

Methanol adsorption and activation by zeolitic protons

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Methanol adsorption and activation by zeolitic protons

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Density functional theory is used to determine the modes of adsorption at low and high coverage of methanol as well as the intermediates involved in the Brønsted acid methanol dehydration to dimethyl ether. Two different reaction pathways were studied. In the first, methanol adsorption and surface methoxy species formation are the initial elementary steps for this reaction. Subsequent dimethyl ether formation by reaction of methanol with the surface methoxy species takes place. The second path involves the simultaneous adsorption and activation of two methanol molecules with formation of dimethyl ether and water in one step. The latter appears to be the preferred route. Additionally, carbon-carbon bond formation from the activation of methanol or dimethyl ether molecules by the surface methoxy groups was studied. The products are ethanol and ethyl methyl ether. Computed infrared spectra of the adsorption of one and two methanol molecules to a zeolitic proton are discussed.

1. INTRODUCTION

The methanol-to-gasoline (MTG) process¹ is one of the most successful routes for the catalytic conversion of methanol to synthetic fuels, e.g. hydrocarbons in the gasoline boiling range (30-200°). Although there is a large amount of literature available in this field (ref. 1-6 and references therein), the results are, often, controversial. With respect to the initial adsorption of methanol at the zeolite, some authors² have assigned the corresponding spectroscopic data to hydrogen-bonded methanol and dimethyl ether on the zeolite surface, while some others^{3,4} have suggested the formation of protonated species as the methoxonium ion, CH_3OH_2^+ . A large variety of different kinetic experiments established that methanol is first dehydrated to dimethyl ether (DME) and that an equilibrium mixture of methanol and DME is converted to olefins, aliphatics and aromatics up to C_{10} . The mechanism of methanol adsorption, dehydration and, specially, the formation of the first C-C bond and the nature of the intermediates involved is still not fully understood.

With respect to methanol adsorption, theoretical calculations show (ref. 5 and references therein) that the protonated species, CH_3OH_2^+ , is not a stable intermediate as initially proposed,^{3,4} but a transition state, corresponding to a maximum in the potential energy surface. Concerning DME formation, different bimolecular mechanisms have been proposed in the literature. Bandiera and Naccache⁶ proposed the initial reaction of one methanol molecule at a Brønsted acid site, H^+ , and another at the adjacent base site, O^{2-} , with

formation of the two species, $[\text{CH}_3\cdot\text{OH}_2]^+$ and $[\text{CH}_3\text{O}]^-$ which upon condensation gives dimethyl ether and water. Kubelková et al.⁴ proposed that methanol is first dehydrated leaving methyl groups bonded to the zeolitic surface. Later on, those surface methoxy groups can react with another methanol molecule to form dimethyl ether. Here we show how methanol can adsorb at low (one methanol molecule) and higher coverages (two methanol) to the zeolitic proton. We also show that two reaction pathways for the production of dimethyl ether can be distinguished. One proceeds via two distinct steps, similar as proposed by Kubelková et al.⁴ The second path involves the simultaneous adsorption and reaction of two methanol molecules with formation of dimethyl ether and water in one step. With respect to C-C bond formation, we have studied the transition states involved in the activation of methanol and DME by the surface methoxy producing ethanol and methyl ethyl ether.

2. METHOD

All calculations in this work are based on density functional theory (DFT),⁷ using the DGAuss program.⁸ Nonlocal exchange and correlation corrections due to Becke and Perdew,⁹ respectively, are included in a self-consistent manner. The basis sets used are of double-zeta quality and include polarization functions for all non-hydrogen atoms.^{10a} A second set of basis functions (A1), the auxiliary basis set,^{10b} is used to expand the electron density in a set of single-particle Gaussian-type functions. They were optimized for use in DFT in order to minimize the basis set superposition error.^{10c} Geometry optimization calculations are carried out to a minimum in the case of reactants, adsorption complexes and products, and to a saddle point in the case of transition states (TS). Unscaled frequencies are presented and zero-point energy corrections included for all structures. See ref. 5 for more technical details.

