



สรุปผลการดำเนินงานวิจัย

โครงการทุนเมธีวิจัยประจำปี 2538

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

เสนอ

ผู้อำนวยการฝ่ายสนับสนุนการวิจัยเชิงวิชาการ
สำนักงานกองทุนสนับสนุนการวิจัย

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วันที่ 6-7 ตุลาคม พ.ศ. 2541



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วันที่.....
เลขทะเบียน.....
เลขเรื่องหนังสือ.....

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วันที่ 6-7 ตุลาคม พ.ศ. 2541

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ห้องสมุด



สารบัญ

หน้า

กิตติกรรมประกาศ

บทคัดย่อ

สารบัญ

ผลการวิจัย

1

- Structures, energetics, vibrational frequencies of zeolitic catalysts, a comparison between density functional and post Hartree-Fock approaches

2

- บทนำ (Introduction)
- วิธีการทดลอง (Methods)
- ผลการทดลองและบทวิจารณ์ (Results and Discussion)
- เอกสารอ้างอิง (References)

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

17

- บทนำ (Introduction)
- วิธีการทดลอง (Methods)
- ผลการทดลองและบทวิจารณ์ (Results and Discussion)
- เอกสารอ้างอิง (References)

- Structures and potential energy surface of faujasitic zeolite / water

30

- บทนำ (Introduction)
- วิธีการทดลอง (Methods)
- ผลการทดลองและบทวิจารณ์ (Results and Discussion)
- เอกสารอ้างอิง (References)

■ Coadsorption of ammonia and methanol on H-zeolites and alkaline-exchanged zeolites	45
■ บทนำ (Introduction)	
■ วิธีการทดลอง (Methods)	
■ ผลการทดลองและบทวิจารณ์ (Results and Discussion)	
■ เอกสารอ้างอิง (References)	
■ Structure and Reaction Pathways in Zeolitic Systems	60
■ บทนำ (Introduction)	
■ วิธีการทดลอง (Methods)	
■ ผลการทดลองและบทวิจารณ์ (Results and Discussion)	
■ เอกสารอ้างอิง (References)	
■ เคมีของซีโอไลต์ (Chemistry of Zeolites)	68
ผลงาน	74
ผลงานที่ตีพิมพ์และกิจกรรมอื่นๆ ที่เกี่ยวข้อง	
ภาคผนวก	
รายงานการเงิน	

กิตติกรรมประกาศ

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บทคัดย่อ

ซีโอไลต์เป็นสารประกอบอะลูมิโนซิลิเกต (crystalline aluminosilicates) มีโครงสร้างเป็นรูปพรมมีโพรงและช่องว่างขนาดตั้งแต่ 2-10 Å ซึ่งเป็นลักษณะพิเศษเฉพาะตัวที่เด่นชัดสมบัติของซีโอไลต์ที่นำมาไปใช้ประโยชน์ เช่น การแลกเปลี่ยนไอออน (ion exchange) การดูดซับ (adsorption) การดูดซับแก๊ส สารอาหาร น้ำ ตลอดจนโมเลกุลอินทรีย์ และสมบัติที่สำคัญมากอย่างหนึ่งคือเป็นตัวเร่งปฏิกิริยา ได้ทำการวิจัยโครงสร้าง พลังงาน ความถี่ของการสั่นของตัวเร่งปฏิกิริยาซีโอไลต์ และ ศึกษาถึงอิทธิพลของโลหะ องค์ประกอบ การเปลี่ยนแปลงโครงสร้าง ต่อโครงสร้างพื้นผิวของตัวเร่งปฏิกิริยา การศึกษาและค้นหา Local structure properties ของซีโอไลต์และซีโอไทป์ เพื่อที่จะเข้าใจถึงบทบาทที่สำคัญของซีโอไลต์แต่ละชนิด และนำมาเป็นโครงสร้างต้นแบบ (Zeolitic prototype) ในการพัฒนาตัวเร่งปฏิกิริยาซีโอไลต์ให้มีประสิทธิภาพสูงขึ้น นอกจากนั้นศึกษากระบวนการการดูดซับของ adsorbate บน ตัวเร่งปฏิกิริยาซีโอไลต์ โดยการศึกษาโครงสร้าง พื้นผิวพลังงานศักย์ (potential energy surface) ของ Faujasite Zeolite กับน้ำ และศึกษากระบวนการดูดซับร่วมและกลไกการเกิดปฏิกิริยาของเมธานอลและแอมโมเนียบน H-zeolite และ Alkaline-exchange zeolite

Abstract

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. In the present research work the surface structure and catalytic properties of different zeolitic clusters have been investigated for the first time via density functional theory (DFT/B3LYP), Hartree-Fock(HF) and Perturbation theory(MP2). This includes

- Structures, energetics and vibrational frequencies of zeolitic catalysts : a comparison between density functional and post-Hartree-Fock approaches
- Cationic, structural, and compositional effects on the surface structure of zeolitic aluminosilicate catalysts
- Structures and potential energy surface of Faujasitic zeolite/water
- Coadsorption of ammonia and methanol on H-zeolites and alkaline-exchanged zeolites
- Structure and reaction pathways for methylamine/zeolite system.

ผลการวิจัย

1. Structures, energetics, vibrational frequencies of zeolitic catalysts:
A comparison between density functional and post Hartree-Fock approaches
2. Cationic, structural, and compositional effects on the surface structure of zeolitic aluminosilicate catalysts
3. Structures and potential energy surface of faujasitic zeolite / water
4. Coadsorption of ammonia and methanol on H-zeolites and alkaline-exchanged zeolites
5. Structure and Reaction Pathways in Zeolitic Systems
6. เคมีของซีโอไลต์ (Chemistry of Zeolites)

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Structures, energetics and vibrational frequencies of zeolitic catalysts: a comparison between density functional and post-Hartree–Fock approaches

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ELSEVIER



Structures, energetics and vibrational frequencies of zeolitic catalysts: a comparison between density functional and post-Hartree–Fock approaches

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Abstract

Structures, energetics and vibrational frequencies of zeolitic cluster models have been investigated with an *ab initio* method at the correlated level involving the second-order Møller–Plesset (MP2) and with the density functional theory (DFT) method including local and non-local spin density functions. Full optimization of structures has been carried out with 3-21G, 6-31G*, 6-311G*, DZVP basis sets. The comparison of geometries of zeolite clusters between the DFT (Becke–Lee–Yang–Parr and Vosko–Wilk–Nusair) and MP2 results agrees with 1 pm for Si–O and O–H, while the weaker Al–O bond length agrees with 2–4 pm depending on the exchange–correlation potential employed. The Si–O(H)–Al, Si–O–H, and Si–O–Si bond angles are in good agreement with MP2. The flexible Si–O–Si angle is well represented by BLYP but not by VWN, the latter yielding angles 12° and 18° smaller than the MP2 and coupled pair functional results, respectively. This suggests that BLYP should be used. The acidity of zeolites at the BLYP/6-311G* level is evaluated by proton affinity; it is virtually identical to that from MP2/DZP and is also close to the result for G1 theory within the desired 10 kJ mol^{−1} accuracy. The DFT OH stretching frequencies of zeolite clusters are predicted to within 4% of the experimental value. The DFT methods are computationally efficient and appear to provide results that are generally of comparable quality to MP2.

Keywords: Density functional theory; MP2; Zeolite

1. Introduction

Zeolites are porous frameworks of crystalline aluminosilicates with a number of interesting physical and chemical properties. The hydroxyl groups in zeolites are acknowledged to be of prime importance for the catalytic properties and have led to numerous industrially important applications [1–11].

It is important to know the structures, energetics

and vibrational frequencies of the Brønsted acidic surface sites which are crucial for understanding the catalytic processes [9–12].

Recently, density functional theory (DFT) has been employed to investigate various chemical systems [13–18]. Not only does it require much less computational effort, but also the DFT results are very encouraging when compared with high level *ab initio* calculations and more reliable experimental data. This leads to the utilization of DFT approaches for large chemical systems.

To the best of our knowledge, no systematic

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investigations of the structure and bonding of zeolitic cluster models have been explored by DFT employing both local (LSD) and non-local spin density (NLSD) approximations. We have selected $\text{H}_3\text{SiOHAlH}_3$, $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$, $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, and $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$ to test and gauge the usefulness of DFT by a direct comparison with the high level ab initio results, and also the available experimental results.

2. Methods and computational details

Full geometry optimization of all zeolitic cluster models was carried out with the DFT methods.

All density functional computations were carried out using the Dgauss program [19] implemented to run on the Cray-YMP EL98 at the NECTEC High Performance Computing Center.

In Dgauss, the electron density is expanded in terms of single-particle Gaussian-type functions, referred to as the "auxiliary basis set". The program includes approximate electron exchange and correlation effects. These contributions are evaluated on a finite grid and can be fitted to another auxiliary basis set. Most integrals are calculated analytically, but some integrals concerning exchange-correlation contributions are evaluated by a numerical integration technique using a finite grid.

Two different exchange-correlation functionals were selected for this investigation, namely the

local density approximation (LDA) and BLYP functionals. For LDA we employed the Vosko–Wilk–Nusair (VWN) correlation function [20]. It is generally believed that the VWN potential represents one of the best analytical functional forms currently available for LSD potentials. Gradient-type corrections have been included self-consistently using the non-local functions of Becke exchange [21] and the Lee, Yang and Parr [22] correlation (BLYP).

The cluster models (H_3SiOH , $\text{H}_3\text{SiOSiH}_3$, $\text{H}_3\text{SiOHAlH}_3$, $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$, $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, and $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$) have been computed with 3-21G, 6-31G*, and 6-311G* basis sets. Additionally, to minimize the basis set superposition error (BSSE) and to improve the quality of valence orbitals, the recommended LSD-optimized orbital basis sets [23] were also employed. The following orbitals were used: (41) for hydrogen atoms, (621/41/1) for oxygen atoms, and (6321/521/1) for Si and Al atoms. The following auxiliary basis sets were used: [4] for hydrogen atoms, [7/3/3] for oxygen atoms, and [9/4/4] for Al and Si atoms. These LSD-optimized orbital basis sets can be considered as double-zeta split valence plus polarization (DZVP) basis sets.

For the ab initio calculations we employed the TURBOMOLE program, which is based on the direct self-consistent field (SCF) method of Almloef and co-workers [24–26]. Two two-electron repulsion integrals are recomputed when needed, rather than being kept. Three basis sets of 3-21G,

Table 1
Optimized parameters for the molecular models of H_3SiOH and $\text{H}_3\text{SiOSiH}_3$

Methods	Basis sets	H_3SiOH			$\text{H}_3\text{SiOSiH}_3$	
		Si–O (pm)	O–H (pm)	Si–O–H (pm)	Si–O (pm)	Si–O–Si (deg)
BLYP	6-31G*	168.2	97.7	114.3	166.7	148.4
	6-311G*	167.3	97.0	118.6	166.4	150.0
VWN	6-31G*	165.8	97.6	115.1	165.0	137.8
	6-311G*	164.9	96.8	119.6	165.1	132.1
MP2	6-31G*	167.2	96.9	116.4	166.0	143.7
	6-311G*	165.5	95.6	121.7	164.3	155.7
CPF	Extended ^a	165.0	95.8	117.7	164.8	151.6

^a [8s, 5p, 3d, 1f/4s, 2p].

Table 2

Optimized parameters for the molecular model $\text{H}_3\text{SiOHAlH}_3$ at the BLYP, VWN, MP2 and HF levels

Methods	Si–O (pm)					
	3-21G*	6-31G*	6-311G*	DZVP	DZVP2	TZVP
BLYP	176.9	173.4	173.1	173.4	173.3	173.0
VWN	174.3	171.2	170.2	171.4	171.1	170.4
MP2	175.8	172.8	171.5	–	–	–
HF	173.6	170.6	169.9	–	–	–
	Al–O (pm)					
	3-21G*	6-31G*	6-311G*	DZVP	DZVP2	TZVP
BLYP	197.5	207.1	207.0	210.9	210.2	209.7
VWN	191.8	199.8	189.4	201.8	201.3	199.1
MP2	194.2	202.6	200.6	–	–	–
HF	192.2	202.2	201.5	–	–	–
	O–H (pm)					
	3-21G*	6-31G*	6-311G*	DZVP	DZVP2	TZVP
BLYP	99.7	97.9	97.1	98.2	97.8	97.5
VWN	99.5	98.1	97.1	98.2	97.8	97.5
MP2	98.6	97.3	96.0	–	–	–
HF	96.6	95.1	94.2	–	–	–
	Al...H (pm)					
	3-21G*	6-31G*	6-311G*	DZVP	DZVP2	TZVP
BLYP	256.1	258.2	261.7	255.5	256.2	256.0
VWN	252.7	245.2	253.5	248.9	250.2	255.2
MP2	256.0	259.7	259.2	–	–	–
HF	249.5	258.1	255.8	–	–	–
	Si–O–Al (deg)					
	3-21G*	6-31G*	6-311G*	DZVP	DZVP2	TZVP
BLYP	125.6	127.6	127.0	131.0	130.8	130.6
VWN	121.6	121.1	125.1	121.9	123.4	125.9
MP2	123.5	123.3	123.8	–	–	–
HF	124.9	126.7	126.2	–	–	–
	Si–O–H (deg)					
	3-21G*	6-31G*	6-311G*	DZVP	DZVP2	TZVP
BLYP	119.2	116.9	119.2	115.7	116.2	116.3
VWN	121.5	116.9	121.2	117.7	118.1	119.5
MP2	118.2	116.5	118.7	–	–	–
HF	119.7	117.6	118.9	–	–	–

6-31G*, and 6-311G* quality are used. In order to obtain the more reliable structures of zeolite, the correlated calculations were performed for the primary unit $\text{H}_3\text{SiOHAlH}_3$. Geometry optimization was terminated when the gradient norm with respect to internal coordinates was less than $10^{-3} E_h a_0^{-1}$. The energy change was then below $5 \times 10^{-6} E_h$. All SCF and second-order Møller–Plesset (MP2)

calculations were carried out on the HP 700 cluster at the Laboratory for Computational and Applied Chemistry at Kasetsart University.

3. Results and discussion

In order to assess the reliability of density

Table 3
BLYP optimized parameters computed for different models

Model	Si–O (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	176.9	173.4	173.4	173.1
H ₃ SiOHAl(OH) ₂ OSiH ₃	175.7	174.6	173.4	173.4
(OH) ₃ SiOHAl(OH) ₃	175.6	174.8	175.2	174.3
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	175.8	173.9	173.1	173.0
Model	Al–O (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	197.5	210.9	207.1	207.0
H ₃ SiOHAl(OH) ₂ OSiH ₃	188.8	197.9	195.3	195.7
(OH) ₃ SiOHAl(OH) ₃	184.8	191.9	190.9	191.7
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	190.0	197.4	196.4	197.6
Model	O–H (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	99.7	98.2	97.9	97.1
H ₃ SiOHAl(OH) ₂ OSiH ₃	99.4	98.1	97.8	97.0
(OH) ₃ SiOHAl(OH) ₃	99.4	98.0	97.8	97.0
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	99.9	98.2	98.0	97.4
Model	Al···H (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	256.1	255.5	258.2	261.7
H ₃ SiOHAl(OH) ₂ OSiH ₃	248.9	255.4	251.6	250.9
(OH) ₃ SiOHAl(OH) ₃	251.8	254.3	255.5	253.7
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	240.5	248.8	243.6	244.0
Model	Si–O–Al (deg)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	125.6	131.0	127.6	127.0
H ₃ SiOHAl(OH) ₂ OSiH ₃	120.2	125.6	124.1	124.0
(OH) ₃ SiOHAl(OH) ₃	119.3	121.4	120.2	119.9
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	128.4	130.0	131.9	131.5
Model	Si–O–H (deg)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	119.2	115.7	116.9	119.2
H ₃ SiOHAl(OH) ₂ OSiH ₃	123.9	119.3	121.8	122.3
(OH) ₃ SiOHAl(OH) ₃	118.8	119.6	118.8	120.8
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	123.7	119.9	121.3	121.9

functional methods (local and non-local approximations) and the validity of the molecular models employed, the structures, proton affinities and vibrational frequencies of the smallest model compound silanol, H₃SiOH, disiloxane, H₃SiOSiH₃, and different cluster models of zeolites (H₃SiOHAlH₃, (OH)₃SiOHAl(OH)₃, H₃SiOHAl(OH)₂OSiH₃, and H₃SiOHAl(OSiH₃)₂OSiH₃)

were computed at different levels of theory using 3-21G, 6-31G*, 6-311G* and DZVP basis sets, as documented in Tables 1–5, and also depicted in Fig. 1. Smaller clusters, H₃SiOHAlH₃, are also computed at MP2 levels employing the corresponding basis sets, and the results were compared with those of the more reliable coupled pair functional (CPF/[8s, 5p, 3d, 1f/4s,

Table 4
VWN optimized parameters computed for different models

Model	Si–O (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	174.3	171.4	171.2	170.2
H ₃ SiOHAl(OH) ₂ OSiH ₃	172.8	171.5	170.8	170.4
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	173.0	171.0	170.7	170.3
Model	Al–O (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	191.8	201.8	199.8	198.4
H ₃ SiOHAl(OH) ₂ OSiH ₃	184.0	190.0	188.9	189.0
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	184.3	190.3	190.4	190.3
Model	O–H (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	99.5	98.2	98.1	97.1
H ₃ SiOHAl(OH) ₂ OSiH ₃	99.3	98.0	97.8	97.2
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	100.2	98.3	98.1	97.4
Model	Al···H (pm)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	252.7	248.9	245.2	253.5
H ₃ SiOHAl(OH) ₂ OSiH ₃	241.9	247.7	245.2	243.7
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	231.2	243.7	241.7	241.0
Model	Si–O–Al (deg)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	121.6	121.8	121.1	125.1
H ₃ SiOHAl(OH) ₂ OSiH ₃	118.2	121.9	122.2	121.8
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	125.0	124.3	125.3	125.1
Model	Si–O–H (deg)			
	3-21G	DZVP	6-31G*	6-311G*
H ₃ SiOHAlH ₃	121.5	117.7	116.9	121.2
H ₃ SiOHAl(OH) ₂ OSiH ₃	127.9	123.3	124.1	125.4
H ₃ SiOHAl(OSiH ₃) ₂ OSiH ₃	130.1	124.5	125.1	125.4

2p)) method of Sauer and Alhrichs [27] and G1 [28,29], as well as available accurate experimental results.

