

collected in Table 2 show the expected pattern. For the fully optimized cluster C, there is close agreement between 6-31G(d) and 6-31G(d,p) results: bond lengths differ by about 0.004 Å for the O–H bond, Si–O and Al–O bonds are virtually equal and Si–O–H bond angles vary by 0.3°. Comparing the fully optimized cluster C with its partially optimized structure, the Al–O bonds of the latter are longer while the Si–O bonds are slightly shorter than the former. The 6-31G(d,p) calculations of the partially optimized structure yields an O–H that is 0.002 Å too short. The comparative results for the optimized 'cluster C' (Si/Al = 4) and optimized 'cluster B' having high silica zeolite (Si/Al = 10) demonstrate the variation of acidity on chemical composition of Si/Al ratio i.e. the acid strength of zeolite increases with decreasing Al content, which is in accordance with recent experimental data [41].

3.2. Proton affinities

Proton affinities (PAs) of Brønsted hydroxyl group in zeolites are considered to be an important feature of catalytic activity. The performance of the B3LYP method in predicting gas phase proton affinities is compared with highly the reliable coupled pair functional method [35] and G1 theory [42,43]. Both theoretical levels are reportedly capable of predicting PAs accurate to within 2 to 3 kcal/mol. All calculated PAs at different basis sets for different cluster models are documented in Table 3.

3.2.1. Silanol

The B3LYP/6-311G(d,p) and B3LYP/6-311 + G(d,p) proton affinities are found to be 368.6 and 363.7 kcal/mol. It is clearly seen that inclusion into the basis of a single diffuse function on heavy atoms,

Table 3
OH bond lengths (Å), proton affinities (PA in kcal/mol) and Mulliken charges of the acidic hydrogens computed with the B3LYP for the different models

Model	Basis set	r_{OH}	PA	q_H
H ₂ O	6-31G(d)	0.969	431.8	0.3871
	6-31G(d,p)	0.965	435.1	0.3049
	6-311G(d)	0.962	425.4	0.3987
	6-311G(d,p)	0.962	429.2	0.2367
	6-311 + G(d,p)	0.962	396.0	0.2529
H ₃ COH	6-311G(d)	0.963	397.2	0.3789
	6-311G(d,p)	0.961	401.2	0.2355
H ₃ SiOH	6-311G(d,p)	0.959	368.8	0.2808
	6-311 + G(d,p)	0.959	363.7	0.2814
H ₃ AlOHSiH ₃	6-311G(d,p)	0.963	314.3	0.3427
	6-311 + G(d,p)	0.963	312.6	0.3303
Cluster C ^a	6-31G(d)	0.971	306.7	0.4768
	6-31G(d,p)	0.968	310.5	0.3777
	6-311G(d)	0.964	304.4	0.4882
	6-311G(d,p)	0.964	307.5	0.3568
Cluster C ^b	6-31G(d)	0.974	303.6	0.4740
Cluster B ^a	6-31G(d)	0.972	300.9	0.4773
	6-311G(d,p)	0.965	301.9	0.3497
H ₃ O ⁺	6-31G(d)	0.982	173.8	0.5576
	6-31G(d,p)	0.976	178.2	0.4653
	6-311G(d)	0.973	176.1	0.5796
	6-311G(d,p)	0.975	176.1	0.4193
	6-311 + G(d,p)	0.976	170.0	0.4182

^a Partially optimized structure.

^b Fully optimized structure.

6-311G(d,p) $\rightarrow$ 6-311 + G(d,p), yields a significant improvement in the PA. The DFT performs perfectly well at the B3LYP/6-311 + G(d,p) level, which is in good agreement with the CPF and G1 results (363.5 and 363.4 kcal/mol).

3.2.2. Zeolites

A nearly linear relationship between the PAs and the net charge on the proton, q_H , has been derived for a set of structurally related molecules (HO–H, H_3CO-H , H_3SiO-H , $H_3SiOHAlH_3$, different types of zeolite cluster models, and H_3O^+) and is illustrated in Fig. 2. As expected, the hydronium cation yields the lowest PA, while the nonacidic water molecule provide the largest PA value. Comparing the PAs of H_3SiOH with $H_3SiO(H)AlH_3$, the PA of the latter is 50.9 kcal/mol lower than the PA of the former which corresponds to the lengthening of the OH in the $H_3SiO(H)AlH_3$. This results from the interaction of the Lewis acid, AlH_3 , with the basic oxygen site in the Lewis acid–base complex, $H_3SiOH \dots AlH_3$. The B3LYP/6-311G + (d,p) result of the PA for $[H_3SiOAlH_3]^-$ is also encouraging. The deviation from the most accurate G1 [38,39] is about 2.86 kcal/mol. The MP2/DZ2P proton affinity yields a virtually identical value to the less expensive B3LYP result (312.5 kcal/mol (MP2) versus 312.6 kcal/mol (B3LYP)).

For cluster C, $Al(OSiH_3)_4H$, the B3LYP/6-311G(d,p) calculation yields a PA value of 307.5 kcal/mol. It is also important to study the dependence of PA on the employed cluster size. On expanding the model cluster from $H_3SiO(H)AlH_3$ to $Al(OSiH_3)_4H$, PA is decreased by 6.8 kcal/mol. For the largest faujasitic zeolite model, Fig. 1b, the PA is evaluated to be 301.9 kcal/mol. Using the systematic deviation between B3LYP/6-311G + (d,p) and G1 theory, our predicted value is estimated to be 294 ± 3 kcal/mol, which is in the range of experimentally determined values of 291–300 kcal/mol [44,45].

3.3. The interaction of faujasitic zeolite with water

3.3.1. Structures and energetics

Two representative cluster models of water adsorption on zeolites are investigated. In one of these, the hydrogen-bonded structures are stabilized on the

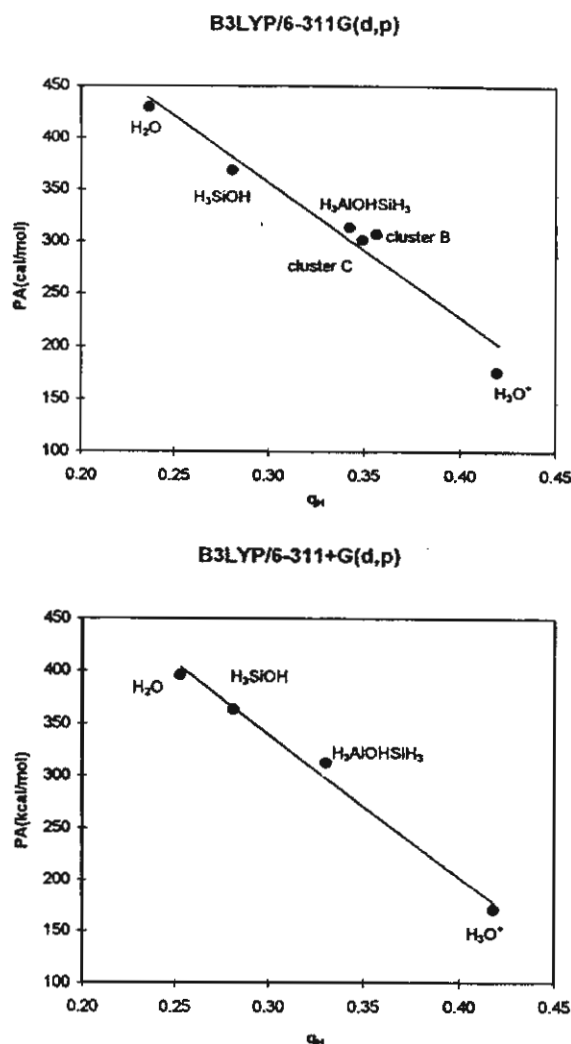


Fig. 2. The proton affinities of a set of structurally related molecules (HO–H, H_3COH , H_3SiO-H , $H_3SiOHAlH_3$, different types of zeolite cluster models, and H_3O^+) as a function of the net charge on the proton, q_H .

bridging OH. The other is a type of protonated model, in which hydronium cation forms two hydrogen bonds towards the unprotonated zeolitic framework. Attempts were made to search for the minimum structure of zeolite cluster model/ H_3O^+ . All investigated cluster models yield only one minimum as hydrogen-bonded water complexes regardless of whether the initial framework structure having H_2O or hydronium ion. It is noted that in the case of ion-pair complexes, an initial structure with a

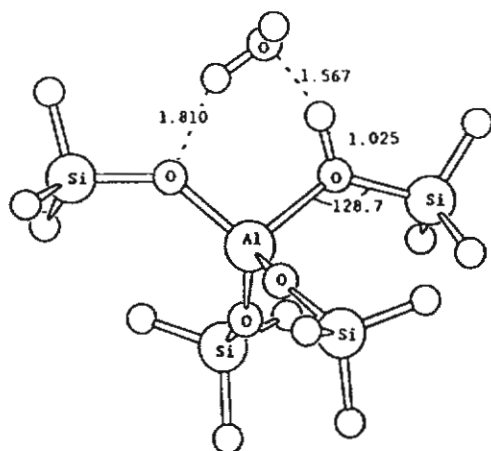


Fig. 3. Schematic representation of molecular model for the cluster C, $\text{Al}(\text{OSiH}_3)_4/\text{H}_2\text{O}$.

hydronium ion is optimized. The OH bond of H_3O^+ and the hydrogen bond angle ($\text{O}\cdots\text{H}-\text{O}$) in the complex is constrained at the optimized H_3O^+ and 180, respectively. The final complex can be derived by removing the fixed internal coordinates from the former constrained optimization structure. Similar conclusions to our predicted results have just recently been reported by Sauer et al. [11]. Recent FT-IR [17] and ab initio [14] studies of H_2O adsorption on zeolite support the direct clear evidence for the hydrogen-bonded adsorption of water. In the present study we concentrate only on the most probable hydrogen-bonded models.

The optimized geometry of cluster C with water (Fig. 3) and the extended model cluster B with water (Fig. 4) are investigated at the B3LYP/6-31G(d) level. The geometric parameters are summarized in Table 4. The results for the surface complexes clus-

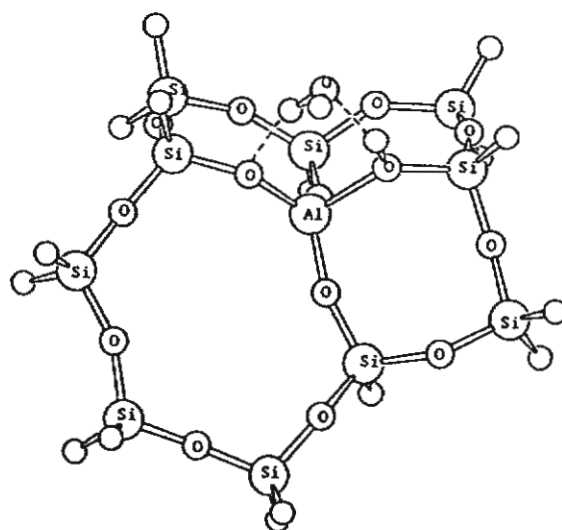


Fig. 4. Schematic representation of molecular model for the faujasitic zeolite/water.

ter C/water and cluster B/water indicate that the adsorbed water can act both as a proton acceptor and as a proton donor. The two hydrogen bonds are part of a cyclic structure, which have also been reported at HF/DZP level of theory by Sauer et al. [13].

The changes in the structural parameters of the faujasitic zeolite upon complexation with water are impressive. The results are in accordance with Gutmann's rules [46], i.e. a lengthening of the bridging O-H bond, a shortening of Al-O adjacent to this bond and a lengthening of Al-O (not adjacent to it).

The intermolecular $\text{O}\cdots\text{O}$ distance in the optimized and rigid structure of faujasite/water adducts (within the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond) are evaluated to be 2.605 and 2.555 Å, respectively. The con-

Table 4
B3LYP optimized structure parameters for $\text{Al}(\text{OSiH}_3)_4/\text{H}_2\text{O}$ (cluster C, cf. Fig. 3) and faujasitic zeolite catalyst/water (cluster B, cf. Fig. 4)

Model/parameter	Rigid cluster C	Optimized cluster C	Rigid cluster B	Optimized cluster B
r_{AlO}	1.961	1.912	1.953	1.909
r_{SiO}	1.729	1.714	1.726	1.710
r_{OH}	0.964	1.026	0.965	1.024
$r_{\text{O(H)}\cdots\text{O}}$	2.598	2.546	2.605	2.555
$r_{\text{H}\cdots\text{O}}$	1.685	1.567	1.693	1.581
$r_{\text{O}\cdots\text{H}}$	1.933	1.811	1.981	1.863
$\angle \text{Al}-\text{O}-\text{Si}$	128.0	128.8	128.7	129.2

tracted O...O distance of the latter model reflects an increase of the binding energy (-20.3 versus -22.5 kcal/mol). The adsorption energy for the largest model investigated, cluster B (Fig. 1b) is -20.3 kcal/mol, which is close to the result for the smaller cluster C (-20.5 kcal/mol, Fig. 1c). The binding energy of the latter cluster can be compared to the MP2 result of Sauer et al. [11] (-20.3 versus -18.98 kcal/mol). The heat of adsorption of water with H-ZSM-5 has been recently obtained by Gorte [[15],[16]], which is an excellent agreement with our largest model (-20.4 versus -20.3 kcal/mol).

In order to check the reliability of the calculated intermolecular O...O distance of faujasite/water, the water dimer was also carried out and compared to the experimental data. The calculated O...O distance of water dimer is found to be 2.909 Å, only 0.009 Å longer than the corresponding MP2 value and 0.03 Å less than the experimentally determined value of the O...O distance [47].

In order to compare the relative acidity with the other types of hydrogen-bonded systems we have performed calculations with the same theoretical model on the systems HF...H₂O (-11.68), HCl...H₂O (-8.94), H₃SiOH...H₂O (-9.52) and H₃SiOHAlH₃...H₂O (-19.24); the values in parentheses are the hydrogen bonding energies in kcal/mol. The B3LYP results suggest that in comparison with hydrogen halides, the faujasitic zeolite/H₂O system is a strong acid.