The molecular system used consisted of one or two methanol molecules, DME, methyl ethyl ether, ethanol and water. Two different clusters, the $\text{H}_3\text{SiOHAlH}_2\text{OSiH}_3$ (or AlH) and $\text{H}_3\text{SiOHAl(OH)}_2\text{OSiH}_3$ (or AlOH), were used to represent the acidic zeolite. Additionally, in some cases, those clusters were also used in their methoxide form, where the acidic proton was replaced by a methyl (CH_3) group. To model the silanol group, the $\text{H}_3\text{SiSi(OH)H}_2$ cluster was used. The cases where a different cluster was used will be specified in the text.

3. RESULTS

It was found that a single methanol molecule can in principle adsorb to the acidic site of a zeolite in two different modes. End-on, shown in Figure 1a, where the hydroxyl group interacts with the zeolitic proton and side-on (Figure 1b) where the C-H group of methanol is directed to the basic oxygen of the zeolite and the oxygen of methanol is directed to the zeolitic proton. In this configuration mode the hydrogen of methanol is pointing away from the surface. Calculations of equilibrium constants between those adsorption modes with respect to the reactants in the gas phase⁵ show that, at room temperature, for each $\approx 4.5 \cdot 10^4$ methanol molecules adsorbed in the end-on mode, only one will be adsorbed in the side-on. The conclusion is that methanol adsorbs preferably in the end-on mode. Adsorption energies are -75 and -45 kJ/mol respectively for the end-on and side-on modes. The calculated harmonic frequencies for the adsorption of one methanol are shown in Table 1. The experimental^{3,4} bands at 2900-2400-1660 cm^{-1} associated to OH stretch and bending modes

are, in reality, pseudo bands due to resonant interactions between the OH stretch of the zeolite and overtone bending mode of the perturbed bridging OH group, the A-B-C¹¹ bands. The harmonic spectrum gives only one of those bands, located at around 2500 cm⁻¹. Only when frequencies are calculated anharmonically, the three band system can be obtained.¹² Within the harmonic approximation for the end-on complex, this band was found at 2400 cm⁻¹.

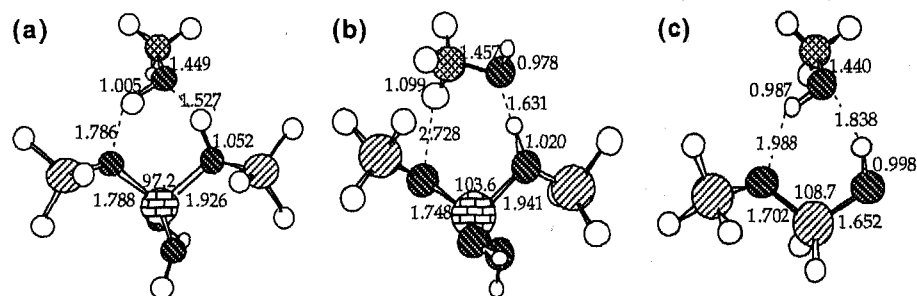


Figure 1. One methanol molecule adsorbed end-on (a) and side-on (b) in the zeolitic acid site as well as at the silanol site (c). \ominus Al, \otimes Si, \bullet C, \bullet O, \circ H. Distances (Å), angles (deg).

DFT seems to give higher CH stretch modes (3086, 3054 and 2972 cm⁻¹) than the experiment^{3,4} (2993, 2958 and 2856 cm⁻¹). This may indicate the DFT underestimates the weak van der Waals interactions between CH₃ and the lattice oxygen. A feature in the experimental^{3,4} spectra that cannot be explained with our models is the sharp peak at 3550 cm⁻¹ measured at low methanol coverages. A possibility is that this band is due to the adsorption of methanol at the external or internal silanol sites.¹³ Therefore the system presented in Figure 1c was also calculated. The interaction of methanol with the silanol group is weaker than with the acidic zeolite, as observed from the difference in distances (Figure 1). The OH shift of methanol adsorbed to the silanol site (3546 cm⁻¹) agrees remarkably well with experimental band^{3,4} at \approx 3550 cm⁻¹. The assignment of this band by another calculation (using the cluster Si(OH)₄, the small 3-21G basis set and obtaining a Hartree-Fock optimized

Table 1
Calculated harmonic frequencies (cm⁻¹) for low and high methanol coverages

