J. Phys. Chem. A **2001,** *105,* 6187−6196

A Reactivity Index Study to Choose the Best Template for a Particular Zeolite Synthesis

Abhijit Chatterjee* and Takashi Iwasaki

Inorganic Materials Section, Tohoku National Industrial Research Institute, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan

Received: November 20, 2000; In Final Form: April 5, 2001

The activity of different representative templating molecules along with zeolite framework is investigated using a range of reactivity indexes using density functional theory (DFT). From the values of local softness and the charge on the hydrogen atom of the bridging hydroxyl, resulting from the presence of aluminum in the framework, it is observed that the acidities of the aluminum containing zeolite type model systems are dependent on several characteristics which are of importance within the framework of hard and soft acids and bases (HSAB) principle. We investigated the local softness of the interacting templates to compare their affinity with the zeolite framework cluster models. The cluster models are chosen to mimic the secondary building units of zeolite crystals for both silicalite and silica aluminates. The conformational flexibility was brought out as common features of those representative organic templates. The influence of the nature of the functional group and alkyl group on the electronic interaction is studied systematically. An a priori rule is formulated to choose the best template for a particular zeolite (e.g., ZSM-5) synthesis. The role of water during nucleation process is monitored in terms of solvation energy to rationalize the fundamental mechanism of crystal growth.

Introduction

At present several organic molecules are widely employed as templating additives in the synthesis mixture of micro and meso porous materials, in which zeolite is an important class of material.[1] There are growing interest in synthesizing new zeolites with novel framework architecture[2−6] along with studies to tailor the catalytic properties of existing materials with well-established structures.[7−10] The general concept of templating is thought of a phenomenon occurring during either the gelation or nucleation process, whereby the organic molecules organize the inorganic tetrahedral units into a particular topology around themselves and thus provide the initial building block for further crystallization of a particular structure type.

There are many theoretical[11−13] studies which deal with denovo designing of structural directing agents for the synthesis of microporous solids. There are also studies predicting the location of templates via a combined Monte Carlo (MC) simulated annealing approach.[14] There is a recent study of Catlow et al.[15] which uses computer simulation in understanding the role of templating in nucleation, growth, and templating in zeolite synthesis. These studies aimed to rationalize the role templates in all silica zeolite synthesis and derived a probable mechanism of it. The effect of aluminum in the framework is not so far studied. The presence of aluminum in the framework results in the Brønsted acidity of the zeolite, which further plays the important role in the catalytic behavior of zeolites. When we study structure directing agents, we need to monitor their interaction with primary building units of zeolite. We believe that templates are not only void fillers but as well as act as charge compensators. To account for the charge part we need to have aluminum in the framework, as the charge-compensating role can be monitored in the presence of Bronsted acidity. ZSM-5 is the most studied zeolite because it's ample application in petroleum industry and its easy synthesis procedure, so we opted for this type of zeolite in the current study to choose the best template for its synthesis from a wide range of templates available. Lok et al.[16] compiled literature information and presented various models to explain the templating phenomenon. It was shown that more than 25 organic molecules, covering a wide variety of compounds, such as mono- or polyalkylamines, mono or poly -amines and -alcohols, and hetrocyclics act as templates for the synthesis of ZSM-5 zeolite. ZSM-5 can also be synthesized in absence of template, where hydrated metal cations play a structure directing role.[17] We in our earlier studies for the first time monitored the structure and electronic properties of 50 different templates used in the synthesis of ZSM-5 zeolite. We explored both the structure-directing as well as the void-filling role of templates using semiempirical quantum chemical calculations.[18] We also studied the effect of nature and number of alkyl groups in the teraalkylammonium cations acting as templates during the synthesis of ZSM-5.[19] There is no scale whatsoever available to use to choose a best template for a particular zeolite. There are contradictory ideas with one supporting the role of templates as void filler and the other accepting its structure-directing as well as charge-balancing roles. There is no study so far to monitor the templating phenomenon in the presence of aluminum in the framework.

The hard soft acid−base (HSAB) principles classify the interaction between acids and bases in terms of global softness. Pearson proposed the global HSAB principle.[20] The global hardness was defined as the second derivative of energy with respect to the number of electrons at constant temperature and external potential, which includes the nuclear field. The global softness is the inverse of this. Pearson also suggested a principle of maximum hardness (PMH),[21] which states that, for a constant external potential, the system with the maximum global hardness

---

* Corresponding author. E-mail: c-abhijit@aist.go.jp. Fax: +81-22-236-6839. Phone: +81-22-237-5211.

10.1021/jp0042617 CCC: $20.00

is most stable. In recent days, DFT has gained widespread use in quantum chemistry. Some DFT-based local properties, e.g., Fukui functions and local softness,[22] have already been used for the reliable predictions in various types of electrophillic and nucleophilic reactions in the case of zeolites and clay materials.[23−26] In our recent studies[27,28] we proposed a reactivity index scale for heteroatomic interaction with zeolite framework, permeation of small gaseous molecules through a zeolite membrane. The reactivity index calculation for zeolites is investigated using quantities emerging in a most natural way from density functional theory.[29] Moreover, Gazquez and Mendez[30] proposed that when two molecules A and B of equal softness interact, thereby implicitly assuming one of the species as nucleophile and the other as an electrophile, a novel bond would likely form between an atom A and an atom B whose Fukui function values are close to each other.

In the present study we used the HSAB principle to locate the nucleophilic site in the range of templates used in ZSM-5 type zeolite synthesis and at the same time monitored the electrophilicity of the zeolite framework structure. We have chosen templates belonging to the following groups, which have shown the best performances in ZSM-5 as well as for other zeolite syntheses: aldehydes, alcohols, amines, and tetraalkylammonium cations. We have given special emphasis to the tetraalkylammonium cations because of their performance over other templating molecules as observed both theoretically and experimentally. These ammonium cations being tetrahedral help the growth of zeolites around themselves. This helps us to scale up the templates in terms of its local softness. This is followed by the study with zeolite clusters interaction with water. This is to rationalize the role of water during nucleation. The result aims to formulate a priori rule to trace the best template available in the business for the synthesis of ZSM-5 type zeolites.

Theory

The Fukui function is defined[22] as follows:

$$f(r) = [\delta\mu/\delta v(r)]_N = [\delta\rho(r)/\delta N]_v \qquad (1)$$

The function f is the local quantity, which has different values at different points (r) in the species, N is the total number of electrons, μ is the chemical potential, and v is the potential acting on an electron due to all nuclei present. Since $\rho(r)$ as a function of N has slope discontinuities, eq 1 provides the following three reaction indices:[22]

$$f^{-}(r) = [\delta\rho(r)/\delta N]_v \text{ (governing electrophillic attack)}$$

$$f^{+}(r) = [[\delta\rho(r)/\delta N]_v \text{ (governing nucleophilic attack)}$$

$$f^{0}(r) = {}^{1}/_{2}[f^{+}(r) + f^{-}(r)] \text{ (for radial attack)}$$

In a finite difference approximation, the condensed Fukui function[31] of an atom, for example, x, in a molecule with N electrons is defined as

$$f_x^{\ +} = [q_x(N + 1) - q_x(N)] \text{ (for nucleophilic attack)}$$

$$f_x^{\ -} = [q_x(N) - q_x(N - 1)] \text{ (for electrophillic attack)}$$

$$f_x^{\ 0} = [\mathrm{q}_x(N + 1) - \mathrm{q}_x(N - 1)]/2 \text{ (for radical attack)} \qquad (2)$$