3.1. Structures

Table 1 illustrates the results for H₃SiOH and H₃SiOSiH₃ structure parameters computed at different levels of theory. It is clearly seen that BLYP/6-311G* and MP2/6-31G* levels yield basically the same results, which are also close to the more accurate CPF structure given in Table 1.

Silanol

Bond lengths involving OH are consistently longer than CPF values (97.0 (BLYP), 96.8 (VWN), and 95.8 pm (CPF)). The DFT results are in good agreement with MP2/6-31G* (96.9 pm). For the Si–O bond length VWN/6-311G* yields a virtually identical value to CPF, while the corresponding value at the BLYP/6-311G* level is 2.3 pm too long. Si–O–H bond angles calculated with both DFT procedures compare well with MP2 and CPF results (119.6°, 118.6°, 116.4°, and 117.7° at the VWN, BLYP, MP2 and CPF levels, respectively).

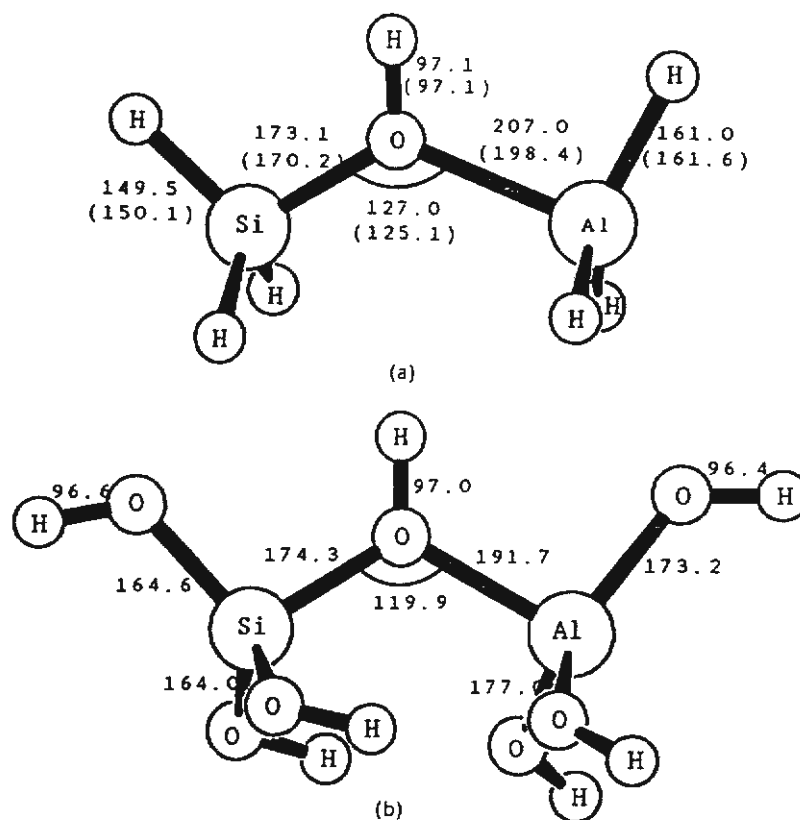


Fig. 1. Schematic representation of molecular models optimized at BLYP/6-311G* and VWN/6-311G* (values in parentheses) for (a) $\text{H}_3\text{SiOHAlH}_3$, (b) $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$, (c) $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, and (d) $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$.

Table 5

Computed OH bond lengths, proton affinities (kJ mol^{-1}), and vibrational frequencies (cm^{-1}) at the VWN and BLYP levels of theory for $\text{H}_3\text{SiOHAlH}_3$, $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ and $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$

Cluster model	Basis set	r_{OH} (pm)		P.A. (kJ mol^{-1})		ν (cm^{-1})	
		VWN	BLYP	VWN	BLYP	VWN	BLYP
$\text{H}_3\text{SiOHAlH}_3$	3-21G	99.5	99.7	1333.5	1343.0	3550.0	3488.6
	6-31G*	98.1	97.9	1295.5	1323.3	3671.3	3662.7
	6-311G*	97.1	97.1	1282.7	1307.9	3789.8	3757.0
	DZVP	98.2	98.2	1284.0	1314.1	3693.7	3660.4
$\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$	3-21G	99.3	99.4	1371.8	1382.4	3610.9	3516.0
	6-31G*	97.8	97.8	1302.5	1324.0	3780.3	3720.8
	6-311G*	97.2	97.0	1296.9	1316.2	3873.1	3812.9
	DZVP	98.0	98.1	1281.9	1310.4	3841.1	3749.4
$\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$	3-21G	100.2	99.9	1305.7	1319.3	3455.0	3451.3
	6-31G*	98.1	98.0	1253.6	1272.5	3675.2	3653.4
	6-311G*	97.4	97.4	1242.3	1261.9	3702.6	3683.7
	DZVP	98.3	98.2	1244.4	1264.9	3655.3	3647.6

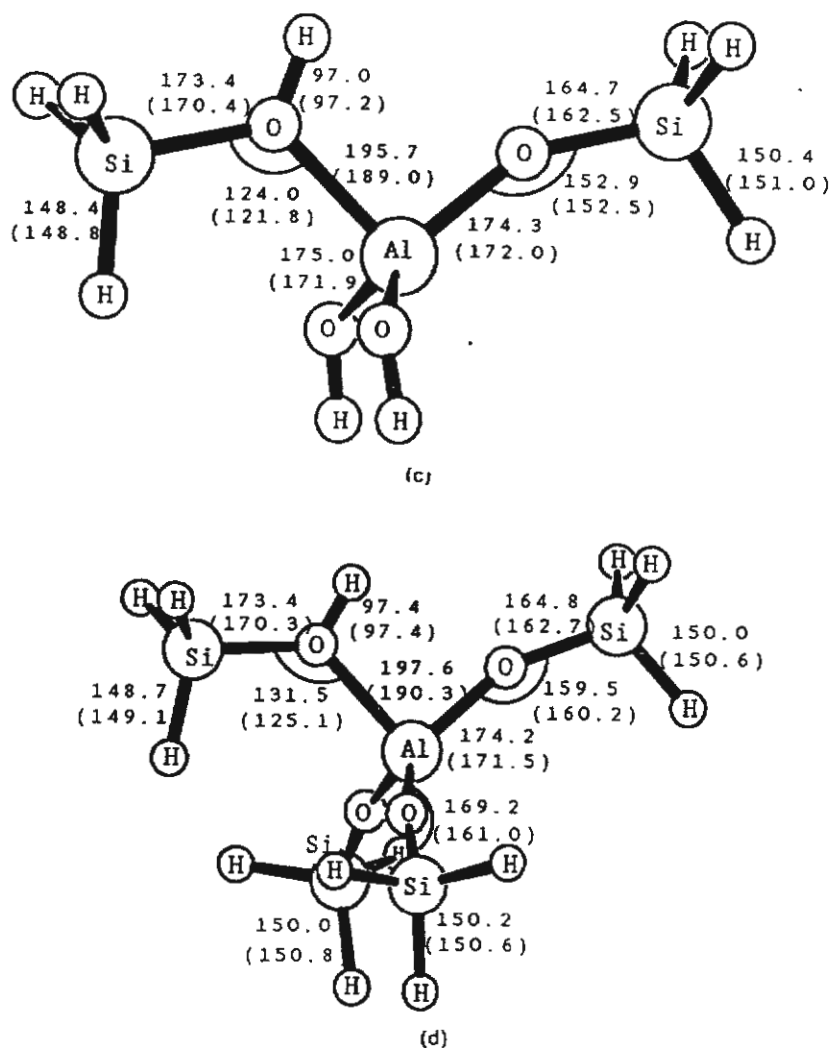


Fig. 1. Continued.

Disiloxane

For $\text{H}_3\text{SiOSiH}_3$, the computed Si-O bond lengths are 166.4 pm (BLYP/6-311G*) and 165.1 pm (VWN/6-311G*), which are in good agreement with the results of 166.0 pm at the MP2/6-31G* and 164.8 pm at the CPF level. However, the VWN Si-O-Si bond angles are too small by about 18° when compared to the CPF result. In contrast with this discouraging result, the BLYP/6-311G* approach yields of 150.0° which is close to the MP2/6-31G* (143.7°) and the most reliable

CPF angle of 151.6°, as well as experimental data ($\approx 144^\circ$) [30].

Zeolites

A systematic deviation in bond lengths can be observed with different methods for $\text{H}_3\text{SiOHAlH}_3$ (see Figs. 2(a)–2(c) and Table 2). Bond lengths concerning hydroxyl O-H calculated at both the DFT-VWN/6-311G* and DFT-BLYP/6-311G* levels are comparable to those computed at the MP2/6-31G* level. The deviation for the O-H

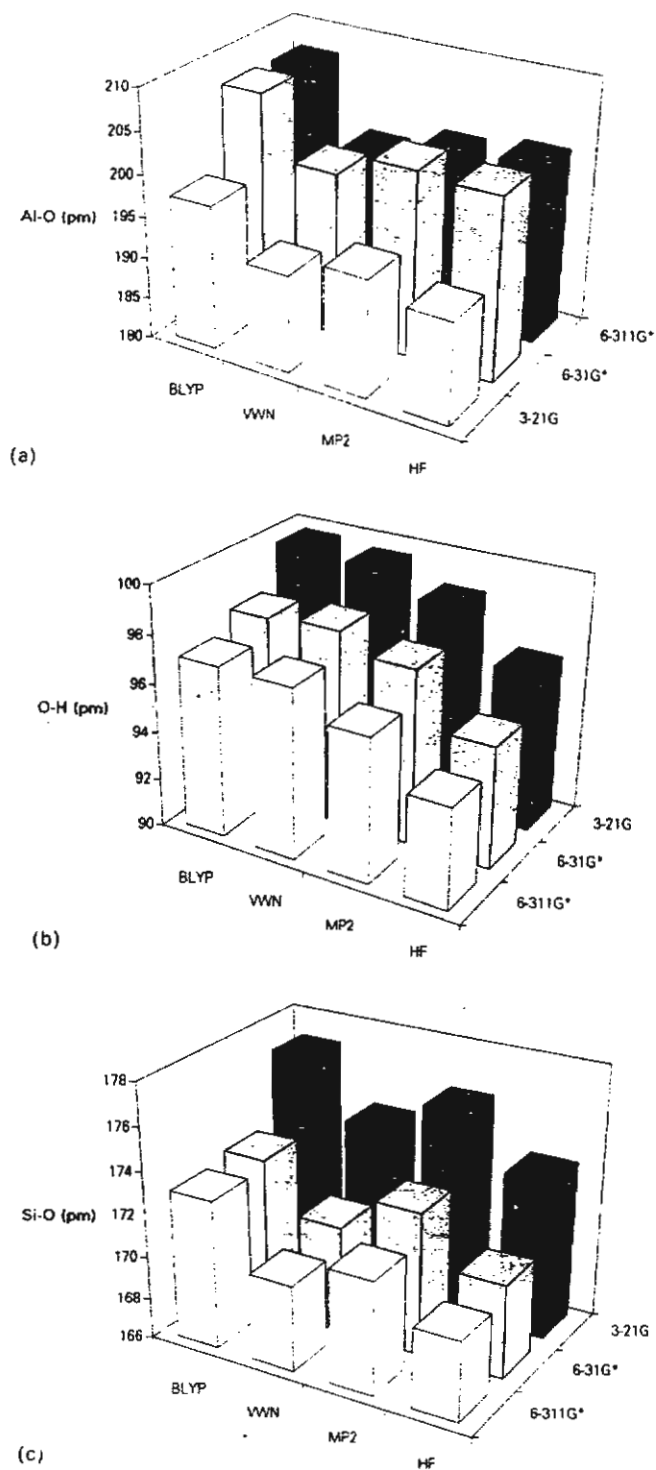


Fig. 2. Optimized parameters — (a) Al–O, (b) O–H, (c) Si–O, (d) Si–O(H)–Al and (e) Si–O–H — for the molecular model $\text{H}_3\text{SiOHAlH}_3$ at the BLYP, VWN, MP2 and HF levels.

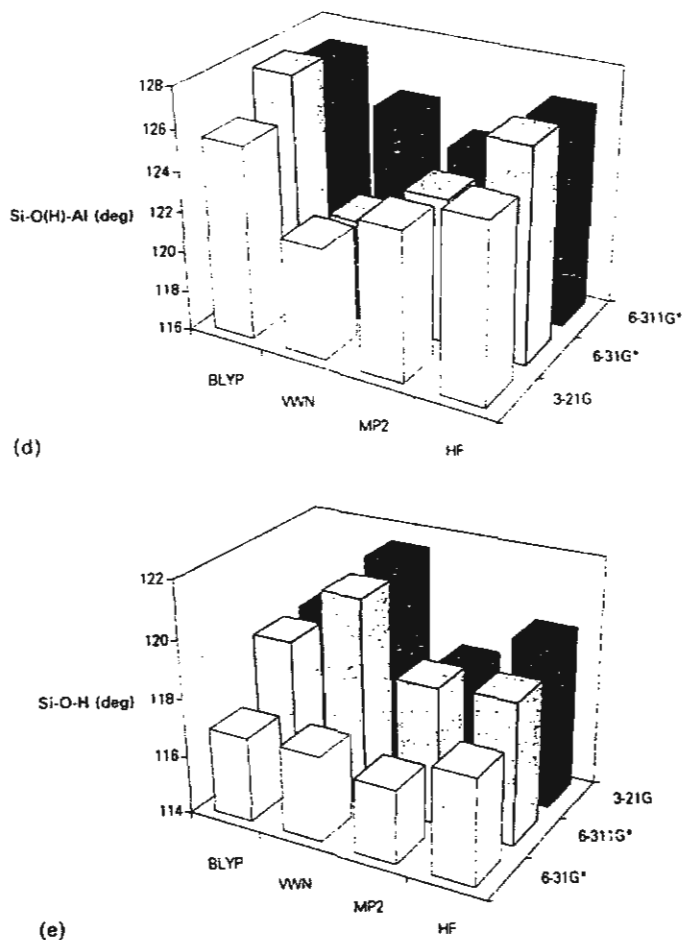


Fig. 2. Continued.

bond length is 1.1 pm at both the DFT-VWN/6-311G* and DFT-BLYP/6-311G* levels, as compared to the MP2/6-311G* level. Inclusion of NLSD has little effect on the O–H and Si–O bonds, but this is not the case for the weaker Al–O bonds: the Si–O, and Al–O bonds are lengthened by 2.9 and 8.7 pm, respectively. At the DFT-VWN/6-311G* level, the OH, Si–O and Al–O bond lengths are 97.1, 170.2 and 198.4 pm, respectively, which are in very good agreement with those determined at the MP2/6-31G* level; the corresponding MP2 values are 97.3, 172.8 and 202.6 pm.

Bond angles calculated at both the DFT/VWN and DFT/BLYP levels are in good agreement with those computed at the MP2 level (see Figs. 2(d)–

2(e)). At the DFT-BLYP/6-311G* level, maximum deviations of 3.2° and 0.5° are calculated for the bond angles of Si–O(H)–Al and Si–O–H, respectively. The corresponding deviation values using DFT-VWN/6-311G* are 1.3° and 2.5°.

There is little effect on the Si–O and Al–O bond lengths, and Si–O–Al and Si–O–H bond angles on going from the DFT-BLYP/6-31G* to the DFT-BLYP/6-311G* level. The same corresponding effect is also observed for the DFT-VWN procedure. However, the bond lengths involving hydrogen atoms, especially the O–H bond, exhibit large deviations: 98.1 vs. 97.1 pm (at VWN/6-31G* and VWN/6-311G*, respectively) and 97.9 vs. 97.1 pm (at BLYP/6-31G* and BLYP/6-311G*, respectively). This implies that at least a 6-311G* basis

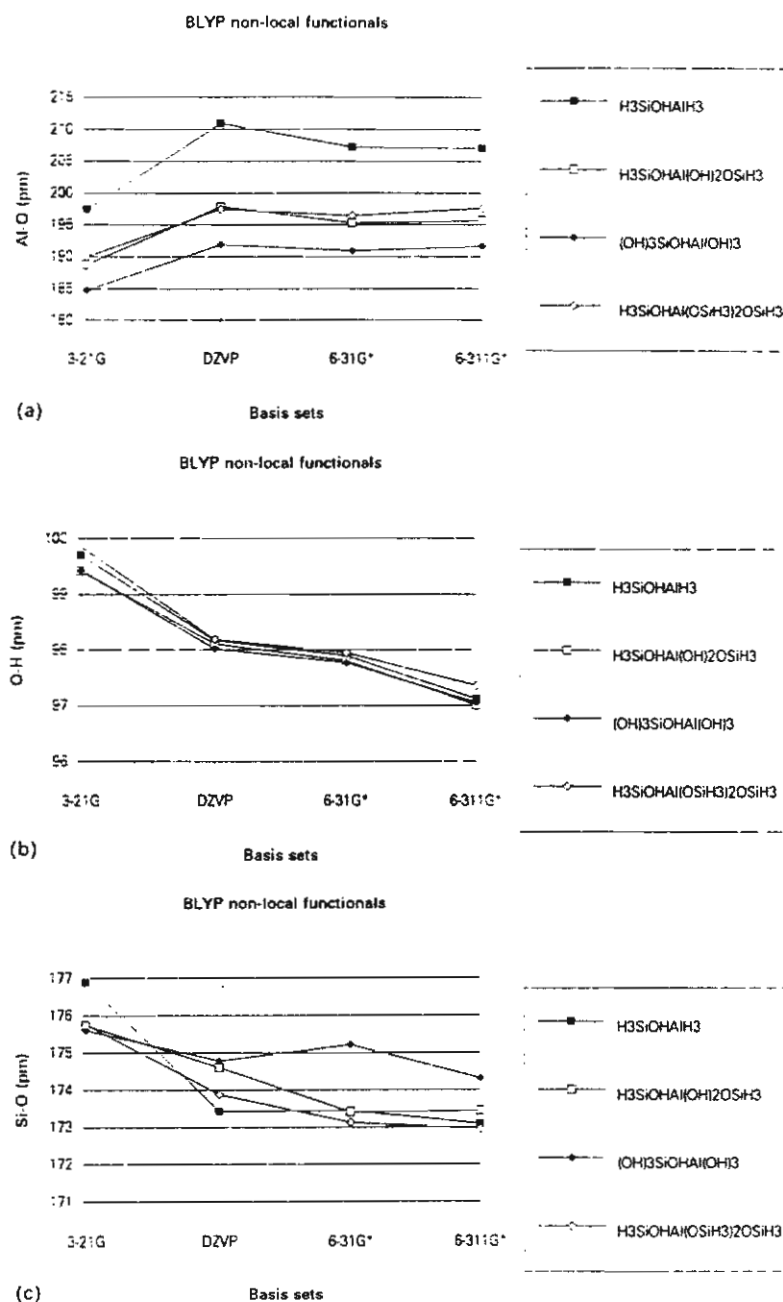


Fig. 3. Variation of calculated (a) Al–O, (b) O–H and (c) Si–O bond lengths with basis sets at the BLYP non-local density functional level.