	One Methanol Molecule				Two Methanol Molecules		
	end-on <i>fig. 1a</i>	silanol <i>fig. 1c</i>	exp. <i>ref. 3</i>	exp. <i>ref. 4</i>	cis <i>fig. 2a</i>	trans <i>fig. 2b</i>	exp. <i>ref. 3</i>
OH stretch _{m/m'}	3237	3546	3545	3576	3307 / 2772	3367 / 2837	3325 ^b
OH stretch _f		3319	2900	2900	1724	1833	2900 ^c
"	2398		2440	2400			2440 ^c
CH stretch _{m/m'}	3086	3075	2993	3008	3069 / 3108	3079 / 3074	2993
"	3054	3023	2958	2961	3038 / 3056	3057 / 3042	2958
"	2972	2955	2856	2858	2957 / 2974	2972 / 2959	2856 ^d
OH bend _{m,i}	1496	641	1687	1660 ^a	1552	1568	1580

(m) 1st. methanol; (m') 2nd. methanol; (f) framework; (i) in-plane. ^a This band has been assigned by ref. 3 due to methoxonium HOH bend. ^b At 1 mbar this band shifts to 3280 cm⁻¹. ^c At high coverages these bands show very low intensity. ^d Assigned due to CH stretch.

structure)¹⁴ at $\approx 3700\text{ cm}^{-1}$ is probably not correct. DFT calculations using the same cluster show this band to be at 3527 cm^{-1} , only a few wavenumbers lower than that for the cluster presented in Figure 1c. It has been shown recently that for methanol adsorbed in a zeolite, only the MP2 optimized structures are able to produce correct NMR and infrared spectra.¹⁵ Experimentally,^{3a} a small shoulder at $\approx 3300\text{ cm}^{-1}$ is observed. This could be associated to OH stretch bands due to methanol adsorbed end-on in the acidic zeolite or due to the disturbed silanol and calculated at 3237 and 3319 cm^{-1} , respectively. Note that this agreement is questionable since for another sample of the same zeolite^{3b} this shoulder was not observed. With respect to the intensities of OH stretch bands of methanol adsorbed to a silanol group (350 and 675 km/mol for methanol and frame, respectively) and methanol OH stretch adsorbed end-on to the acidic site (840 km/mol) the assignment is not completely consistent. Possibly the very broad band from the strongly perturbed methanol OH stretch (adsorbed end-on in the acidic site) overlaps with the band due to perturbed OH silanol stretch. The narrow band at $\approx 3550\text{ cm}^{-1}$ can be due to the methanol OH stretch adsorbed to the silanol sites.

Two of the possible modes of adsorption of methanol at higher coverages are shown in Figure 2. The difference between them is the position of the methyl groups, at the same side (named "cis", Figure 2a) or opposite side (named "trans", Figure 2b) of the plane defined by the oxygen atoms O₍₁₋₂₋₃₋₄₎. The cis structure is just a few kilojoules more stable than the trans structure, -130 and -125 kJ/2mol of methanol, respectively. Note that the adsorption energy for these two structures is given with respect to the adsorption of two methanol molecules. Half of it ($\approx 65\text{ kJ/mol}$) should be compared to the experiment. Two different experimental heat of adsorption for methanol in H-ZSM5 zeolite, -63 ^{16a} and -115 kJ/mol ,^{16b} were reported in the literature. Our results agree pretty well with the first.^{16a}

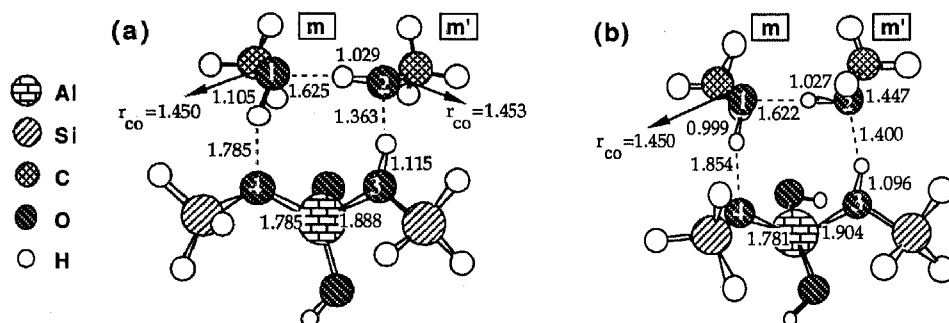


Figure 2. Two methanol molecules adsorbed in the zeolitic acid site. (Distances in Å).