Where q_x is the electronic population of atom x in a molecule. In density functional theory, the hardness g is defined as[32]

$$\eta = {}^{1}/_{2}(\delta^2\mathrm{E}/\delta\mathrm{N}^2)v(r) = {}^{1}/_{2}(\delta\mu/\delta N)v$$

The global softness S is defined as the inverse of the global hardness g.

$$S = {}^{1}/_{2}\eta = {}^{1}/_{2}(\delta N/\delta\mu)v$$

The local softness $s(r)$ can be defined as

$$s(r) = (\delta\rho(r)/\delta\mu)v \qquad (3)$$

Equation 3 can also be written as

$$s(r) = [\delta\rho(r)/\delta N]v[\delta N/\delta\mu]v = f(r)S \qquad (4)$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in HSAB principle. Using the finite difference approximation, S can be approximated as

$$S = 1/(\mathrm{IE} - \mathrm{EA}) \qquad (5)$$

where IE and EA are the first ionization energy and electron affinity of the molecule, respectively. Atomic softness values can easily be calculated by using eq 4, namely:

$$s_x^{\ +} = [q_x(N + 1) - q_x(N)]S$$

$$s_x^{\ -} = [q_x(N) - q_x(N - 1)]S$$

$$s_x^{\ 0} = S[q_x(N + 1) - q_{\mathrm{x}}(N - 1)]/2 \qquad (6)$$

Computational Methodology and Models. In the present study, all calculations have been carried out with DFT[33] using DMOL code of MSI Inc. BLYP[34,35] exchange correlation functional and DNP basis set[36] was used through out the calculation. BLYP has already shown its credibility for explaining weak hydrogen bond type interactions in comparison to MP2 level calculations.[37,38] It is also useful in describing the interaction of heteroatomic molecules with zeolite framework cluster.[27] The basis set superposition error (BSSE) was also calculated for the current basis set in nonlocal density approximation (NLDA) using the Boys−Bernardi method.[39] The theory of reactivity index calculations is mentioned elsewhere in details.[27] Single-point calculations of the cation and anion of each molecule at the optimized geometry of the neutral molecule were also carried out to evaluate Fukui functions and global and local softness. The condensed Fukui function and atomic softness were evaluated using eqs 2 and 6, respectively. The gross atomic charges were evaluated by using the technique of electrostatic potential (ESP) driven charges. It is well-known that Mulliken charges are highly basis set dependent, whereas the ESP driven charges show less basis set dependence[27,40,41] and are better descriptors of the molecular electronic density distribution.

Calculations have been performed on clusters of different formula to mimic the crystal growth in zeolites. In the case of zeolite the primary building units are the silicon or aluminum tetrahedra, which combines in the presence of templates and water to form the secondary building units which are five-membered rings followed by the rearrangement to grow a crystal of zeolite. We designed the cluster with that background. The nature of silica species in gel has been studied using ^{29}Si NMR, liquid chromatography, and other experimental techniques.[42−44] However, due to the presence of so many different clusters

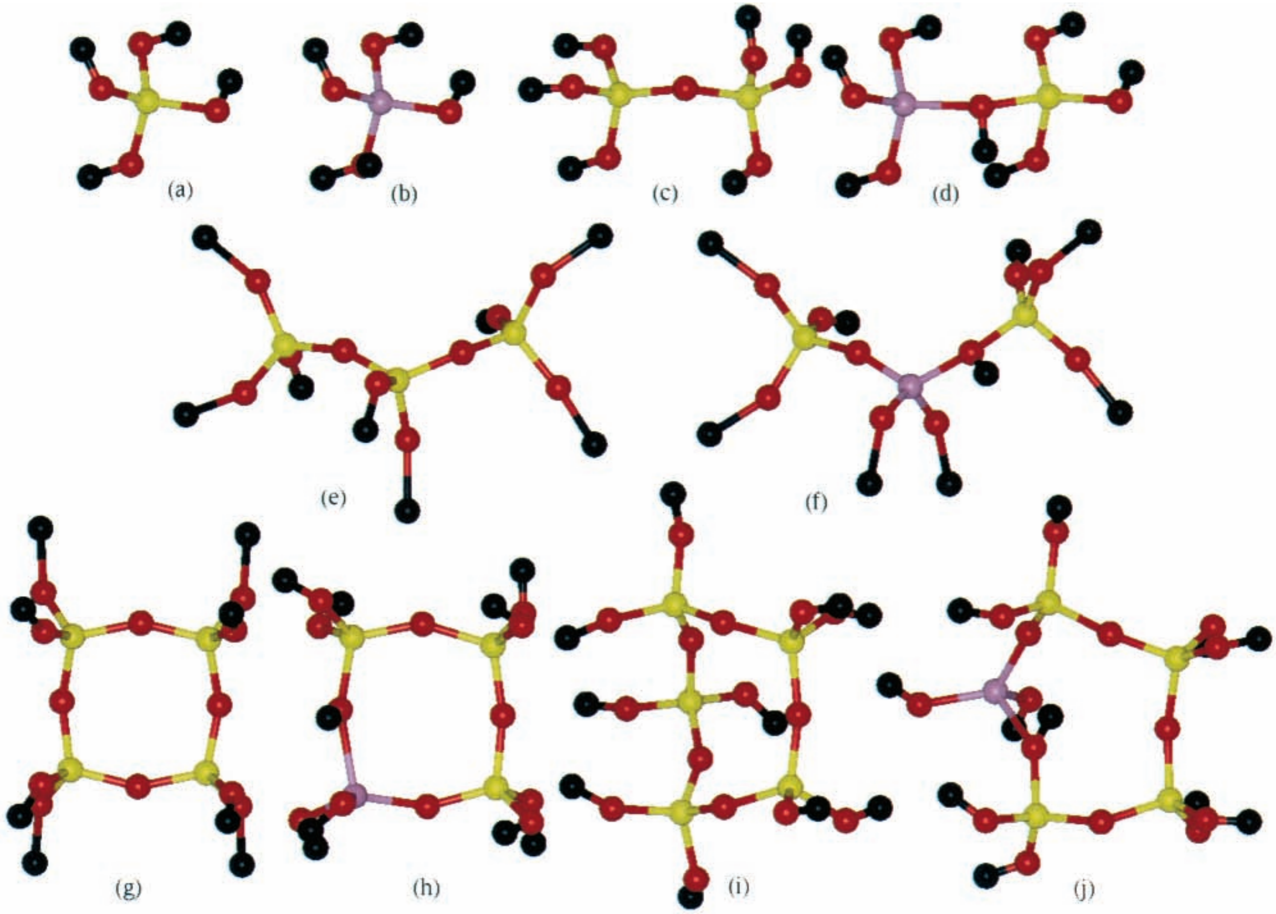

Figure 1. Cluster models of Zeolite framework with the formulas (a) SiO_4H_4, (b) AlO_4H_5, (c) $Si_2O_7H_6$, (d) $AlSiO_7H_7$, (e) $Si_3O_{10}H_8$, (f) $Si_2AlO_{10}H_9$, (g) $Si_4O_{12}H_8$, (h) $Si_3AlO_{12}H_9$, (i) $Si_5O_{15}H_{10}$, and (j) $Si_4AlO_{15}H_{11}$. The color code is as follows: red, oxygen; yellow, silicon; violet, aluminum; black, hydrogen.

