

# Density Functional Investigations into the Adsorption of Methanol on Isomorphously Substituted ZSM-5

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**Abstract:** The adsorption of methanol in the acid sites of zeolites has attracted a great deal of attention because of its relevance to the industrial methanol to gasoline conversion process. In this work, the B3LYP hybrid density functional method was used to investigate the adsorption behavior of methanol on Brönsted acid sites in B, Al, Ga and Fe isomorphously substituted ZSM-5 zeolites. The optimized structures reveal a physisorbed methanol interacting with the zeolite framework through two hydrogen bonds. The order of the computed adsorption energy correlates with the acid strength of the isomorphously substituted ZSM-5: B-ZSM-5 << Fe-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5. The adsorption difference between methanol and ammonia is compared.

**Key words:** methanol, adsorption, substituted ZSM-5, hydrogen bond, density functional theory

## 1. Introduction

The interaction of molecules with the acid sites in zeolites has attracted a great deal of attention because it is the first step in the chemical reactions catalyzed by acidic zeolites. Many studies were carried out to analyze the interactions of the Brönsted sites with a wide range of probe bases like CO [1–3], NH<sub>3</sub> [4–6], CH<sub>3</sub>OH [7–11] and H<sub>2</sub>O [12,13]. For the interaction of NH<sub>3</sub> with the acid sites in (Si, Al)-zeolites, for example, the proton transfer has been observed and NH<sub>3</sub> is transformed into an ammonium ion (NH<sub>4</sub><sup>+</sup>) [6].

As the main commercial catalyst for methanol conversion, the interactions between methanol and the Brönsted acid sites in ZSM-5 have been experimentally [7–9] and theoretically [10,11] studied. Despite considerable efforts, a detailed understanding of these interactions is still lacking, and whether the methanol physically or chemically adsorbed on zeolites is still heavily debated [7–11]. There are two

possible adsorption forms: (1) a neutral complex in which the adsorbed methanol is attached to the acidic site via hydrogen bonds (physisorption), (2) and an ion-pair complex in which the protonated methanol interacts via two protons with the negatively charged zeolite framework site (chemisorption)[14].

It was shown that metals such as B, Ga, or Fe can be introduced into the ZSM-5 framework [15–17]. Metal atom doping can modify the acidity and pore structure of zeolites. The doped materials have different catalytic behaviors with altered activity, selectivity and stability, offering the potential to design zeolites for novel applications. For example, B-ZSM-5 is promising for methanol conversion [18,19]. Experiments showed that the selectivity for complete methanol conversion to olefins on various metal-doped ZSM-5 zeolites varied as follows: Ga=Cr<V<Ge<Mn<La=Al<Ni<Zr=Ti<Fe<Co=Pt [20]. Despite many investigations on isomorphously substituted zeolites, the doping effects of metals on

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structures, acid sites, adsorption behaviors and catalytic reactivity are not well understood.

In this paper, we report a density functional theory study on the adsorption of methanol on Brønsted acid sites in B, Al, Ga and Fe doped ZSM-5. The adsorption energy, local structure and electronic properties of the adsorbate complexes are discussed in detail, and the adsorption difference between methanol and ammonia is compared.

## 2. Computational details

The coordinates of the atoms in the zeolite model are taken from the crystal structure of ZSM-5 by van Koningsveld *et al* [21]. There are 12 distinct tetrahedral sites ( $T_1, T_2, \dots, T_{12}$ ) in the unit cell. In this paper, the  $T_{12}$  site is selected because of its location at the intersection of the straight and sinusoidal channels, which is characteristic of ZSM-5 for significant interaction between the bridging hydroxyl and adsorbed molecules and thus the catalytic active sites.

Clusters containing eight tetrahedral centers with M at the  $T_{12}$  site and a proton attached to  $O_{10}$  with the formula  $((OH)_3SiO)_3-Si-O(H)-M(OSi(OH)_3)_3$  (denoted as M-8TH, M=B, Al, Ga,

Fe, Figure 1) are employed to represent the Brønsted acid sites in ZSM-5 zeolites. As shown in Figure 2(a), the initial structure to model  $CH_3OH$  adsorption on ZSM-5 is on the basis of the partially optimized M-8TH clusters and the free optimized  $CH_3OH$  molecule. The formed adsorption clusters (later referred to as M-8TH( $CH_3OH$ )) are partially optimized with  $O_3Si-O(H)-MO_3$  and  $CH_3OH$  allowed to relax, while the rest of the clusters are fixed at their location in the ZSM-5 structure. This allows the atoms in the vicinity of the acid site, the substituent and the adsorbate to relax, while the clusters retain their positions in the zeolite lattice. The equilibrium configuration of the M-8TH( $CH_3OH$ ) clusters is shown in Figure 2(b).