The calculated harmonic frequencies for high methanol coverages are presented in Table 1. Especially the calculated frequencies for the trans structure (Figure 2b) agree remarkably well with the experiment.³ In the experimental spectra for high methanol coverages (1mbar) the shoulders observed at ≈ 2900 - 2450 - 1650 cm^{-1} are the residual A-B-C pattern due to hydrogen bonded methanol molecule adsorbed end-on in the acidic site. The small shoulder in the experimental spectrum^{3a} at $\approx 3550\text{ cm}^{-1}$, more intense than in the spectrum for low methanol coverages (the absorbance unity increases from 0.130 to 0.190), is consistent with the decrease in the silanol OH stretch intensity at 3730 cm^{-1} . This suggests an

increase in the adsorption of methanol to the silanol sites. The increase in intensity of CH stretch bands can be attributed to a summation effect resulting from the presence of two methyl groups in the same spectral region. The OH stretch of a methanol molecule (m) interacting with the basic oxygen of the frame is shifted to $\approx 3350\text{ cm}^{-1}$, which agrees very well with the experiment.³ The OH stretch for the other methanol molecule (m'), strongly perturbed by the presence of the first (m) and the acidic proton, shifts to much lower wavenumbers, $\approx 2800\text{ cm}^{-1}$. This contradicts the assignment of a band at this position in the experimental³ spectrum as due to CH stretching mode. The shift of OH stretch frequency of the frame is very large, calculated at $\approx 1800\text{ cm}^{-1}$. Its identification in the experimental spectra is complicated due to the presence of several very broad bands in this region.

The reaction energy diagram presented in Figure 3 shows the first path (Path I) for dimethyl ether formation. In the diagram, results for the AlH cluster are presented. The hydride termination of the silicon atoms are not shown in the figure. The first step is the methanol dehydration with formation of surface methoxy species. In Figure 3 only the important steps for the dehydration are presented. A more detailed path is presented in ref. 5. The adsorption of an additional methanol molecule to the surface methoxy species results in the formation of dimethyl ether. The rate limiting step for this reaction is the dehydration of the first methanol molecule, which presents a true activation barrier of $+215\text{ kJ/mol}$. This is over 50 kJ/mol higher than the second step, DME formation ($+160\text{ kJ/mol}$). The transition states involved in both reaction steps (PI-ts1, 2) are very similar. The methyl group in both TS's assume a carbenium like geometry with a hybridization very near to sp^2 .

