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Influence of zeolite composition on the selectivity of alkylation reaction for the synthesis of *p*-isobutylethylbenzene: a computational study

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Abstract

In this paper, we describe our computational approach to understand the factors influencing the selectivity of alkylation reactions over zeolite catalysts. Firstly, the shape, size and flexibility of the alkylated products are correlated to their diffusion behaviour inside zeolites. Secondly, the influence of pore architecture and the dimension of various large pore zeolites on diffusion characteristics of alkylaromatics are brought out. Further, we study the isomorphous substitution of Al, Ga or B in the place of Si and their consequent influence in the selectivity of alkylation reaction. We apply hard–soft acid–base (HSAB) principle which provides the properties to describe the acidity and reactivity of zeolites. The analysis of the results indicates that the shape selectivity in the alkylation reaction is also controlled by the molecular orbital properties in addition to the geometry constraints. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hard–soft acid–base (HSAB) principle; *p*-Isobutylethylbenzene; Zeolites; Mulliken population

1. Introduction

Indeed, the shape selectivity of organic transformations inside zeolite arises due to the selective fitting of the required product molecules. However, this necessary condition of molecular fitting is not sufficient enough to achieve high selectivity. The intrinsic electronic structure and consequent properties of zeolite catalysts also control the shape selectivity in the catalytic reactions. Demand for the specialistic chemicals and environmental considerations are the reasons which led to search for solid acid catalyst

replacements to conventional Lewis acid catalysts. The success in applying zeolite catalysts for the shape selective synthesis of fine chemicals is hindered by the formation of small amounts of by-products. Controlling the by-products formation as an impurity in the processes to manufacture pharmaceuticals, electronic grade chemicals, etc. necessitate the understanding of the process at electronic level.

The diffusional behaviours of the molecules inside zeolites play the major role in the shape selective catalytic processes and membrane applications. Hence, there are several experimental [1–11] and molecular modelling [9–14] efforts to understand the diffusion characteristics. Among the molecular modelling techniques, Monte Carlo calculations

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[15,16] and molecular dynamics calculations [17–19] are extensively used. In a recent study [20], we brought out the power of force-field based energy minimisation calculations for such applications.

When the molecules diffuse through materials with pore diameters in the range of 4–9 Å, the diffusion behaviour fits the configurational regime which is beyond the Knudsen and regular regions. In the configurational regimes, the diffusivity of molecules spans 10-order of magnitude in diffusivity, namely from 10^{-4} to 10^{-14} cm²/s [21]. In this paper, we report the results on the energy minimisation studies of diffusion characteristics and the quantum chemical studies of the influence of isomorphous substitution on the acidity and shape selective properties of zeolites.

2. Theory and computational details

The concept of HSAB was introduced by Pearson [22] based on the polarisation properties of acid and base centres. In this study, the global softness (S) and the local softness (s) calculated using Hartree–Fock techniques for zeolite cluster models are used to locate the preferential ethylation position of isobutylbenzene. The global hardness is defined as the second derivative of the energy with respect to the number of particles for a given external potential:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\bar{r})} = \left(\frac{\partial \mu}{\partial N} \right)_{v(\bar{r})}, \quad (1)$$

where E is the total energy, N is the number of electrons of a chemical species and μ is the chemical potential. The corresponding global softness is expressed in terms of the inverse of global hardness as

$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2} \right)_{v(\bar{r})} = \left(\frac{\partial N}{\partial \mu} \right)_{v(\bar{r})}. \quad (2)$$

By applying the finite difference approximation, we get what are known as the operational global hardness and softness as

$$\eta = \frac{\text{IP} - \text{EA}}{2}, \quad (3)$$

$$S = \frac{1}{\text{IP} - \text{EA}}, \quad (4)$$

where IP and EA are the first ionisation potential and

electron affinity of the species. The local softness $s(\bar{r})$ may be defined as

$$s(\bar{r}) = \left(\frac{\partial \rho(\bar{r})}{\partial \mu} \right)_{v(\bar{r})}, \quad (5)$$

so that, $\int s(\bar{r}) d\bar{r} = S$.