3.3.2. Analytical potentials

The interaction of faujasite catalyst with water for different conformations has been calculated at DFT and HF levels of theory. The Hartree–Fock calculations were performed with the effective-core potential and corresponding basis sets of Stevens et al. [48–50] (denoted as SBKJC) in valence double-zeta contraction. For the DFT calculations the B3LYP functional and the 6-31G(d) basis set were used. In order to construct potential functions for faujasitic zeolite/water, four main steps have been employed: (1) selection of the dimer conformations, (2) performing the B3LYP/6-31G(d) and HF/SBKJC calculations, (3) selecting the analytical form, and (4) fitting the computed DFT/B3LYP and HF/SBKJC energies to the selected functional forms.

The water geometry has been kept at the experimental values ($r_{\text{OH}} = 0.9572$ Å, $\angle\text{HOH} = 104.52^\circ$ [51]), while the faujasite structure has been taken from the B3LYP/6-311G(d,p) optimization. Fig. 5 shows the faujasitic zeolite/water potential curves as a function of the O...H distance for three different levels of theory. The figure also reveals that HF/STO-3G yields a steeper minimum at a shorter distance than B3LYP/6-31G(d). This large difference shows that calculations on the STO-3G level are not useful here. The HF/SBKJC results are encouraging when compared to B3LYP/6-31G(d). The two potential curves are quite similar despite of the fact that the HF/SBKJC calculations are much

Table 5
Atomic charges for water and faujasite (cluster B)

Water molecule				
O = -0.7401				
H = 0.3700				
Faujasite (Cluster B)				
H1 = -0.1356	H10 = -0.1445	H14 = -0.1465	H15 = -0.1449	H16 = -0.1365
H21 = 0.5165	H23 = -0.1490	H24 = -0.1663	H28 = -0.1197	H33 = -0.1630
H34 = -0.1621	H35 = -0.1613	H36 = -0.1313	H38 = -0.1551	H39 = -0.1428
H41 = -0.1650	H42 = -0.1639	O3 = -1.1567	O4 = -1.0252	O5 = -1.0110
O9 = -1.1400	O11 = -1.1141	O12 = -1.0356	O13 = -1.0424	O17 = -1.0340
O22 = -1.0249	O25 = -1.0048	O26 = -1.0156	O27 = -1.0398	O32 = -1.0168
O37 = -1.0271	Al6 = 1.9752	Si2 = 1.5934	Si7 = 1.3417	Si8 = 1.3511
Si18 = 1.6386	Si19 = 1.6427	Si20 = 1.6616	Si29 = 1.3454	Si30 = 1.3438
Si31 = 1.3254	Si40 = 1.3404			

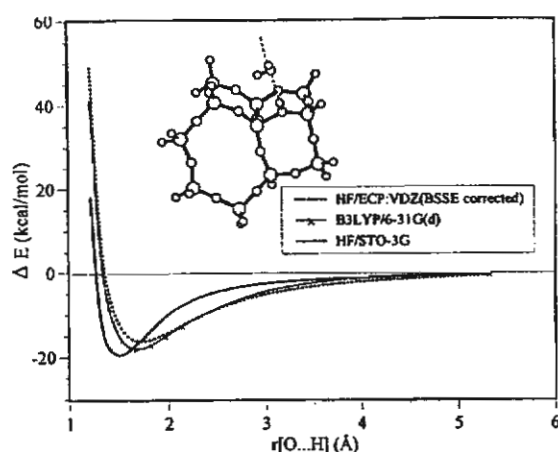


Fig. 5. Comparison of adsorption energies from B3LYP/6-31G(d), HF/ECP-VDZ, and HF/STO-3G for the faujasitic zeolite/water system.

faster (on an SGI Challenge about 50 times). After testing a variety of functional forms, a simple 2–6–10–12 potential energy expression for the interaction of faujasitic zeolite with water was employed:

$$E_{\text{fit}}^{\text{z-w}}(r_{ki}) = \sum_{k,i} \left[\frac{q_k q_i}{r_{ki}} + \frac{A_{ki}}{r_{ki}^2} + \frac{B_{ki}}{r_{ki}^6} + \frac{C_{ki}}{r_{ki}^{10}} + \frac{D_{ki}}{r_{ki}^{12}} \right]$$

Table 6

The fitted parameters of the potential energy functions (see text)

Parameter	A	B	C	D
H1–O	-1.0331905×10^2	1.8382883×10^2	-1.5083348×10^2	8.9420565×10^1
H1–H	1.2645426×10^2	-2.8999846×10^2	2.4324152×10^2	-5.5234880×10^2
H2–O	2.8574043×10^1	5.2740608×10^2	-3.3482893×10^2	-2.6299890×10^2
H2–H	-8.3599299×10^1	1.4191032×10^2	5.9935692×10^1	-1.0575208×10^2
O1–O	-2.2914121×10^1	1.3536682×10^3	-3.9274513×10^3	6.0327825×10^3
O1–H	-9.2895111×10^1	1.2641836×10^2	-3.6371045×10^1	1.2479447×10^1
O2–O	2.5865495×10^2	-1.3296107×10^3	1.5674254×10^5	-3.4876443×10^5
O2–H	-1.1555464×10^2	2.1024226×10^2	-1.9198437×10^2	1.0763633×10^2
O3–O	2.8803433×10^2	-6.7006798×10^2	1.0924449×10^5	-2.4821535×10^5
O3–H	-1.4723644×10^2	1.9241469×10^2	6.6505733×10^2	-1.0651945×10^3
O4–O	-7.4289775×10^1	1.9661823×10^3	4.0700384×10^3	-1.2381189×10^4
O4–H	-1.3862499×10^2	4.6499706×10^1	7.3627116×10^3	1.8873061×10^3
O5–O	-3.2716430×10^0	8.9273658×10^1	2.8112535×10^5	-1.1607496×10^6
O5–H	-1.1941986×10^2	1.4535989×10^2	2.1379764×10^3	-3.3723297×10^3
O6–O	-1.1715990×10^2	1.5436984×10^3	2.0774143×10^4	-8.0412282×10^4
O6–H	-9.7118742×10^1	1.7816578×10^2	-1.3496463×10^2	7.1361063×10^1
Si1–O	-5.7071178×10^1	-2.3134268×10^3	8.2071595×10^4	-4.9494428×10^4
Si1–H	2.8669836×10^2	-2.9201129×10^2	3.0196516×10^3	-3.7259970×10^3
Si2–O	1.6333832×10^2	-4.9009698×10^0	3.4294755×10^5	-1.4582774×10^5
Si2–H	2.3662032×10^2	-1.2223283×10^0	2.2845654×10^4	-5.9072913×10^4
Al–O	-5.1438777×10^2	1.1459039×10^3	1.3088621×10^5	-5.1532513×10^5
Al–H	1.1556943×10^2	5.7061768×10^2	-9.1190710×10^3	1.4812055×10^4

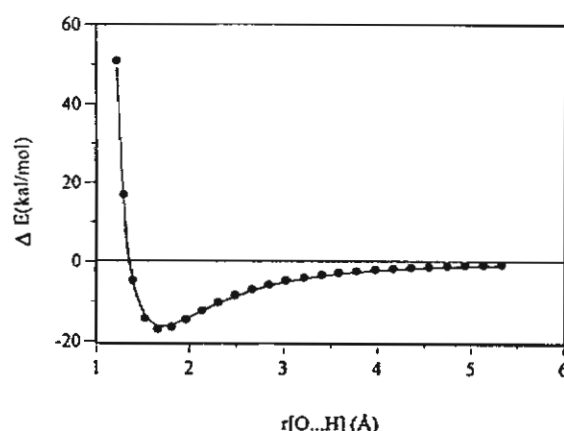


Fig. 6. Comparison between ab initio energy surface data (Δ) and analytical potential curves (lines) for the configuration presented in Fig. 4.

r_{ki} is the distance between atom k on the zeolite molecule and atom i on the water molecule. q_k and q_i are atomic charges taken from a Mulliken population analysis (cf. Table 5). A_{ki} , B_{ki} , C_{ki} and D_{ki} are the parameters determined by least-squares fitting. The fitted parameters of the potential energy functions are tabulated in Table 6 (in kcal/mol). The quality of the fit is illustrated in Figs. 6 and 7. Fig. 6

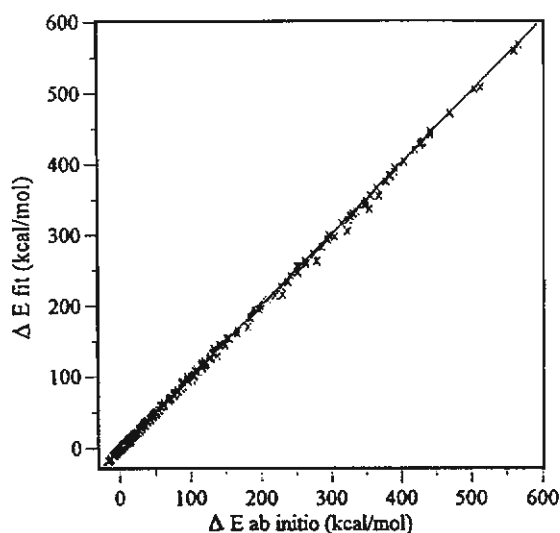


Fig. 7. Correlation between interaction energy ($\Delta E_{\text{ab initio}}$) from the ab initio calculations and those derived from analytical expressions as described in the text.

shows the fitted values for the same curve as Fig. 5 whereas Fig. 7 illustrates the correlation between all ab initio and fitted energies. The standard deviation obtained between fitted and ab-initio energies is 2.14 kcal/mol. Since among the 500 points used in the fitting there are many with high energies, this is a good value. Our newly developed potentials will be further employed in the simulation of zeolite/water system.

4. Conclusions

We have presented a density-functional study of faujasitic zeolites and their complexes with water using the B3LYP functionals and the basis sets 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311 + G(d,p). The agreement between DFT/B3LYP-6-311 + G(d,p) proton affinities and the corresponding CPF and G1 values are excellent. Comparing the older BLYP and VWN functionals with the recently introduced B3LYP functionals, the latter yields superior accuracy. This artificial significant lengthening effect on the weaker Al–O bond in the BLYP and VWN calculations does not occur with B3LYP. The Si–O(H)–Al and Si–O–H bond angles of zeolites do not appreciably depend on the

inclusion of non-local effects in the density functional. The 6-31G(d) basis set in the DFT prediction of the faujasite structure yields good results and is an economic choice for large systems. The predicted PA of the faujasitic catalyst is estimated to be 294 ± 3 kcal/mol, which is in the range of experimentally determined value of 291–300 kcal/mol. The faujasite catalyst/water structure (see Fig. 1b) is stabilized at the bridging O–H group by two H-bonds with binding energy of -20.3 kcal/mol. Comparison with hydrogen halides and related complexes of water demonstrates that the faujasite is a strong acid. An analytical potential for the interaction of faujasitic zeolite with water was derived by fitting the ab initio interaction energies which we plan to employ in simulations studies of petrochemical catalyst/water systems.

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Coadsorption of ammonia and methanol on H-zeolites and
alkaline-exchanged zeolites

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Abstract

The interactions of methanol and ammonia on H-zeolites (H-Z) and alkaline-exchanged zeolites (Na-Z) have been investigated using Hartree–Fock (HF) and density functional theory (DFT) approaches. Full optimization of all clusters and their complexes has been optimized at B3LYP/6-31G* and HF/6-31G* theoretical levels. The reaction mechanism of coadsorption of methanol and ammonia on H-Z is that the ammonia is found to bound to the Brønsted acid site of H-Z, yielding ammonium cation, which in turn operates as an active site for methanol. The result of coadsorption processes indicates that the stronger base ammonia is preferentially bonded to the Brønsted acid sites of H-Z, while methanol is interacted with the Lewis acid of Na-Z. Our findings are in excellent agreement with very recently reported data (Kogelbauer, A., Grundling, G., Lercher, J.A., *J. Phys. Chem.* 100 (1996) 1852–1837). © 1997 Elsevier Science B.V.

Keywords: Quantum chemical calculations; Adsorption; Catalysis; Zeolites; Methanol–ammonia interaction

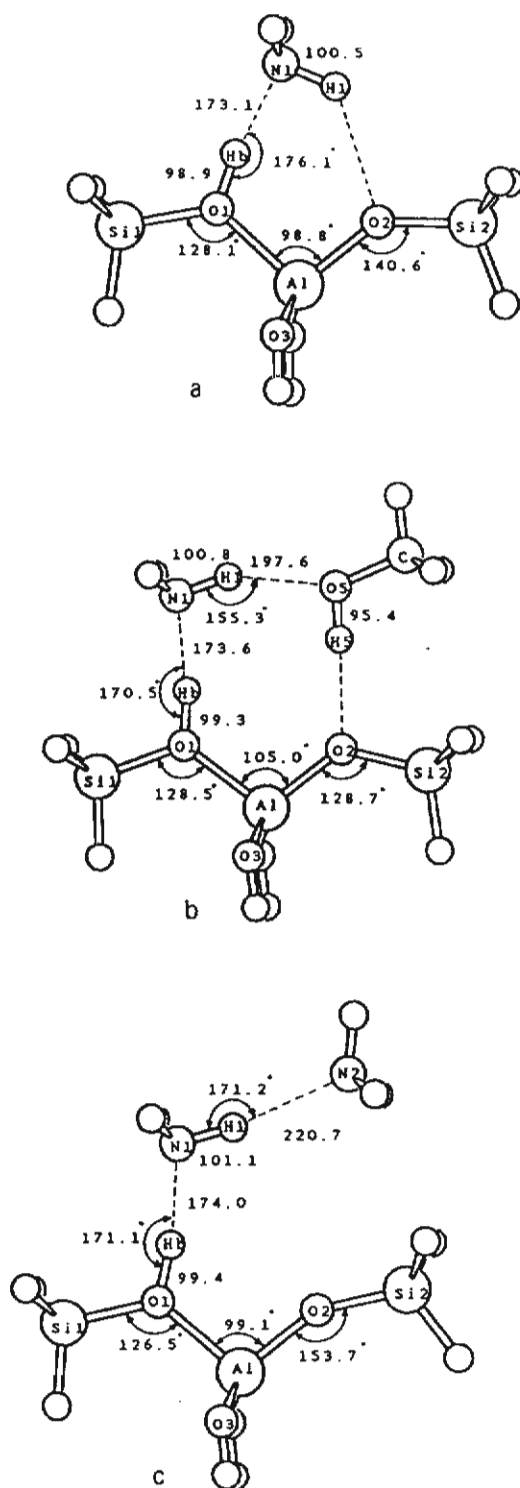
1. Introduction

The acidity of zeolitic catalysts released from the surface hydroxyls (Si-OH-Al) is responsible for their catalytic function and has led to numerous important industrial applications, such as the application of catalysts and adsorbents in petrochemical processes and for the production of fine chemicals [1–15]. Of particular interest in this active research is the products generated from the adsorption of methanol (i.e. conversion of methanol to gasoline) [16–21] and the coadsorption of methanol and ammonia [22,23] (production of methylamines, which are essential chemical building subunits for important industrial materials such as resins, fibers,

dyes and pharmaceuticals). One of the crucial steps of these chemically interesting systems involves the probed molecules adsorption on the catalyst surface. In spite of a large number of documents about zeolite research, details of the structures and reaction mechanisms of adsorption and, particularly of coadsorption, are still incomplete and only partially solved [17,23]. This understanding is the basis for the rational design of improved catalysts.