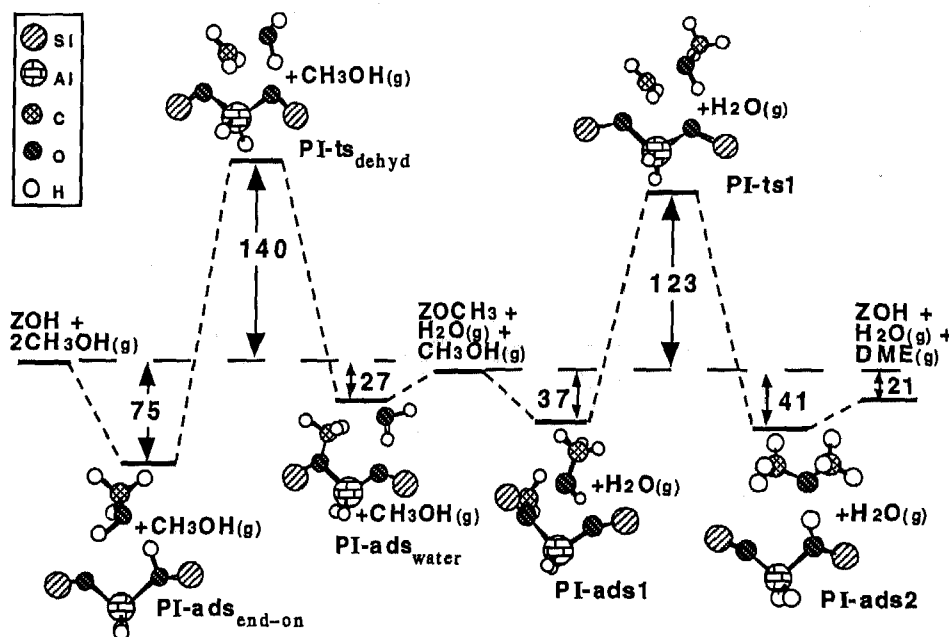


Figure 3: Path I: Reaction energy diagram for methanol dehydration to dimethyl ether via a surface methoxy species (kJ/mol).

The reaction energy diagram for the second path (Path II) of methanol dehydration is shown in Figure 4. Here the larger AlOH cluster is used, but again the hydride termination of the silicon atoms is not shown. The first step in this second path is the simultaneous adsorption of two methanol molecules at the acidic site, PII-ads1 in Figure 4. This is followed by the rotation of one of the methanol molecules in such way that the methyl group is able to interact with the hydroxyl group of the other methanol molecule (PII-ads2). In the transition state PII-ts2 water is seen to be almost formed. The central methyl group has clearly characteristics of a carbenium ion. The left-side methanol transfers its proton back to the surface, regenerating the acidic site while, simultaneously, DME is formed. Via this transition state, rather complex, DME and water are formed in only one step. The surface complex formed after the reaction is strongly hydrogen bonded to the frame, as it is seen from the high energy necessary to desorb the products formed, +80 kJ/mol. The activation barrier for the calculated transition state (PII-ts2) with respect to the reactants is very low, +15 kJ/mol. Including the adsorption energy for the two methanol molecules (+130 kJ/mol) the true barrier for this path becomes +145 kJ/mol. It is 70 kJ/mol lower than the limiting step for Path I, +215 kJ/mol. This enables one to conclude that Path II will have preference over Path I. An experimental true activation barrier⁶ for methanol dehydration to DME for dealuminated H-Mordenite was reported to be +80 kJ/mol. This number seems to be too low, specially comparing to one of the reported heat of adsorption for methanol, +115 kJ/mol.^{16b}

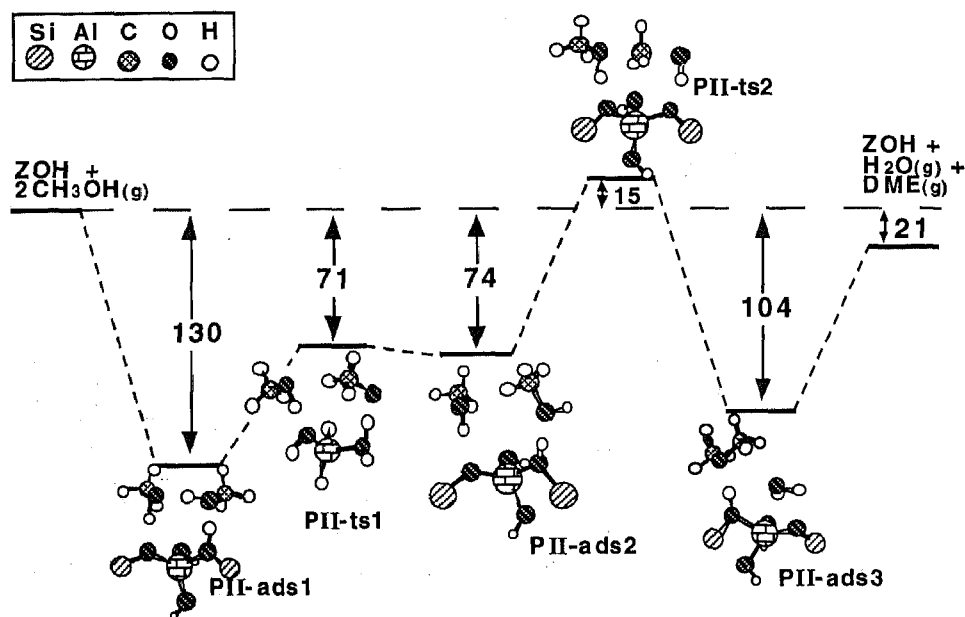


Figure 4: **Path II:** Reaction energy diagram for methanol dehydration to dimethyl ether via an associative mechanism (kJ/mol).