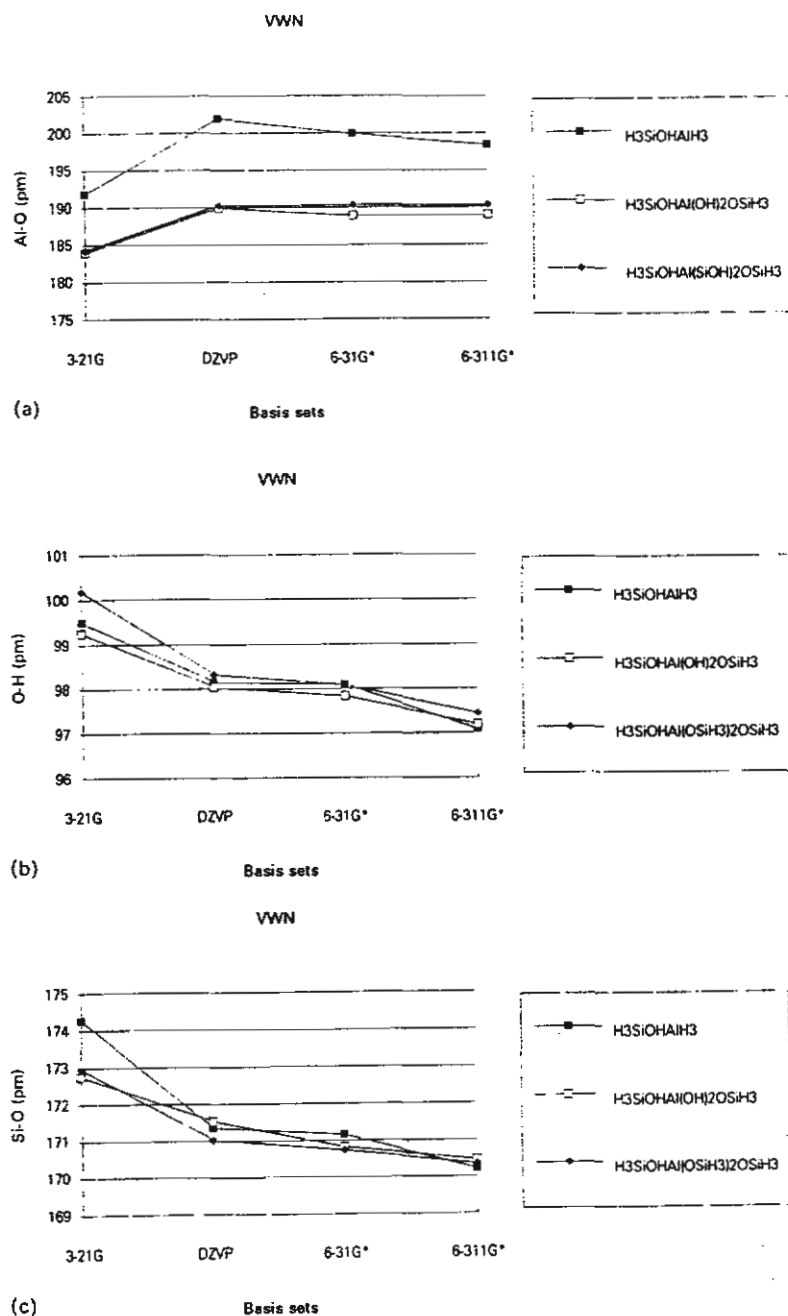


Fig. 4. Variation of calculated (a) Al-O, (b) O-H and (c) Si-O bond lengths with basis sets at VWN local density functional level.

set is required for the system involving hydrogen bonding.

Considering Tables 3 and 4, it is clearly seen that $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$ provides a better model than the widely employed $\text{H}_3\text{SiOHAlH}_3$. The smallest model yields an Al–O bond length that is too long compared with that of $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$. On increasing the level of basis set from 3-21G to 6-31G* to 6-311G*, the Al–O bond lengths of the cluster models increase whereas the Si–O and O–H bond lengths decrease, as shown in Figs. 3 and 4. The results obtained with the 6-311G* basis sets show that the Al–O bond lengths are contracted by 9.4 and 8.1 pm at the BLYP and VWN levels, respectively, while the Si–O bond lengths of these methods are almost identical upon expanding the model from $\text{H}_3\text{SiO}(\text{H})\text{AlH}_3$ to $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$ (see also Tables 3 and 4).

Further support for the reliability of using the $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$ unit in computations is given by the results of NMR studies: the Al...H distance of H-faujasite has been estimated to be 238 ± 4 pm [1], when our computed distances of $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$ are 244.0 and 241.0 pm (at the BLYP/6-311G* and VWN/6-311G* level, respectively), whereas the corresponding distances of $\text{H}_3\text{SiO}(\text{H})\text{AlH}_3$ are 261.7 and 253.5 pm (at BLYP/6-311G* and VWN/6-311G*, respectively).

Tables 3 and 4 also give other important parameters, including the O–H distance which plays an important role in catalytic properties. The hydroxyl O–H bond length obtained from a neutron diffraction study of acidic faujasite [31,32] was 100 ± 20 pm. It should be noted that for $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ our BLYP/6-311G* OH bond length was calculated to be 97.0 pm, which is in very good agreement with the recent MP2/DZP result of 96.8 pm [33].

In order to observe changes in structure and bonding on going from the anionic framework site to Brønsted acid site, the anionic clusters were also computed at the 3-21G, 6-31G* and 6-311G* levels of theory. In the following discussion, we refer to the BLYP results obtained with the largest basis set, 6-311G*. Removal of a proton from the protonated cluster of H_3SiOHAl -

$(\text{OSiH}_3)_2\text{OSiH}_3$ strengthens the Si–O(H) and Al–O(H) bonds (173.0 pm vs. 160.6 pm for Si–O(H), and 197.6 pm vs. 174.8 pm for Al–O(H)). The Si–O–Al angle (148.2°) in the deprotonated cluster is larger (by 16.7°) than the Si–O(H)–Al angle (131.5°) at the bridging hydroxyl site. The average Al–O bond length of the four Al–O bonds of the protonated form was calculated to be 179.9 pm, whereas for the anionic framework it was found to be 174.4 pm, which is in good agreement with the available experimental value of 174.5 pm determined by X-ray diffraction measurement of the zeolite [34].

3.2. Proton affinities

Proton affinities of Brønsted hydroxyl in zeolites can be used as a basis for the activity of catalysts in catalytic processes.

We can evaluate the performance of the DFT procedure in predicting gas phase proton affinities by comparison with highly reliable theoretical values of G1 and coupled pair functional levels. All calculated proton affinities at different basis sets for different cluster models are documented in Table 5.

Silanol

The calculated VWN/6-311G* and BLYP/6-311G* proton affinities are evaluated to be 1495.2 and 1520.4 kJ mol^{-1} . It can be seen that NLSD performs perfectly well at the BLYP/6-311G* level, which is in good agreement with the CPF (1521 kJ mol^{-1}) [27] and G1 ($1490.3 \text{ kJ mol}^{-1}$) [28,29] results.

Zeolites

The BLYP proton affinities of zeolites are reduced on passing from 3-21G to 6-311G*, as shown in the following (VWN results in parentheses): 35.1 (50.8) kJ mol^{-1} for $\text{H}_3\text{SiO}(\text{H})\text{AlH}_3$, 66.2 (74.9) kJ mol^{-1} for $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ and 57.4 (63.4) kJ mol^{-1} for $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$. The improvement on going from 3-21G to 6-311G* is quite large, with a maximum difference of 75 kJ mol^{-1} .

The result of the proton affinity for the $\text{H}_3\text{SiOAlH}_3^-$ molecule with BLYP/6-311G* is also

encouraging. The deviation from the most accurate G1 [29,30] is about 12 kJ mol^{-1} . The MP2/6-31G* proton affinity yields a virtually identical value to the less expensive BLYP result ($1307.9 \text{ kJ mol}^{-1}$ (MP2) vs. $1307.9 \text{ kJ mol}^{-1}$ (BLYP)). DFT results may be further improved by enlarging the basis to a size comparable to 6-311 + G (3df,2p) in order to obtain a deviation within the desired 10 kJ mol^{-1} accuracy from experimental data.

For $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, the BLYP/6-311G* yields a value 2 kJ mol^{-1} lower than MP2/DZP [33]. This agreement reflects the similar computed OH bond lengths at both levels of theory (96.8 pm (MP2) vs. 97.1 pm (BLYP)). It is also important to study the dependence of proton affinities on the employed cluster size. On expanding the model cluster from $\text{H}_3\text{SiOHAlH}_3$ to $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$, the proton affinities are decreased by 40 and 46 kJ mol^{-1} with the LSD and NLSD procedures, respectively. For the largest model of our work, the proton affinities are calculated to be 1242 and 1262 kJ mol^{-1} with LSD and NLSD, respectively. Using the systematic deviations between DFT and G1 theory, our predicted value is estimated to be 1215 kJ mol^{-1} , which is in the range of experimentally determined values of $1180\text{--}1333 \text{ kJ mol}^{-1}$ [35,36]. The calculated AM1 proton affinity of $\text{Si}_{47}\text{AlO}_{114}\text{H}_{37}$, which is by far the largest zeolite cluster, is estimated to be 1295 kJ mol^{-1} [37]. In order to properly study the acidity of the bridging hydroxyl group in zeolites, such a modestly-sized cluster model of $\text{H}_3\text{SiOHAl}(\text{OSiH}_3)_2\text{OSiH}_3$ at least is needed.

3.3. Vibrational frequencies

It has been noted previously by Pople et al. [38] that the frequencies obtained at the HF and MP2 levels using the 6-31G* basis set have been found to yield vibrational frequencies that are about 12% and 6% too high, respectively, on average compared with the experimentally observed frequencies.

It is one of our aims to evaluate the performance of DFT procedures in predicting vibrational frequencies, ν_{OH} . The ν_{OH} of zeolites increases with the size of the basis functions (see Table 5). The improvement on going from 3-21G to

6-311G* is quite large, with a maximum of 297 cm^{-1} .

Silanol

The VWN and BLYP OH frequencies, ν_{OH} , of 3807.2 and 3751.3 cm^{-1} are in agreement with MP2/6-31G* calculations (3841.6 cm^{-1}). They are also in agreement with the Morse MP2 OH stretching frequency of Bates and Dwyer [39] (3818 cm^{-1}). The HF/6-31G* ν_{OH} of 4148 cm^{-1} is 306 cm^{-1} higher than the MP2/6-31G* value. This is due partly to the neglect of electron correlation.

Zeolites

The VWN and BLYP OH frequencies, ν_{OH} , of $\text{H}_3\text{SiOHAlH}_3$ are 3789.8 and 3757.0 cm^{-1} , respectively. Andrews and Handy [40] have recently presented harmonic vibrational frequencies of this molecule at MP2/DZP. Their ν_{OH} is 3800 cm^{-1} , in agreement with our results. The DFT result is about 300 cm^{-1} lower than the SCF/6-31G* result reported by Fleischer et al. [41]. Their calculation at this level is 4090 cm^{-1} which is known to yield an overly high ν_{OH} . Calculations of the vibrational frequencies of all cluster models of zeolites employed here indicated that ν_{OH} are located in the region $3683\text{--}3757 \text{ cm}^{-1}$, which can be compared to the range of experimentally determined values of $3520\text{--}3630 \text{ cm}^{-1}$. It is well known that the observed ν_{OH} depends on the number of aluminium atoms and the distribution of the $\equiv\text{SiOHAl}\equiv$ groups in the zeolite framework [42]. With the aim of quantifying the quality of the DFT data for zeolite clusters, we have compared our results with the most recent experimental data [43]. The maximum deviation occurs in the case of $\text{H}_3\text{SiO}(\text{H})\text{Al}(\text{OH})_2\text{OSiH}_3$. If we consider the relative error, we find for our models a deviation of 2–5% from the experimental data depending on the models employed. In the case of closest agreement, a deviation of less than 2% is derived for $\text{H}_3\text{SiO}(\text{H})\text{Al}(\text{OSiH}_3)_2\text{OSiH}_3$ at the BLYP level, compared to experimental results.

4. Conclusions

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 set (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 ν_{OH} 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.

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

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Abstract

The cationic, structural, and compositional influences on the structure and bonding of zeolitic aluminosilicates have been investigated with the density functional theory (DFT) method including local (VWN) and non-local spin density functionals (BLYP). Full optimization of structures has been carried out at the 6-31G^{*}/VWN and 6-31G^{*}/BLYP levels of theory for the different types of the $\equiv\text{Si}-\text{OH}-\text{Al}\equiv$ unit in the secondary building unit of the zeolite cluster models $[(\text{OH})_8\text{H}_x\text{Al}_y\text{Si}_{8-x}\text{O}_{12}]^{x-y-} (x, y = 0, 1, 2, 4)$ and the silica model $(\text{OH})_8\text{Si}_8\text{O}_{12}$. Changes in the environment of the silicon and aluminium framework atoms with a given Si/Al ratio generate new different acid sites. The validity of Loewenstein's $\equiv\text{Al}-\text{O}-\text{Al}\equiv$ avoidance rule is confirmed but Dempsey's $\equiv\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Al}\equiv$ avoidance rule does not hold with double four-membered ring aluminosilicate (D4R). The proton affinity (PA) of the silica model $(\text{OH})_8\text{Si}_8\text{O}_{12}$ at BLYP/6-31G^{*} are evaluated to be 1403 ± 15 kJ/mol which is in good agreement with the experimentally observed value of 1390 ± 25 kJ/mol. Proton affinities of Brønsted hydroxyl groups in H forms of zeolites associated with different Si/Al ratios indicate that the higher the ratio, the less the proton is constrained which results in a stronger acid strength. Cations are found to have profound effects on the structure and bonding of zeolite clusters. The H ion has a strong perturbation on the important parameters i.e. Si–O, Al–O, OH bond lengths while the Li(I) has a modest effect. The PA of the Brønsted OH groups in the zeolitic frameworks interacting with their cations are 1272.4 and 1279.3 kJ/mol for $\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ and $\text{LiH}(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$, respectively, which correspond with decreasing bond lengths of the OH groups. These results indicate that the acid strength of the OH groups within the zeolitic framework is also determined by the presence of cations, in addition to compositional and structural effects.

1. Introduction

Zeolites are porous frameworks of crystalline aluminosilicates with a number of interesting physical and chemical properties. The hydroxyl groups in zeolites are of primary significance for the catalytic properties and have led to numerous industrially

important applications, such as adsorbents and catalysts [1–10].

The performance of zeolitic catalysts depends on the framework composition (the Si/Al ratio) and the framework topology (the environment of the Si and Al atoms).

The widely utilized primary building unit [11–15] $\text{H}_3\text{SiOHAlH}_3$ is too limited to investigate the effects mentioned above. The two-site binding model of

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$\text{H}_3\text{Si}-\text{OH}-\text{Al}(\text{OH})_2-\text{O}-\text{SiH}_3$ [16–21], which can be employed for studying the details of interaction with the adsorbed molecules i.e. H_2O , NH_3 and methanol still involves two Si tetrahedra and only one Al tetrahedron. Important information of the nature, the strength and the number of acid sites is limited if a small cluster is employed for modelling.

Extension of the cluster model from $\text{H}_3\text{SiOHAlH}_3$ over $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ to more realistic models of double four-membered rings (D4R) should therefore permit us to investigate the cationic and compositional effects on the surface structure of zeolite aluminosilicate catalysts.

Recently the density functional theory (DFT) has been employed to investigate various chemical systems [22–27]. Not only does it require much less computational effort, but also the DFT results are very encouraging when compared with high level ab initio calculations and more reliable experimental data [27]. This leads to the utilization of DFT approaches for large chemical systems.

To the best of our knowledge, no systematic investigations of the cationic, structural, and compositional effects on the structure and bonding of zeolitic cluster models have been carried out by DFT employing both local (LSD) and non-local density (NLSD) approximations. In addition to the DFT calculations, smaller models have been studied at HF and MP2 levels.

2. Methods and computational details

Full geometry optimization of the zeolitic cluster models $\text{H}_3\text{SiOHAlH}_3$, $\text{H}_3\text{SiOHAl}(\text{OH})_2-\text{OSiH}_3$, as well as the more realistic models of double four-membered rings (D4R: $(\text{OH})_8\text{Si}_8\text{O}_{12}$, $(\text{OH})_8\text{Si}_7\text{AlOXO}_{11}$, $(\text{OH})_8\text{Si}_6\text{Al}_2\text{OHXO}_{11}$, $(\text{OH})_8\text{Si}_4\text{Al}_4\text{H}_4\text{O}_{12}$, where X represents H^+ and Li^+ , was carried out with the density functional theory methods.

All density functional computations were carried out by the DGAUSS program [28] implemented to run on the Cray-YMP EL98 at the NECTEC High Performance Computing Center.

Two different exchange correlation functionals were selected for this investigation, namely the LDA and BLYP functionals. For local density approximation (LDA) we employed the Vosko–Wilk–Nusair

(VWN) correlation function [29]. It is generally believed that the VWN potential represents one of the best analytical functional forms currently available for LSD potentials. Gradient-type corrections have been included self-consistently using the non-local functions of Becke exchange [30] and the Lee, Yang and Parr [31] correlation (BLYP). Studies [32,33] have shown that these functionals yield harmonic frequencies with mean absolute errors less than those of MP2 and produce respectable geometries.

All cluster models mentioned above have been computed with 6-31G* basis sets. Additionally, to minimize the basis set superposition error (BSSE) and to improve the quality of valence orbitals, the recommended LSD-optimized orbital basis sets [34] were also employed. The following orbitals were employed: (41) for the hydrogen atom, (621/41/1) for the oxygen atom, and (6321/521/1) for Si and Al atoms. The following auxiliary basis sets were used: [4] for the hydrogen atom, [7/3/3] for the oxygen atom, and [9/4/4] for Al and Si atoms. These LSD-optimized orbital basis sets can be considered as double-zeta split valence plus polarization (DZVP) basis sets.