present in solution, it is difficult to study their properties individually by experiment. There are many theoretical works to calculate the structure, energetics of these silica clusters.[45,46] We designed linear clusters until trimers followed by four- and five-membered rings. We have started from monomeric [$T(OH)_4$], dimeric [$(OH)_3$-T-O-T-$(OH)_3$], and trimeric [$(OH)_3$-T-O-T$(OH)_2$-O-T-$(OH)_3$] clusters to represent open and noncyclic clusters. Clusters containing monomer aluminum are constructed with the formula Al(OH)H; this formula accounts for the charge of the cluster as well as the added hydrogen will make all the aluminum-containing clusters the same from the Bronsted proton point of view. Clusters with four-member and five-membered rings follow the same order as mentioned above. The cluster models are shown in Figure 1. The representative template models are shown in Figure 2. The interacting templates were fully optimized with a fixed cluster for the evaluation of interaction energy. Because the validity of HSAB principle demands the satisfaction of the condition of equal local softness between two different interacting species, our aim is to compare the local softness values of the atoms of the interacting molecules along with the zeolite framework cluster. The atoms for which those values will be closer will be considered as the most probable sites of interaction. For the electrophillic center we need to calculate s_x^+ values, and for the nucleophilic center we need to calculate the s_x^- values. However, in addition we have also evaluated f_x^+ and f_x^- values for all the atoms in electrophilic and nucleophilic site, respectively. This will help us to compare the suitability of one of the parameters between f and s in the general statement of the HSAB principle as mentioned in earlier paragraphs.

Results and Discussion

The aim of the current communication is to propose a way to choose the best template for the synthesis of a particular zeolite ZSM-5 from a range of various representative templates. The templates are involved in the nucleation process so we have chosen different clusters to mimic the growth of the crystal during nucleation. The global softness values of the zeolite cluster models both all silica and clusters containing aluminum replacing one silicon as well as interacting template molecules calculated using DFT are presented in Tables 1 and 2, respectively. The nucleophilic condensed local softness s_x^- and condensed Fukui function f_x^- have been calculated for all the representative templates using the ESP methodologies and are presented in Tables 3 −9. The values of electrophilic condensed local softness s_x^+ and condensed Fukui function f_x^+ of the individual atoms of the cluster models obtained through ESP technique at DFT level are shown in Tables 10−14. It is observed from Tables 1 and 2 that the global softness values for the interacting molecular species are generally higher than that of the zeolite cluster models with the exceptions for lower molecular weight templating molecules. So to test the local HSAB principle, it seems to be important to analyze which of the local softness values or Fukui functions or reactive indices for the constituent atoms of the cluster models and interacting molecular species will be the more reliable parameters. First,

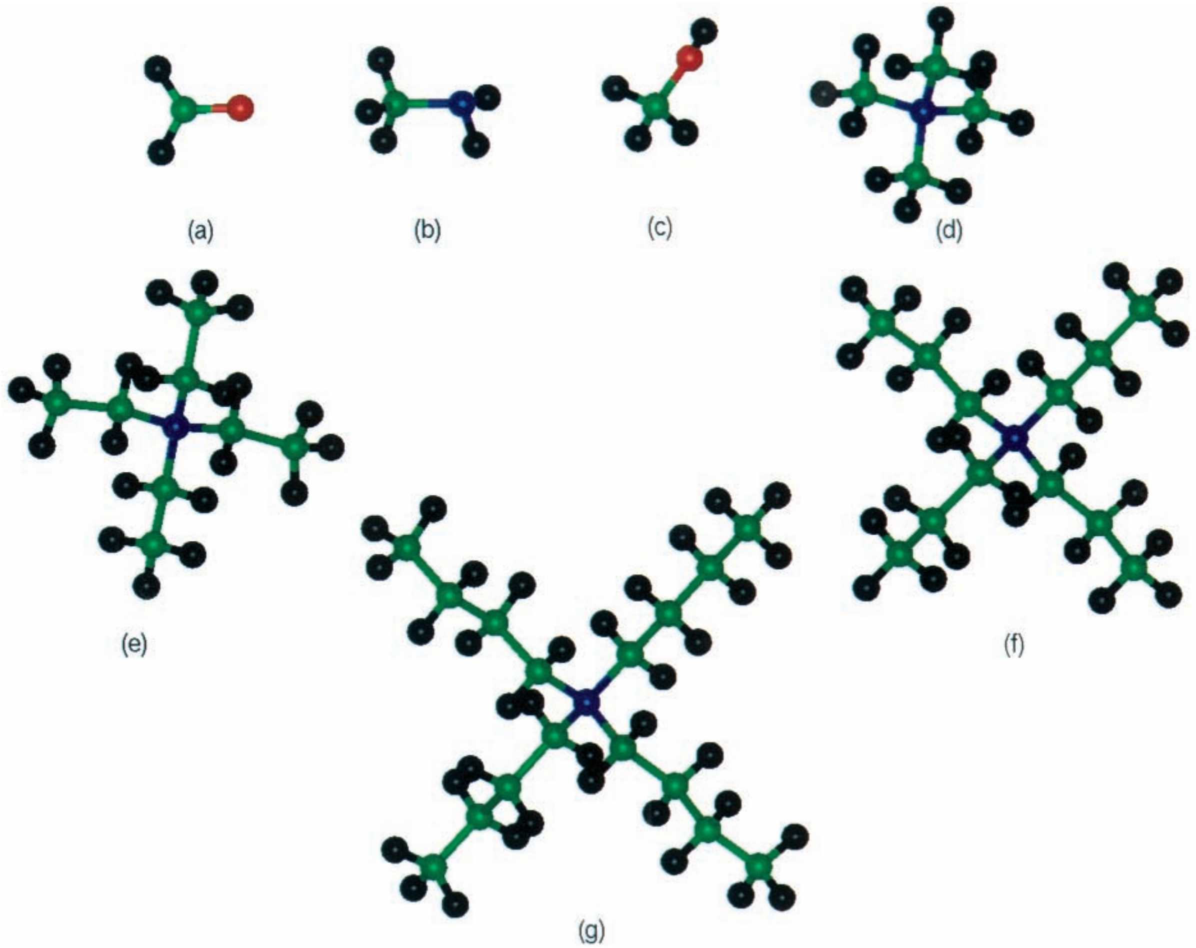

Figure 2. Structures of representative templates used (a) formaldehyde, (b) methylamine, (c) methanol, (d) tetramethylammonium cation, (e) tetraethylammonium cation, (f) tetrapropylammonium cation, and (g) tetrabutylammonium cation. The color code is as follows: red, oxygen; black, hydrogen; blue, nitrogen; green, carbon.

TABLE 1: Global Softness Values (in au) for Zeolite Clusters

framework cluster	global softness (au)
SiO_4H_4	2.329102
AlO_4H_5	2.588617
$Si_2O_7H_6$	2.583979
$AlSiO_7H_7$	2.751788
$Si_3O_{10}H_8$	2.773155
$Si_2AlO_{10}H_9$	2.910360
$Si_4O_{12}H_8$	0.434725
$Si_3AlO_{12}H_9$	0.394119
$Si_5O_{15}H_{10}$	0.551349
$Si_4AlO_{15}H_{11}$	0.301032

TABLE 2: Global Softness Values (in au) for Interacting Representative Template Molecules

template	global softness (au)
CH_2O	2.186270
CH_3NH_2	2.251091
CH_3OH	2.092838
$(CH_3)_4N^+$	7.177720
$(CH_3CH_2)_4N^+$	8.541898
$(CH_3CH_2CH_2)_4N^+$	8.713078
$(CH_3CH_2CH_2CH_2)_4N^+$	9.117432

TABLE 3: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Formaldehyde as Obtained from the ESP Technique at the DFT Level

constituent atoms	f_x^-	s_x^-
C	0.072	0.154
O	0.329	0.719
H	0.280	0.612
H	0.280	0.612

TABLE 4: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Methanol as Obtained from ESP Technique at DFT Level

constituent atoms	f_x^-	s_x^-
C	0.049	0.102
O	0.310	0.648
H	0.078	0.163
H	0.167	0.349
H	0.264	0.552
H	0.264	0.552

the fascination of interaction for the active sites present in zeolite cluster models with each of the templating molecules are calculated using local softness values and an activity order is proposed. This is followed by the interaction energy of the individual molecule with the best feasible zeolite framework cluster to justify the proposed order. A comparison of the trends observed in these two sets of results was studied and a qualitative scale has been proposed to choose the best template for a particular zeolite.

