] D. Hoebbel and W. Weiker, Z. Anorg. Allg. Chem., 418 (1975) 35.
[2] K.J. Cavell, A.F. Masters and K.G. Wilsher, Zeolites, 2 (1982) 244.
[3] E.G. Derouane, J. B.Nagy and Z. Gabelica, Zeolites, 2 (1982) 299.
[4] G. Giordono, F. Crea and A. Nastro, J. Therm. Anal., 36 (1990) 2233.
[5] L.M. Parker, D.M. Bibby and J.E. Patterson, Zeolites, 4 (1984) 168.
[6] H. van Koningsveld, H. van Bekkum and J.C. Jansen, Acta Crystallogr. B, 43 (1987) 127.
[7] K.J. Chao, J.C. Lin, Y. Wang and G.H. Lee, Zeolites, 6 (1986) 35.
[8] K.F.M.G.I. Scholle, W.S. Veeman, P. Frenken and G.P.M. van der Valden, J. Phys. Chem., 88 (1984) 3395.
[9] A. Nastro and R. Aiello, Stud. Surf. Sci. Catal., 44 (1989) 227.
[10] T. Song and R. Xu, J. Solid State Chem., 88 (1990) 577.
[11] T.A.M. Twomey, M. Mackay, H.P.C.E. Kuipers and R.W. Thompson, Zeolites, 14 (1994) 162.
[12] IZA Synthesis Commission Report, Zeolites, 13 (1993) 399.
[13] S. Mintova, V. Valtchev and I. Kanov, Zeolites, 13 (1993) 102.
[14] S. Prasad and R. Vetrivel, Recent Developments in Catalysis, B. Viswanathan and C.N. Pillai (Eds.), Narosa Publishing House, 1991, p. 175.
[15] S. Prasad and R. Vetrivel, J. Phys. Chem., 96 (1992) 3092.
[16] E.B. de Vos, J.C. Jansen, B. van de Graaf and H. van Bekkum, Zeolites, 13 (1993) 216.
[17] T.V. Harris and S.I. Zones, Stud. Surf. Sci. Catal., 84 (1994) 29.
[18] R.G. Bell, D.W. Lewis, P. Voigt, C.M. Freeman, J.M. Thomas and C.R.A. Catlow, Stud. Surf. Sci. Catal., 84 (1994) 2075.
[19] P.A. Cox, A.P. Stevens, L. Banting and A.M. Gorman, Stud. Surf. Sci. Catal., 84 (1994) 2115.
[20] M. Nowotny, J.A. Larcher and H. Kessler, Zeolites, 11 (1991) 454.
[21] M.J.S. Dewar and W.J. Thiel, J. Am. Chem. Soc., 99 (1977) 4899.
[22] A. Redondo and P.J. Hay, J. Phys. Chem., 97 (1993) 11754.
[23] J.G. Fripiat, F. Berger-Andre, J.M. Andre and E.G. Derouane, Zeolites, 3 (1983) 306.
[24] E.G. Derouane and J.G. Fripiat, Zeolites, 5 (1985) 165.
[25] A. Chatterjee and R. Vetrivel, Microporous Mater., 3 (1994) 211.
[26] R.H. Daniels, G.I. Kerr and L.D. Rollman, J. Am. Chem. Soc., 100 (1978) 3097.
[27] B.M. Lok, T.R. Cannan and C.A. Messina, Zeolites, 3 (1983) 282.
[28] J.L. Casci, Stud. Surf. Sci. Catal., 28 (1986) 215.
[29] K.R. Franklin and B.M. Lowe, Stud. Surf. Sci. Catal., 49A (1989) 179.
[30] H. Gies and B. Marler, Zeolites, 12 (1992) 42.