We have studied the ethanol formation from the reaction between methanol and a surface methoxy species. In this case, nonlocal corrections were included only to the final

local optimized structure energy. The small $\text{HO}(\text{CH}_3)\text{Al}(\text{OH})_3$ cluster was used to represent the surface methoxy. The activation barrier with respect to reactants in the gas phase is rather high, +284 kJ/mol. The TS is presented in Figure 5a. The arrows represent the reaction coordinate according to the only imaginary mode. There it can be seen the transfer of a hydrogen atom from the methyl group of methanol to the zeolitic surface and the simultaneous C-C bond formation between the methyl of methanol and the surface methoxy species. The surface methoxy group resembles a carbenium ion, with a geometry nearly trigonal planar. Also methyl ethyl ether formation from DME plus a surface methoxy species presents a rather high activation barrier with respect to reactants, +246 kJ/mol. Here the methoxy AlH cluster was used and nonlocal corrections included at the end of the optimization. The transition state, shown in Figure 5b, is very similar to the one just discussed for ethanol formation.

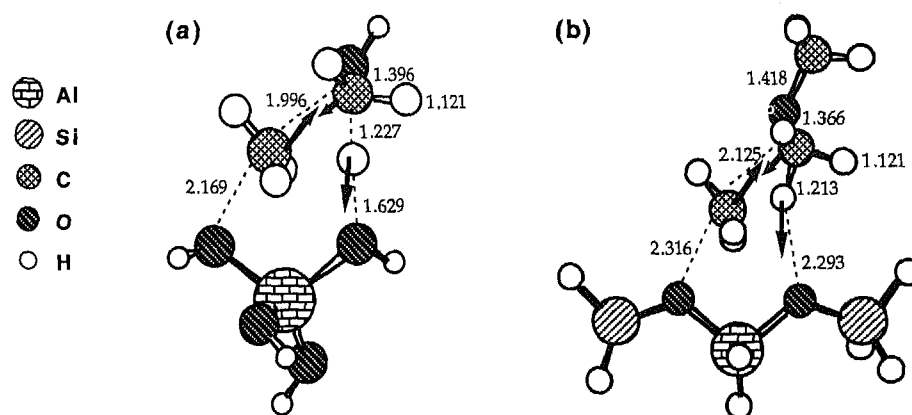


Figure 5. TS for ethanol and methyl ethyl ether formation. The arrows represent the reaction coordinate for the most important atoms. Distances in Å.

4. CONCLUSIONS

DFT was used to study the adsorption of methanol at low and high coverages as well as its dehydration to dimethyl ether. The experimental^{3,4} infrared spectra at low coverages can be interpreted as follows: the three bands at 2900-2450-1650 cm^{-1} are the A-B-C pattern¹¹ resulting from a perturbed OH stretch mode of the zeolitic proton. The spectral region at 3250-3350 cm^{-1} contains a very broad band resulting from the overlap of bands due OH stretch of methanol (adsorbed end-on at the acidic site of the zeolite) and disturbed silanol OH stretch. The band observed experimentally at 3550 cm^{-1} is possibly due to the OH stretch of methanol adsorbed to silanol sites. The experimental spectra at high methanol adsorption coverages show a new broad band at 3350 cm^{-1} , that can be assigned due to one methanol OH stretch interacting with the zeolite basic site. A sharp band at 2850 cm^{-1} was shown to be due to OH stretch of a second methanol molecule interacting with the other adsorbed methanol molecule.

Two reaction pathways for dimethyl ether formation were examined. The first, involving initial formation of a surface methoxy species followed by DME formation, was

found to have a barrier over 50 kJ/mol higher than the second, involving the associative adsorption and reaction of two methanol molecules. We conclude that the surface methoxy species is not a necessary intermediate for the dimethyl ether formation. The formation of ethanol and ethyl methyl ether via a surface methoxy species involves high activation barriers, +284 and +246 kJ/mol, respectively. For both reactions, the transition states formed are very similar and have characteristics of carbenium ion. The methyl group is stabilized by the surface basic oxygen.

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