In this work, the interactions of methanol and ammonia with H-zeolites (H-Z) and alkaline-zeolites (Na-Z) are investigated for the first time by the density functional theory (DFT), and Hartree–Fock (HF) with the aim of; a) investigating the important consequences of different types of adsorbed probe molecules at low and high coverages, i.e. $(\text{CH}_3\text{OH})_n$, $(\text{NH}_3)_n$, $(\text{CH}_3\text{OH})(\text{NH}_3)$ and $(\text{NH}_3)(\text{CH}_3\text{OH})$, where

* Corresponding author.



n denotes the amount of probed molecule coverages; b) determining the reaction mechanism of coadsorption; c) comparing the influence of H-Z and Na-Z on the coadsorption structure of methanol and ammonia.

2. Method

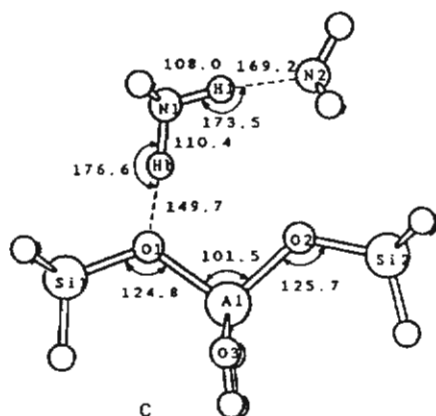
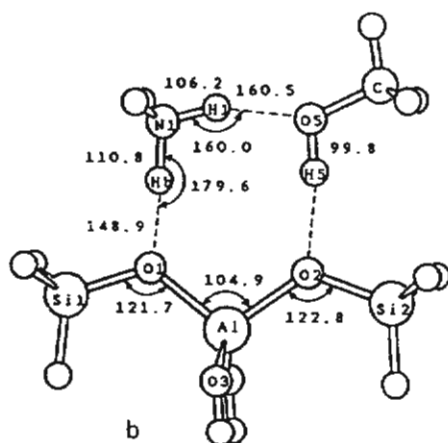
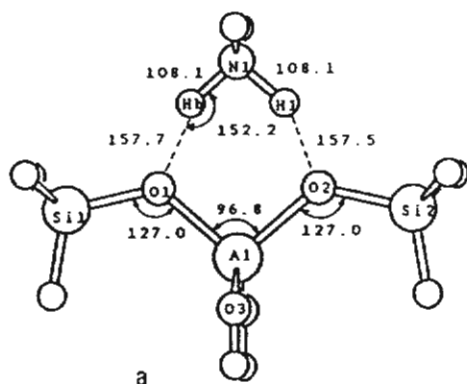
We employed the adsorption clusters illustrated in Figs. 1–3 as the models of the probed molecules' adsorption on zeolites $[H_3SiOHAl(OH)_2OSiH_3]/[NH_3][CH_3OH]$, and $[H_3SiOHAl(OH)_2OSiH_3]/[CH_3OH][NH_3]$, and their possible ion-pair species. The alkaline-exchanged systems, $[H_3SiONaAl(OH)_2OSiH_3]/[NH_3][CH_3OH]$ and $[H_3SiONaAl(OH)_2OSiH_3]/[CH_3OH][NH_3]$ are modelled for the coadsorption of methanol and ammonia on Na-exchanged zeolites (see Fig. 4 and Fig. 5). The isolated Na-complexes, $Na(I)/[NH_3][CH_3OH]$, and $Na(I)/[CH_3OH][NH_3]$ are also included for comparison. We have also investigated the adsorption of methanol and ammonia at low and high coverages, with similar absorbent models of $[H_3SiOHAl(OH)_2SiH_3]/[CH_3OH]$, $[H_3SiOHAl(OH)_2OSiH_3]/[CH_3OH]_2$, $[H_3SiOHAl(OH)_2OSiH_3]/[NH_3]$, $H_3SiOHAl(OH)_2OSiH_3]/[NH_3]_2$. In the models employed, the clusters have been terminated by hydrogen atoms.

Full geometry optimization of the cluster models mentioned above was carried out with the DFT methods employing the B3LYP density functional. This functional has been recently demonstrated to yield accurate results for the molecular structures and vibrational frequencies for zeolites [24–26]. All density functional computations were performed using the program Gaussian-94 [27].

For the HF calculations, we employed the TURBO-MOLE code [28,29] which is based on the direct SCF method of Almloef et al. [30]. Geometry optimizations were terminated when the gradients norm with respect of internal coordinates was less than $10^{-3} E_h/a_0$. The energy change was then below $5 \times 10^{-6} a.u.$

The computations were carried out using DEC

Fig. 1. Schematic representation of molecular models for the systems Brønsted acid site $[H_3SiOHAl(OH)_2OSiH_3]$: (H-Z): a) $[H_3SiOHAl(OH)_2OSiH_3]/[NH_3]$; b) $[H_3SiOHAl(OH)_2OSiH_3]/[NH_3][CH_3OH]$; c) $[H_3SiOHAl(OH)_2OSiH_3]/[NH_3]_2$.



Alphastation 250 and HP 9000/700 workstations at the Laboratory for Computational and Applied Chemistry at Kasetsart University.

3. Results and discussion

3.1. Coadsorption of ammonia and methanol on H-zeolite (H-Z)

3.1.1. Interaction of ammonia and methanol on H-Zeolite

The fully optimized geometrical structures constrained at C_s symmetry for $[H_3SiOAl(OH)_2OSiH_3]/[NH_3][CH_3OH]$ (see Fig. 1b) were investigated at HF levels of theory using 6-31G* basis set. The optimized parameters for the two theoretical approaches are summarized in Table 1.

Comparing the HF structure of $H_3SiOAl(OH)_2OSiH_3$ with the B3LYP structure, it is seen that the Si–O, Al–O and O–H bonds of the former are shorter than with the latter (see Table 2). Note that the HF results always yield an OH bond which is too short as compared to the experimental result [31].

Further support for the reliability of using this model is confirmed by the results of NMR measurement [32]: the Al...H of H-faujasite has been estimated to be 238 ± 4 pm whereas our computed distances at the B3LYP and HF levels of theory are 239.7 and 241.6 pm, respectively.

The changes in the structural parameters of tertiary upon complexation are in line with Gutmann's rules [33], i.e. a lengthening of the bridging OH bond, a shortening of Al–O and a lengthening of Al–O (not adjacent to the bridging OH bond).

In order to compare the structure and bonding with the related types of adsorbed molecules, we have also performed calculations on the systems H-Z/[NH₃], H-Z/[NH₃]₂, H-Z/[CH₃OH][NH₃], and H-Z/[CH₃OH][CH₃OH] (see Table 4). The results suggest that the H-Z/[NH₃][CH₃OH] is energetically favoured in the coadsorption process of methanol and ammonia. The methanol has a pronounced effect on the H-Z/[NH₃] complex, indicating the capability of donating a

Fig. 2. Schematic representation of molecular models for the deprotonated framework $[H_3SiOAl(OH)_2OSiH_3]^{-(Z^-)}$: a) $[H_3SiOAl(OH)_2OSiH_3]^{-(Z^-)}/[NH_4]^+$; b) $[H_3SiOAl(OH)_2OSiH_3]^{-(Z^-)}/[NH_4]^+[CH_3OH]$; c) $[H_3SiOAl(OH)_2OSiH_3]^{-(Z^-)}/[NH_4]^+[NH_3]$.

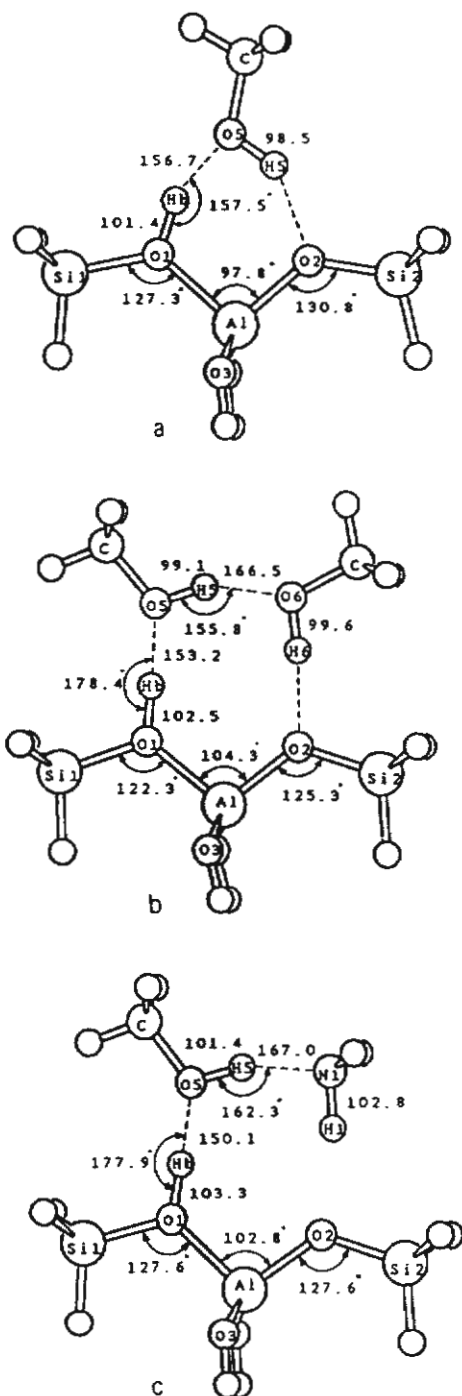


Fig. 3. Schematic representation of molecular models for the systems Brønsted acid site $[H_3SiOAl(OH)_2OSiH_3]$ (H-Z): a) $[H_3SiOAl(OH)_2OSiH_3]/[CH_3OH]$; b) $[H_3SiOAl(OH)_2OSiH_3]/[CH_3OH]$; c) $[H_3SiOAl(OH)_2OSiH_3]/[CH_3OH][NH_3]$.

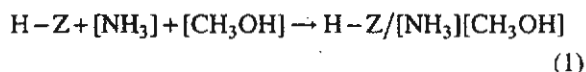
zeolitic proton onto the adsorbed ammonia. The Brønsted OH bonds of zeolitic catalysts are lengthened for the $H-Z/[NH_3][CH_3OH]$ as compared to the corresponding binary complex of $H-Z/[NH_3]$ (99.3 vs. 98.9 pm, see Fig. 1a,b).

3.1.2. Ion-pair formation

The optimized structure parameters of $[H_3SiOAl(OH)_2SiH_3]^-/[NH_4]^+$, $[H_3SiAl(OH)_2SiH_3]^-/[NH_4]^+$ $[NH_3]$ and $[H_3SiOAl(OH)_2SiH_3]^-/[NH_4]^+[CH_3OH]$ are reported. For the system $[H_3SiOAl(OH)_2SiH_3]^-/[NH_4]^+$, the ammonium cation forms two very strong hydrogen bonds towards the negatively charged zeolite (see Fig. 2a). The Al–O1, and Al–O2 distances are virtually equal and about 4.6 pm longer than that found in the anionic zeolite. For the high coverages, the ammonia is found to bond to the Brønsted acid site of H-Z, yielding ammonium cation, which operates as the centre site for further hydrogen bonding to methanol of ammonia (see Fig. 2b and 2c).

Attempts have been to observe the $Z^-/[CH_3OH_2]^+$ $[NH_3]$; an initial structure with a methoxonium ion is optimized. The OH bond of $[CH_3OH_2]^+$ and the hydrogen bond angle (O–H...N) in the complex is constrained at the optimized $[CH_3OH_2]^+$ and 180° , respectively. However, during the optimization, the proton of $[CH_3OH_2]^+$ is transferred to the ammonia molecule, and the final equilibrium complex $H-Z/[CH_3OH][NH_4]^+$ is obtained. Note that this complex is achieved only at B3LYP, while only hydrogen-bonded $H-Z/[CH_3OH][NH_3]$ is obtained at the HF level of theory.