Combining Eqs. (5) and (2) we can write

$$s(\bar{r}) = \left(\frac{\partial \rho(\bar{r})}{\partial N} \right)_{v(\bar{r})} \cdot \left(\frac{\partial N}{\partial \mu} \right)_{v(\bar{r})} = f(\bar{r}) \cdot S = \left(\frac{\partial \mu}{\partial v(\bar{r})} \right)_N \cdot S, \quad (6)$$

where $f(\bar{r})$ is defined as the Fukui function by Parr and Yang [23]. $f(\bar{r})$ defines the sensitivity of chemical potential to the local external perturbation at point r . From the definition of the local softness, one can infer that local softness can also be used as a reactivity measure. Local HSAB principle states that the local softness is a better reactivity descriptor with respect to the reaction partner. The definitions of $f(\bar{r})$ and $s(\bar{r})$ involve derivatives of $\rho(\bar{r})$ with respect to the number of electrons. A finite difference scheme has been used to define three different types of local softness for nucleophilic, electrophilic and radical attacks as given below:

$$s_k^+ = [\rho_k(N_0 + 1) - \rho_k(N_0)] \cdot S, \quad (7)$$

$$s_k^- = [\rho_k(N_0) - \rho_k(N_0 - 1)] \cdot S, \quad (8)$$

$$s_k^0 = \frac{1}{2}[\rho_k(N_0 + 1) - \rho_k(N_0 - 1)] \cdot S, \quad (9)$$

where $\rho_k(N_0)$, $\rho_k(N_0+1)$, and $\rho_k(N_0-1)$ are the Mulliken population on atom k in the N_0 , (N_0+1) , and (N_0-1) electron systems, respectively.

The quantum chemical calculations have been carried out at the ab initio Hartree–Fock level with DZV basis set. The calculation of IP and EA as the difference of separate SCF energy values of neutral and monopositive or mononegative ions of the same cluster model is explained elsewhere [24]. The Hartree–Fock calculations were carried out by GAMESS package developed by Schmidt et al. [25] in an SGI-Indy workstation.

3. Results and discussion

Small subtle changes in molecular sizes can have large effect on their diffusivity. The influence of

diffusion characteristics on the selectivity is studied by energy minimisation calculations. The electronic properties control the electrophilic and nucleophilic reactivity of atoms in the molecule. The influence of electronic properties on the selectivity is studied by Hartree–Fock quantum chemical calculations.

3.1. Influence of the diffusion characteristics on the selectivity

Zeolites have been found to be effective catalysts [26] for the selective synthesis of *p*-isobutylethylbenzene which is the key intermediate in the production of α -(4-isobutylphenyl) propionic acid, popularly known as ibuprofen [27]. In our earlier work [20], we described the influence of the size and shape of the isomers of IBEB and the pore diameter and architecture of several large pore zeolites on the diffusion characteristics. The diffusion energy barriers calculated for the three isomers in large pore zeolites are given in Table 1. The salient outcome from the results in Table 1 could be summarised as:

1. The selectivity is more pronounced in zeolites with 1d pores such as MOR, MTW and OFF.
2. The zeolites, such as FAU and LTL, with cages larger than the size of the molecules (having 2d or 3d pore architecture) do not show selectivity.
3. The molecule–zeolite lattice interactions control the diffusion mechanism; the molecules prefer orientations and configurations inside pores, where there is a maximum interaction between the surface of the zeolite and alkyl groups.

Table 1
The diffusion energy barriers in kJ/mol for the three isomers of IBEB in large-pore zeolites

Zeolites	Molecules		
	<i>o</i> -IBEB	<i>m</i> -IBEB	<i>p</i> -IBEB
Faujasite	32.74	28.38	31.65
Zeolite L	40.87	43.69	28.43
Mazzite	50.78	9.78	10.69
Mordenite	95.69	17.95	6.44
Offretite	149.68	30.00	15.43
Cancrinite	–	81.51	14.65
ZSM-12	243.60	38.21	19.13

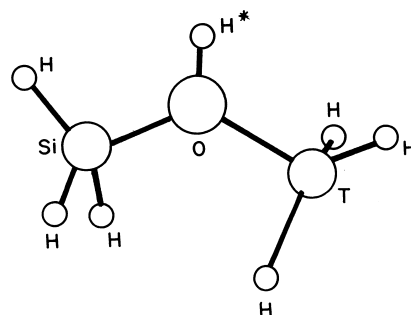


Fig. 1. The geometry of the cluster model used to study the influence of chemical composition on the acidic properties; T=Al, Ga or B; H⁺=Bronsted acid site. The geometry is fully optimised using DZV basis set. The properties calculated for these cluster models are given in Table 2.