For the ab initio calculations we employed the TURBOMOLE program, which is based on the direct SCF method of Almloef et al. [35–37]. The two-electron repulsion integrals are recomputed when needed, rather than being kept. In order to obtain zeolite structures at a (more reliable) higher level of theory some models, e.g. the primary building unit $\text{H}_3\text{SiOHAlH}_3$, are also evaluated at the correlated level of theory. Geometry optimization was terminated when the gradient norm with respect to the internal coordinates was less than $10^{-3} E_h a_0^{-1}$. The energy change was then below $5 \times 10^{-6} E_h$. All SCF and MP2 calculations were carried out on the HP 700 cluster at the Laboratory for Computational and Applied Chemistry at Kasetsart University.

3. Results and discussion

3.1. Comparison of density functional theory and post-Hartree–Fock results with experimental results

The different types of $\equiv\text{Si}-\text{O}(\text{H})-\text{Al}\equiv$ units in the double four-membered ring of the zeolite frame-

Table 1
Optimized parameters for H_3SiOH , $\text{H}_3\text{SiOSiH}_3$ and $\text{H}_3\text{SiOHAlH}_3$ at various methods

Model	Method	Basis set	Si–O (pm)	Al–O (pm)	O–H (pm)	Si–O–Si (deg)	Si–O–Al (deg)	Si–O–H (deg)
H_3SiOH	BLYP	6-31G*	168.2	–	97.7	–	–	114.3
		6-311G*	167.3	–	97.0	–	–	118.6
		DZVP	168.6	–	97.8	–	–	116.0
	VWN	6-31G*	165.8	–	97.6	–	–	115.1
		6-311G*	164.9	–	96.8	–	–	119.6
		DZVP	166.1	–	97.7	–	–	117.0
	MP2	6-31G*	167.2	–	96.9	–	–	116.4
		6-311G*	165.5	–	95.6	–	–	121.7
	HF	6-31G*	164.7	–	94.6	–	–	119.0
		6-311G*	163.6	–	93.7	–	–	124.2
	CPF	extended ^a	165.0	–	95.8	–	–	117.7
$\text{H}_3\text{SiOSiH}_3$	BLYP	6-31G*	166.7	–	–	148.4	–	–
		6-311G*	166.4	–	–	150.0	–	–
		DZVP	167.5	–	–	140.3	–	–
	VWN	6-31G*	165.0	–	–	137.8	–	–
		6-311G*	165.1	–	–	132.1	–	–
		DZVP	164.7	–	–	149.1	–	–
	MP2	6-31G*	166.0	–	–	143.7	–	–
		6-311G*	164.3	–	–	155.7	–	–
	HF	6-31G*	162.7	–	–	166.4	–	–
		6-311G*	162.0	–	–	180.0	–	–
	CPF	extended ^a	164.8	–	–	151.6	–	–
$\text{H}_3\text{SiOHAlH}_3$	BLYP	6-31G*	173.4	207.1	97.9	–	127.6	116.9
		6-311G*	173.1	207.0	97.1	–	127.0	119.2
		DZVP	173.4	210.9	98.2	–	131.0	115.7
	VWN	6-31G*	171.2	199.8	98.1	–	121.1	116.9
		6-311G*	170.2	189.4	97.1	–	125.1	121.2
		DZVP	171.4	201.8	98.2	–	121.9	117.7
	MP2	6-31G*	172.8	202.6	97.3	–	123.3	116.5
		6-311G*	171.5	200.6	96.0	–	123.8	118.7
	HF	6-31G*	170.6	202.2	95.1	–	126.7	117.6
		6-311G*	169.9	201.5	94.2	–	126.2	118.9

^a = [8s,5p,3d,1f/4s,2p].

Table 2
BLYP optimized parameters computed for $\text{H}_3\text{SiOAlH}_3^-$, $\text{H}_3\text{SiOHAlH}_3$, $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3$ and D4R cluster models and their complexes with ions

BLYP/6-31G*						
System	Si–O (pm)	Al–O (pm)	O–H (pm)	Al...H (pm)	Si–O–Al (deg)	Si–O–H (deg)
$\text{H}_3\text{SiOAlH}_3^-$	163.0	184.5	–	–	127.1	–
$\text{H}_3\text{SiOHAlH}_3$	173.4	207.1	97.9	258.2	127.6	116.9
$\text{H}_3\text{SiOLiAlH}_3$	167.5	190.6	178.5 ^a	170.3	128.6	142.3
$\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3$	173.4	195.3	97.8	251.6	124.1	121.8
$\text{H}_3\text{SiOLiA}(\text{OH})_2\text{OSiH}_3$	167.3	186.0	182.6 ^a	258.3	124.8	146.2
$\text{H}(\text{OH})_8\text{AlSi}_7\text{O}_{12}$	171.9	194.6	98.2	248.9	131.0	116.1
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (a)	173.3	193.7	98.2	248.9	131.0	116.1
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (b)	175.5	194.0	98.4	240.8	137.2	116.1
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (c)	169.8	199.8	98.4	247.6	133.4	119.3
$\text{LiH}(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$	172.8	194.1	98.1	248.4	131.2	116.6
$\text{H}_4(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{12}$	176.4	191.4	98.1	247.0	132.4	113.6

^a = Li(I)...O.

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Table 3

VWN optimized parameters computed for $\text{H}_3\text{SiOAlH}_3^-$, $\text{H}_3\text{SiOAlH}_3$, $\text{H}_3\text{SiOAl(OH)}_2\text{OSiH}_3$, D4R cluster models and their complexes with ions

VWN/6-31G *						
System	Si–O (pm)	Al–O (pm)	O–X (pm)	Al...H (pm)	Si–O–Al (deg)	Si–O–H (deg)
$\text{H}_3\text{SiOAlH}_3^-$	161.2	180.9	–	–	125.4	–
$\text{H}_3\text{SiOAlH}_3$	171.2	199.8	98.1	245.2	121.1	116.9
$\text{H}_3\text{SiOLiAlH}_3$	165.8	186.5	176.2 ^a	251.1	127.6	142.9
$\text{H}_3\text{SiOAl(OH)}_2\text{OSiH}_3$	170.8	188.9	97.8	245.2	122.2	124.1
$\text{H}_3\text{SiOLiAl(OH)}_2\text{OSiH}_3$	165.2	182.1	179.1 ^a	254.8	119.4	150.8
$\text{H(OH)}_8\text{AlSi}_7\text{O}_{12}$	168.6	189.2	98.4	243.0	129.9	118.8
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (a)	169.7	188.6	98.4	243.6	130.8	117.0
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (b)	170.5	186.9	98.4	241.8	130.4	117.4
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (c)	166.3	191.7	97.6	226.5	134.4	127.9
$\text{LiH(OH)}_8\text{Al}_2\text{Si}_6\text{O}_{12}$	169.4	188.6	98.3	242.5	130.4	118.1
$\text{H}_4(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{12}$	172.5	186.2	98.3	240.7	132.8	115.3

^a = Li(I)...O.

Table 4

Computed OH bond lengths and proton affinities (kJ/mol) at BLYP for the zeolite cluster models

BLYP					
System	Basis set	r_{OH} (pm)	q_{H}	$ q_{\text{O}} \cdot q_{\text{H}} $	PA (kJ/mol)
H_3SiOH	6-311G *	97.0	0.405	0.294	1520.4
$\text{H}_3\text{SiOHAlSiH}_3$	6-311G *	97.1	0.454	0.372	1307.9
$\text{H}_3\text{SiOHAl(OH)}_2\text{OSiH}_3$	6-311G *	97.0	0.466	0.395	1316.2
$(\text{OH})_8\text{Si}_8\text{O}_{12}$	6-31G *	97.7 [†]	–	–	1403.1
$\text{H(OH)}_8\text{Al}_1\text{Si}_7\text{O}_{12}$	6-31G *	98.2	0.477	0.333	1249.1
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (a)	6-31G *	98.2	0.475	0.333	1272.4
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (b)	6-31G *	98.4	0.475	0.335	–
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (c)	6-31G *	98.4	0.476	0.327	–
$\text{H}_4(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{12}$	6-31G *	98.1	0.458	0.318	1285.2
$\text{LiH(OH)}_8\text{Al}_2\text{Si}_6\text{O}_{12}$	6-31G *	98.1	0.474	0.332	1279.3

[†] = terminal hydroxyl groups =SiOH.

Table 5

Computed OH bond lengths and proton affinities (kJ/mol) at VWN for the zeolite cluster models

VWN					
System	Basis set	r_{OH} (pm)	q_{H}	$ q_{\text{O}} \cdot q_{\text{H}} $	PA (kJ/mol)
H_3SiOH	6-311G *	96.8	0.434	0.317	1495.2
$\text{H}_3\text{SiOHAlSiH}_3$	6-311G *	97.1	0.487	0.396	1282.7
$\text{H}_3\text{SiOHAl(OH)}_2\text{OSiH}_3$	6-311G *	97.2	0.498	0.413	1296.9
$(\text{OH})_8\text{Si}_8\text{O}_{12}$	6-31G *	97.5 [†]	–	–	1413.2
$\text{H(OH)}_8\text{Al}_1\text{Si}_7\text{O}_{12}$	6-31G *	98.4	0.504	0.351	1233.6
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (a)	6-31G *	98.4	0.503	0.329	1255.8
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (b)	6-31G *	98.4	0.502	0.329	–
$\text{H}_2(\text{OH})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (c)	6-31G *	97.6	0.498	0.318	–
$\text{H}_4(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{12}$	6-31G *	98.3	0.499	0.330	1265.8
$\text{LiH(OH)}_8\text{Al}_2\text{Si}_6\text{O}_{12}$	6-31G *	98.4	0.501	0.327	1241.4

[†] = terminal hydroxyl groups =SiOH.

works with different Si/Al ratio computed using the DFT/BLYP and DFT/VWN methods are documented for the first time in Tables 1–5, and illustrated in Figs. 1–4. In order to compare the reliability of the DFT structure the highly symmetrical model compound $\text{H}_8\text{Si}_8\text{O}_{12}$ was fully optimized at the SCF/DZP level of theory and the results were compared with the more reliable experimental data. In addition to various isomers of the D4R model clusters the smaller models H_3SiOH , $\text{H}_3\text{SiOSiOH}_3$, $\text{H}_3\text{SiOHAlH}_3$, $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$, $\text{H}_3\text{SiOAl}(\text{OH})_2$ – OHSiH_3 are also included at the SCF, DFT and MP2 methods.

The comparison of the geometry of the smaller zeolitic models between the DFT (Becke–Lee–Yang–Parr and Vosko–Wilk–Nasair) and MP2 results agrees with 1 pm for Si–O and O–H, while the weaker Al–O bond lengths agree with 2–4 pm depending on the exchange-correlation potential employed. The Si–O(H)–Al, Si–O–H, and Si–O–Si parameters are in good agreement with MP2. The flexible Si–O–Si angle of $\text{H}_3\text{SiOSiH}_3$ is well represented by BLYP but not by VWN, the latter giving angles 12° and 18° smaller than MP2 and coupled pair functional results, respectively. This suggests that BLYP should be employed for a silica model.

For $(\text{OH})_8\text{Si}_8\text{O}_{12}$, Fig. 1a, the calculated values of $r(\text{Si–O})$ and $\angle\text{Si–O–Si}$ are 165.1 pm and 140.1° for BLYP/6-31G*, 162.8 pm and 137.2° for VWN/6-31G*, and 162.8 pm and 160.6° for SCF/DZP levels of theory. All DFT structures are in reasonable agreement with the experimental data ($r(\text{Si–O}) = 161.9$ pm and $\angle\text{Si–O–Si} = 148^\circ$ [38]).

Considering the D4R model $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$, Fig. 1b, it is clearly seen that the unperturbed bridging hydroxyl unit, $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$ is a better model than the widely employed $\text{H}_3\text{SiOHAlH}_3$ (Table 1). The smallest model yields an Al–O(H) bond length that is 12.4 pm too long, as compared with the D4R. There is a major difference between the D4R and the unperturbed models in the OH bond length. The D4R is more acidic than the unperturbed models, which is partly due to the larger SiOHAl angle of the former (131.1° versus 120.2°). Unfortunately, at present we cannot perform calculations at the 6-311G* level of theory for our largest model of $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$ since this would take too much computer time. Thus, we have to rely on the 6-31G*

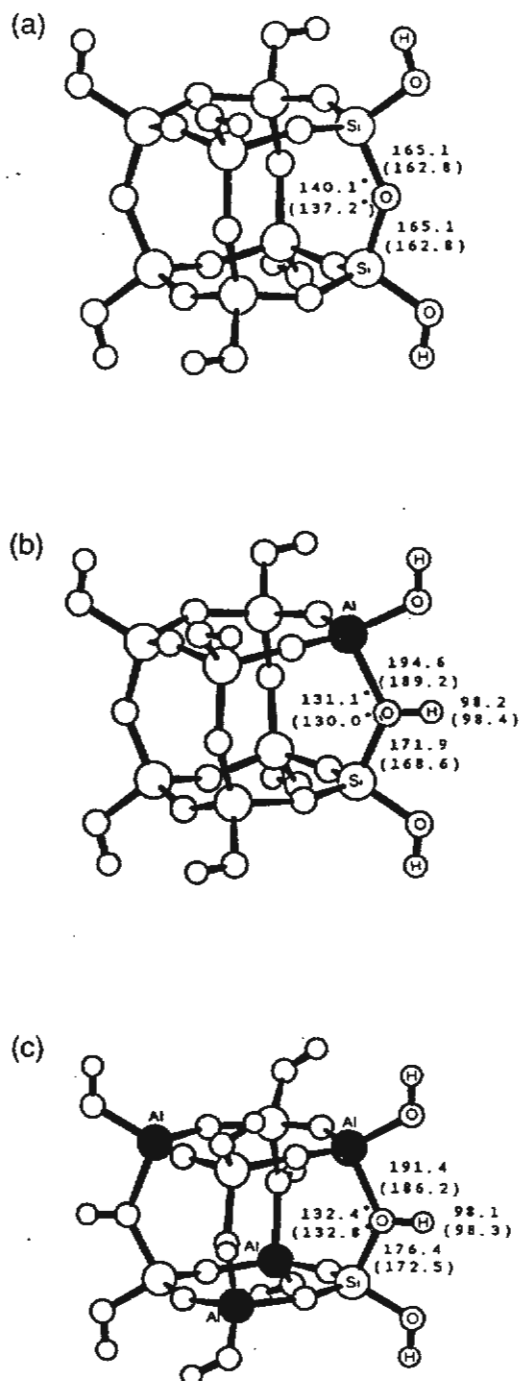


Fig. 1. Composition and variation of D4R with varying Si/Al ratio calculated at BLYP/6-31G* and VWN/6-31G* (values in parentheses). (a) $(\text{OH})_8\text{Si}_8\text{O}_{12}$, (b) $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$ and (c) $\text{H}_4(\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{12}$.

results to estimate the changes of the selected parameters i.e. Si–O, Al–O and OH bonds on expansion of the $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$ to the $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$ model. The results obtained for $(\text{OH})_3\text{SiOHAl}(\text{OH})_3$ with the 6-31G* basis set indicate that $r(\text{Al–O(H)})$ is lengthened by 0.8 pm and $r(\text{Si–O(H)})$ and $r(\text{O–H})$ are contracted by 0.9 and 0.8 pm, respectively, upon expanding the basis set from 6-31G* to 6-311G*.

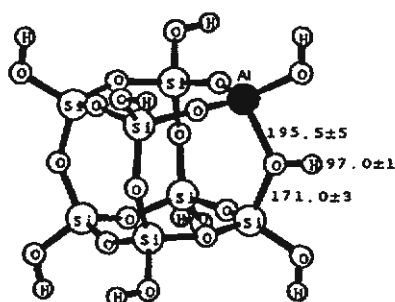
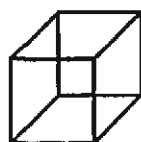
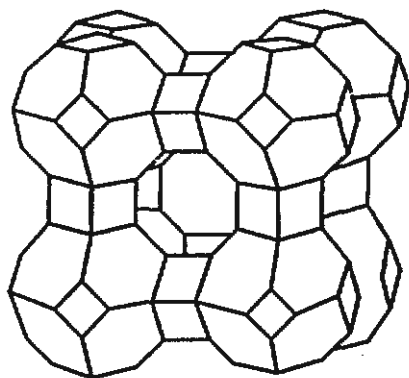


Fig. 2. Predicted local structure of Linde-type A zeolitic catalysts.

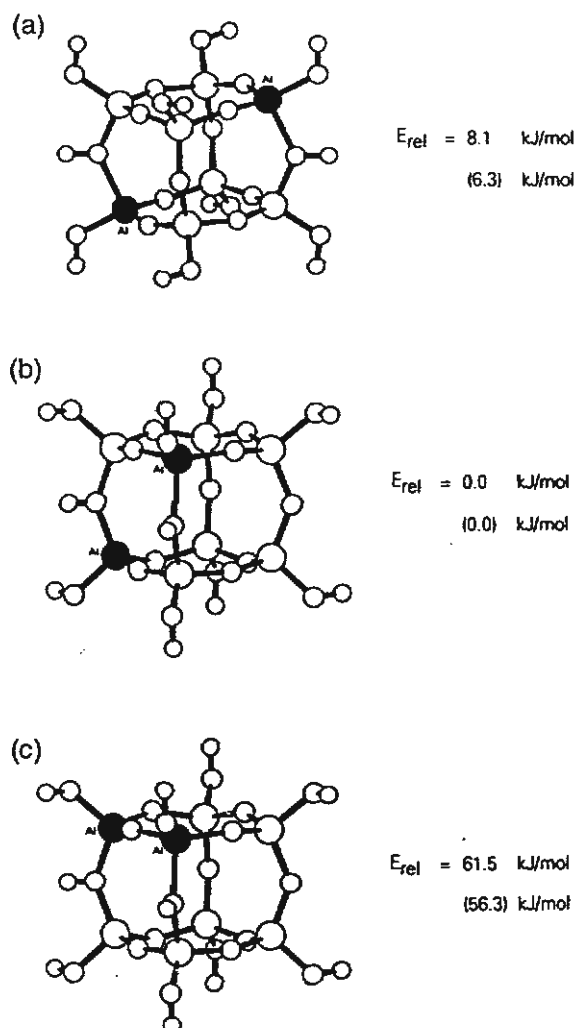


Fig. 3. Relative isomer stability of D4R within given Si/Al ratio (6/2) calculated at BLYP/6-31G* and VWN/6-31G* (values in parentheses).