The energy for conversion of $[H_3SiOAl(OH)_2SiH_3]/[NH_3][CH_3OH]$ to $[H_3SiOAl(OH)_2SiH_3]^-/[NH_4]^+[CH_3OH]$ is 0.74 kcal/mol. The details of the sorption processes were evaluated as follows. The coadsorption energy of ammonia and methanol on the cluster zeolite (H-Z) is the energy of reaction



Whilst for an anion (Z^-) and ammonium cation (NH_4^+), the energies are those of the reactions

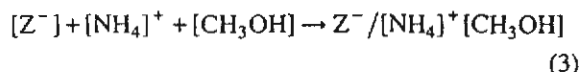


The energy for reaction (2a) is called the deprotonation energy and the protonation energy is represented by

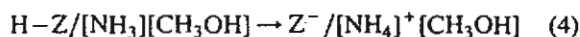
Table 1
HF/6-31G* and B3LYP/6-31G* optimized structure parameters for $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]$, $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]^+$, $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]_2$ and $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]^+[\text{CH}_3\text{OH}]$

Bond/pm or angle/deg	H-Z/[NH ₃]		H-Z/[NH ₃] ₂		H-Z/[NH ₃] ⁺		Z'/[NH ₃] ⁺ [NH ₃]		Z'/[NH ₃] ⁺ [CH ₃ OH]	
	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP
Al-O1	190.4	190.0	189.4	182.2	180.3	182.2	180.1	182.8	180.9	182.7
Al-O2	173.5	172.4	174.8	182.2	180.3	182.2	177.4	178.5	178.5	180.6
Al-O3	172.2	172.5	172.4	174.2	173.1	174.2	173.6	175.1	173.6	174.8
Al-O4	172.2	172.5	172.4	174.2	173.1	174.2	173.6	175.1	173.6	174.8
< Al-O >	177.1	176.8	177.2	178.2	176.7	178.2	176.2	177.9	176.6	178.2
Si1-O1	168.7	168.5	169.4	165.4	162.9	165.4	162.3	165.3	163.3	166.1
Si2-O2	161.5	160.2	163.7	165.4	162.9	165.4	160.6	163.4	162.6	165.0
O1-Hb	98.9	99.4	99.3	157.7	167.7	157.7	163.7	149.7	158.7	148.9
N1-H1	100.5	101.1	100.8	108.1	104.0	108.1	102.6	108.0	102.8	106.2
N1-N2	-	321.0	-	-	-	-	296.3	276.8	-	-
N1-O1	271.4	272.7	272.0	258.4	263.4	258.4	267.4	260.0	264.4	259.6
N1-O5	-	-	292.3	-	-	-	-	-	269.4	262.8
O5-H5	-	-	95.4	-	-	-	-	-	96.4	99.8
Si1-O1-Al	128.1	126.5	128.5	127.1	128.7	127.1	130.6	124.8	124.0	121.7
Si2-O2-Al	140.6	153.7	128.7	127.0	128.6	127.0	131.9	125.7	124.7	122.8
O1-Al-O2	98.8	99.1	105.0	96.8	100.8	96.8	99.4	101.5	106.2	104.9
N1-H1-N2	-	171.2	-	-	-	-	161.7	173.5	-	-
O1-Hb-N1	171.6	171.1	170.5	152.5	150.8	152.5	170.3	176.6	177.7	179.6
N1-H1-O5	-	-	155.3	-	-	-	-	-	159.2	160.0

reaction (2b). For an ion-pair, $Z^-/[NH_4]^+[CH_3OH]$, the complexation energy is the energy of the reaction



Finally, the conversion energy of a covalent structure to an ion-pair structure is the sum of the energies of the three reactions above, i.e.



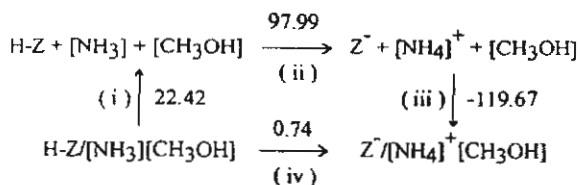
The reaction energies of each step are summarized in the schematic diagram in Scheme 1. From the reaction energies (see Table 4) of all the complexes, we can propose the reaction mechanism of coadsorption of methanol and ammonia on H-Z as depicted in Scheme 2.

3.2. Coadsorption of methanol and ammonia on Na-zeolites (Na-Z)

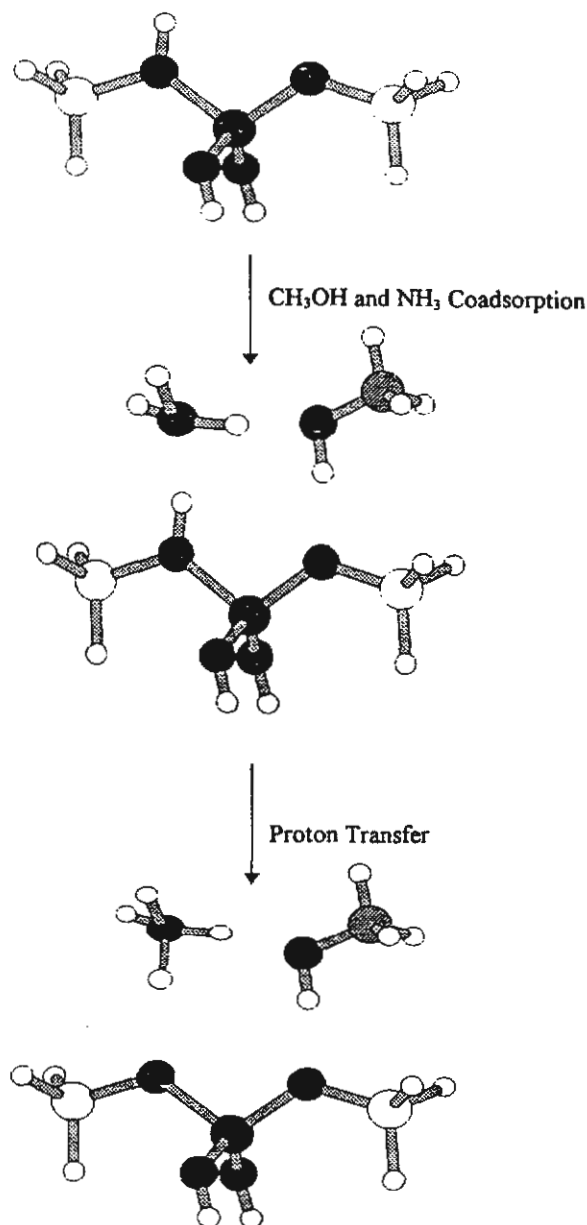
The effect of the cation on the structure of zeolitic catalysts and the coadsorption process is investigated at B3LYP/6-31G* and HF/6-31G* levels of theory. The fully optimized geometry structures for Na-Z, Na-Z/[NH₃], Na-Z/[CH₃OH], Na-Z/[NH₃][CH₃OH] and Na-Z/[CH₃OH][NH₃] are documented in Table 3.

3.2.1. The Na(I)/zeolite complex

The Na(I) does not bind with a particular bridging oxygen atom in the $[AlO_4]^-$ but is symmetrically bidentated to the O1 and O2 of the $[AlO_4]^-$ tetrahedron and the interaction has ionic character. The symmetric binding between Na(I) and $[AlO_4]^-$ has been confirmed by an ESR experiment [34]. The optimized Na(I)...O distance is found to be 216.0 pm and the corresponding energy is 134.09 kcal mol⁻¹. Table 3 further indicates that the charge compensating Na(I) can affect the $\equiv Si-O-Al \equiv$ by weakening the Si-O and Al-O bonds, as compared to the anionic framework (see Table 2).



Scheme 1.



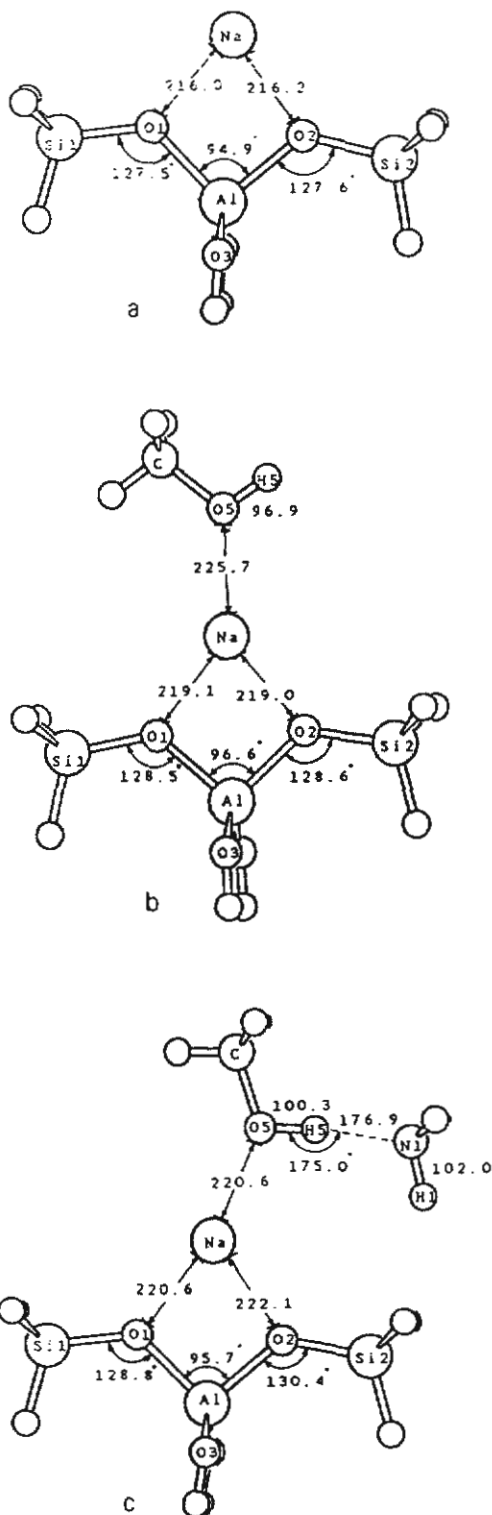
Scheme 2.

3.2.2. The Na-Z/[CH₃OH] complex

The optimized Na(I)...O(Z) distance in the Na-Z/[CH₃OH] complex is 2.8 pm larger than in the Na(I)/zeolite complex. The Na...O(m) equilibrium distance of the Na-Z/[CH₃OH] complex is about 7.7 pm longer than the corresponding distance in the isolated Na(I) complex, Na(I)/[CH₃OH], in

Table 3
HF/6-31G* and B3LYP/631G* optimized structure parameters for $H_3SiONaAl(OH)_2OSiH_3$, $H_3SiONaAl(OH)_2OSiH_3/[NH_3]$, $H_3SiONaAl(OH)_2OSiH_3/[CH_3OH]$, $H_3SiONaAl(OH)_2OSiH_3/[CH_3OH][NH_3]$ and $H_3SiONaAl(OH)_2OSiH_3/[NH_3][CH_3OH]$

Bond/pm or angle/deg	Na-Z		Na-Z/[NH ₃]		Na-Z/[CH ₃ OH]		Na-Z/[NH ₃][CH ₃ OH]		Na-Z/[CH ₃ OH][NH ₃]	
	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP
Al-O1	180.3	182.0	179.8	181.5	179.8	181.5	179.6	181.2	179.6	181.3
Al-O2	180.4	182.0	179.8	181.4	179.8	181.4	179.8	181.4	179.7	181.2
Al-O3	172.8	174.1	173.1	174.4	173.1	174.4	173.1	174.4	173.1	174.5
Al-O4	172.8	174.1	173.1	174.4	173.1	174.4	173.1	174.4	173.1	174.5
< Al-O >	176.6	178.0	176.4	177.9	176.4	177.9	176.4	177.8	176.4	177.9
Si1-O1	162.8	164.9	162.3	164.4	162.3	164.5	162.3	164.4	162.3	164.4
Si2-O2	162.8	164.9	162.3	164.4	162.3	164.4	161.7	163.5	161.7	163.6
N1-H1	-	-	100.5	102.1	-	-	100.8	10.28	100.4	102.0
O1-O5	-	-	-	-	424.0	420.8	-	-	438.7	436.9
O1-N1	-	-	439.0	433.0	-	-	450.9	449.2	-	-
O5-N1	-	-	-	-	-	-	310.6	298.6	289.0	276.9
O1-Na	217.6	216.0	220.9	219.5	220.6	219.1	221.7	220.7	221.7	220.6
N1-Na	-	-	242.3	238.8	-	-	239.6	235.7	-	-
O5-Na	-	-	-	-	-	-	-	-	-	-
O5-H5	-	-	-	-	227.8	225.7	-	-	223.6	220.6
Si1-O1-Al	129.8	127.5	131.0	128.6	94.8	96.9	94.8	97.0	96.4	100.3
Si2-O2-Al	130.1	127.6	131.0	128.6	131.1	128.5	131.4	129.0	131.1	128.8
O1-Al-O2	96.5	94.9	97.1	95.5	97.0	96.6	97.1	95.5	97.2	95.7
O1-Na-O5	-	-	-	-	142.0	142.2	-	-	160.3	170.0
O1-Na-N1	-	-	142.7	141.7	-	-	155.7	159.7	-	-
O5-H5-N1	-	-	-	-	-	-	-	-	176.0	175.0
N1-H1-O5	-	-	-	-	-	-	168.7	168.8	-	-



accordance with the lower binding energy; $\Delta E(\text{Na(I)}/\text{CH}_3\text{OH}) = -31.08 \text{ kcal mol}^{-1}$, $\Delta E(\text{Na-Z}/\text{CH}_3\text{OH}) = -18.39 \text{ kcal mol}^{-1}$.

One point of interest is that the Na-Z/[CH₃OH] leads to an increased positive charge for the methanol hydrogen by about 0.0462. This suggests that the ability of the methanol molecule to form a hydrogen bond as a proton-donor molecule is enhanced with Na-Z attached to the methanol oxygen atom. We note that the absolute values from Mulliken population analysis are not very reliable, and also depend on the basis set employed. However, within closely related structures a useful value will be yielded.