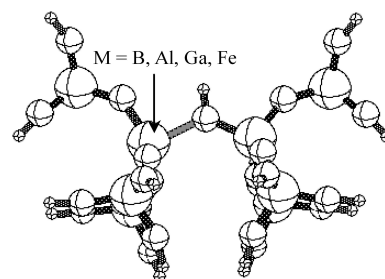


Figure 1. M-8TH (M=Al, Ga, Fe and B) cluster models representing the acid sites in ZSM-5 with M at the  $T_{12}$  site

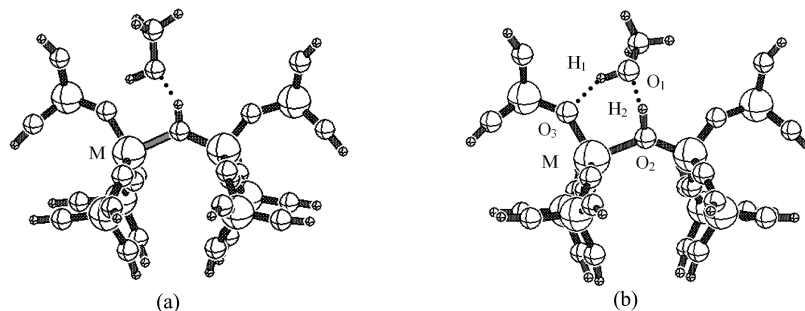


Figure 2. Configuration of the M-8TH( $CH_3OH$ ) models representing the adsorption of  $CH_3OH$  on ZSM-5 clusters  
(a) initial configuration, (b) the partially optimized configuration

The B3LYP hybrid density functional method and LAV3P\*\* basis set implemented within the Jaguar program [22] are used to determine cluster geometries, energies and population analysis. The LAV3P\*\* basis set has been proven to be adequate for the study of acidity in zeolite clusters [23]. In the present study, no corrections were made for basis-set-superposition-error (BSSE) because it is expected to be roughly the same for each of the clusters examined, and we are only interested in the trends of  $CH_3OH$  adsorption energy with the nature of the substituents.

## 3. Results and discussion

Table 1 shows the energy of  $CH_3OH$  adsorption on the isomorphously substituted ZSM-5 zeolites,  $\Delta E_{ads}$ , which is calculated by  $\Delta E_{ads} = [E(M-8TH) + E(CH_3OH)] - E(M-8TH(CH_3OH))$ . It is obvious that stronger acid sites would have larger adsorption energy. The calculated  $\Delta E_{ads}$  of  $CH_3OH$  on isomorphously substituted ZSM-5 increases in the order: B-ZSM-5  $\ll$  Fe-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5, paralleling the increasing strength in Brønsted acidity

of B, Al, Ga and Fe substituted ZSM-5 predicted from experimental [24] and theoretical studies [23]. In addition, the calculated adsorption energies of CH<sub>3</sub>OH

(94.6 kJ/mol at B3LYP/LAV3P\*\* level) on Al-8TH compare well with the experimental adsorption heat of 110–118 kJ/mol [25].

**Table 1. The energy of methanol adsorption on isomorphously substituted ZSM-5 M-8TH clusters**

Sample	$E(\text{M-8TH}(\text{CH}_3\text{OH}), \text{ au})$	$E(\text{M-8TH}, \text{ au})$	$\Delta E_{\text{ads}} (\text{kJ/mol})$
Al	−2037.87346	−1922.11566	94.6
Ga	−2037.88826	−1922.13153	91.6
Fe	−2058.20006	−1942.44396	90.0
B	−2060.66048	−1944.91470	62.8