Using this systematic change in bond lengths (Table 1), the local structure of $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$ can be reliably predicted (Fig. 2). The predicted results can be compared with the closely related experimental results observed by Feher et al. [39] ($r(\text{Si–O}) = 165.2$ versus 161.8 pm and $r(\text{Al–O}) = 179.5$ versus 174.5 pm).

Further support for the reliability of the $\equiv\text{Si–OH–Al}\equiv$ subunits by our calculations is given from NMR studies. Klinowski et al. have estimated the internuclear distance between aluminium and proton

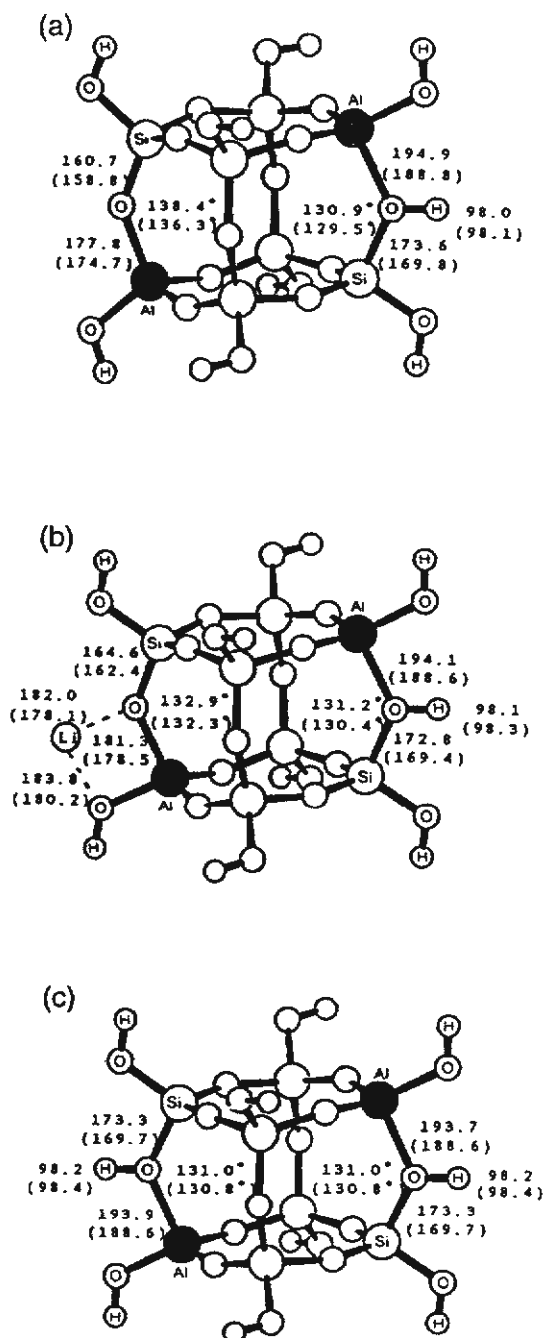


Fig. 4. Cationic effects on the catalytic acid sites of D4R calculated at BLYP/6-31G* and VWN/6-31G* (values in parentheses). (a) $\text{H}(\text{OH})_8\text{Si}_6\text{Al}_2\text{O}_{12}$, (b) $\text{LiH}(\text{OH})_8\text{Si}_6\text{Al}_2\text{O}_{12}$ and (c) $\text{H}_2(\text{OH})_8\text{Si}_6\text{Al}_2\text{O}_{12}$.

nuclei in a Brønsted acid site, $r(\text{Al-H})$, of H-faujasite [40] and H-ZSM5 [41] to be 238.0 ± 4 and 245.0 ± 4 pm, respectively, whereas our computed $r(\text{Al-H})$ distance is 243.0 pm.

Tables 3 and 4 also show another important parameter, the $r(\text{O-H})$ distance which is of prime importance for catalytic properties. From neutron diffraction studies of the acidic faujasite, Cheetham et al. [42,43] have determined the OH distance to be 100 ± 20 pm, whereas our predicted value is 97.0 ± 1 pm. The result of lattice energy minimizations is also found to be as large as 100.0 pm. Such an unrealistic deviation is partly due to the Morse potential used in the simulation as already noted by Schröder et al. [44].

In order to observe changes in the structure and bonding on going from the anionic framework site $[(\text{OH})_8\text{Si}_7\text{AlO}_{12}]^-$ to the Brønsted acid site $(\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12})$, the anionic framework was also computed. Removal of a proton from the protonated D4R strengthens the Si-O and Al-O bonds (171.9 versus 160.0 pm for Si-O and 194.6 versus 178.5 pm for Al-O). The Si-O-Al angle (138.4°) in the deprotonated D4R is larger (by 7.3°) than that at the bridging hydroxyl site (131.1°). The average Al-O bond length of the four Al-O bonds of the deprotonated D4R was calculated as 177.3 pm whereas for the protonated D4R it was found to be 179.5 pm, which can be compared with the available experimental value of 174.5 pm found by X-ray diffraction measurements of the zeolite [45].

3.2. Proton affinities

Proton affinities of Brønsted hydroxyl groups in zeolites can be used as a basis for investigating the role of both composition and structure in describing the activity of catalysts in catalytic processes.

We can evaluate the performance of the DFT procedure in predicting gas phase proton affinities by comparing with highly reliable theoretical values of G1 and coupled pair functionals and experimental results. All calculated proton affinities for different cluster models are documented in Tables 4 and 5.

Silanol. The calculated VWN/6-311G* and BLYP/6-311G* proton affinities are evaluated to be 1495.2 and 1520.4 kJ/mol. It can be seen that NLSD performs perfectly well at the BLYP/6-

311G* level, which is in good agreement with the CPF (1521 kJ/mol) [46] and G1 (1490.3 kJ/mol) [47,48] results.

Octanuclear silsesquioxanes (cf. Fig. 1a). The calculated BLYP/6-31G* and VWN/6-31G* proton affinities of $(\text{OH})_8\text{Si}_8\text{O}_{12}$ are evaluated to be 1403.0 and 1413.2 kJ/mol which is in good agreement with the recent experimental result $(1390 \pm 25 \text{ kJ/mol})$ [49]. As can be seen that the calculated proton affinity of the most widely employed model H_3SiQH does not well represent silica which yields over 100 kJ/mol above the observed data. Thus the double four-membered silicate ring is highly recommended for studying the protonation process of a surface silica.

Zeolite. The result of the proton affinity for the $\text{H}_3\text{SiOAlH}_3$ molecule with BLYP/6-311G* is encouraging. The MP2/6-31G* proton affinity yields a virtually identical value to the less expensive BLYP result (1307.9 (MP2)) (see Table 4).

For $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, BLYP/6-311G* yields a 2 kJ/mol lower value than MP2/DZP [50]. This agreement reflects the similar computed OH bond lengths at both levels of theory (96.8 pm (MP2) versus 97.1 pm (BLYP)). It is also important to study the dependence of proton affinities on the employed cluster models. On expanding the model cluster from $\text{H}_3\text{SiOHAlH}_3$ to $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$, the proton affinities are decreased by 14 and 8 kJ/mol with VWN and BLYP procedures, respectively.

For the largest model of our work, the proton affinities are calculated to be 1233.6 and 1249.1 kJ/mol with LSD and NLSD, respectively. Using the systematic deviations between BLYP/6-311G* and BLYP/6-31G*, our predicted value is estimated to be 1234 kJ/mol, which is in the range of experimentally determined values of $1192 \pm 29 \text{ kJ/mol}$ [49].

Proton affinities of three types of Brønsted hydroxyl groups in H forms of zeolites associated with different Si/Al ratios are also determined, Tables 4 and 5, (i) $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$: (PA) = 1249.1 kJ/mol, (ii) $\text{H}_2(\text{OH})_8\text{Si}_6\text{Al}_2\text{O}_{12}$: (PA) = 1272.4 kJ/mol, (iii) $\text{H}_4(\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{12}$: (PA) = 1285.2 kJ/mol. The higher the Si/Al ratio, the less the proton is constrained which results in a stronger acid strength. These results indicate that the proton affinities are

proved to be dependent on the composition (Si/Al ratio) and the structure (distribution of the $\equiv\text{Si}-\text{OH}-\text{Al}\equiv$ groups) in the zeolite framework.

3.3. The structural and compositional effects on the properties of zeolites

$\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$, 1b, with one catalytically active bridging hydroxyl group represents the "high" Si/Al zeolite corresponding to a ratio of 7. The Si–O(H), Al–O(H), and OH bond lengths at BLYP/6-31G* (VWN/6-31G*) are evaluated to be 171.9(168.6), 194.6(189.2), and 98.16(98.42) pm, respectively, where the values in parentheses are obtained at the VWN/6-31G* level. In this model the Al–O(H) bond is 0.7 pm shorter, the Si–O(H) bond 1.5 pm shorter, the OH distance is 0.36 pm longer, and the Si–O(H)–Al angle is more than 7° larger than in $\text{H}_3\text{Si}-\text{OH}-\text{Al}(\text{OH})_2-\text{OSiH}_3$. This smaller cluster is widely employed as a two-site binding model when better methods and larger basis sets can be used. Compared with $\text{H}_4(\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{12}$, 1c, with four Brønsted acid sites representing the "low" Si/Al zeolite (Si/Al = 4/4), the Si–O(H) distance in the "high" Si/Al zeolite is shorter by 4.5 pm, whereas the Al–O(H) bond length is longer by about 3.2 pm (Table 2). The net charge on the H proton, q_{H} , in compound 1b is about 0.019 higher than in compound 1c, in accordance with the larger OH distance of the former as compared to the latter. These data indicate that $\text{H}(\text{OH})_8\text{Si}_7\text{AlO}_{12}$ is more acidic than $\text{H}_4(\text{OH})_8\text{Si}_4\text{Al}_4\text{O}_{12}$. We note that absolute values from Mulliken population analysis are not very reliable, and are also basis set dependent [51]. However, comparison with closely related structures will give us certainly a very meaningful value.

$\text{H}_2(\text{OH})_8\text{Si}_6\text{Al}_2\text{O}_{12}$, 3, with three isomers (3a, 3b, and 3c) is found to be a useful cluster model for structural investigations. Isomer 3a can be viewed as the structure with the largest Al...Al distance in the double four-membered zeolite ring. The calculated energy of this isomer is 8.1 kJ/mol less stable than that of the isomer 3b, in which two Al atoms are located in the same four-membered zeolite ring. Similar results for high-silica faujasite is also observed by Schroeder et al. [52] and Limtrakul et al. [53], which is in contradiction to Dempsey's rule

(i.e. an increased stability of the Al–O–Si–O–Al linkage in a zeolite framework structure). Using the relative stability of these isomers, the well known Loewenstein's rule, which states that two tetrahedrally coordinated aluminium atoms will not locate adjacent to each other ($\equiv\text{Al–O–Al}\equiv$), 3c, has been once again confirmed by us. Results of all the three isomers considered here show that the effects of local environment (other than chemical contents) are explicitly included.

On the basis of the charges on the hydroxyl proton, the OH bond lengths, the ionicity of the OH bonds and the proton affinities (see Tables 4 and 5), the Brønsted acidity is proved to be dependent on the number of aluminium atoms and the different environment of the $\equiv\text{Si–OH–Al}\equiv$ groups in the zeolite framework.

3.4. Cationic effect on structure and bonding of zeolites

The selected geometrical parameters, proton affinities, charges on protons, bridging OH bonds of the $\text{H}_2(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ and $\text{LiH}(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$, zeolite clusters are given in Tables 2–5, and illustrated in Fig. 4. Comparison of H^+ and Li^+ cations indicates that the Al–O bond is lengthened by 15.9 and 3.5 pm for H^+ and Li^+ ions complexes, respectively. The Si–O bond is also weakened: it is about 12.6 pm for $\text{H}_2(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ and 3.9 pm for $\text{LiH}(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$. The Al–O–Si bridging angles are more bent in $\text{H}_2(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ than in $\text{LiH}(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ (131.0° versus 132.9°). The OH bond is evaluated to be 98.1 pm whereas the O...Li bond is 182.0 pm. The marked difference between these cations is that the H^+ is singly bonded while the Li^+ is doubly bonded to the zeolitic framework structure.

The proton affinities of Brønsted OH groups in the zeolitic framework are 1272.4 and 1279.3 kJ/mol for $\text{H}_2(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$ and $\text{LiH}(\text{HO})_8\text{Al}_2\text{Si}_6\text{O}_{12}$, respectively, which corresponds with the decreased OH bond lengths (see Tables 4 and 5). These results indicate that the acid strength of the OH groups within the zeolitic framework is also determined by the presence of cations, in addition to the compositional and structural effects mentioned in Section 3.3; thus, the acid strength depends on the amount of

electron density transferred from the anionic framework to the cation which balances its negative charges.

4. Conclusions

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 $(\text{OH})_8\text{H}_y\text{Al}_x\text{Si}_{8-x}\text{O}_{12}^{(x-y)-}$ ($x, y = 0, 1, 2, 4$) and the silica model $(\text{OH})_8\text{Si}_8\text{O}_{12}$ 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 SiOHAl 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.

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Structures and potential energy surface of Faujasitic zeolite/water

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Structures and potential energy surface of Faujasitic zeolite/water

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Abstract

The structures and the potential energy surface of the system faujasitic zeolite/water have been investigated by Hartree–Fock, second-order Moller–Plesset (MP2) and by the density functional theory (DFT) calculations, using five basis sets 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311 + G(d,p). The DFT calculations employ the Becke–3–Lee–Yang–Parr (B3LYP) and Becke–Lee–Yang–Parr (BLYP) density functional, and, for comparisons, the local density approximation with the Vosko–Wilk–Nusair (VWN) functional. The B3LYP approach is found to yield better agreement with the corresponding experimental results than the VWN and BLYP functionals. The B3LYP and MP2 levels of theory yield basically the same results. Results of B3LYP with a 6-311 + G(3df,2p) basis set are also very close to those of the very accurate coupled pair functional (CPF) method. Also proton affinities (PA) computed by B3LYP reproduce the corresponding CPF and G1 results very well. The predicted PA of faujasitic catalyst is estimated to be 294 ± 3 kcal/mol, which is in the range of the experimentally determined value of 291–300 kcal/mol. The interaction of faujasite catalyst with water has revealed that the structures can be stabilized by the formation of two hydrogen bonds with water molecules adsorbed at the bridging hydroxyl groups which can act either as a proton acceptor or as a proton donor. Comparison of the faujasite complexes with silanol and hydrogen halides has demonstrated that the faujasitic zeolite is a strong acid. The potential energy surfaces of faujasite zeolite/water has been investigated and analytical interaction potentials have been derived.

1. Introduction

Zeolites are microporous materials widely investigated for their numerous industrially important applications, e.g. as sorbents, catalysts, and molecular sieves [1–8]. The zeolitic framework structures of crystalline aluminosilicates present regular cavities

and open channels of molecular dimensions which allow molecular probes to interact with the Brønsted acidic sites. Their catalytic property of zeolite is involved with the site originating from bridging hydroxyl groups in zeolitic catalysts.

For understanding the catalytic processes [9–18] it is of prime importance to know the structure and properties of Brønsted acidic sites, as well as the potential energy surface of the adsorbate/zeolite system.

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Density functional theory (DFT) has been increasingly exploited to study various chemical systems [19–24]. Requiring less computational effort, DFT results compare well with high level *ab initio* calculations and reliable experimental data. The quality of DFT results is determined largely by the density functional employed. The Becke–3–Lee–Yang–Parr (B3LYP) functional, recently introduced by Stephens et al. [25], a modification of the BLYP functional [26], is often regarded as one of the best available choices. Bauschlicher and Partridge [27], and other groups [28] have demonstrated that this density functional can be employed to yield accurate results about molecular structures, atomic energies and harmonic vibrational frequencies for a large set of small molecules. To the best of our knowledge, no systematic investigations of the faujasitic zeolite properties have yet been performed with this functional.

In the present work, the catalytic properties of zeolites have been investigated for the first time via DFT employing B3LYP and the basis sets ranging from 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p), to 6-311 + G(3df,2p) with the aims of: (a) comparing the changes in structures and bonding on going from the smallest possible model to the more realistic cluster models; (b) determining the influence of the structure on the catalytic properties of zeolites; (c) predicting a local solid acid catalyst site of zeolite and comparing the structural parameters with available experimental data; (d) obtaining the potential energy surface of system zeolites/water and (e) investigating the effects of the size of the basis set.

2. Method and models

We employed different clusters, $\text{AlSi}_{10}\text{O}_{14}\text{H}_{17}$, $\text{Al}(\text{OSiH}_3)_4\text{H}$, $\text{H}_3\text{SiOHAlH}_3$ and H_3SiOH , illustrated in Fig. 1b–e, as the representative models of zeolites. We consider that to simulate the local framework of these clusters correctly, at least four silicon atoms and one aluminium atom have to be included in the model clusters. In the model employed, the dangling bonds of ‘surface’ oxygen atoms are saturated by hydrogen atoms. The $\text{Al}(\text{OSiH}_3)_4\text{H}$ cluster, denoted as ‘cluster C’ (Fig. 1c), represents the active acidic site of zeolite. In this model the dangling bonds of the Si atoms are terminated by H

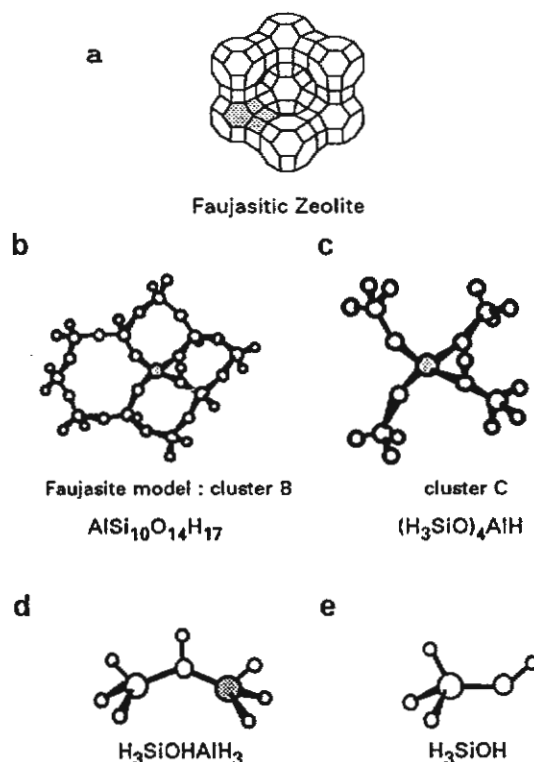


Fig. 1. Cluster models of faujasite zeolite.

atoms with a fixed Si–H bond length of 1.487 Å, and the Si–H bonds are aligned with the corresponding Si–O bonds of the structure of faujasite [29]. The local active site structure has been achieved by allowing the AlO_4H unit to relax, while the remainder SiH_3 groups are being fixed. In order to observe the effect of full relaxation, this cluster is compared to its fully optimized $\text{Al}(\text{OSiH}_3)_4\text{H}$ structure.