4. The molecules do not prefer the sites closer to side-pockets or channel intersection (as in the case of CAN) along the pore.
5. When the pore diameter is small, the molecules have unfavourable interaction indicating that the strain may lead to coking inside the pores.
6. Zeolites with elliptical 1d-channel such as MOR show better selectivity than zeolites with circular 1d-channel.

3.2. Influence of the chemical composition on the selectivity

The cluster model chosen to study the influence of isomorphous substitution of Al, Ga or B in place of Si is shown in Fig. 1. Although a larger cluster model is desired, we observed that the cluster models where the T atoms are terminated by –OH groups are unsuitable, because it is known to overemphasise the ionic nature in zeolites [28] and create unrealistic electrostatic potential [29,30]. The oxygen atoms bridging a T and H (T–O–H) have larger electronegativity than the oxygen atoms bridging two Ts (T–O–T). Due to the unrealistic electrostatic potential created by O in T–O–H in the vicinity of Bronsted acid sites, the proton affinity, which is a measure of Bronsted acidity, obtained for the cluster terminating with –OH groups is also an overemphasised value (as much as 30 kcal/mol). Further, the geometry optimisation of the cluster containing heteroatoms, which are terminated by –OH groups, lead to unrealistic geometry [31]. Thus, although the cluster terminating with –OH groups

resembles close to the true composition, the electrostatics created by the –OH groups are unrealistic to derive the properties related to Pearson acidity. In contrast, as shown in this work, the cluster terminated with hydrogen atoms simulates the partial ionic nature of Si–O bonds correctly. It has to be noted that even a small cluster model such as $\text{H}_3\text{Si–O–SiH}_3$ is useful to give more realistic results for the localised properties, which control several catalytic phenomena.

The exact prediction of the acid strength of these isomorphously substituted zeolite observed in the experimental studies [32–34] is used as criterion to fix the calculation parameters. Si–O–T bridge was bonded to hydrogen atoms to fix the boundary conditions. The Si–H and T–H distances were fixed as 1.5 Å with the H atoms lying along the vector of neighbouring O. The initial geometry of these cluster models is derived from the crystal structure reported for the faujasite lattice. Trial calculations were carried out for the initial geometry and for the geometry where peripheral hydrogen atoms were held fixed, where only the geometry of central atoms was optimised. However, to make it a general utility for all zeolites, the geometry of all the atoms in these cluster models was optimised.

Trial calculations were also carried out with several basis sets. Several basis sets, starting from minimal STO-3G, through 3-21G, 6-31G, up to DZV were used. While the minimal basis set was not able to reproduce the experimentally observed acidity trend, 3-21G was not suitable to predict the local softness. The 6-31G and DZV gave comparable results. The basis sets STO-3G, 3-21G and 6-31G were earlier used by Brand et al. [29,30] to calculate the molecular

electrostatic potential (MEP) map. These basis sets predicted an MEP minima at the oxygen of the Si–O–Si as –58.2, –67.0 and –36.1 kcal/mol, respectively. We found that calculations on larger pentameric cluster models are useful to confirm the influence of the basis sets and the MEP predicted by 6-31G is a realistic value [35]. Thus, a basis set quality of 6-31G or more is needed for reliable results. The results reported here are derived using DZV basis set.

The electronic structures were calculated for the neutral, anionic and cationic cluster models. The global softness of the cluster models and the local softness on the acidic sites were computed according to the method described in the previous section. The results of the cluster models shown in Fig. 1 using the DZV basis sets are given in Table 2. With the above described geometry and size of the cluster as well as the basis set, all the properties such as electron population on bridging oxygen (q_{O}), acidic proton (q_{H}), the ionicity of O–H bond ($q_{\text{O}}q_{\text{H}}$) and the optimised O–H distance are useful in describing the acidity trend. The global softness and local softness are more sensitive to the chemical composition. The local softness is shown to be the best descriptor of the acidity and reactivity of the zeolites.