Note:  $E(\text{CH}_3\text{OH}, \text{ au}) = -115.72187$

The structure of the optimized M-8TH(CH<sub>3</sub>OH) clusters is presented in Figure 2(b), and some selected bond distances are listed, with those of the bare M-8TH clusters for comparison, in Table 2 [23]. The optimized M-8TH(CH<sub>3</sub>OH) structure corresponds to the neutral substrate, and CH<sub>3</sub>OH interacts with the zeolite framework through two hydrogen bonds. One is through the acidic proton of the zeolite and the oxygen of methanol with an O—H bond distance of 0.145–0.159 nm as the major interaction. Another

weaker hydrogen bond is formed by the methanol proton and an oxygen in the zeolite framework with an O—H bond distance of 0.173–0.196 nm. In addition, the O<sub>1</sub>—H<sub>2</sub> and O<sub>3</sub>—H<sub>1</sub> bond distances correspond to the acidity of M-ZSM-5, which is in turn consistent with the adsorption energy. Associated with these interactions, the O—H bond in both methanol and the zeolite is elongated, while the M—O bonds become shorter compared to the bare M-8TH clusters.

**Table 2. Selected bond lengths (in nm)<sup>a</sup> of CH<sub>3</sub>OH, M-8TH and M-8TH(CH<sub>3</sub>OH) clusters**

Samples		$d_{\text{C}-\text{O}_1}$	$d_{\text{O}_1-\text{H}_1}$	$d_{\text{O}_1-\text{H}_2}$	$d_{\text{O}_3-\text{H}_1}$	$d_{\text{O}_2-\text{H}_2}$	$d_{\text{M}-\text{O}_2}$
M-8TH(CH <sub>3</sub> OH)	CH <sub>3</sub> OH	0.142	0.096	—	—	—	—
	Al	0.143	0.099	0.145	0.175	0.105	0.192
	Ga	0.142	0.099	0.146	0.173	0.104	0.202
	Fe	0.142	0.099	0.153	0.176	0.102	0.209
	B	0.142	0.098	0.159	0.196	0.101	0.186
M-8TH	Al	—	—	—	—	0.097	0.198
	Ga	—	—	—	—	0.097	0.203
	Fe	—	—	—	—	0.097	0.213
	B	—	—	—	—	0.097	0.374

a. The numbering of atoms follows those designated in Figure 2(b)

It is worth noting that in the bare B-8TH cluster, the B—O bond distance is too long (0.374 nm) to have any interactions between B and O atoms. This is because the small size of B<sup>3+</sup> favors trigonal rather than tetrahedral coordination. Experiments showed that the interaction of Lewis base such as water or ammonia with an acid site in B-containing zeolite can lead to the formation of tetrahedral coordinated boron [26]. In our present work, B undergoes a reversible change from trigonal to tetrahedral coordination when CH<sub>3</sub>OH is adsorbed, which is confirmed by the B—O distance of 0.186 nm in the B-8TH(CH<sub>3</sub>OH) cluster. The fact that methanol is not protonated by the acid sites of zeolites agrees with

the findings of Haase and Sauer [11] from molecular dynamics simulations based on density functional theory, indicating that the substitution of different metals affects the strength of the interaction between molecules and zeolites but not the type of adsorption.

The Mulliken atomic charges associated with the selected atoms in the free optimized methanol, the bare M-8TH clusters and the adsorbate complexes of M-8TH(CH<sub>3</sub>OH) are presented in Table 3. By analyzing the charges on each atom, it can be found that the local electronic structures of the adsorbate complexes are in good agreement with the bonding properties of the substrate and the adsorbed molecules. Because of the formation of hydrogen bonds between

methanol and the substrates, the O—H bonds in both methanol and the zeolite were polarized, leading to the increased charges on O<sub>1</sub>, O<sub>2</sub>, H<sub>1</sub>, and H<sub>2</sub> atoms

compared to the free CH<sub>3</sub>OH molecule and bare M-8TH clusters. This in turn resulted in the charge increase on the substituents (M) and methyl C atom.

**Table 3. Mulliken atomic charges of the selected atoms of CH<sub>3</sub>OH, M-8TH and M-8TH(CH<sub>3</sub>OH) clusters<sup>a</sup>**

Samples		$q_C$	$q_{O_1}$	$q_{H_1}$	$q_{H_2}$	$q_{O_2}$	$q_M$
M-8TH(CH <sub>3</sub> OH)	CH <sub>3</sub> OH	-0.067	-0.531	0.306	—	—	—
	Al	-0.085	-0.585	0.403	0.461	-1.028	1.720
	Ga	-0.085	-0.587	0.399	0.452	-0.990	1.581
	Fe	-0.084	-0.580	0.398	0.438	-0.961	1.061
	B	-0.082	-0.564	0.368	0.425	-0.903	0.927
M-8TH	Al	—	—	—	0.396	-0.903	1.718
	Ga	—	—	—	0.388	-0.874	1.562
	Fe	—	—	—	0.390	-0.873	1.069
	B	—	—	—	0.364	-0.837	0.886

a. The numbering of atoms follows those designated in Figure 2(b)