The $\text{AlSi}_{10}\text{O}_{14}\text{H}_{17}$ cluster, denoted as ‘cluster B’ (Fig. 1b) consists of three four-membered rings (4MR) and one six-membered ring (6MR), representing the ‘high’ Si/Al zeolite (Si/Al = 10). This cluster can also be exploited to investigate the structural and compositional influences on the catalytic properties of faujasite.

Full geometry optimization of the mentioned cluster models was carried out with the DFT methods employing the B3LYP density functional. Again the basis sets 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p), and 6-311 + G(3df,2p) were used. Additionally, calculation with the Becke–Lee–Yang–Parr

(BLYP) [26] and Vosko–Wilk–Nusair (VWN) [30] functionals were performed for some models. All density functional computations were carried out using the program Gaussian-94 [31].

For the HF calculations we employed the TURBOMOL code [32,33] which is based on the direct SCF method of Almloef et al. [34]. In order to obtain the more reliable structures of zeolites, the correlated calculations were also included for the smallest model. Geometry optimization was terminated when the gradients norm with respect to internal coordinates was less than $10^{-3} E_h/a_0$. The energy change was then below 5×10^{-6} au.

The computations were carried out using an SGI power challenge XL computer at the Innsbruck University computing center, and DEC AlphaStation 250/4 266 and HP 9000/700 workstations at the Laboratory for Computational and Applied Chemistry at Kasetsart University.

3. Results and discussion

3.1. Structures

Table 1 illustrates the results for H_3SiOH and H_3COH structural parameters computed at different levels of theory. It is clearly seen that B3LYP density functional results are superior to the BLYP and VWN. The B3LYP and MP2 levels yield basically the same results, the B3LYP/6-311 + G(3df,2p) is also very close to the most accurate CPF [35] structure given in Table 1.

3.1.1. Silanol

B3LYP bond lengths involving bridging OH are virtually identical to CPF [35] value (cf. Table 1). For the Si–O bond length again B3LYP yield an excellent value to CPF, while the corresponding value at the BLYP level is about 0.02 Å too long. Si–O–H bond angles calculated with all DFT approaches compare well with MP2 and CPF data. Again a good agreement takes place for its anion, H_3SiO^- , where B3LYP values of Si–O = 1.580 Å, Si–H = 1.531 Å and O–Si–H = 117.1° are compared to the CPF values of 1.563, 1.529 and 117.3°, respectively. The same trends are also observed for methanol (cf. Table 1).

3.1.2. Zeolite

The extension of 6-311G(d) basis set with the polarization functions on the hydrogen atoms influences the B3LYP structure only slightly. The O–H, Si–O, and Al–O bonds differ by less than 0.001 Å, the SiO(H)Al and Si–O–H bond angles differ by about less than 0.5° (Table 2). These results indicate that the B3LYP structural parameters are converged for the cluster C, $Al(OSiH_3)_4H$ at B3LYP/6-311G(d) level of theory and the extension of the basis set will not lead to different structure results.

Comparing the cluster C, $Al(OSiH_3)_4H$, with the widely employed model cluster, $H_3SiOHAlH_3$ (Table 2), it is clearly seen that the smallest model yields an Al–O bond length that is too long. On increasing the levels of basis set from 6-31G(d) to 6-311G(d,p), the Al–O and Si–O bond lengths of the cluster models increase, as tabulated in Table 2.

Table 1
Optimized parameters for the molecular models of H_3SiOH and H_3COH at different levels of theory with the 6-311 + G(3df,2p) basis set (bond distances in Å, bond angles in degrees)

Method	H_3SiOH			H_3COH		
	r_{SiO}	r_{OH}	$\angle_{Si-O-H}$	r_{CO}	r_{OH}	$\angle_{C-O-H}$
HF	1.630	0.937	121.4	1.398	0.938	110.3
VWN	1.644	0.967	118.9	1.400	0.969	109.2
BLYP	1.673	0.968	118.2	1.439	0.971	108.5
B3LYP	1.654	0.958	119.3	1.421	0.960	109.1
MP2	1.655	0.957	118.6	1.418	0.959	108.5
CPF ^a	1.650	0.958	117.7	1.419	0.959	108.1
Expt.	—	—	—	1.421	0.963	108.1

^a 6s, 5p, 2d, 1f/ 5s, 3p, 2d, 1f/ 3s, 2p basis set.

The results obtained with 6-311G(d,p) basis sets show that the Al–O bond lengths is contracted by 0.11 Å, while the S–O bond length is lengthened by 0.013 Å upon expanding the model cluster from $\text{H}_3\text{SiOHAlH}_3$ to $\text{Al}(\text{OSiH}_3)_4\text{H}$.

Further support for the reliability of using the cluster C, $\text{Al}(\text{OSiH}_3)_4\text{H}$ in computation is given by the results of NMR studies: the Al...H distance of H-faujasite has been estimated to be 2.380 ± 0.04 Å [36], whereas our computed distances in the fully optimized cluster C are 2.400 and 2.416 Å with 6-31G(d) and 6-31G(d,p) basis sets, respectively. The calculated distances of $\text{H}_3\text{SiOHAlH}_3$ are 2.539 Å (6-31G(d)) and 2.537 Å (6-31G(d,p)).

Table 2 also provides other vital parameters, including the O–H distance which plays an important role in catalytic properties. The hydroxyl O–H bond length derived from neutron diffraction measurement of acidic faujasite [37,38] is 1.000 ± 0.02 Å. Our O–H bond lengths (Table 2) are in good agreement with the previously predicted O–H bond distance [39].

In order to investigate changes in structure and bonding on going from the anionic framework site to Brønsted acid site, removal of a proton from the cluster C, $\text{Al}(\text{OSiH}_3)_4\text{H}$ strengthens the Si–O(H)

and Al–O(H) bonds (1.729 versus 1.602 Å for Si–O(H), and 1.961 versus 1.758 Å for Al–O(H)). The Si–O–Al angle in the deprotonated cluster is larger by 50.9° than the bridging $\equiv \text{SiO(H)}-\text{Al} \equiv$ angle (128.0°). The average Al–O bond length of the four Al–O bonds of the neutral form was calculated to be 1.778 Å, whereas the anionic framework it was found to be 1.755 Å, which is in good agreement with the available experimental value of 1.745 Å determined by X-ray diffraction study of zeolite [40]. The use of the 6-31G(d) basis set in the DFT prediction of the faujasite structure also yields good results and will be the basis set of choice in B3LYP calculations on much larger systems.

In order to know more about the nature of Brønsted acid site in Faujasitic zeolite, the larger cluster with three 4-membered oxygen rings and 6-membered oxygen ring around the active site has also been included (see Fig. 1b). In this 'cluster B' model, we have permitted full optimization of the site, AlO_4H , constraining the rest of the cluster fixed at the structure of faujasite [29]. In doing so, the 'cluster B' can lead to a structure that can mimic the real faujasitic zeolite framework, since full optimization of (sub-) structures can some times lead to wrong results, as noted by Sauer [39]. The results

Table 2
B3LYP optimized geometrical parameters computed for $\text{H}_3\text{SiOHAlH}_3$, $(\text{H}_3\text{SiO})_4\text{AlH}$ (cluster C), and $\text{AlO}_4\text{Si}_{10}\text{H}_{17}$ (cluster B) (distances in Å, angles in degrees).

System	Basis set	r_{OH}	$r_{\text{SiO(H)}}$	$r_{\text{AlO(H)}}$	r_{AlH}	$\langle r_{\text{AlO(H)}} \rangle$	$\angle_{\text{Si-O-H}}$	$\angle_{\text{SiO(H)Al}}$
$\text{H}_3\text{SiOHAlH}_3$	6-31G(d)	0.969	1.716	2.037	2.539	—	117.7	132.2
	6-31G(d,p)	0.966	1.715	2.037	2.537	—	118.0	131.9
	6-311G(d)	0.962	1.714	2.037	2.533	—	119.1	130.9
	6-311G(d,p)	0.963	1.715	2.041	2.535	—	118.5	131.7
	6-311 + G(d,p)	0.963	1.718	2.048	2.543	—	118.7	131.3
$\text{Al}(\text{OSiH}_3)_4\text{H}^a$	6-31G(d)	0.971	1.732	1.964	2.505	1.772	118.8	128.4
	6-31G(d,p)	0.968	1.731	1.964	2.499	1.772	119.2	128.1
	6-311G(d)	0.964	1.729	1.961	2.499	1.770	119.4	127.6
	6-311G(d,p)	0.964	1.729	1.961	2.499	1.769	119.2	128.0
$\text{Al}(\text{OSiH}_3)_4\text{H}^b$	6-31G(d)	0.974	1.733	1.948	2.400	1.778	117.2	123.5
	6-31G(d,p)	0.970	1.732	1.947	2.416	1.777	117.5	123.0
	6-311G(d)	0.962	1.734	1.936	2.556	1.774	118.4	121.7
	6-311G(d,p)	0.963	1.735	1.938	2.561	1.775	117.9	121.8
$\text{AlSi}_{10}\text{O}_{14}\text{H}_{17}^a$	6-31G(d)	0.972	1.729	1.956	2.508	1.773	117.6	128.8
	6-311G(d,p)	0.965	1.726	1.953	2.499	1.770	117.9	128.7

^a Partial optimization.

^b Full optimization.

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

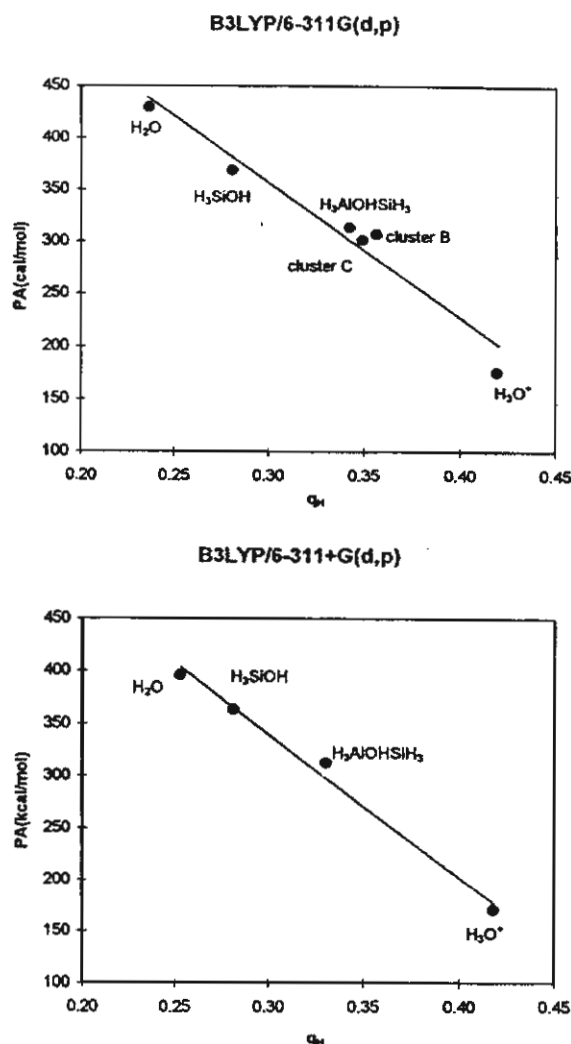


Fig. 2. The proton affinities of a set of structurally related molecules (HO–H, H_3COH , H_3SiO-H , $H_3SiOHAlH_3$, different types of zeolite cluster models, and H_3O^+) as a function of the net charge on the proton, q_H .

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

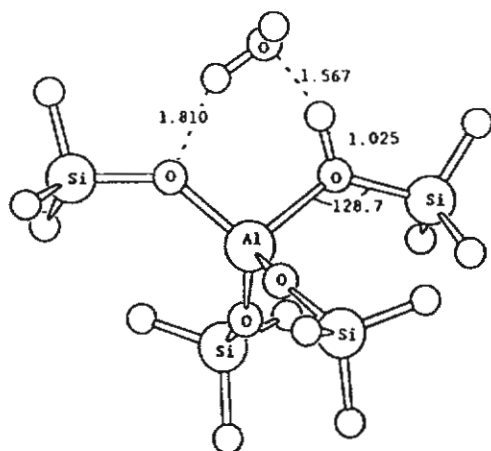


Fig. 3. Schematic representation of molecular model for the cluster C, $\text{Al}(\text{OSiH}_3)_4/\text{H}_2\text{O}$.

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-

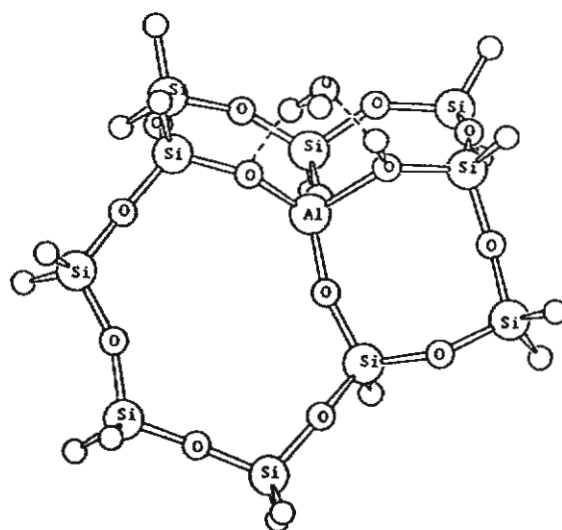


Fig. 4. Schematic representation of molecular model for the faujasitic zeolite/water.

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			

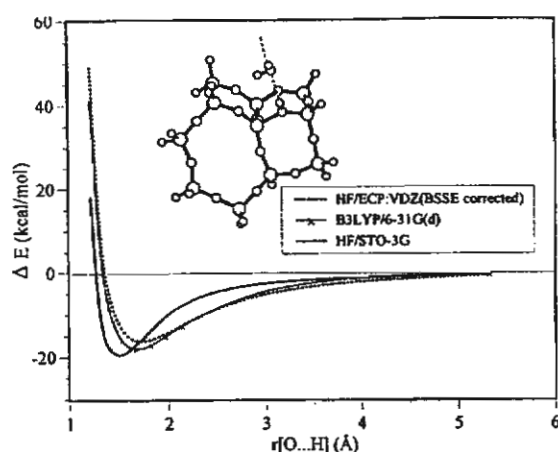


Fig. 5. Comparison of adsorption energies from B3LYP/6-31G(d), HF/ECP-VDZ, and HF/STO-3G for the faujasitic zeolite/water system.

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

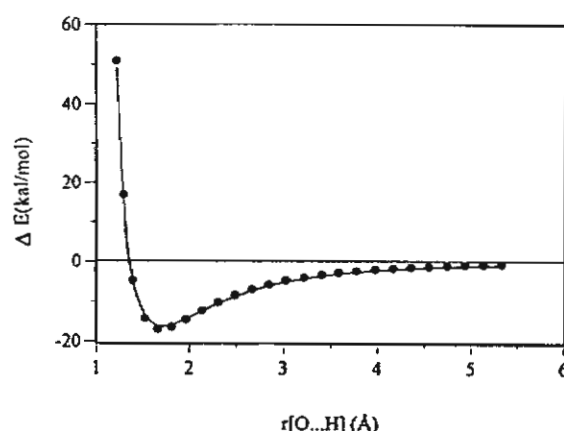


Fig. 6. Comparison between ab initio energy surface data (Δ) and analytical potential curves (lines) for the configuration presented in Fig. 4.

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

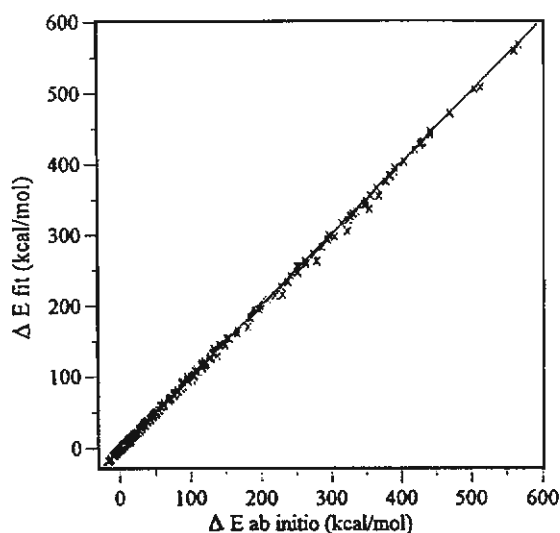


Fig. 7. Correlation between interaction energy ($\Delta E_{\text{ab initio}}$) from the ab initio calculations and those derived from analytical expressions as described in the text.

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.