(*a*) *Activity of Zeolite Cluster Models in Terms of Reactivity Index.* To choose the best template we first need to know the active site in the zeolite framework. We compared the activity for clusters having all silicon to the clusters containing one aluminum replacing silicon. We are not mimicking the Si/Al ratio of the zeolite synthesis but approximating a situation taking into consideration the presence of aluminum. This is to see the

TABLE 5: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Methylamine as Obtained from the ESP Technique at the DFT Level

constituent atoms	f_x^-	s_x^-
C	0.256	0.578
N	0.277	0.623
H	0.001	0.003
H	0.001	0.003
H	0.105	0.236
H	0.105	0.236
H	0.105	0.236

TABLE 6: Condensed Local Softness and Fukui Functions for the N and the Atoms of One Alkyl Chain of Tetramethyl Ammonium Cation as Obtained from the ESP Technique at the DFT Level

constituent atoms	f_x^-	s_x^-
N	0.014	0.100
C	0.015	0.106
H	0.077	0.552
H	0.078	0.559
H	0.076	0.545

TABLE 7: Condensed Local Softness and Fukui Functions for the N and the Atoms of One Alkyl Chain of Tetraethyl Ammonium Cation as Obtained from the ESP Technique at the DFT Level

constituent atoms	f_x^-	s_x^-
N	0.006	0.051
C	0.008	0.068
H	0.059	0.503
H	0.058	0.495
C	0.014	0.119
H	0.062	0.529
H	0.046	0.392
H	0.047	0.401

TABLE 8: Condensed Local Softness and Fukui Functions for the N and the Atoms of One Alkyl Chain of Tetrapropyl Ammonium Cation as Obtained from the ESP Technique at the DFT Level

constituent atoms	f_x^-	s_x^-
N	0.002	0.017
C	0.005	0.043
H	0.044	0.383
H	0.044	0.383
C	0.002	0.017
C	0.003	0.026
H	0.041	0.357
H	0.026	0.226
H	0.026	0.226
H	0.038	0.331
H	0.038	0.331

TABLE 9: Condensed Local Softness and Fukui Functions for the N and the Atom of One Alkyl Chain of Tetrabutyl Ammonium Cation as Obtained from the ESP Technique at the DFT Level

constituent atoms	f_x^-	s_x^-
N	0.048	0.437
C	0.008	0.072
H	0.043	0.392
H	0.043	0.392
C	0.024	0.218
C	0.005	0.045
C	0.004	0.036
H	0.029	0.264
H	0.017	0.154
H	0.017	0.154
H	0.014	0.127
H	0.014	0.127
H	0.058	0.528
H	0.058	0.528

TABLE 10: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Monomeric Zeolite Cluster as Obtained from the ESP Technique at the DFT Level

	SiO_4H_4		AlO_4H_5	
constituent atoms	f_x^+	s_x^+	f_x^+	s_x^+
Si/Al	0.296	0.689	0.464	1.201
O	−0.053	−0.123	−0.054	−0.139
H	0.176	0.409	0.119	0.308
O	−0.024	−0.055	−0.059	−0.152
H	0.232	0.540	0.189	0.489
O	−0.073	−0.170	−0.063	−0.163
H	0.240	0.558	0.132	0.341
O	−0.054	−0.125	−0.041	−0.106
H	0.261	0.607	0.131	0.339
H			0.181	0.468

TABLE 11: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Dimeric Zeolite Cluster as Obtained from ESP Technique at the DFT Level

$Si_2O_7H_6$			$AlSiO_7H_7$		
constituent atoms	f_x^+	s_x^+	constituent atoms	f_x^+	s_x^+
Si	0.140	0.361	Al	0.256	0.704
O	−0.003	−0.007	O	0.003	0.008
H	0.071	0.183	H	0.059	0.162
O	0.042	0.108	O	−0.001	0.002
H	0.062	0.160	H	0.044	0.121
O	0.093	0.240	O	−0.008	−0.022
H	0.063	0.162	H	0.036	0.099
Si	0.245	0.633	O	−0.025	−0.069
O	0.019	0.049	H	0.027	0.074
H	0.104	0.269	Si	0.217	0.597
O	−0.019	−0.049	O	−0.007	−0.019
O	−0.008	−0.020	H	0.056	0.154
H	0.081	0.209	O	−0.028	−0.077
O	−0.009	−0.023	H	0.078	0.215
H	0.118	0.305	O	0.006	0.016
			H	0.286	0.787

effect of aluminum in the activity of the zeolite framework. Previous calculations involving nucleation move around all silica systems. So they have neglected the charge-compensating part. The condensed local softness (s_x^+) and condensed Fukui function (f_x^+) values governing nucleophilic attack, for the individual atoms of the cluster models, obtained through the ESP technique at the DFT level are shown in Tables 10−14. From the global softness values presented in Table 1, it is observed that the values are less for both four- and five-membered rings irrespective of their compositions. The lower values are partly due to spin contamination. Along with it, we observed that the global softness values for clusters containing aluminum are more than for those containing all silicon for noncyclic clusters. The trend is reversed for the ring systems. For the local properties it is observed that, for both the monomers irrespective of silicon or aluminum, the most electrophilic is the central silicon or aluminum atom. The bridging hydrogen present in the aluminum cluster is active but on a smaller scale compared to that of central silicon: this may be due to the location of another hydrogen in the vicinity of the bridging hydrogen present in the cluster. Now for dimers, the result tabulated in Table 11 shows that for all silicon clusters the most active atom toward a nucleophilic agent is one of the silicon atoms. The highest nucleophilicity for the dimer cluster with aluminum and silicon resides on the Brønsted proton attached to the bridging oxygen. This trend is similar for the trimers as well. The most nucleophilicity lying on the central silicon of the all silicon cluster with the Brønsted proton being the site with highest nucleophilicity for trimer clusters

TABLE 12: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Trimeric Zeolite Cluster as Obtained from the ESP Technique at the DFT Level

	$Si_3O_{10}H_8$		$Si_2AlO_{10}H_9$	
constituent atoms	f_x^+	s_x^+	f_x^+	s_x^+
Si/Al	0.138	0.383	0.180	0.524
H	0.088	0.244	0.019	0.055
O	−0.001	−0.002	−0.010	−0.029
O	−0.005	−0.013	−0.017	−0.049
O	0.018	0.050	0.006	0.017
H	0.107	0.297	0.039	0.113
H	0.099	0.274	0.048	0.139
Si	0.116	0.322	0.117	0.340
H	0.094	0.261	0.050	0.145
O	0.016	0.044	−0.014	−0.040
O	−0.003	−0.008	−0.001	−0.002
H	0.078	0.216	0.036	0.105
O	−0.002	−0.005	−0.012	−0.034
H	0.053	0.146	0.064	0.186
Si	0.073	0.202	0.147	0.428
H	0.077	0.213	0.054	0.157
H	0.086	0.238	0.057	0.166
O	−0.017	−0.047	−0.019	−0.055
O	−0.021	−0.058	0.004	0.012
O	−0.007	−0.019	−0.009	−0.026
O	0.012	0.033	0.007	0.020
H			0.231	0.672