In our previous research [23] considering the adsorption of NH<sub>3</sub> on M-8TH (M=B, Al, Ga and Fe) clusters, it was found that NH<sub>3</sub> became protonated (NH<sub>4</sub><sup>+</sup>) for M=Al and Ga with proton transfer, while only physisorbed NH<sub>3</sub> for M=Fe and B. The different types of adsorption arise from the different acidity of the substituted zeolite. For methanol and water adsorptions, the situation is much more complicated. The principal debate has focused on whether both the physisorbed and chemisorbed (ion pair) structures are minima on the potential energy surface and/or which is more stable. Finite cluster calculations on methanol adsorption have shown that only the physisorbed (not protonated) form of methanol is a minimum for 3T and 4T clusters, [27] and the ion pair structure (protonated) is found to be a transition state for proton transfer between two framework oxygens. Calculations [28,29] on periodic zeolite models demonstrated that the adsorption depends on the zeolite framework and methanol loading. In chabazite, proton transfer can occur provided methanol is adsorbed in the eight-ring. However, in sodalite structure methanol is simply physisorbed.

While experimentally, FTIR studies carried out

by Mirth *et al* [30] indicated the formation of methoxonium ions in the H-ZSM-5 zeolite for low methanol coverages, but <sup>2</sup>H NMR investigations and <sup>1</sup>H MAS NMR spin-echo experiments on adsorbate complexes consisting of one methanol molecule per acid site showed a rapid exchange of hydroxy protons between SiOHAl groups and hydrogen bonded neutral and/or protonated adsorbate complexes [31,32]. A more recent solid state NMR study proved that the adsorption of methanol on bridging OH groups in H-ZSM-5 led to the formation of neutral 2-fold hydrogen-bonded adsorbate complexes consisting of one methanol molecule per SiOHAl group or partially protonated methanol clusters formed by three methanol molecules per SiOHAl group [9]. Present calculations on one methanol molecule adsorption in one acid site of H-ZSM-5 support this finding.

Whether a base molecule can be protonated by the acid sites of zeolites depends not only on the zeolite acidity (*i.e.* the different topology of zeolites) but also on the proton affinities of the base molecule. Table 4 presents the proton affinities of ammonia, methanol and water. It is shown that the proton affinity (calc/expt, in kJ/mol) of NH<sub>3</sub> (859.0/858.1 [33])

**Table 4. Proton affinities (kJ/mol) of NH<sub>3</sub>, CH<sub>3</sub>OH and H<sub>2</sub>O**

Samples	PA (Experiment)	PA (Calculated) <sup>a</sup>	PA (Calculated) <sup>b</sup>
NH <sub>3</sub>	858.1[33]	871.9	859.0
CH <sub>3</sub> OH	773.6[34]	771.1	759.8
H <sub>2</sub> O	696.6[34]	716.3	693.7

a. At B3LYP/6-31G\*\*+ZPE (B3LYP/6-31G\*\*)

b. At CCSD(T)/6-311+G\*\*/B3LYP/6-311+G\*\*+ZPE(B3LYP/6-311+G\*\*)

is larger than that of CH<sub>3</sub>OH (181.6/184.9 [34]) and H<sub>2</sub>O (165.8/166.5 [34]), indicating that it is more difficult for methanol and water to be protonated than ammonia by a given acid site.

#### 4. Conclusions

Density functional theory calculations on the adsorption of methanol on acid sites in B, Al, Ga and Fe isomorphously doped ZSM-5 showed a physisorbed methanol, stabilized by two hydrogen bonds. The calculated adsorption energy in the order: B-ZSM-5 << Fe-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5 correlates with the increased strength of the Brønsted acidity. In contrast to methanol, NH<sub>3</sub> is converted into ammonium ion (NH<sub>4</sub><sup>+</sup>) via proton transfer and therefore a chemisorption process for M=Al and Ga. The adsorption states depend on properties of both zeolites and adsorbates.

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