3.2.3. The Na-Z/[CH₃OH]/[NH₃] complex

The changes in structural parameters of the coadsorption complexes Na-Z/[CH₃OH]/[NH₃] are in agreement with Gutmann's rule [33], i.e. a lengthening of the methanol OH bond, a shortening of Na...O(m), a lengthening of Na...O(Z), and a shortening of the Al–O (adjacent to sodium atom) and Si–O bonds, as illustrated in Fig. 4c. The optimized Na(I)...O(m) distance in the Na-Z/[CH₃OH]/[NH₃] is 5.1 pm smaller than in the Na-Z/[CH₃OH] complex, where O(m) and O(Z) denote methanol oxygen and oxygen of zeolite, respectively. The rotational energy barrier around the O–H...N bond of the Na-Z/[CH₃OH]/[NH₃] complex is lower than KT. Thus Na-Z does not seem to hinder the free rotation of the ammonia molecule.

Another additional point of interest is that the OH...N distance is contracted from the 289.2 pm found in the H-bonded dimers of CH₃OH...NH₃ to 276.9 pm for Na-Z/[CH₃OH]/[NH₃]. This reduced O–H...N distance reflects an increase of binding energy due to the Na-Z. This can also be simply rationalized on the basis of the hydrogen atom population. The Na-Z leads to a decrease in electron density at the methanol proton in the Na-Z/[CH₃OH]/[NH₃] of 0.1088 units, compared to 0.0588 units in the CH₃OH...NH₃.

From the reaction energies in Table 4, the reaction mechanism may be proposed as depicted in Scheme 3.

Fig. 4. Schematic representation of molecular models for the systems: a) [H₃SiONaAl(OH)₂OSiH₃]/(Na-Z); b) [H₃SiONaAl(OH)₂OSiH₃]/[CH₃OH]; c) [H₃SiONaAl(OH)₂OSiH₃]/[CH₃OH]/[NH₃].

Table 4
Computed binding energies

Systems	Binding energy ($-\Delta E/\text{kcal mol}^{-1}$)	
	HF/6-31G*	B3LYP/6-31G*
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{CH}_3\text{OH}]$	13.50	18.48
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{CH}_3\text{OH}]_2$	21.51	29.60
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{CH}_3\text{OH}][\text{NH}_3]$	22.13	31.64
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_3]$	15.81	–
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_4]^+$	112.25	120.96
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_3]_2$	21.47	–
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_4]^+[\text{NH}_3]$	120.08	130.02
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_3][\text{CH}_3\text{OH}]$	22.42	–
$[\text{H}_3\text{SiOAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_4]^+[\text{CH}_3\text{OH}]$	119.67	131.59
$[\text{H}_3\text{SiONaAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_3]$	19.72	21.57
$[\text{H}_3\text{SiONaAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{NH}_3][\text{CH}_3\text{OH}]$	27.07	31.03
$[\text{H}_3\text{SiONaAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{CH}_3\text{OH}]$	17.33	18.39
$[\text{H}_3\text{SiONaAl}(\text{OH}_2)\text{OSiH}_3]/$ $[\text{CH}_3\text{OH}][\text{NH}_3]$	30.34	35.76

Scheme 2 and Scheme 3 indicate that when the methanol and ammonia are coadsorbed, the methanol preferentially adsorbs on Na-Z, while the ammonia binds favorably to H-Z. Our findings are in excellent agreement with very recent experimental data [23].

4. Conclusion

We have carried out HF and B3LYP methods with 6-31G* basis set to investigate the coadsorption of methanol and ammonia on H-zeolites (H-Z) and alkaline-exchanged zeolites (Na-Z). Comparing HF and B3LYP results with available experimental data, the B3LYP yields structural parameters which are in good agreement with experimental data. The Al...H distance of zeolite has been estimated experimentally as 238 ± 4 pm, whereas our B3LYP value is 239.7 pm.

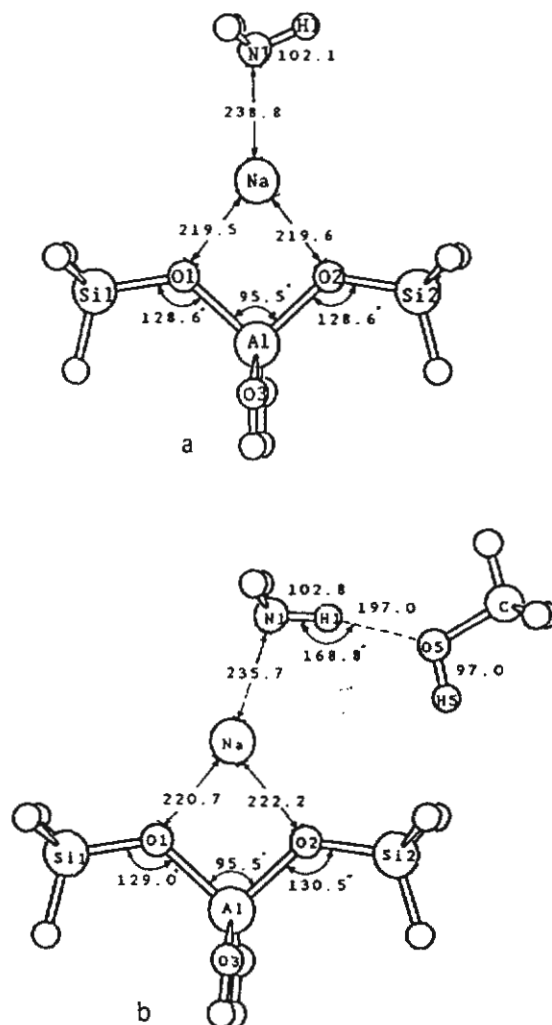
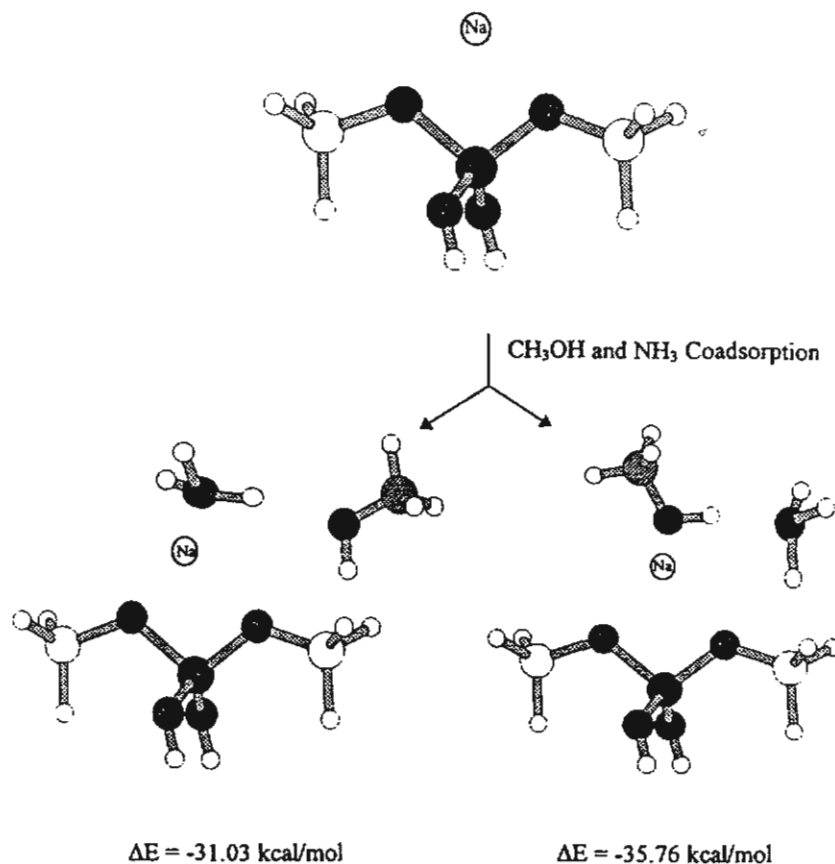


Fig. 5. Schematic representation of molecular models for the systems: a) $[\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3]$; b) $[\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3][\text{CH}_3\text{OH}]$.

A comprehensive study of the coadsorption of adsorbate molecules with the surface hydroxyl reveals several interesting points. Structure Na-Z $[\text{CH}_3\text{OH}][\text{NH}_3]$ is lower in energy than Na-Z $[\text{NH}_3][\text{CH}_3\text{OH}]$, which suggests that the former is more favourable in the coadsorption process. The reaction mechanism of coadsorption of methanol and ammonia on H-Z is that the ammonia is found to stabilize to the Brønsted acid site of H-Z, generating an ammonium cation, which acts as an active site for methanol.



Scheme 3.

The results obtained in the present study are very useful from the experimental point of view, since the adsorption and coadsorption processes on the surface site are found to play a significant role in catalytic processes.

Acknowledgements

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Structure and Reaction Pathways for Methylamine/Zeolite System

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ABSTRACT

Reaction pathways of methylamine synthesis from methanol and ammonia on zeolite (ZOH) have been carried out using Hartree-Fock (HF) and density functional theory (DFT) approaches. Structures of the adsorption reactants, transition states, intermediates, and adsorption products were optimized at DFT(B3LYP) and HF levels of theory using 6-31G(d). Four different reaction pathways, including Langmuir-Hinshelwood (methanol and ammonia are both bound to Brønsted acid sites) and Eley-Rideal (two adsorbing molecules react; methanol is unbound, the ammonia is bound to a Brønsted acid site) mechanisms of methylamine production, were investigated. The reaction pathway which involves dehydration of one methanol and generating surface methoxy species was found to possess a substantially higher activation energy barrier. The lower corresponding energy was estimated for methoxy-zeolite formation from coadsorption of CH_3OH and NH_3 at Brønsted acid sites. The reaction pathways involving an associative reaction were, however, found to be more preferable in methylamine formation.

INTRODUCTION

For many years, zeolites have been found in industrial applications as catalysts in petrochemical processes, because of their unique catalytic activity, excellent selectivity as well as superior stability in many important conversions and upgrading processes as compared to other materials [1]. The acidity of zeolitic catalysts released from the surface hydroxyls ($\equiv\text{Si}-\text{OH}-\text{Al}\equiv$) is responsible for catalytic function [2-3]. The structure of such catalytic sites and their mode of interaction with simple adsorbates have been investigated as a crucial step in elucidating the catalytic reaction mechanism occurring at these active sites.

Of particular interest in this active research is the products generated from the adsorption of methanol (i.e., conversion of methanol to gasoline) and the coadsorption of methanol and ammonia (the production of methylamines which are essential chemical building subunits for important industrial materials such as resins, fibers, dyes and pharmaceuticals) [4]. One of the crucial steps of these chemically interesting systems involves the adsorption of probed molecules on the catalyst surface.

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In spite of a large number of documents about zeolite research, the details of structures and reaction mechanisms of adsorption [2,5-8], and particularly of coadsorption [9] are still incomplete and only partially solved.

METHODS

We employed the adsorption clusters illustrated in Figure 1-5 as the models of all possible adsorption reactants: $[\text{XOHAl}(\text{OH})_2\text{OX}]/[\text{CH}_3\text{OH}]$, $[\text{XOHAl}(\text{OH})_2\text{OX}]/[\text{CH}_3\text{OH}][\text{NH}_3]$, $[\text{XOHAl}(\text{OH})_2\text{OX}]/[\text{NH}_3][\text{CH}_3\text{OH}]$; adsorption surface methoxy intermediates, $[\text{XOCH}_3\text{Al}(\text{OH})_2\text{OX}]/[\text{NH}_3]$, $[\text{XOCH}_3\text{Al}(\text{OH})_2\text{OX}]/[\text{H}_2\text{O}]/[\text{NH}_3]$, $[\text{XOCH}_3\text{Al}(\text{OH})_2\text{OX}]/[\text{H}_2\text{O}]$; transition state complexes, and adsorption products, $[\text{XOHAl}(\text{OH})_2\text{OX}]/[\text{CH}_3\text{NH}_2]$, $[\text{XOHAl}(\text{OH})_2\text{OX}]/[\text{CH}_3\text{NH}_2]/[\text{H}_2\text{O}]$; where $\text{X}=\text{H}$ and SiH_3 , hereafter referred to as 1T and 3T cluster models for $\text{HOHAl}(\text{H})_2\text{OH}$ and $\text{H}_3\text{SiOHAl}(\text{H})_2\text{OSiH}_3$, respectively.

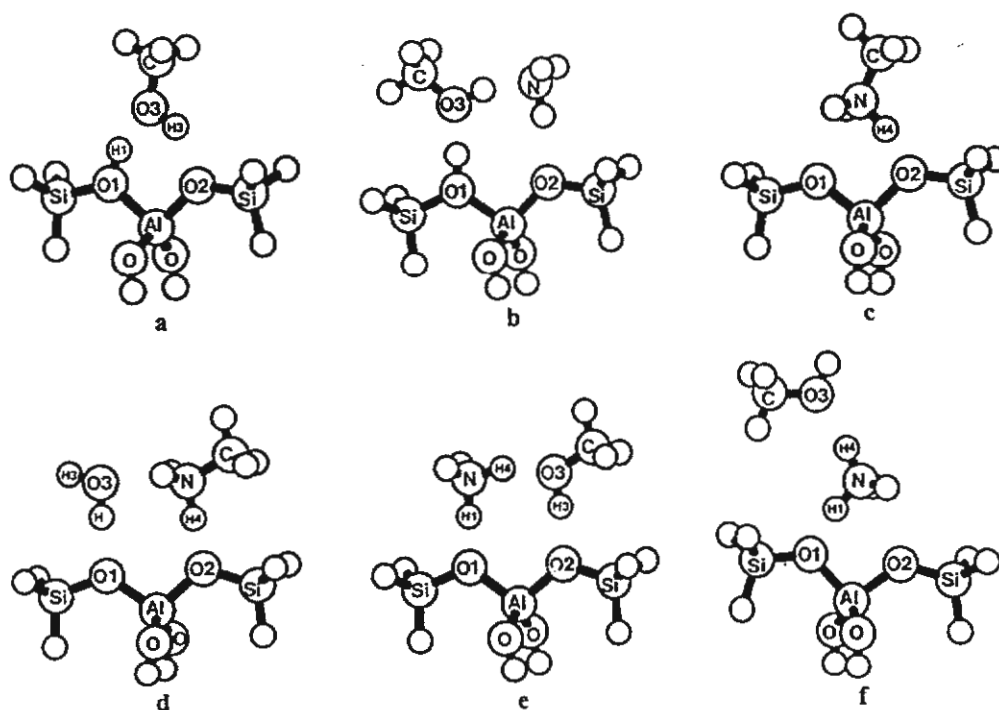


Figure 1. Optimized structures for different adsorption complexes ($\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ (3T), $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3/\text{CH}_3\text{OH}$ (1a), $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3/\text{CH}_3\text{OH}/\text{NH}_3$ (1b), $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]^-/[\text{CH}_3\text{NH}_3]^+$ (1c), $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]^-/[\text{CH}_3\text{NH}_3]^+/\text{H}_2\text{O}$ (1d), $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]^-/\text{CH}_3\text{OH}/[\text{NH}_4]^+$ (1e), $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]^-/[\text{NH}_4]^+/\text{CH}_3\text{OH}/$ (1f)) at B3LYP/6-31G(d) level of theory.