TABLE 13: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Four Membered Ring Zeolite Cluster as Obtained from the ESP Technique at the DFT Level

	$Si_4O_{12}H_8$		$Si_3AlO_{12}H_9$	
constituent atoms	f_x^+	s_x^+	f_x^+	s_x^+
H	0.168	0.073	0.148	0.058
H	0.168	0.073	0.188	0.074
H	0.165	0.072	0.160	0.063
H	0.165	0.072	0.149	0.059
H	0.161	0.069	0.125	0.049
H	0.161	0.069	0.140	0.055
Si	−0.080	−0.034	−0.131	−0.051
Si	−0.080	−0.034	−0.117	−0.046
Si/Al	−0.093	−0.040	0.035	0.014
Si	−0.093	−0.040	−0.031	−0.012
H	0.165	0.072	0.121	0.047
H	0.165	0.072	0.191	0.075
O	0.042	0.018	0.019	0.007
O	0.042	0.018	0.008	0.003
O	−0.057	−0.024	−0.075	−0.029
O	−0.057	−0.024	−0.089	−0.035
O	0.042	0.018	0.095	0.037
O	0.042	0.018	0.023	0.009
O	0.024	0.010	0.069	0.027
O	0.024	0.010	−0.014	−0.005
O	0.035	0.015	0.018	0.007
O	0.035	0.015	0.002	0.007
O	−0.064	−0.027	−0.120	−0.047
O	−0.083	−0.036	−0.137	−0.053
H			0.207	0.081

TABLE 14: Condensed Local Softness and Fukui Functions for All the Constituent Atoms of Five Membered Ring Zeolite Cluster as Obtained from the ESP Technique at the DFT Level

	$Si_5O_{15}H_{10}$		$Si_4AlO_{15}H_{11}$	
constituent atoms	f_x^+	s_x^+	f_x^+	s_x^+
Si	0.029	0.016	0.146	0.044
H	0.082	0.045	0.189	0.056
H	0.120	0.066	0.078	0.023
H	0.107	0.059	0.097	0.029
Si/Al	0.067	0.037	−0.058	−0.017
Si	−0.023	−0.012	−0.104	−0.031
H	0.089	0.049	0.102	0.031
H	0.100	0.055	0.153	0.046
H	0.066	0.036	0.113	0.034
Si	−0.130	−0.007	−0.167	−0.050
H	0.113	0.062	0.119	0.035
H	0.044	0.024	0.064	0.019
H	0.071	0.039	0.146	0.044
Si	0.044	0.024	−0.075	−0.022
H	0.113	0.062	0.144	0.043
O	0.005	0.002	0.061	0.018
O	0.080	0.044	0.058	0.017
O	−0.014	−0.007	−0.013	−0.003
O	0.018	0.009	0.049	0.015
O	0.006	0.003	−0.013	−0.003
O	0.002	0.001	−0.003	−0.001
O	0.016	0.008	−0.009	−0.002
O	0.023	0.013	0.002	0.001
O	−0.038	−0.020	−0.068	−0.020
O	0.002	0.001	−0.006	−0.002
O	−0.012	−0.006	−0.026	−0.008
O	−0.026	−0.014	−0.083	−0.024
O	−0.043	−0.023	−0.069	−0.020
O	−0.025	−0.013	−0.081	−0.024
O	−0.003	−0.001	0.007	0.002
H			0.255	0.076

with one Al. For the ring clusters the trend is similar for the clusters with one Al but for all silicon clusters the nucleophilicity lies on the surrounding hydrogens, which were attached with the terminal silicons for charge neutralization. Now the idea behind this study is to monitor the crystal growth in zeolite synthesis. For the all silicon clusters from monomer to trimer the active site toward nucleophilic attack is Si, whereas the active sites for the ring clusters are the terminal hydrogens. This shows that primarily crystal growth is through the Si atom of the monomer; in the ring clusters it is almost the same except with a limitation of the cluster design. We have replaced the terminal silicons by hydrogens for charge neutrality; those hydrogens are at the nearest neighboring silicon distance. When the ring structure is formed, the intracluster Si atoms lose activity in comparison with the terminal hydrogens (in place of Si). In terms of the local softness (s_x^+) for clusters with all silicon, the trend of activity is as follows:

$$\text{monomer} > \text{dimer} > \text{trimer} > \text{four-membered ring} > \text{five-membered ring}$$

For the clusters with aluminum, the idea is same to monitor the crystal growth. We designed the clusters in a way to monitor the activity of Bronsted proton as well, because it is well-known that Bronsted proton is the active center in the aluminosilicates. Now here except for the monomer, for all other clusters the active center is the Bronsted proton attached to the bridging oxygen. The activity of the Al center in the monomer is supported by a work of Catlow et al:[47] it shows that the energetics of small aluminosilicate clusters has a marked influence on controlling the Si/Al distribution in zeolites. It shows that the condensation of a silica monomer with an Al monomer is energetically favorable by 27 kcal/mol. The order for the clusters with one aluminum assuming the active center as the central aluminum is the same as that with an all-silicon cluster:

$$\text{monomer} > \text{dimer} > \text{trimer} > \text{four-membered ring} > \text{five-membered ring}$$

Apart from the aluminum monomer, all the clusters with one aluminum the active site is the bridging hydrogen attached at the oxygen linked with one aluminum and one silicon. With that hydrogen being the active site, the order of activity is

$$\text{dimer} > \text{trimer} > \text{four-membered ring} > \text{five-membered ring}$$

From the results it can be seen that the activity of smaller clusters is greater, and it is greater for linear clusters in comparison to the ring clusters. Two things can be proposed at this point: (1) the crystal growth starts from the monomer increases linearly toward ring formation and (2) the activity of the individual clusters is very much dependent on the environment. The results categorically show that the activity of the zeolite cluster is dependent on the presence of aluminum. Now we will compare the electrophilicity of each atom of the individual representative template molecules with the corresponding site of interest or with the site of the framework with highest nucleophilicity, which will help us further to achieve our goal of choosing the best template available for the synthesis of a particular zeolite (ZSM-5).

(*b*) *Interaction with Formaldehyde as a Template with Framework Clusters*. Formaldehyde is the smallest template used in the ZSM-5 type zeolite synthesis. Table 3 shows that both s_x^- and f_x^- values obtained at the DFT level are higher for the carbonyl oxygen atom, indicating that the carbonyl oxygen atoms are preferable electrophilic site. From the s_x^+ and f_x^+ values for the atoms of the zeolite cluster models as discussed above, preferable nucleophilic sites could also be monitored. If we match the s_x^- and f_x^- values of the formaldehyde molecule with s_x^+ and f_x^+ values of the zeolite clusters, it can be clearly seen that s_x^- as well as f_x^- values of the carbonyl oxygen atom of formaldehyde match well with the s_x^+ and f_x^+ values of the hydrogen atom of bridging O−H group present in the Al-substituted monomer through pentamer and the silicon atom of monomer and dimer for all silicon clusters.

(*c*) *Interaction with Methanol as a Template with Framework Clusters*. Table 4 shows that both s_x^- and f_x^- values obtained at the DFT levels with the ESP method are higher for the hydroxyl oxygen atom, indicating that the oxygen atom is a preferable electrophilic site. These values are matching well with the s_x^+ and f_x^+ values of hydrogen atom of bridging O−H group present in Al-substituted monomer through pentamer and silicon atom of monomer and dimer for all silicon clusters.