Calculations were also carried out on the isobutylbenzene (IBB) molecule in order to understand the position (*o*-, *m*- or *p*-), where ethylation occurs in this molecule and the results are given in Table 3. It is observed that the density of the frontier orbitals is higher in the *ortho* and *para* positions and the local softness value at the carbon atom in the *para* position of IBB is more than those on the carbon atoms in the *ortho* and *meta* positions. The net charges calculated

Table 2
The electronic properties of fully optimised $\text{H}_3\text{Si}(\text{OH})\text{TH}_3$ (where T=Al, Ga or B) cluster model

Properties ^a	Cluster model		
	SiAl:H	SiGa:H	SiB:H
Total energy (a.u.)	–609.7107	–2288.9799	–392.4691
Mulliken population:			
q_{O} (a.u.)	–1.147	–1.111	–1.015
q_{H} (a.u.)	0.497	0.489	0.487
Ionicity of O–H bond: $ q_{\text{O}} q_{\text{H}} $ (a.u.)	0.570	0.544	0.495
O–H distance (Å)	0.953	0.952	0.949
Global softness (a.u.)	2.350	2.339	2.107
Local softness: s_{H}^+ (a.u.)	0.232	0.206	0.198

^aFor the description of the properties, please see the text.

Table 3
The electronic properties of the fully optimised molecule

Properties	Isobutylbenzene
Total energy (a.u.)	−386.7332
Global softness (a.u)	2.522
Mulliken charges (a.u)	
<i>o</i> -C	−0.318
<i>m</i> -C	−0.192
<i>p</i> -C	−0.219
Local softness	
<i>o</i> -C	0.119
<i>m</i> -C	0.043
<i>p</i> -C	0.384

indicate that nucleophilic attack will take place in the order: *ortho*>*para*>*meta*. Hence a proton or an alkylating agent is expected to produce more *ortho* isomer. However, based on the local softness values, an alkylating agent with higher softness value is expected to attack the *para* position.

The formation of surface alkoxy groups due to the activation of alcohols is an established fact in the literature. Quantum chemical cluster calculations in the literature also have indicated the formation of surface alkoxy groups on the Bronsted acid sites [36]. Hence we carried out calculations on the cluster models shown in Fig. 2 in order to understand the

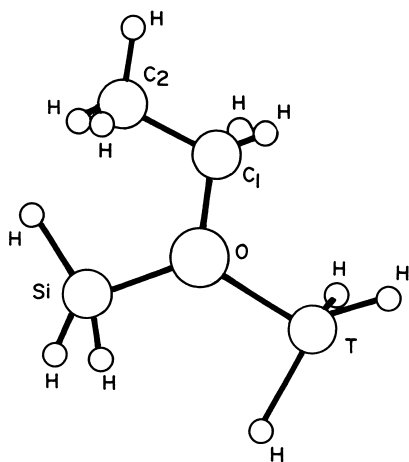


Fig. 2. The geometry of the cluster model used to study the alkylating agent, namely the surface ethoxy group; T=Al, Ga or B. The proton at the Bronsted acid site is replaced by the ethyl group. The properties calculated for C₁, C₂ and the ethyl group are given in Table 4.

ethylation capability of zeolites with different chemical composition. The alkylating agent is modelled by replacing the acidic hydrogen by an ethyl group. The zeolitic O–C₁ of C₂H₅ group distance is fixed at 1.8 Å and the geometry of all the other atoms in the cluster model, shown in Fig. 2, is optimised. The interaction of alkylating agent (–C₂H₅ group) with the zeolite cluster is relevant. However, the cluster model is not large enough to simulate all the interactions between the –C₂H₅ group and the zeolite. To study the adsorption of guest molecules over the zeolite host lattice, we need to choose a very large cluster model, which can simulate all the chemical and physical interactions. Quantum chemical calculations with reasonable accuracy on such cluster models are still computationally demanding. Hence, optimising and obtaining the exact O–C distance is not possible with the present cluster model and it was fixed at 1.8 Å, as used in the previous calculations [37,38]. Thus, this set of calculations bring out the influence of chemical composition on the reactivity only. The reactivity parameters such as electrophilicity and nucleophilicity of atoms in small cluster models could be calculated and correlated to selectivity observed in catalytic reactions. The influence of chemical composition on the local geometry of the adsorption complex is not probed. Further, the alkylation process is expected to undergo via a concerted mechanism, wherein the proton in the Bronsted acid site is also involved and hence more detailed calculations are needed to obtain the O–C distance. The O–C distance will be dependent on the chemical composition, but by fixing the O–C distance at 1.8 Å, we study the influence of chemical composition through the nonbonded interactions. The results of the calculations are given in Table 4. The global softness values and ionicity of O–C₂H₅ bond are found to follow the trend of the acid strength of these zeolites. The group softness of the –C₂H₅ group shows clear dependence on the chemical composition, although the net charges on the individual carbon atoms of –C₂H₅ group do not show any correlations.