Full geometry optimization of the cluster models mentioned above was carried out with the DFT methods employing B3LYP density functional. This functional has been recently

demonstrated to yield accurate results about molecular structures, and vibrational frequencies for zeolites [10-11]. Transition state searches were performed using an eigenvalue-following algorithm [12]. On each optimized cluster, a vibrational analysis was made in order to obtain the normal modes. Final energies of some adsorption complexes were improved from point calculations at B3LYP/6-311+G(3df,2p) theoretical level. All density functional computations were performed using the program Gaussian-94 [13].

For the HF calculations, we employed the TURBOMOLE code [14] which is based on the direct SCF method. Geometry optimization was terminated when the gradient norm with respect to internal coordinates was less than $10^{-3} E_h/a_0$. The energy change was then below 5×10^{-6} a.u.

The computations were carried out using DEC Alphastation 250 and HP 9000/700 workstations at the Laboratory for Computational and Applied Chemistry at Kasetsart University.

RESULTS AND DISCUSSION

Four different reaction pathways of methylamine synthesis have been investigated, as depicted in Figures 2-5.

The first reaction pathway for methylamine formation: One methanol molecule is adsorbed on the catalyst surface to yield $ZOCH_3$, followed by the interaction of ammonia to yield $MeNH_2$.

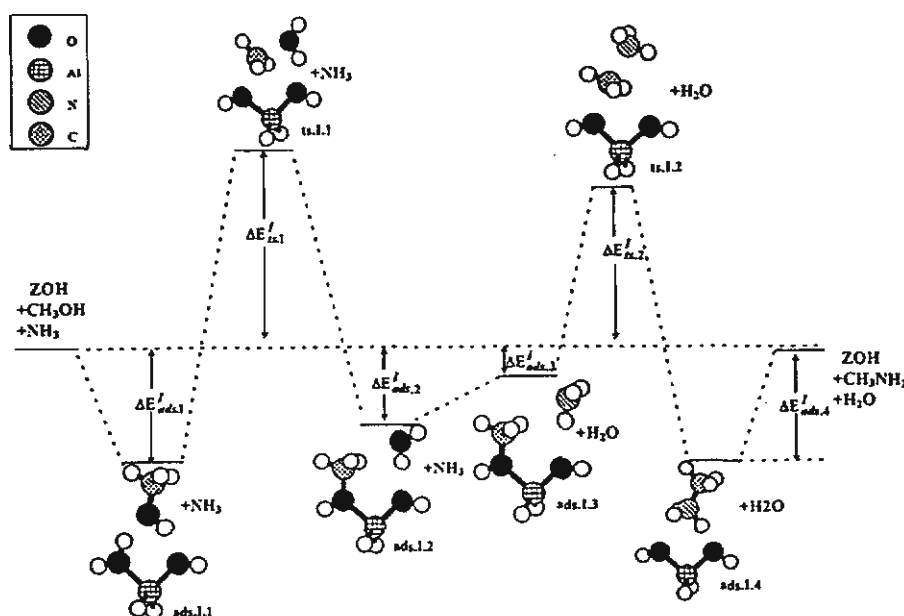


Figure 2. Path I: One CH_3OH is adsorbed on ZOH , $ZOCH_3$ generated, and the interaction of NH_3 with $ZOCH_3$ to yield methylamine.

The first reaction mechanism involves only one CH_3OH molecule adsorbed on the zeolitic acid site, ZOH/CH_3OH (see ads.I.1, Figure 2) which is then dehydrated and leaves a methyl group attached to the zeolite basic oxygen, $ZOCH_3$.

The adsorption energies of ZOH/CH₃OH were found to be -56.48 and -77.32 kJ/mol for 3T cluster models at HF and B3LYP levels of theory, respectively, which is in agreement with other theoretical values ranging from -56 to -89 kJ/mol [2,7,8] depending on the method and cluster size employed. Sauer's HF estimate of the adsorption energy of the large cluster (11T model fragment of faujasite) was -83.0 kJ/mol after correction for electron correlation, ZPE and BSSE. Experimental estimates of the heat of adsorption in acidic zeolites range from -63 [15] and -110 to -120 kJ/mol [referenced in ref. 2].

Parameters	3T	1a	1b	1c	1d	1e	1f
Al-O1	194.67	190.80	189.45	179.55	180.01	182.70	182.71
Al-O2	173.89	177.18	176.69	183.14	182.78	180.57	179.35
O1-H1	97.30	101.36	103.34	-	173.52	148.87	151.13
O1-O3	-	253.28	253.45	-	272.72	382.63	461.78
O2-O3	-	267.96	372.47	-	398.68	267.46	553.16
O3-H3	-	98.48	101.38	-	96.74	99.84	96.81
O1-N	-	-	406.18	263.98	361.00	259.68	259.27
O2-N	-	-	299.77	256.69	260.72	379.21	268.22
O3-N	-	-	265.38	-	258.72	262.75	284.99
O2-H3	-	181.22	340.31	-	487.34	168.09	620.88
O2-H4	-	-	197.82	147.55	150.89	333.32	371.66
N-H1	-	-	331.31	-	274.99	110.81	109.61
N-H4	-	-	102.81	110.77	109.87	106.16	103.57
O1-Al-O2	89.66	97.84	102.83	97.88	103.20	104.86	98.23
O1-H1-O3	-	157.51	177.90	-	175.70	116.14	139.10
O1-H1-N	-	-	130.57	-	105.20	179.56	167.71
O2-H3-N	-	-	61.73	-	31.27	108.71	-
O2-H4-N	-	-	170.82	166.96	178.00	107.62	-
O3-H4-N	-	-	70.34	-	59.45	159.99	172.32
Al-O1-H1	-	113.35	122.80	-	131.69	125.00	105.94
Al-O2-H4	-	-	131.03	105.78	120.04	96.47	99.44
Al-O1-O3	-	98.22	124.04	-	130.12	81.58	134.47
Al-O2-N	-	-	127.89	100.19	120.88	80.99	98.50
-ΔE (kJ/mol)	-	77.31	132.40	101.61	151.27	148.04	132.80

Table 1: Optimized structure parameters (distances in pm and angles in deg.) and binding energies (kJ/mol) for different adsorption complexes (cf. Figure 1).

The activation energy, $\Delta E_{act}^\ddagger$, is quite high, +245.79 kJ/mol. However, this value compares well with the results of Sinclair and Catlow [5] 250 and 244 kJ/mol at the DFT/DZVP and DFT/DZVP levels of theory, respectively. The high value of $\Delta E_{act}^\ddagger$ indicates that this catalytic route may therefore only play a minor role in methanol activation over acidic zeolites. A similar conclusion for DME formation from methanol has been noted by Catlow group [5].

The optimized geometrical parameters of zeolitic clusters with methylamine are reported for the first time and summarized in Table 1. The results for the surface complex cluster indicate that the adsorbed methylamine interacts strongly with the Brønsted acid sites of zeolite and form protonated methylamine cation, $[\text{CH}_3\text{NH}_3]^+$, on the catalytic surface with the adsorption energy of -101.61 kJ/mol. The change in the structural parameters of zeolite upon complexation with methanol are impressive. The results are in line with Gutmann's rule [16], i.e. a lengthening of the bridging O-H bond, a shortening of Al-O adjacent to this bond, and a lengthening of Al-O (not adjacent to it).

The intermolecular O-H...N hydrogen bond in the ZOH/MMA complex, $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{NH}_3]^+$, is evaluated to be 256.69 pm, less than that found in the neutral complexes. The contracted intermolecular distance of the complex reflects an increase of the binding energy (-101.61 versus -83.56 kJ/mol). The energy for conversion of $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{NH}_3]^+$ to $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{NH}_2]$ is -18.05 kJ/mol. The result implies that the desorbed CH_3NH_2 is difficult to generate without the help of other adsorbates, e.g. NH_3 molecules in this study.

The second reaction pathway for methylamine formation: Simultaneous adsorption of CH_3OH and NH_3 on ZOH generating TS structure for methylamine formation.

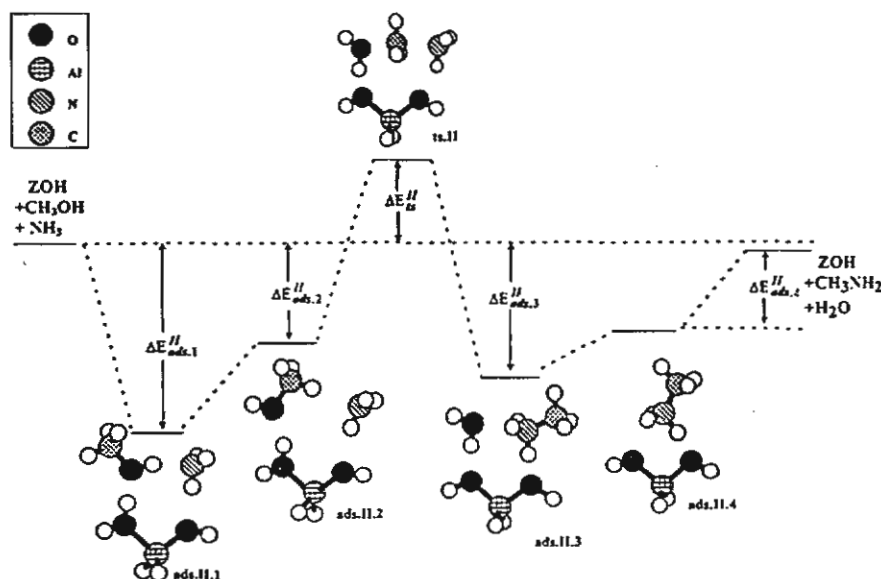


Figure 3. Path II: Simultaneous adsorption of CH_3OH and NH_3 on ZOH, generating a transition state structure for methylamine formation.

Structures of adsorption reactants, adsorption surface methoxy intermediates, and the adsorption products are shown in Figure 3. Selected optimized geometrical structures are tabulated in Table 1.

The starting adsorption reactants involve methanol and ammonia simultaneously adsorbed on ZOH (ads.II.1 in Figure 3). The adsorption energy ($\Delta E_{\text{ads.II.1}}^{\text{II}}$) for this adsorption complex is found to be -132.40 kJ/mol. Although no identical system has been published so far, our calculated adsorption energy, $\Delta E_{\text{ads.II.1}}^{\text{II}}$, of chemically different admolecules of methanol and ammonia should be compared also to the adsorption energy of chemically identical admolecules of two methanol molecules (-123.85 kJ/mol (B3LYP) for $3\text{T}/[\text{CH}_3\text{OH}]_2$). These energy values can also be compared to the initial theoretical investigations of adsorption energy of two methanol molecules at the zeolitic surface [2,7-8]. Gale's DFT/BLYP estimated adsorption energy of the two methanols was -119.16 kJ/mol for 4Tcluster model [8]. Limtrakul [7] reported similar adsorption energies of -56.48 kJ/mol for the first and -35.52 kJ/mol for the second methanol from calculations at the HF theoretical level.

In order to search for the transition state complex of methylamine formation, the preferred configuration, (ads.II.2, Figure 3), has to be selected. This adsorption complex, ads.II.2, can be achieved by rotating the methanol molecule in such a way that the methyl group can be attached by the nucleophile, NH_3 . The structure of transition state may be derived from the $\text{S}_{\text{N}}2$ reaction between the methoxonium cation and nucleophile NH_3 . The activation energy barrier related to the adsorption complex, ads.II.2 is evaluated to be -126.09 kJ/mol, which is less stable than the ads.II.1 by 57.47 kJ/mol. The overall activation energy barrier related to the ads.II.1 for this reaction route becomes 183.56 kJ/mol. The activation energy at B3LYP/6-311G+(3df,2p)//B3LYP/6-31G(d) level of theory was 171.98 kJ/mol, which is about 12 kJ/mol lower than the fully optimized B3LYP/6-31G(d) structure.

The third reaction pathway for methylamine formation: Methanol and Ammonia are simultaneously adsorbed on ZOH generating ZOCH_3 , which interacts with the ammonia promoter to yield methylamine.

The side-on MeOH/NH_3 adsorption, ads.III.2 (Figure 4) is supposed to be the precursor for the formation of surface methoxy intermediate, ads.III.4, which may further interact with ammonia to yield methylamine. However, the most stable adsorption reactants, ads.III.1, where ammonia is adsorbed on the zeolitic acid site, is about 40 kJ/mol more stable than the side-on MeOH/NH_3 adsorption (ads.III.2). The $\Delta E_{\text{act}}^{\text{III}}$ which is related to ads.III.1 is found to be 197.10 kJ/mol. This activation energy barrier is very much lower than $\Delta E_{\text{act}}^{\text{I}}$ obtained from the first type of reaction pathway. It is clearly due to the lesser strain in the transition-state structure, ts.III.1. The three-center angle of the transition-state structure is calculated to be ca. 170° , which is close to the optimum angle of 180° for an $\text{S}_{\text{N}}2$ mechanism. The result indicates that the influence of the adsorbed ammonia is to significantly decrease $\Delta E_{\text{act}}^{\text{III}}$, which enhances the methylation reaction. Due to the lower activation energy, $\Delta E_{\text{act}}^{\text{III}}$, as compared to $\Delta E_{\text{act}}^{\text{I}}$ of the first reaction route, this reaction route may play a significant role in methylamine synthesis.