(*d*) *Interaction with Methylamine as a Template with Framework Clusters*. Table 5 shows that both s_x^- and f_x^- values obtained in DFT are higher for the nitrogen atom, indicating that the nitrogen center is the preferable electrophilic site. As mentioned earlier, the hydrogen atom of bridging O−H group present in the Al-substituted monomer through pentamer and the silicon atom of monomer and dimer for all silicon clusters behaves as a nucleophile. The values of s_x^+ and f_x^+ match very well with the s_x^- and f_x^- values of the carbon atom of methylamine. This shows the accountability of this softness values in predicting the experimental trend as well as making it also possible to locate the interaction site of the interacting species correctly.

(*e*) *Interaction with Alkylammonium Cations as a Template with Framework Clusters*. The alkylammonium cations are the best template used for ZSM-5 type zeolite synthesis as observed experimentally. So we have studied exhaustively the different alkylamines from the smallest possible to the highest used in the synthesis of zeolites. The results are shown in Tables 6−9. It is observed that for all the ammonium cations the terminal hydrogens attached with the terminal carbon shows the greatest eletrophilicity. Now, X-ray crystal structure report of TPA inside ZSM-5 reveals the fact that the terminal methyl group of TPA is directed toward the framework inside the gel.[48] The results are in perfect match with the s_x^+ and f_x^+ values of hydrogen atom of bridging O−H group present in the Al-substituted monomer through pentamer and the silicon atom of monomer and dimer for all silicon clusters.

From the above results we can safely say that the noncyclic clusters grow in the presence of the templates. The active sites of templates have a favorable unisite interaction with the framework cluster to form a pseudo bond.

(*f*) *The Reactivity Index Scale.* The aim of the current study is to choose the best template for the synthesis of a particular zeolite from a range of different templates. We here are trying to rationalize an understanding of interaction of hetroatomic molecules (templates) with zeolite framework and to propose a scale in terms of reactivity index. First we will summarize our observations from the results obtained so far. It is observed from Tables 1 and 2 that the zeolite framework has higher value for global softness in comparison to interacting molecules except for the alkylammonium cations. The order of the global softness of interacting molecules is in the order:

$$\mathrm{TBA} > \mathrm{TPA} > \mathrm{TEA} > \mathrm{TMA} > \mathrm{CH_3NH_2} > \mathrm{CH_2O} > \mathrm{CH_3OH}$$

We presented the results of condensed local softness and Fukui functions of most electrophilic atom of the interacting molecules from ESP technique at DFT level. The results show that in terms of Fukui functions and local softness these interacting template molecules can be arranged in the order:

$$\mathrm{TPA} < \mathrm{TBA} < \mathrm{TEA} < \mathrm{TMA} < \mathrm{CH_3NH_2} < \mathrm{CH_3OH} < \mathrm{CH_2O}$$

This is the trend of the activity of templates among the range of templates suitable for a particular zeolite (here ZSM-5) synthesis. These templates, especially the ammonium cations, are common templates used in zeolite synthesis. So knowledge of activity of these templates will help to extrapolate the findings to another type of zeolite material.

(*g*) *Differences in the Condensed Softness between the Organic Templates and the Si/Al Cluster.* The differences in the condensed softness between the organic templates and the Si/Al cluster have been shown in Table 15. The results are the difference of local softness between the most nucleophilic site of the zeolite clusters and the most electrophilic site of the templates. We also monitored the ratio of the local softness values obtained for the most electrophilic site to the most nucleophilic site. The results are shown in Table 16. We wish to extract the qualitative trend observed from these results. The results obtained from Tables 15 and 16 contain the same information that the activity of the templates TPA > TBA > TEA > TMA > CH_3NH_2 > CH_3OH > CH_2O is only valid for the clusters $Si_3O_{10}H_8$ > $Si_3AlO_{12}H_9$ > $Si_4AlO_{15}H_{11}$ > $Si_4O_{12}H_8$ > $Si_5O_{15}H_{10}$. The current results show that TPA shows better activity toward ring clusters in comparison to that with linear clusters with an exception of an all silicon trimer. Smaller templating molecules still behave better than the tetraalkylammonium ions while interacting with linear clusters. This gives us a very interesting conclusion. All of the studied templates are used for zeolite synthesis, and it is observed experimentally those tetraalkylammonium templates and especially the TPA gives better crystallinity. We observe the same trend here, as TPA shows favorable interaction with ring clusters. In an other way, TPA helps the condensation of smaller fragments. As well there are other parameters involved in the real story, i.e., during synthesis of zeolite water is present in the medium which may have a influence in the condensation of the small fragments (monomers). This needs a further study involving templates,

TABLE 15: Difference between Condensed Local Softness Values between the Most Nucleophilic Site of the Zeolite Clusters and the Most Electrophilic Site of Interacting Organic Template Molecules

	differences between condensed local softness ($s_x^+ - s_x^-$) for templates						
zeolite cluster	CH_2O	CH_3OH	CH_3NH_2	TMA	TEA	TPA	TBA
SiO_4H_4	0.152	0.223	0.248	0.312	0.342	0.488	0.343
AlO_4H_5	0.482	0.553	0.578	0.642	0.672	0.818	0.673
$Si_2O_7H_6$	−0.086	−0.015	0.010	0.074	0.104	0.250	0.105
$AlSiO_7H_7$	0.068	0.139	0.164	0.228	0.258	0.404	0.259
$Si_3O_{10}H_8$	−0.336	−0.265	−0.240	−0.176	−0.146	0.000	−0.145
$Si_2AlO_{10}H_9$	−0.047	0.024	0.049	0.113	0.143	0.289	0.144
$Si_4O_{12}H_8$	−0.646	−0.575	−0.550	−0.486	−0.456	−0.310	−0.455
$Si_3AlO_{12}H_9$	−0.638	−0.567	−0.542	−0.478	−0.448	−0.302	−0.447
$Si_5O_{15}H_{10}$	−0.653	−0.582	−0.557	−0.493	−0.463	−0.317	−0.462
$Si_4AlO_{15}H_{11}$	−0.643	−0.572	−0.547	−0.483	−0.453	−0.307	−0.452

TABLE 16: Ratio of Condensed Local Softness Values between the Most Nucleophilic Site of the Zeolite Clusters and the Most Electrophilic Site of Interacting Organic Template Molecules

zeolite cluster	ratio of condensed local softness (s_x^-/s_x^+) for templates						
	CH_2O	CH_3OH	CH_3NH_2	TMA	TEA	TPA	TBA
SiO_4H_4	0.825	0.743	0.715	0.641	0.607	0.439	0.606
AlO_4H_5	0.598	0.539	0.518	0.465	0.440	0.318	0.439
$Si_2O_7H_6$	1.135	1.023	0.984	0.883	0.835	0.605	0.834
$AlSiO_7H_7$	0.913	0.823	0.791	0.710	0.672	0.486	0.670
$Si_3O_{10}H_8$	1.877	1.691	1.626	1.459	1.381	1.000	1.378
$Si_2AlO_{10}H_9$	1.069	0.964	0.927	0.831	0.787	0.569	0.785
$Si_4O_{12}H_8$	9.849	8.876	8.534	7.657	7.246	5.246	7.232
$Si_3AlO_{12}H_9$	8.876	8.000	7.691	6.901	6.530	4.728	6.518
$Si_5O_{15}H_{10}$	10.893	9.818	9.439	8.469	8.015	5.803	8.000
$Si_4AlO_{15}H_{11}$	9.460	8.526	8.197	7.355	6.960	5.039	6.947