Acknowledgements

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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

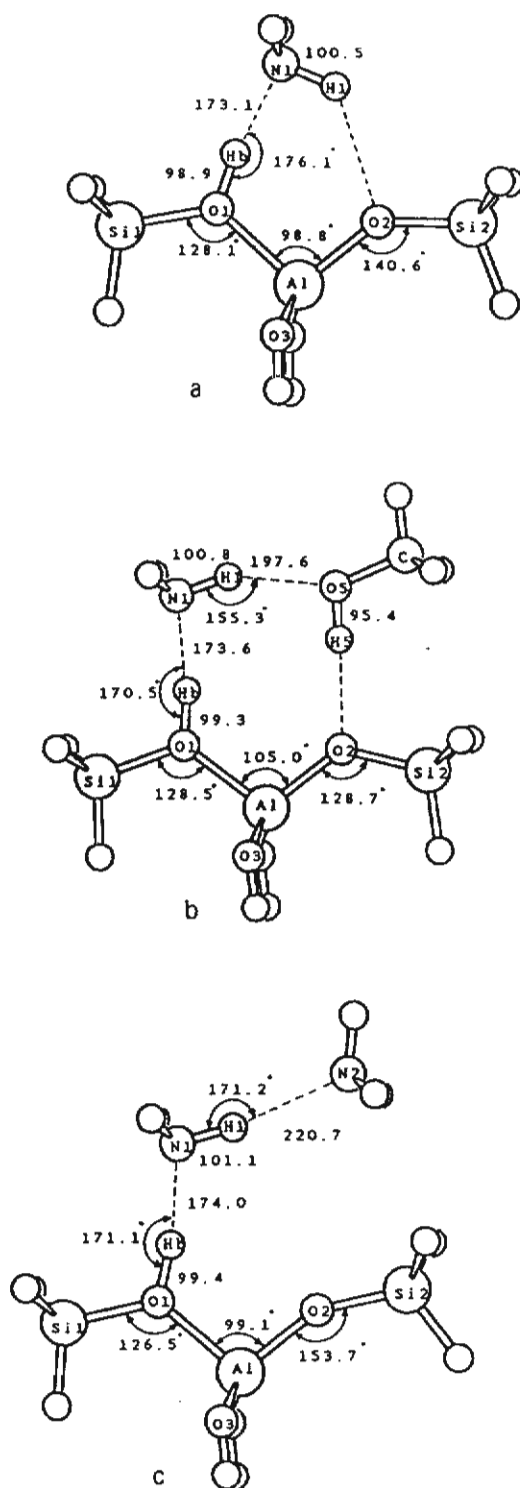
1. Introduction

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

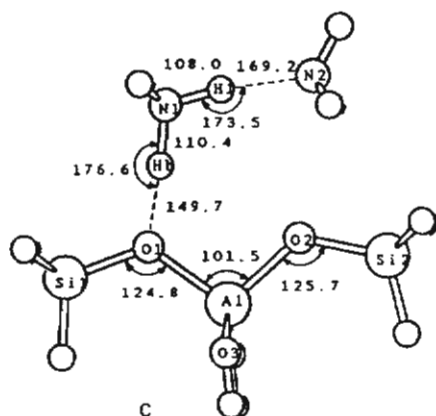
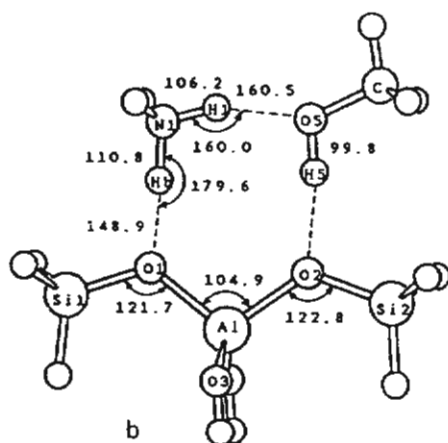
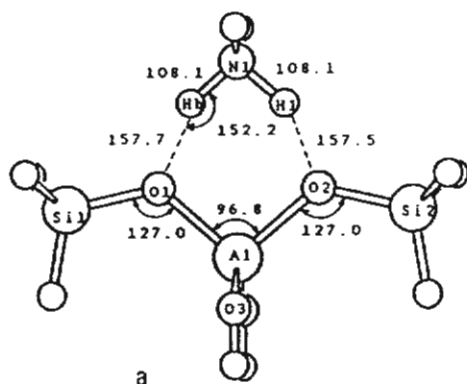
We employed the adsorption clusters illustrated in Figs. 1–3 as the models of the probed molecules' adsorption on zeolites $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3][\text{CH}_3\text{OH}]$, and $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{OH}][\text{NH}_3]$, and their possible ion-pair species. The alkaline-exchanged systems, $[\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3][\text{CH}_3\text{OH}]$ and $[\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{OH}][\text{NH}_3]$ are modelled for the coadsorption of methanol and ammonia on Na-exchanged zeolites (see Fig. 4 and Fig. 5). The isolated Na-complexes, $\text{Na}(\text{I})/[\text{NH}_3][\text{CH}_3\text{OH}]$, and $\text{Na}(\text{I})/[\text{CH}_3\text{OH}][\text{NH}_3]$ 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 $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{OH}]$, $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{OH}]_2$, $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3]$, $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]_2$. 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 $5 \times 10^{-6} \text{ a.u.}$

The computations were carried out using DEC

Fig. 1. Schematic representation of molecular models for the systems Brønsted acid site $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]$: (H-Z): a) $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3]$; b) $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3][\text{CH}_3\text{OH}]$; c) $[\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3]_2$.



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) $[H_3SiOAl(OH)_2OSiH_3]^{-(Z^-)}/[NH_4]^+[NH_3]$.

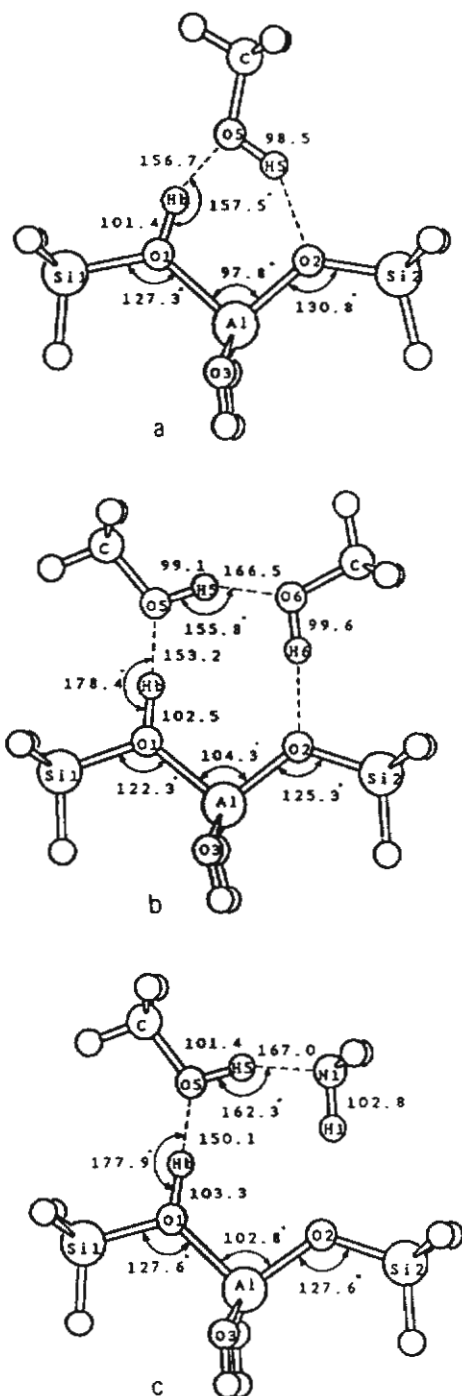


Fig. 3. Schematic representation of molecular models for the systems Brønsted acid site $[H_3SiOHAl(OH)_2OSiH_3]$ (H-Z): a) $[H_3SiOHAl(OH)_2OSiH_3]/[CH_3OH]$; b) $[H_3SiOHAl(OH)_2OSiH_3]/[CH_3OH]$; c) $[H_3SiOHAl(OH)_2OSiH_3]/[CH_3OH][NH_3]$.

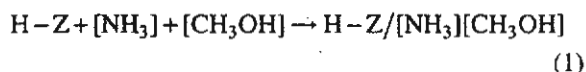
zeolitic proton onto the adsorbed ammonia. The Brønsted OH bonds of zeolitic catalysts are lengthened for the $H-Z/[NH_3][CH_3OH]$ as compared to the corresponding binary complex of $H-Z/[NH_3]$ (99.3 vs. 98.9 pm, see Fig. 1a,b).

3.1.2. Ion-pair formation

The optimized structure parameters of $[H_3SiOHAl(OH)_2OSiH_3]^-/[NH_4]^+$, $[H_3SiAl(OH)_2SiH_3]^-/[NH_4]^+$ $[NH_3]$ and $[H_3SiOHAl(OH)_2SiH_3]^-/[NH_4]^+[CH_3OH]$ are reported. For the system $[H_3SiOHAl(OH)_2SiH_3]^-/[NH_4]^+$, 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 $[H_3SiOHAl(OH)_2SiH_3]/[NH_3][CH_3OH]$ to $[H_3SiOHAl(OH)_2SiH_3]^-/[NH_4]^+[CH_3OH]$ 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

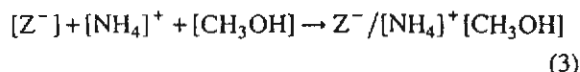


The energy for reaction (2a) is called the deprotonation energy and the protonation energy is represented by

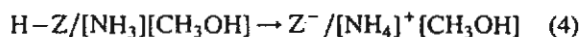
Table 1
HF/6-31G* and B3LYP/6-31G* optimized structure parameters for $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]$, $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]^+$, $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]_2$ and $\text{H}_3\text{SiOHA}(\text{OH})_2\text{OSiH}_3/[\text{NH}_3]^+[\text{CH}_3\text{OH}]$

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.



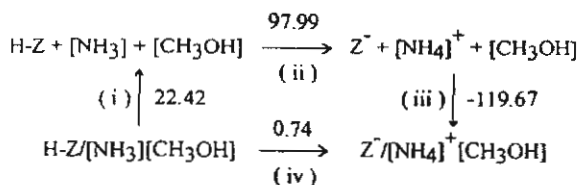
The reaction energies of each step are summarized in the schematic diagram in Scheme 1. From the reaction energies (see Table 4) of all the complexes, we can propose the reaction mechanism of coadsorption of methanol and ammonia on H-Z as depicted in Scheme 2.

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

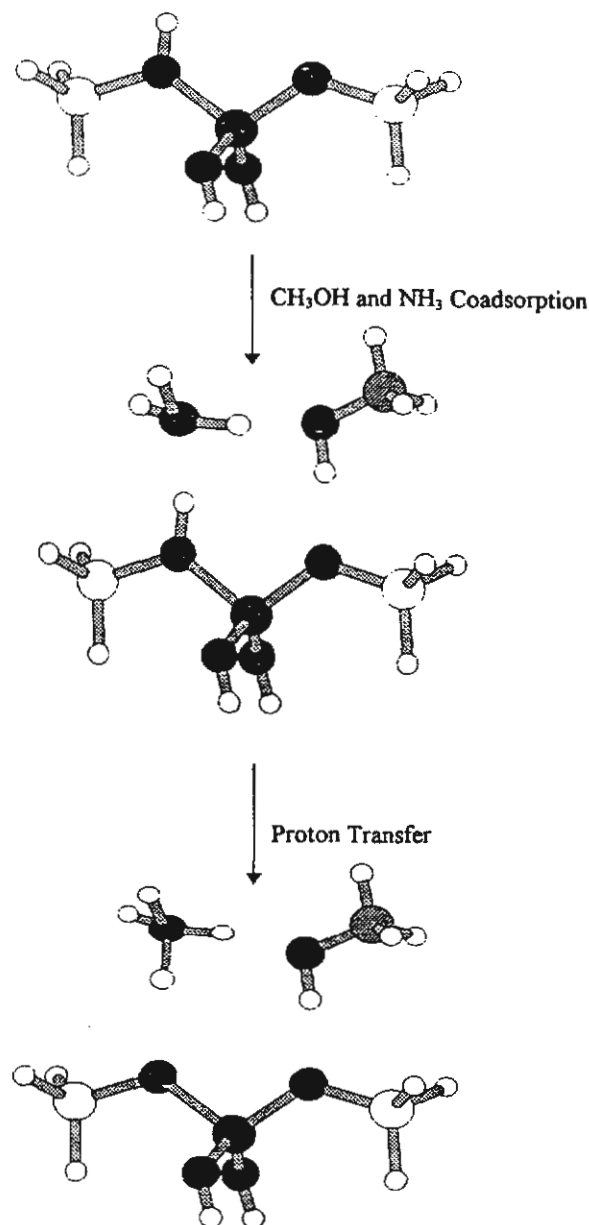
The effect of the cation on the structure of zeolitic catalysts and the coadsorption process is investigated at B3LYP/6-31G* and HF/6-31G* levels of theory. The fully optimized geometry structures for Na-Z, Na-Z/[NH₃], Na-Z/[CH₃OH], Na-Z/[NH₃][CH₃OH] and Na-Z/[CH₃OH][NH₃] are documented in Table 3.

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.



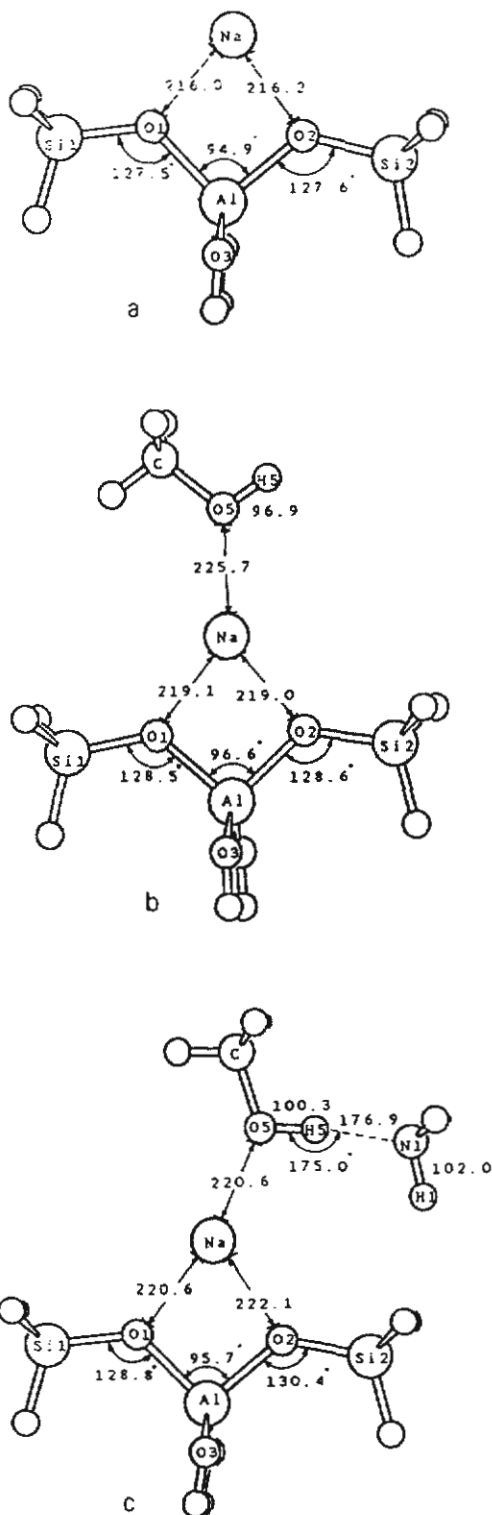
Scheme 2.

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 $\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3$, $\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_2[\text{NH}_3]$, $\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_2[\text{CH}_3\text{OH}]$, $\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_2[\text{CH}_3\text{OH}][\text{NH}_3]$ and $\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_2[\text{NH}_3][\text{CH}_3\text{OH}]$

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.

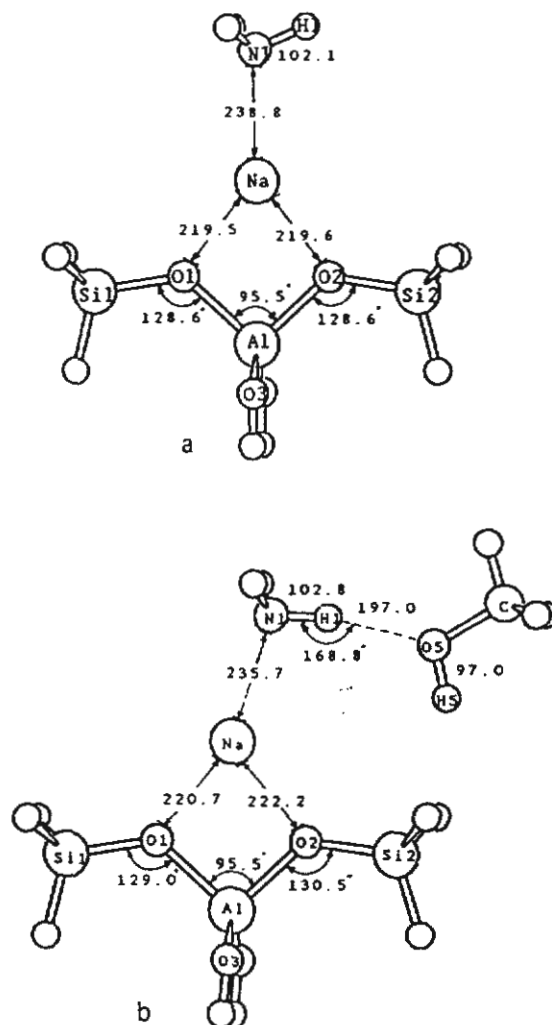
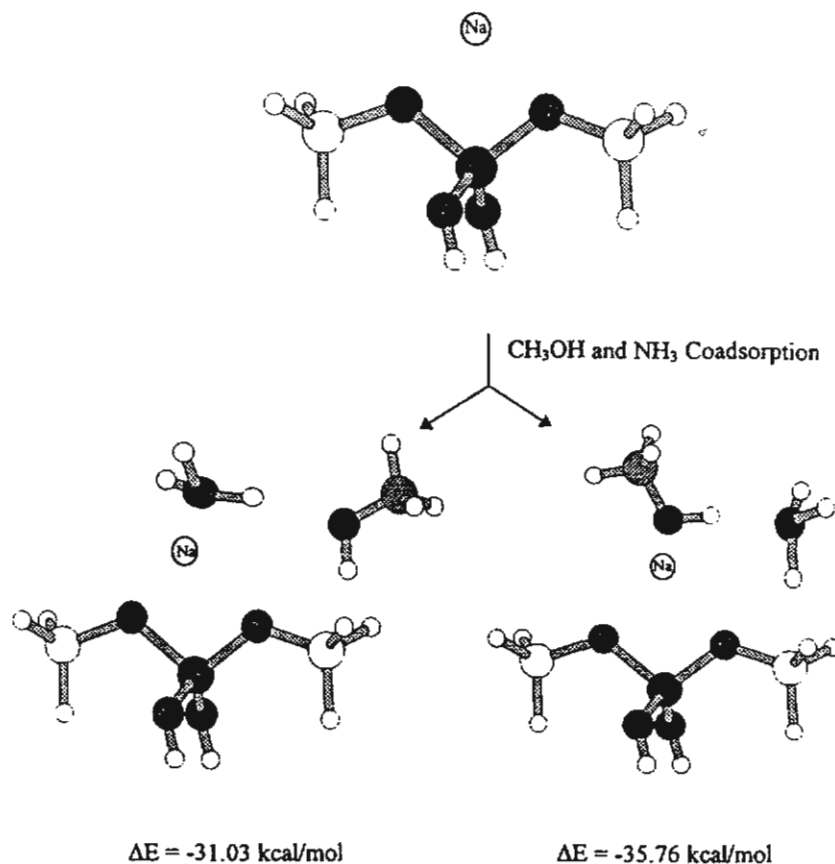


Fig. 5. Schematic representation of molecular models for the systems: a) $[\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3]$; b) $[\text{H}_3\text{SiONaAl}(\text{OH})_2\text{OSiH}_3]/[\text{NH}_3][\text{CH}_3\text{OH}]$.