4. Conclusion

Shape selectivity in zeolites during alkylation reaction can be understood from molecular modelling

Table 4

The electronic properties of fully optimised $\text{H}_3\text{Si}(\text{OC}_2\text{H}_5)\text{TH}_3$ (where T=Al, Ga or B) cluster models

Properties	Cluster model		
	SiAl:Et	SiGa:Et	SiB:Et
Total energy (a.u.)	−687.7180	−2366.9882	−470.4728
Mulliken population:			
q_{O} (a.u.)	−1.197	−1.143	−1.014
q_{C_2} (a.u.) (methyl carbon)	−0.490	−0.489	−0.494
q_{C_1} (a.u.) (methylene carbon)	0.053	0.053	0.069
$q_{\text{C}_2\text{H}_5}$ (a.u.)	0.614	0.596	0.601
Ionicity of O–C ₂ H ₅ bond: $ q_{\text{O}}q_{\text{C}_2\text{H}_5} $ (a.u.)	0.735	0.681	0.609
O–C ₂ H ₅ distance (Å)	1.800	1.800	1.800
Global softness (a.u.)	2.627	2.600	2.455
Group softness: $S_{\text{C}_2\text{H}_5^+}$ (a.u.)	1.975	1.914	1.847

studies. The size, shape and the flexibility of reactant and product molecules are accurately derived. The fitting of these molecules inside various zeolites are analysed qualitatively by molecular graphics methods. Quantitatively, the interaction energy between the guest molecules and host lattice are calculated by force–field based energy minimisation calculations. The diffusional energy barriers calculated from such calculations are arising due to the pore dimensions, channel architecture, cage architecture and the specific interactions between the molecules and zeolite lattice.

Achieving a very high selectivity with zeolite catalysts is an essential requirement to use them for the production of fine chemicals. Although the shape selectivity is the major controlling factor, there are several studies in literature to show that electronic factors also play a subtle role in controlling selectivity. In this study, we show that Pearson acidity based on HSAB principle is an important parameter to describe the selectivity. The local softness, a parameter to quantify Pearson acidity, is derivable from quantum chemical calculations. The acid strength and the softness are correlated to the catalytic activity and the selectivity, respectively, in orbital-controlled reactions. It is possible to estimate the relative acid strength due to the variation in the chemical compositions. The local softness of molecule is useful to identify the selectivity in catalytic reactions. Thus the acid strength and local softness are the “indicators” derivable from quantum chemical calculations.

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References

- [1] C.N. Satterfield, J.R. Katzer, *Adv. Chem. Ser.* 102 (1971) 193.
- [2] M. Bülow, P. Struve, G. Finger, C. Redszus, K. Ewrhardt, W. Schirmer, J. Kärger, *J. Chem. Soc., Faraday Trans. I* 76 (1980) 597.
- [3] W.O. Haag, R.M. Lago, P.B. Weisz, *Faraday Dis. Chem. Soc.* 72 (1981) 317.
- [4] R.R. Eckman, A.J. Vega, *J. Phys. Chem.* 90 (1986) 4679.
- [5] H. Pfeifer, *Phys. Rep.* C26 (1976) 293.
- [6] H. Jobic, A. Renouprez, M. Bee, C. Poinson, *J. Phys. Chem.* 90 (1986) 1059.
- [7] Y. Yasuda, A. Yamamoto, *J. Catal.* 93 (1985) 176.
- [8] J. Caro, M. Bülow, H. Jobic, J. Kärger, B. Zibrowius, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.), *Advances in Catalysis*, vol. 39, Academic Press, New York, 1993, p. 351.
- [9] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- [10] J. Karger, D.M. Ruthven, *Diffusion in zeolites and other microporous solids*, Wiley, New York, 1992.
- [11] B.F. Chmelka, D. Raftery, A.V. McCormick, L.C. de Menorval, R.D. Levine, A. Pines, *Phys. Rev. Lett.* 66 (1991) 580.
- [12] J. Kärger, M. Petzold, H. Pfeifer, S. Ernst, J. Weitkamp, *J. Catal.* 136 (1992) 283.
- [13] J. Xiao, J. Wei, *Chem. Eng. Sci.* 47 (1992) 1143.