TABLE 17: Total Energy of the Framework and Interacting Molecules along with the Interaction Energy for Each of the Individual Representative Template Molecules with Zeolite Framework at Their Optimized Configurations

	interaction energy	
molecule	total energy (au)	BSSE corrected (kcal/mol)
$Si_2AlO_{10}H_9$ (FW)	−1571.435	
CH_2O	−114.516	
CH_3NH_2	−95.833	
CH_3OH	−115.721	
$(CH_3)_4N^+$	−214.138	
$(CH_3CH_2)_4N^+$	−371.253	
$(CH_3CH_2CH_2)_4N^+$	−528.435	
$(CH_3CH_2CH_2CH_2)_4N^+$	−685.617	
FW + CH_2O	−1685.982	−20.33
FW + CH_3NH_2	−1667.308	−23.22
FW + CH_3OH	−1687.190	−21.96
FW + $(CH_3)_4N^+$	−1785.617	−24.54
FW + $(CH_3CH_2)_4N^+$	−1942.736	−25.85
FW + $(CH_3CH_2CH_2)_4N^+$	−2099.940	−32.19
FW +$(CH_3CH_2CH_2CH_2)_4N^+$	−2257.108	−29.12

water, and clusters together to propose the mechanism of nucleation. But at this point we may qualitatively say that TPA behaves as a better performer in terms of better crystallinity. As we aim to choose the best template in terms of its role toward synthesis of ZSM-5, we need to monitor the crystal growth. To monitor that, one has to perform interaction energy calculation, which then can help to quantify the results in terms of choosing the best template available for the synthesis of zeolite.

(*h*) *Interaction Energy Calculation.* We need to verify this trend by interaction energy calculation, which will plausibly say whether the active site we located through Fukui function calculations are worthy or not. These calculations are aimed to validate the proposition of activity order of templates proposed. The interaction energy calculation was performed using DFT with BLYP functional. The validity of current methodology in predicting the interaction energy is tested elsewhere.[27,28] It shows that our current methodology can reproduce the binding energy of the smaller models with an error of ±0.1 kcal/mol. The trimer cluster model is a rational choice between cluster sizes, realistic picture for the zeolite crystals, and CPU time. The cluster is fixed throughout the calculation and the configuration of the interacting molecules was optimized. For each case, the most electrophilic atom (as observed from the reactive index values) of the interacting molecules was placed at a distance of 2 Å from the most nucleophilic site of the zeolite cluster. This has been done based on the chemical intuition and also supported by the crystallographic observation.[48] The crystallographic results are for TPA and TBA inside zeolite before calcinations. There the terminal methyl group is pointed toward the bridging oxygen, we used the same basics for choosing the conformations. This results in a more accurate initial conformation, which is now based on intuition, local softness values, which determine the active site for both interacting species and the framework, supported by experimental results. The results of total energy of the framework cluster and the individual interacting molecule along with the adsorption complex and interaction energy (BSSE corrected) of the individual molecule are shown in Table 17. The interaction energy values fall in the range of 20.33 kcal/mol to 32.19 kcal/mol. The interaction energy value for methanol is in perfect match with the ab initio calculation using same basis set by Greatbanks et al.[49] We will not emphasize on the numbers; rather, we will analyze the trend. The interaction energy trend for alkylammonium cations matches with our earlier results. The overall trend as observed from the interaction energy calculations are as follows:

$$\mathrm{TPA} > \mathrm{TBA} > \mathrm{TEA} > \mathrm{TMA} > CH_3NH_2 > CH_3OH > CH_2O$$

So from the DFT based local parameter descriptor can conclusively locate the active site in the interacting molecular species as well as by comparing with the parametric value for zeolites we can choose the best candidate for a particular reaction. Because here the zeolite structure is very general, the interacting species location is sensible, which further helps in mimicking the reaction condition in a nice way. This also validates our earlier proposition that for unisite interaction the reactivity index scale is the proper descriptor to develop a qualitative scale for a range of molecules.

(*i*) *Solvation Energy Calculation for Zeolite Cluster Models.* The calculations so far performed were on clusters formed in a vacuum. As in the case of zeolite synthesis, the solvation will exert a crucial role in terms of its stability. This study is aimed to trace the role of aluminum in the zeolite synthesis in terms of choosing the best template for a particular zeolite synthesis. So far, the results show that electrophilicity is more pronounced

TABLE 18: Solvation Energies (kcal/mol) per Si or Al Calculated with DMOL/COSMO

framework cluster	COSMO solvation energy (kcal/mol) per Si	COSMO solvation energy (kcal/mol) per Al
SiO_4H_4	−10.04	
AlO_4H_5		−12.47
$Si_2O_7H_6$	−9.78	
$AlSiO_7H_7$		−11.7
$Si_3O_{10}H_8$	−8.96	
$Si_2AlO_{10}H_9$		−9.93
$Si_4O_{12}H_8$	−7.55	
$Si_3AlO_{12}H_9$		−8.04
$Si_5O_{15}H_{10}$	−5.86	
$Si_4AlO_{15}H_{11}$		−7.49

for clusters with aluminum substitution. To validate this we need to monitor the influence of solvation on the clusters involved in this study. We used here the COSMO method developed by Klamt et al.[50] This method has been introduced to DFT code by Andzelm et al.[51] The COSMO model is a continuum solvation model, in which the solute forms a cavity within the solvent of specific permittivity, represented by dielectric continuum. The dielectric medium is polarized by the charge distribution of the solute, and the response of the dielectric medium is described by screening charges on the surface of the cavity. The free energy of solvation ΔG can be calculated as

$$\Delta G = (E + \Delta G_{\text{nonelectrostaic}}) - E^0$$

where E^0 is the total energy of the molecule in a vacuum and E is the total energy of the molecule in the solvent. $\Delta G_{\text{nonelectrostaic}}$ is the nonelectrostaic contribution from the dispersion and cavity formation effects, obtained by fitting the free energies of hydration for linear chain alkanes as a function of surface area.[52] We used DNP basis set and BLYP functional throughout the COSMO calculations. The results are shown in Table 18. The results show that solvation energy decreases with increase in the silicon content. A recent study using DMOL/ COSMO has shown the mechanism of condensation of silicate monomers to form a dimer species.[53] These calculations give a detailed account on the energetics and predicted activation energies in the range of 11−16 kcal/mol. These values are again a perfect match with those obtained for zeolite nucleation using synchrotron radiation techniques.[54] The results for the clusters containing one aluminum show the same trend with lower solvation energy. These results show that frameworks with aluminum will be a better choice for synthesis. At the same time it also validates the need for aluminum being present in the zeolite framework. Our Fukui function results propose that the templates will have a more favorable interaction with clusters containing aluminum and that also for the noncyclic ones. The solvation energy shows also the same trend for both noncyclic and ring clusters.