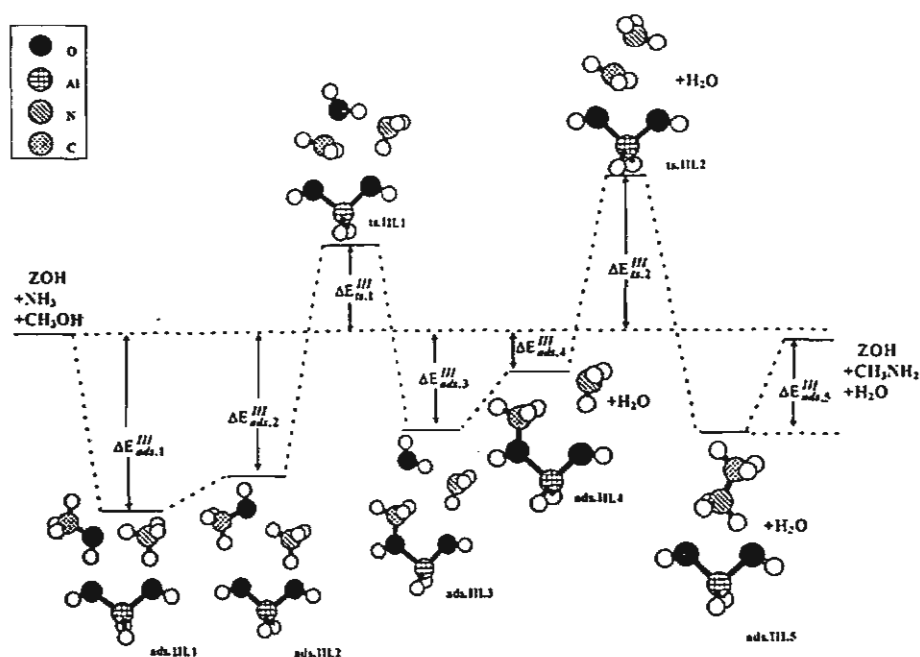


Figure 4. Path III: Both CH_3OH and NH_3 are adsorbed on ZOH, ZOCH_3 is generated via $\text{S}_{\text{N}}2$ with the help of the promoter NH_3 , and the interaction of NH_3 with ZOCH_3 to yield methylamine formation.

The fourth reaction pathway for methylamine formation: Eley-Rideal mechanism where only NH_3 is adsorbed on the Brønsted acid site, followed by CH_3OH binding to the adsorbed NH_3 , generating TS structure.

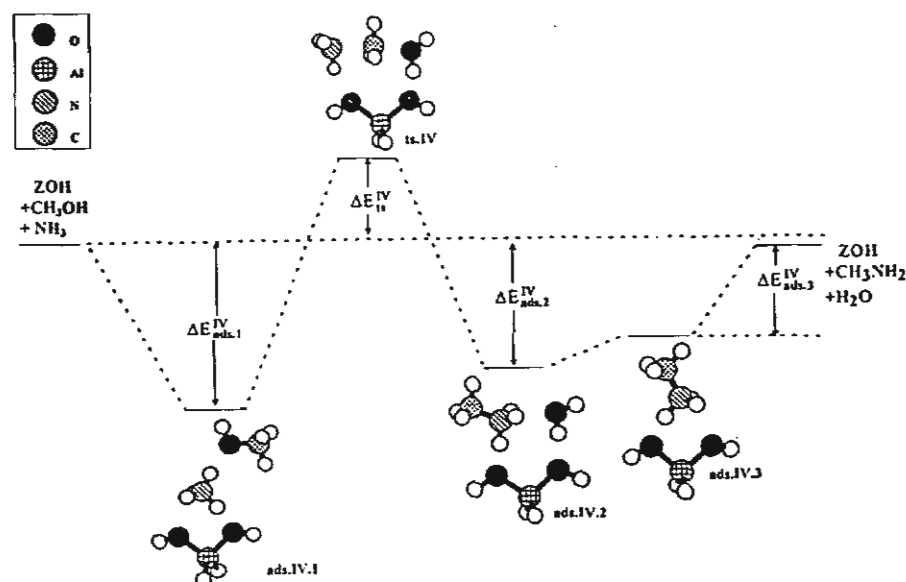


Figure 5. Path IV: Only NH_3 is adsorbed on the Brønsted acid site, CH_3OH is bound to the adsorbed NH_3 , generating transition state structure which is converted to methylamine formation.

The aforementioned second and third reaction pathways, which involve the binding of both methanol and ammonia to Brønsted acid sites, follow a Langmuir-Hinshelwood mechanism.

In contrast, the last reaction pathway is dictated by the Eley-Rideal mechanism where only NH_3 is adsorbed on the Brønsted acid site, followed by CH_3OH binding to the adsorbed NH_3 . To obtain the desired product, methoxonium cation is first generated via the Eley-Rideal precursor complex, which then reacts with ammonia, and loses water to yield a protonated methylamine. $\Delta E_{\text{TS}}^{\text{IV}}$ related to the Eley-Rideal configuration is found to be 183.85 kJ/mol.

CONCLUSIONS

We conclude that paths II, III, IV are the suggested reaction pathways, but paths (II and IV) involving the associative mechanism are the more preferred reaction routes due to a lower activation energy as compared to the path III. The results obtained in the present study are very useful from the experimental point of view, since the adsorption and coadsorption processes on the surface site are found to play a significant role in the catalytic process.

ACKNOWLEDGEMENTS

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เคมีของซีโอไลต์

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ซีโอไลต์คืออะไร ? มีสมบัติอย่างไร?

ซีโอไลต์เป็นสารประกอบอะลูมิเนียมซิลิเกต (1) (crystalline aluminosilicates) มีโครงสร้างเป็นรูพรุนมีโพรงและช่องว่างขนาดตั้งแต่ 2-10 Å (ตารางที่ 1) ซึ่งเป็น

ลักษณะพิเศษเฉพาะตัวที่เด่นชัด สมบัติของซีโอไลต์ที่นำเอาไปใช้ประโยชน์ เช่น การแลกเปลี่ยนไอออน (ion exchange) การดูดซับ (adsorption) การดูดซับแก๊ส สารอาหาร น้ำ ตลอดจนโมเลกุลอินทรีย์ และสมบัติที่สำคัญมากอย่างหนึ่งคือเป็นตัวเร่งปฏิกิริยา

ตารางที่1 คุณลักษณะของซีโอไลต์ชนิดต่าง ๆ (2)

สัญลักษณ์	ชื่อ	ขนาดของโพรง (Å)	อัตราส่วน Si/Al
FAU	Faujasite	7.4	1.25 (Zeolite X) 2.80 (Zeolite Y)
LTL	Zeolite L	7.1	3
MOR	Modenite	6.5 × 7.0	5
MFI	ZSM-5	5.3 × 5.6 5.1 × 5.5	22
BEA	Zeolite Beta	7.6 × 6.4 5.5 × 5.5	30

เคมีของซีโอไลต์

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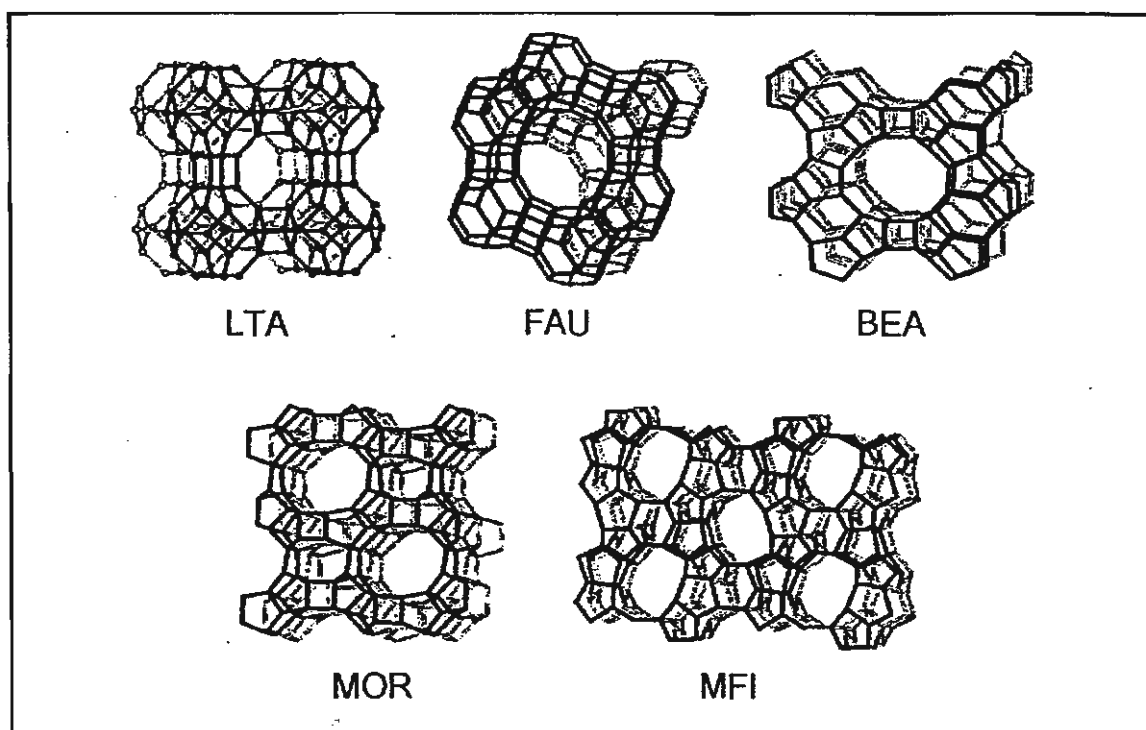
ซีโอไลต์คืออะไร ? มีสมบัติอย่างไร?

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ลักษณะพิเศษเฉพาะตัวที่เด่นชัด สมบัติของซีโอไลต์ที่นำมาใช้ประโยชน์ เช่น การแลกเปลี่ยนไอออน (ion exchange) การดูดซับ (adsorption) การดูดซับแก๊ส สารอาหาร น้ำ ตลอดจนโมเลกุลอินทรีย์ และสมบัติที่สำคัญมากอย่างหนึ่งคือเป็นตัวเร่งปฏิกิริยา

ตารางที่1 คุณลักษณะของซีโอไลต์ชนิดต่างๆ (2)

สัญลักษณ์	ชื่อ	ขนาดของโพรง (Å)	อัตราส่วน Si/Al
FAU	Faujasite	7.4	1.25 (Zeolite X) 2.80 (Zeolite Y)
LTL	Zeolite L	7.1	3
MOR	Modenite	6.5 × 7.0	5
MFI	ZSM-5	5.3 × 5.6 5.1 × 5.5	22
BEA	Zeolite Beta	7.6 × 6.4 5.5 × 5.5	30



รูปที่ 1 แสดงโครงสร้างซีโอไลต์ชนิดต่างๆ

ซีโอไลต์ทำอะไรได้บ้าง ?

1. การแลกเปลี่ยนไอออน (ion exchange)

ในปัจจุบันนิยมใช้ซีโอไลต์เป็นส่วนผสมในการทำสารซักล้าง โดยจะใช้ซีโอไลต์แทนสารฟอสเฟต (phosphates) ซึ่งเป็นตัว water softening agents ที่อันตรายต่อสิ่งแวดล้อม ซีโอไลต์ (zeolite A) มีโลหะโซเดียมซึ่งสามารถแลกเปลี่ยนกับโลหะแคลเซียมและแมกนีเซียมได้เป็นอย่างดีและไม่เป็นอันตรายต่อสิ่งแวดล้อม

การบำบัดน้ำเสีย ซีโอไลต์สามารถขจัด แอมโมเนียจากน้ำเสีย โดยการแลกเปลี่ยน

เปลี่ยนแอมโมเนียมแคตไอออนกับโลหะโซเดียมที่อยู่ในโพรงซีโอไลต์ได้เป็นอย่างดี ดังนั้นซีโอไลต์ที่สังเคราะห์ขึ้นสามารถบำบัดน้ำเสียได้เป็นอย่างดี นอกจากนั้นยังสามารถใช้ ขจัดไอโซโทปกัมมันตรังสี (cesium and strontium radioisotopes) จากกากนิวเคลียร์ (nuclear wastes)

2. การดูดซับ (adsorption)

มีการใช้ซีโอไลต์เป็นตัวดูดซับสารต่างๆ รวมทั้งการประยุกต์ใช้ในระบบการทำให้แห้ง (drying) กระบวนการทำให้บริสุทธิ์ (purification) และ กระบวนการแยกสาร (separation)

3. การเร่งปฏิกิริยา (catalysis)

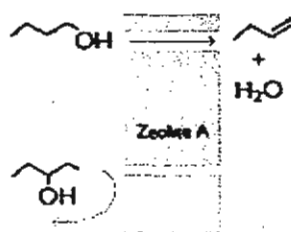
นักเคมีทำการสังเคราะห์สารที่มีโครงสร้างคล้ายซีโอไลต์ และเรียกสารกลุ่มนี้ว่า molecular sieves จากการสังเคราะห์และออกแบบโครงสร้างจึงทำให้สารดังกล่าวมีคุณค่าและ คุณประโยชน์ที่สำคัญในอุตสาหกรรมปิโตรเคมี เช่น ใช้เป็นตัวเร่งปฏิกิริยาในกระบวนการเปลี่ยนแปลงเมทานอลเป็นไฮโดรคาร์บอน (methanol to olefin) และ การแตกตัวด้วยตัวเร่งปฏิกิริยา (catalytic cracking) เป็นต้น