- [14] C.R.A. Catlow (Ed.), *Modelling of Structure and Reactivity in Zeolites*, Academic Press, London, 1992.
- [15] S.J. Goodbody, K. Watanabe, D. MacGowan, J.P.R.B. Walton, N. Quirke, *J. Chem. Soc., Faraday Trans. 87* (1991) 1951.
- [16] C.M. Freeman, C.R.A. Catlow, J.M. Thomas, S. Brode, *Chem. Phys. Lett.* 186 (1991) 137.
- [17] S. Yashonath, P. Santikary, *J. Phys. Chem.* 97 (1993) 13778.
- [18] R.L. June, A.T. Bell, D.N. Theodorou, *J. Phys. Chem.* 96 (1992) 1051.
- [19] D. Dumont, D. Bougeard, *Zeolites* 15 (1995) 650.
- [20] R.C. Deka, R. Vetrivel, *J. Catal.* 174 (1998) 88.
- [21] P.B. Weisz, *Chemtech*, August 1973, p. 498.
- [22] R.G. Pearson, *J. Am. Chem. Soc.* 85 (1963) 3533.
- [23] R.G. Parr, W. Yang, *J. Am. Chem. Soc.* 106 (1984) 4049.
- [24] S. Krishnamurty, R.K. Roy, R. Vetrivel, S. Iwata, S. Pal, *J. Phys. Chem. A*, 101 (1997) 7253.
- [25] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.
- [26] Y. Tokumoto, I. Shimizu, S. Inoue, *Eur. Pat. Appl.*, EP 414 207, 27 February 1991.
- [27] J.-P. Riew, A. Boucherle, H. Cousse, G. Mouzin, *Tetrahedron* 42 (1986) 4095.
- [28] S.R. Blaszkowski, R.A. van Santen, *J. Phys. Chem.* 99 (1995) 11728.
- [29] H.V. Brand, L.A. Curtiss, L.E. Iton, *J. Phys. Chem.* 96 (1992) 7725.
- [30] H.V. Brand, L.A. Curtiss, L.E. Iton, *J. Phys. Chem.* 97 (1993) 12773.
- [31] J. Sauer, in: C.R.A. Catlow (Ed.), *Modelling of Structure and Reactivity in Zeolites*, Academic Press, London, 1992.
- [32] C.T. Chu, C.D. Chang, *J. Phys. Chem.* 89 (1985) 1569.
- [33] J. Datka, M. Kawalek, *J. Chem. Soc., Faraday Trans.* 89 (1993) 1829.
- [34] S.V. Awate, P.N. Joshi, M.J. Eapen, V.P. Shiralkar, *J. Phys. Chem.* 97 (1993) 6042.
- [35] R. Vetrivel, R.C. Deka, A. Chatterjee, M. Kubo, E. Broclawik, A. Miyamoto, in: J.S. Murray, K. Sen (Eds.), *Molecular Electrostatic Potentials – Concepts and Applications*, Elsevier, Amsterdam, 1996, p. 509.
- [36] P.E. Sinclair, C.R.A. Catlow, *J. Chem. Soc., Faraday Trans.* 92 (1996) 2099.
- [37] A. Corma, G. Sastre, P. Viruela, C. Zicovichwilson, *J. Catal.* 136 (1992) 521.
- [38] A. Corma, F. Llopi, P. Viruela, C. Zicovichwilson, *J. Am. Chem. Soc.* 116 (1994) 134.