Conclusion

This is the first study to choose the best template for a particular zeolite synthesis by estimating the individual activity of templating molecules and the framework cluster in terms of reactivity index and then validating the results through interaction energy calculations. We here are successful in justifying the charge-compensating role of templates, which is observable while through the favorable interaction of the templates with the framework containing aluminum. Thus, the role of aluminum has also been monitored. This paves a novel qualitative way of estimating the activity of interacting template molecules to choose a matrix for their usage, which is prime need for tailoring zeolite synthesis. The reactivity index results show that by calculating a range of templates we can successfully predict which template will be suitable for a particular zeolite synthesis. We tested our results with a very well-known zeolite ZSM-5 which can be available as both silicalite and silica aluminate. Along with that it is the most studied zeolite with ample applications. From our calculations it is observed that TPA is the best template for zeolite ZSM-5 synthesis, which also validates our earlier proposition as well as experimental observation. At the same time we could qualitatively scale a series of templates to find the best choice. We still need to work on the Si/Al ratio, to formulate an a priori rule for the synthesis. We need to perform calculations involving template, water, and the cluster to propose the nucleation mechanism. Then only we can extrapolate this finding to a general zeolite synthesis. But at this point we show from the solvation energy that presence of aluminum in the gel favors growth. The templates have unisite interaction with the zeolite framework at the time of growth. Once the ring structure is formed, the template has a less active role. The results show the beauty of reactivity index in exploring complicated host−guest phenomenon. The optimistic results paves way for future study involving other parameters of interest such as temperature and pressure using ab initio molecular dynamics to formulate an a priori rule for the zeolite synthesis.

References and Notes

(1) Barrer, R. M. *Hydrothermal Chemistry of Zeolites;* Acedmic Press: London, 1982.

(2) Akoporiaye, D. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2456.

(3) Zones, S. I.; Nakagawa, Y.; Lee, G. S.; Chen. C. Y.; Yuen, L. T. *Micrporous Mesoporous Mater.* **1998**, *21*, 199.

(4) Yoshikawa, M.; Wagner, P.; Lovall, M.; Tsuji, K.; Takewaki, T.; Chen. C. Y.; Beck, L. W.; Jones, C.; Tsapatsis, M.; Zones, S. I.; Davis, M. E. *J. Phys. Chem. B* **1998**, *102*, 7139.

(5) Shantz, D. F.; Fild, C.; Koller, H.; Lobo, R. F. *J. Phys. Chem. B.* **1999**, *103*, 10858.

(6) Cambell, B. J.; Bellusi, G.; Carluccio, L.; Perego, G.; Cheetham, A. K.; Cox, D. E.; Millini, R. *Chem. Commun.* **1998**, 1725.

(7) Lee, Y. J.; Carr, S. W.; Praise, J. B. *Chem. Mater.* **1998**, *10*, 2561.

(8) Armor, J. N. *Microporous Mesoporous Mater.* **1998**, *22*, 451.

(9) Yunfeng, L.; Gonzalez, C.; Kale, R. P.; Prabhakar, S.; Lopez, G. P.; Brinker, C. J. *Chem. Mater.* **1999**, *11*, 1223.

(10) Feuerstein, M.; Lobo, R. F. *Chem. Mater.* **1998**, *10*, 2197.

(11) Lewis, D. W.; Freeman, C. M.; Catlow, C. R. A. *J. Phys. Chem.* **1995**, *99*, 11194.

(12) Boyett, R. E.; Stevens, A. P.; Ford, M. G.; Cox, P. A. *Stud. Surf. Sci. Catal.* **1996**, *105*, 117.

(13) Lewis, D. W.; Willock, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, G. J. *Nature* **1996**, *382*, 604.

(14) Stevens, A. P.; Gorman, A. M.; Freeman, C. M.; Cox, P. A. *J. Chem. Soc., Faraday Trans.* **1996**, 92. 2065.

(15) Catlow, C. R. A.; Coombes, D. S.; Lewis, D. W.; Pereira, J. C. G. *Chem. Mater.* **1998**, *10*, 3249.

(16) Lok, B. M.; cannan, T. R.; Messina, C. A. *Zeolites* **1983**, *3*, 282.

(17) Shiralkar, V. P.; Clearfield, A. *Zeolites* **1989**, *9*, 363.

(18) Chatterjee, A.; Vetrivel, R. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4313.

(19) Chatterjee, A. *J. Mol. Catal. A.* **1997**, *120*, 155.

(20) Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(21) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

(22) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(23) Langenaeker, W.; Demel, K.; Geerlings, P. *J. Mol. Struct. (THEOCHEM)* **1992**, *259*, 317.

(24) Langenaeker, W.; Proft, F. De.; Geerlings, P. *J. Phys. Chem.* **1995**, *99*, 6624.

(25) Langenaeker, W.; Proft, F. De.; Geerlings, P. *J. Phys. Chem. A* **1998**, *102*, 5944.

(26) Chandra, A. K.; Geerlings, P.; Nguyen, M. T. *J. Org. Chem.* **1997**, *62*, 6419.

(27) Chatterjee, A.; Iwasaki, T.; Ebina, T. *J. Phys. Chem. A* **1999**, *103*, 2489 and references therein.

(28) Chatterjee, A.; Iwasaki, T. *J. Phys. Chem. A* **1999**, *103*, 9857.

(29) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(30) Gazquez, J. L.; Mendez, F. *J. Phys. Chem.* **1994**, *98*, 4591.

(31) Yang, W.; Mortier, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 5708.

(32) Pearson, R. G.; Parr, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(33) Kohn, W.; Sham. L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(34) Becke, A. *J. Chem. Phys.* **1988**, *88*, 2547.

(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 786.

(36) Bock, C. W.; Trachtman, M. *J. Phys. Chem.* **1994**, *98*, 95.

(37) (a) Sim, F.; St-Amant, A.; Papai, I.; Salahub, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 4391. (b) Kim, K.; Jordan, K. D. *J. Phys. Chem.* **1994**, *98*, 10089.

(38) Chandra, A. K.; Nguyen, M. T. *Chem. Phys.* **1998**, *232*, 299.

(39) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(40) Proft, F. D.; Martin, J. M. L.; Geerlings, P. *Chem. Phys. Lett.* **1996**, *250*, 393.

(41) Geerlings, P.; Proft, F. D.; Martin, J. M. L. In *Recent Developments in Density Functional Theory*; Seminario, S., Ed.; Theoretical and Computational Chemistry 5; Elsevier, Amsterdam, 1996; pp 773−780.

(42) Keefer, K. D. In *Better Ceramics through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Elsevier Science Publishing Co.: New York, 1984; Vol. 32, p 15.

(43) Kinrade, S.D.; Swaddle, T.W. *Inorg. Chem.* **1988**, *27*, 4253.

(44) Knight, C. T. G. *Zeolites* **1990**, *10*, 140.

(45) Sauer, J. *Chem. Rev.* **1989**, *89*, 199.

(46) Moravetski, V.; Hill, J. R.; Eichler, U.; Cheetham, A. K.; Sauer, J. *J. Am. Chem. Soc.* **1996**, *118*, 13015.

(47) Catlow, C. R. A.; George, A. R.; Freeman, C. M. *J. Chem. Soc., Chem. Commun.* **1996**, 1311.

(48) Koningsveld, H. V.; Bekkum, H. V.; Jansen, J. C. *Acta Crystallogr. Sect. B* **1987**, *43*, 127.

(49) Greatbanks, S. P.; Hillier, I. H.; Sherwood, P. *J. Chem. Phys.* **1996**, *105*, 3770.

(50) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799.

(51) Andzelm, J.; Kölmel, C.; Klamt, A. *J. Chem. Phys.* **1995**, *103*, 9312.

(52) Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016.

(53) Pereira, J. C. G.; Price, G. D.; Catlow, C. R. A. *J. Chem. Soc., Chem. Commun.* **1998**, 1387.

(54) Davies, A. T.; Sankar, G.; Catlow, C. R. A.; Clark, S. M. *J. Phys. Chem. B* **1997**, *101*, 10115.