ซีโอไลต์มีสมบัติเป็นกรด (Brønsted acid sites) และมีโครงสร้างเป็นรูพรุน และเป็นโพรง ทำให้มีสมบัติโดดเด่น เช่น มีความสามารถในการเลือกเกิดปฏิกิริยาตามรูปร่าง (shape selectivity) ซึ่งอาจแบ่งได้เป็น 3 แบบ ได้แก่ การเลือกเกิดปฏิกิริยาตามรูปร่างของสารตั้งต้น (reactant shape selectivity) การเลือกเกิดปฏิกิริยาตามรูปร่างของสารผลิตภัณฑ์ (product shape selectivity) และการเลือกเกิดปฏิกิริยาตามรูปร่างของสถานะแทรนซิชัน (transition state shape selectivity)

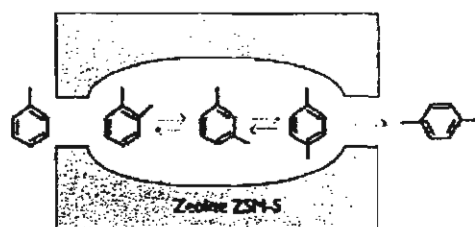
การเลือกเกิดปฏิกิริยาตามรูปร่างของสารตั้งต้น (reactant shape selectivity) ซีโอไลต์จะสามารถเร่งปฏิกิริยาสูญเสียน้ำ (dehydration) ของ 1-butanol ได้อย่างดี แต่ไม่ทำปฏิกิริยากับ 3-pentanol ซึ่งมีขนาดใหญ่กว่า (ดูรูปที่ 2.1)

การเลือกเกิดปฏิกิริยาตามรูปร่างของสารผลิตภัณฑ์ (product shape selectivity) ปฏิกิริยาเมทิลเลชัน (methylation) ของโทลูอีนซึ่งเกิดขึ้นภายในโพรงของซีโอไลต์ ZSM5 จะเกิดขึ้นที่ตำแหน่งพารา (para) เพื่อเกิดเป็นพาราไซลีน (p-xylene) ซึ่งมีขนาดเล็กกว่าสารผลิตภัณฑ์ชนิดอื่นๆ (ดูรูปที่ 2.2)

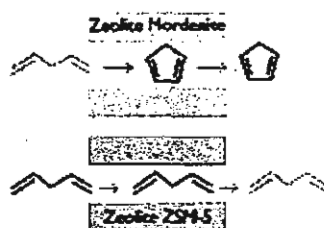
การเลือกเกิดปฏิกิริยาตามรูปร่างของสถานะแทรนซิชัน (transition-state selectivity) ปฏิกิริยาการเกิดวงแหวน (cyclization) ของ 2,4-pentadiene สามารถเกิดขึ้นภายในโพรงของซีโอไลต์ mordenite แต่ไม่สามารถเกิดขึ้นภายในโพรงของซีโอไลต์ ZSM5 ซึ่งมีขนาดของโพรงเล็กกว่าสถานะแทรนซิชัน (ดูรูปที่ 2.3)



2.1 การเลือกเกิดปฏิกิริยาตามรูปร่างของสารตั้งต้น (reactant shape selectivity)



2.2 การเลือกเกิดปฏิกิริยาตามรูปร่างของสารผลิตภัณฑ์ (product shape selectivity)



2.3 การเลือกเกิดปฏิกิริยาตามรูปร่างของสถานะทรานซิชัน (transition-state selectivity)

รูปที่ 2 แสดงลักษณะการเลือกเกิดปฏิกิริยาตามรูปร่างของสารตั้งต้น, สารผลิตภัณฑ์ และ สถานะทรานซิชัน

งานวิจัยเกี่ยวกับซีโอไลต์

ซีโอไลต์มีมากกว่า 600 ชนิด (2538) แต่พอจะแบ่งกลุ่มตามชนิดของโครงสร้าง ได้ประมาณ 40 ชนิด องค์ประกอบหลักที่ทำให้ซีโอไลต์มีสมบัติแตกต่างกันคือ อัตราส่วนของ ซิลิกอน และ อะลูมิเนียม การเปลี่ยนอัตราส่วนดังกล่าวมีผลก่อให้เกิดการเปลี่ยนแปลงกัมมันตภาพเชิงเร่งปฏิกิริยา (catalytic activity) และความเสถียรของ โครงสร้างซีโอไลต์

การแทนที่ธาตุ Si และ Al ด้วยธาตุอื่น เช่น Ga, Ge, P, B และ Fe ในโครงสร้างซีโอไลต์ทำให้เกิด acidic bridging hydroxyl ($\equiv\text{AlOH-Ga}\equiv$, $\equiv\text{Si-OH-Ga}\equiv$, $\equiv\text{Si-OH-B}\equiv$) ซึ่งก่อให้เกิดการเปลี่ยนแปลง

สภาพมีขั้ว (polarity) และความเป็นกรดของซีโอไลต์

การศึกษาและวิจัยถึงความสัมพันธ์ของโครงสร้างและกัมมันตภาพเชิงเร่งปฏิกิริยาทำให้เราสามารถออกแบบและสังเคราะห์ซีโอไลต์ที่มีสมบัติใหม่ๆ เพื่อนำมาใช้ในปฏิกิริยาเคมีต่างๆ ได้ตามต้องการ และขณะนี้ได้มีการศึกษาและวิจัยเกี่ยวกับซีโอไลต์เมมเบรน (zeolite membrane) เพื่อใช้ในการแยกสารประกอบไฮโดรคาร์บอน (3) นอกจากนี้ได้มีการสังเคราะห์ transition-metal oxide cluster ขึ้นภายในโพรงของซีโอไลต์เพื่อนำมาใช้ในปฏิกิริยาออกซิเดชันของสารประกอบไฮโดรคาร์บอน (4)

กลุ่มเคมีซีโอไลต์และวิศวกรรมตัวเร่ง
ของภาควิชาเคมี และวิศวกรรมเคมี
มหาวิทยาลัยเกษตรศาสตร์ ได้ศึกษาและวิจัย
ในหัวข้อต่อไปนี้ (5-14)

- Adsorption and coadsorption in zeolite
- Molecular aspects of heterogeneous catalysis
- Surface reaction dynamics in zeolitic catalysts
- Catalytic cracking (reaction & mechanism)
- Development of new and/or better catalytic reaction pathways via the explorative computational methods and the synthesis of new catalytic materials
- Other areas of developing use of zeolite like environmental chemistry

กิตติกรรมประกาศ

ขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัยและสถาบันวิจัยและพัฒนา
แห่งมหาวิทยาลัยเกษตรศาสตร์

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ผลงาน

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การเชื่อมโยงทางวิชาการกับนักวิชาการอื่นๆทั้งในและนอกประเทศ

- Chemical Engineering Department, Kasetsart University. In close collaboration with Chemical Engineering Department at Washington University, USA.
Industrial applications of zeolite catalysis.
- Chemistry Department, University of Utah, Utah, USA.
Development and Exploration of embedded Cluster Approach and Direct Dynamics for heterogeneous catalysis
- Laboratory for Molecular Spectroscopy, Bordeaux University, France.
Surface Characterization of Advanced Materials
- Institutes of Inorganic and Theoretical Chemistry, University of Innsbruck and University of Vienna.
Computer Simulations of Surface Physical Chemistry and Drug Design.
- Molecular Simulations Inc., Sydney, Australia.
Computer Aided Materials and Drug Design.
- Institute of Physical Chemistry & Electrochemistry, University of Karlsruhe, Germany.
Development and Exploration of Computational chemistry codes.

Computer Simulations of Surface Physical Chemistry and Drug Design.

- Molecular Simulations Inc., Sydney, Australia.

Computer Aided Materials and Drug Design.

- Institute of Physical Chemistry & Electrochemistry, University of Karlsruhe, Germany.

Development and Exploration of Computational chemistry codes.

ภาคผนวก

The Surface Structure and Catalytic Properties of Zeolite and Molecular Sieve Catalysts

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Executive Summary

Rational catalyst design, notably zeolites and molecular sieves, represents one of the most rewarding challenges in catalysis research. Zeolites possess three dimensional microporous crystalline solid. Their catalytically active acid-sites within the complex porous framework structure provide unique properties that make them very attractive industrial materials. They play a significant role in chemicals and fuels production worth over \$1000 billion per year. Zeolites and molecular sieves can be tailored or chosen to maximize the product of target molecules by employing state-of-the-art techniques. Our aim is to develop strategies for tailoring the structural and chemical properties of catalyst materials and to explore the potential of new catalytic materials.

- Structures, energetics and vibrational frequencies of zeolitic catalysts : a comparison between density functional and post-Hartree-Fock approaches Limtrakul, J. and Tantanak D, J. Molecular Structure, 358 (1996) 179-193.

We have carried out LSD and NLSD functional methods with 3-21G, 6-31G*, 6-311G* and DZVP basis sets to investigate the structures, energetics and vibrational frequencies for silanol, disiloxane, and different zeolite clusters. Some smaller models have also been calculated at the MP2 level. The individual geometrical parameters calculated at the BLYP and VWN levels with a modestly sized basis sets (6-311G*) generally yield good results compared to MP2 with much less computational effort. Comparing BLYP and VWN results with MP2, the former has a significant lengthening effect on the weaker A-O bond which does not occur with the latter. The Si-O(H)-Al and Si-O-H bond angles of zeolites are not appreciably affected by the inclusion of NLSD. However, the NLSD was found to be important for a better description of the floppy Si-O-

Si bond angle for disiloxane. The proton affinity of $\text{H}_3\text{SiOHAlH}_3$, a widely employed model of a Brønsted acid site in zeolites, is virtually identical to that of MP2/DZP and is also close to the result from G1 theory within the desired 10 kJ mol⁻¹ accuracy. For this cluster model, the BLYP VOH value is calculated to within 130 cm⁻¹ of the experimental value. We expect that the same accuracy from the BLYP/6-311G* procedure will be applied to larger zeolite clusters in the future.

- Structures and potential energy surface of Faujasitic zeolite/water

Limtrakul, J. and Treesukol, P., Chemical Physics, 215 (1997) 77-87.

We have presented a density functional study of faujasitic zeolites and their complexes with water using the B3LYP functionals and the basis sets 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311+G(d,p). The agreement between DFT/B3LYP-6-311+G(d,p) proton affinities and the corresponding CPF and G1 values are excellent. Comparing the older BLYP and VWN functionals, with the recently introduced B3LYP functionals, the latter yields superior accuracy. This artificial significant lengthening effect on the weaker Al-O bond in the BLYP and VWN calculations does not occur with B3LYP. The Si-O(H)-Al and Si-O-H bond angles of zeolites do not appreciably depend on the inclusion of non-local effects in the density functional. The 6-31G(d) basis set in DFT prediction of the faujasitic structure yields good results and is an economic choice for large systems. The predicted PA of the faujasitic catalyst is estimated to be 294 ± 3 kcal/mol, which is in the range of experimentally determined value of 291-300 kcal/mol. The faujasite catalyst/water structure is stabilized at the bridging O-H group by two H-bonds with binding energy of -20.3 kcal/mol. Comparison with hydrogen halides and related complexes of water demonstrates that the faujasite is a strong acid. An analytical potential for the interaction to faujasitic zeolite with water was derived by fitting the ab initio interaction energies which we plan to employ in simulations studies of petrochemical catalyst/water systems.

- Coadsorption of ammonia and methanol on H-zeolites and alkaline-exchanged zeolites

Limtrakul J. and Onthong U. J. Molecular Structure 435 (1998) 181-192.

We have carried out HF and B3LYP methods with 6-31G* basis set to investigate the coadsorption of methanol and ammonia on H-zeolites (H-Z) and alkaline-exchanged zeolites (Na-Z). Comparing HF and B3LYP results with available experimental data, the B3LYP yields structural parameters which are in good agreement with experimental data. The Al...H distance of zeolite has been estimated experimentally as 238 ± 4 pm, where as our B3LYP value is 239.7

pm. A comprehensive study of the coadsorption of adsorbate molecules with the surface hydroxyl reveals several interesting points. Structure Na-Z[CH₃OH][NH₃] is lower in energy than Na-Z[NH₃] [CH₃OH], which suggests that the former is more favourable in the coadsorption process. The reaction mechanism of coadsorption of methanol and ammonia on H-Z is that the ammonia is found to stabilize to the Brønsted acid site of H-Z, generating an ammonium cation, which acts as an active site for methanol.

- Cationic, structural, and compositional effects on the surface structure of zeolitic aluminosilicate catalysts

Limtrakul, J. and Tantanak, J. Chemical Physics, 208 (1996) 331-340.

The cationic, structural and compositional effects on the structure and bonding of different types of $\equiv\text{Si-OH-Al}\equiv$ units in the secondary building unit of zeolite cluster models (OH)₈H_yAl_xSi_{8-x}O₁₂ (x, y=0, 1, 2, 4) and the silica model (OH)₈Si₈O₁₂ have been investigated with the DFT method. Full optimization of all mentioned structural isomer clusters have been carried out at VWN/6-31G* and BLYP/6-31G*. All isomers of the double four-membered ring aluminosilicate (D4R) demonstrate that Dempsey's rule may be violated in this type of zeolite. The well-known Loewenstein's $\equiv\text{Al-O-Al}\equiv$ avoidance rule has been once again confirmed by us. The results of D4R with varying Si/Al ratio indicate that the higher the ratio, the lesser the proton is restricted which results in a higher acidic strength. The cations, H⁺ and Li⁺, are found to have a profound effect on the important structural parameters (Si-O, Al-O, O-H bonds and SiOAl angle) of D4R. The marked difference between the cations is that the H⁺ is singly bonded while the Li⁺ is doubly bonded to the framework. This excellent results indicate that the catalytic activity of zeolites is also enhanced by the presence of cations, in addition to a compositional effect.