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.

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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.

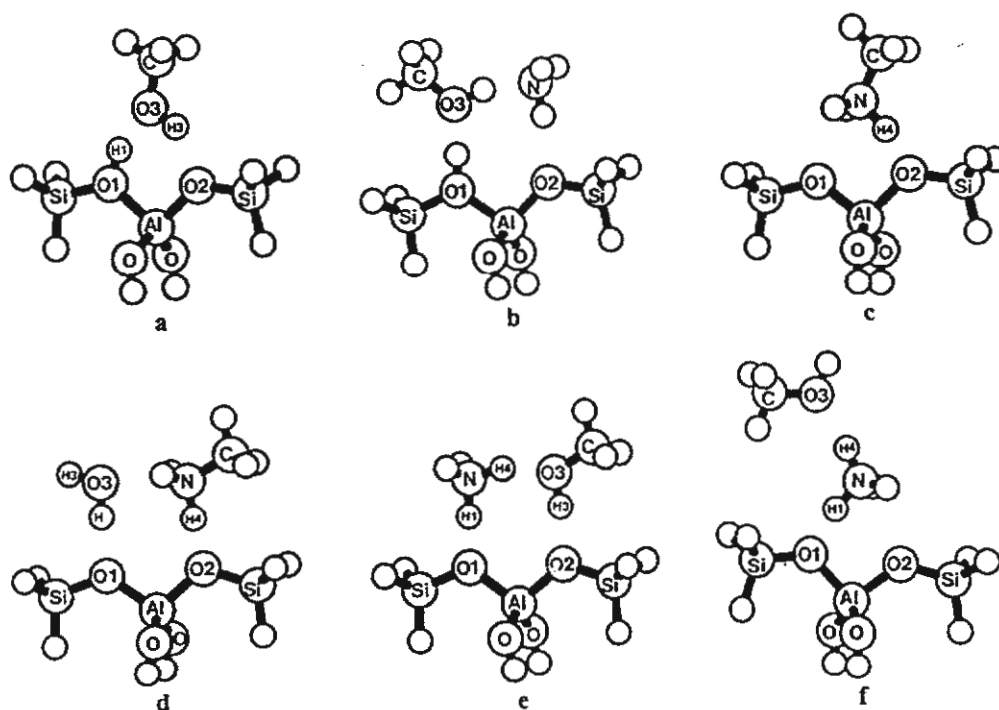


Figure 1. Optimized structures for different adsorption complexes ($\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3$ (3T), $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3/\text{CH}_3\text{OH}$ (1a), $\text{H}_3\text{SiOHAl}(\text{OH})_2\text{OSiH}_3/\text{CH}_3\text{OH}/\text{NH}_3$ (1b), $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]^-/[\text{CH}_3\text{NH}_3]^+$ (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 $MeNH_2$.

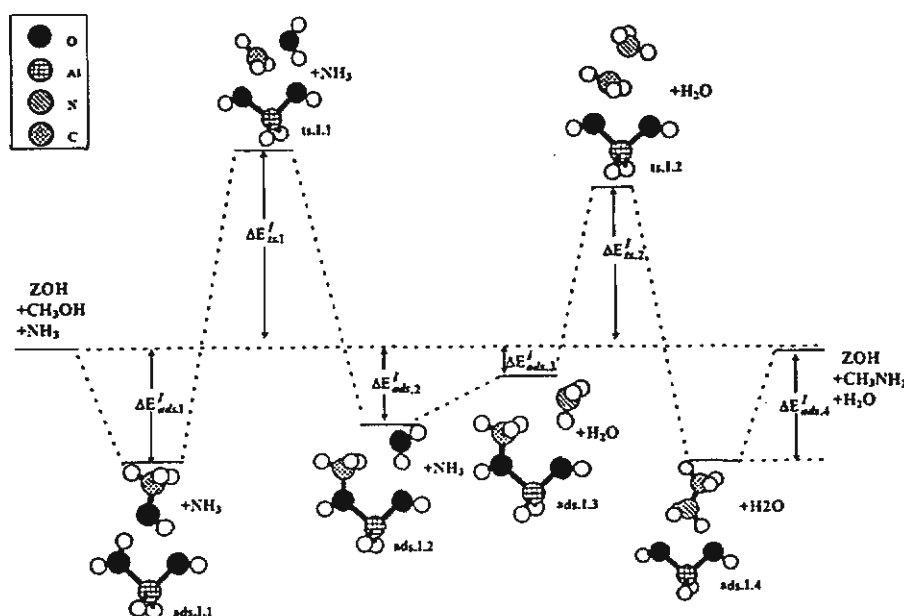


Figure 2. Path I: One CH_3OH is adsorbed on ZOH , $ZOCH_3$ generated, and the interaction of NH_3 with $ZOCH_3$ to yield methylamine.

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 $[\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3]/[\text{CH}_3\text{NH}_2]$ 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.

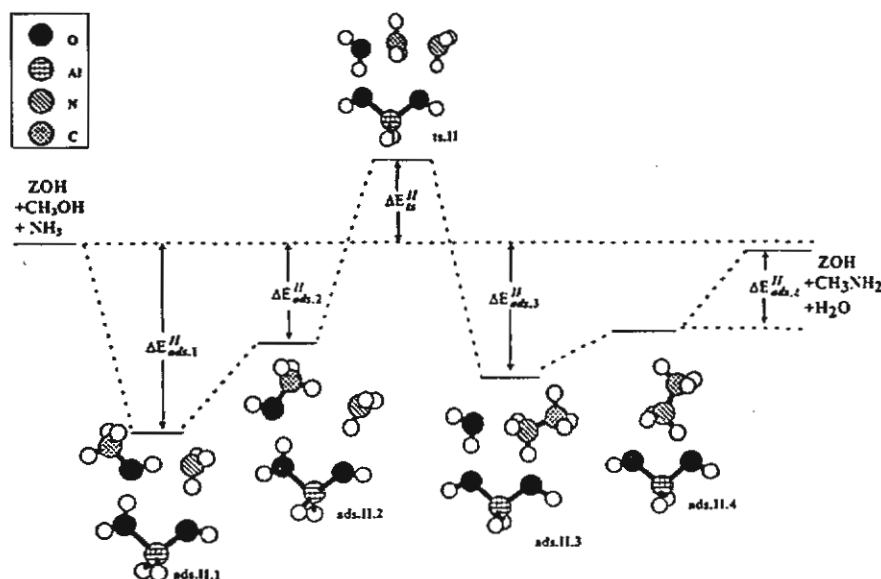


Figure 3. Path II: Simultaneous adsorption of CH_3OH and NH_3 on ZOH, generating a transition state structure for methylamine formation.

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.

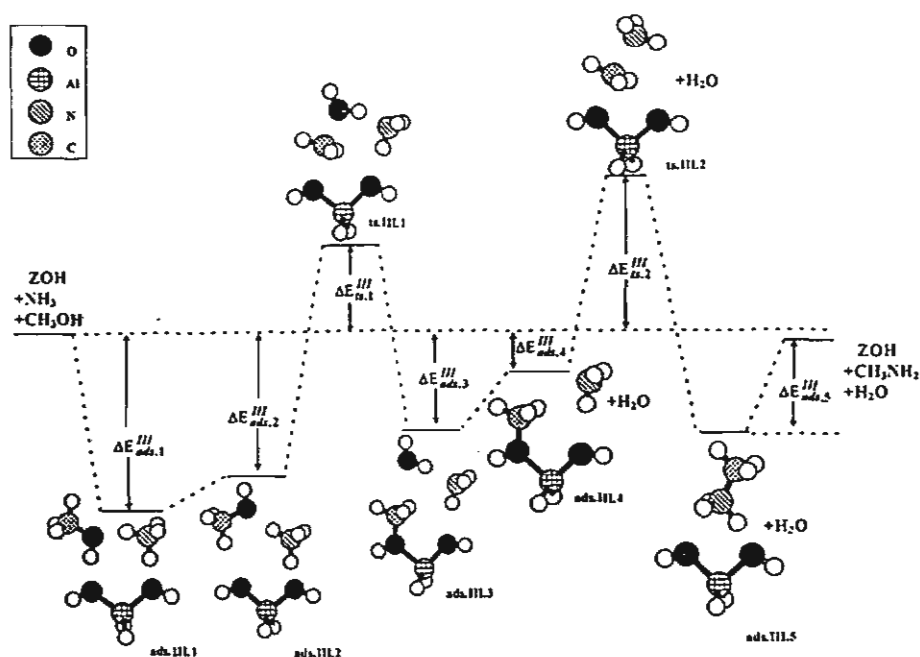


Figure 4. Path III: Both CH₃OH and NH₃ are adsorbed on ZOH, ZOCH₃ is generated via S_N2 with the help of the promoter NH₃, and the interaction of NH₃ with ZOCH₃ to yield methylamine formation.

The fourth reaction pathway for methylamine formation: Eley-Rideal mechanism where only NH₃ is adsorbed on the Brønsted acid site, followed by CH₃OH binding to the adsorbed NH₃, generating TS structure.

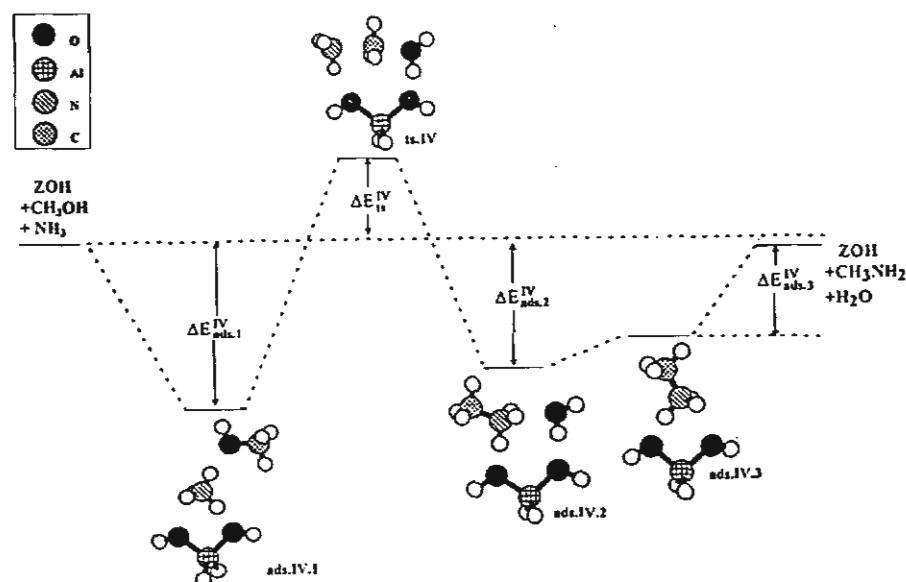


Figure 5. Path IV: Only NH₃ is adsorbed on the Brønsted acid site, CH₃OH is bound to the adsorbed NH₃, generating transition state structure which is converted to methylamine formation.

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

จำรัส ลิ้มตระกูล

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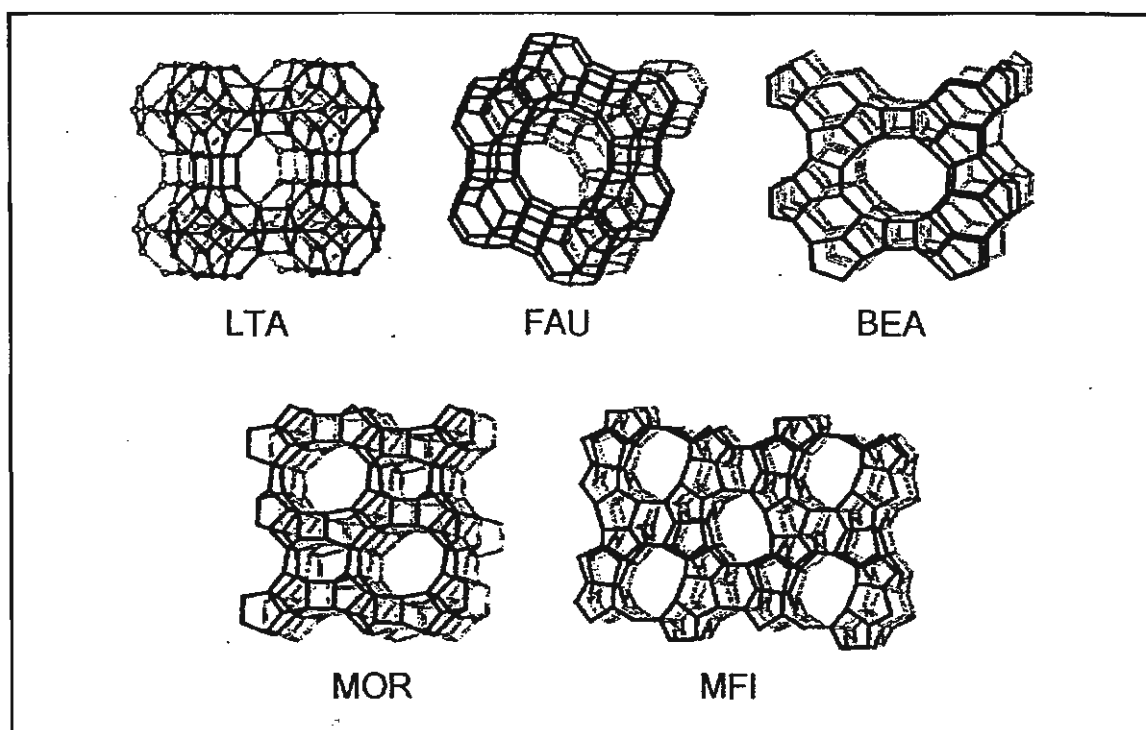
ซีโอไลต์คืออะไร ? มีสมบัติอย่างไร?

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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
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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)

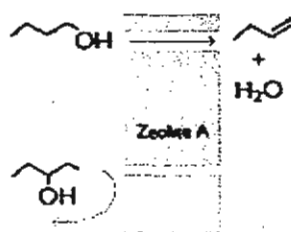
นักเคมีทำการสังเคราะห์สารที่มีโครงสร้างคล้ายซีโอไลต์ และเรียกสารกลุ่มนี้ว่า molecular sieves จากการสังเคราะห์และออกแบบโครงสร้างจึงทำให้สารดังกล่าวมีคุณค่าและ คุณประโยชน์ที่สำคัญในอุตสาหกรรมปิโตรเคมี เช่น ใช้เป็นตัวเร่งปฏิกิริยาในกระบวนการเปลี่ยนแปลงเมทานอลเป็นไฮโดรคาร์บอน (methanol to olefin) และ การแตกตัวด้วยตัวเร่งปฏิกิริยา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

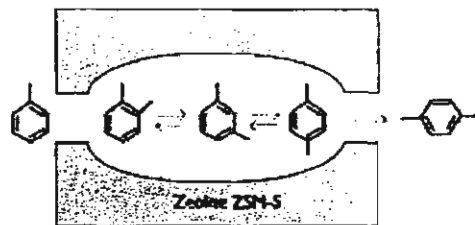
การเลือกเกิดปฏิกิริยาตามรูปร่างของสารตั้งต้น (reactant shape selectivity) ซีโอไลต์จะสามารถเร่งปฏิกิริยาสูญเสียน้ำ (dehydration) ของ 1-butanol ได้อย่างดี แต่ไม่ทำปฏิกิริยากับ 3-pentanol ซึ่งมีขนาดใหญ่กว่า (ดูรูปที่ 2.1)

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

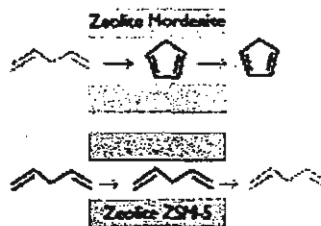
การเลือกเกิดปฏิกิริยาตามรูปร่างของสถานะแทรนซิชัน (transition-state selectivity) ปฏิกิริยาการเกิดวงแหวน (cyclization) ของ 2,4-pentadiene สามารถเกิดขึ้นภายในโพรงของซีโอไลต์ mordenite แต่ไม่สามารถเกิดขึ้นภายในโพรงของซีโอไลต์ ZSM5 ซึ่งมีขนาดของโพรงเล็กกว่าสถานะแทรนซิชัน (ดูรูปที่ 2.3)



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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- นักวิจัยที่มีผลงานตีพิมพ์ของเมธีวิจัย สกว. ประจำปี 2539
- นักวิจัยที่มีผลงานตีพิมพ์ของเมธีวิจัย สกว. ประจำปี 2540
- รางวัลผลงานวิจัยดีเด่นทางเคมีในรูปโปสเตอร์ในการประชุมวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย ครั้งที่ 22 ประจำปี 2539
- รางวัลผลงานวิจัยดีเด่นทางเคมีในการประชุมวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย ครั้งที่ 23 ประจำปี 2540
- รางวัลนักวิจัยดีเด่นแห่งชาติสาขาเคมี และเภสัช ประจำปี 2541 จากสภาวิจัยแห่งชาติ
- บุคลากรผู้มีผลงานดีเด่นทางวิชาการ มหาวิทยาลัยเกษตรศาสตร์ ประจำปีการศึกษา 2541
- ผลงานวิจัยดีเด่นสาขาวิทยาศาสตร์และเทคโนโลยี "ครบรอบยี่สิบงานวิจัย มก. สถาบันวิจัย มก.

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- ศักยภาพของนักวิทยาศาสตร์ไทย องค์ปาฐก "ปาฐกถาศาสตราจารย์ ดร.แถบ นีละนิธิ" 23 สิงหาคม 2541 ณ ห้องราชเทวี 2 โรงแรมเอเชีย กรุงเทพมหานคร
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- Structure and Reactivity in Zeolites กรมวิทยาศาสตร์บริการ กระทรวงวิทยาศาสตร์เทคโนโลยีและสิ่งแวดล้อม กรุงเทพมหานคร
- Catalyst Design 11 กันยายน 2541 คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์ กรุงเทพมหานคร
- หลักสูตร วท.บ.เคมี แนวใหม่ มหาวิทยาลัยทักษิณ สงขลา
- บรรณาธิการวารสาร KU Science Journal

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.