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Theoretical Study of C–C Bond Formation in the Methanol-to-Gasoline Process

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Abstract: Density functional theory is used to study one of the most successful routes to the production of synthetic fuels, the conversion of methanol to gasoline (MTG process) with an acidic zeolite. With our calculations we have determined transition states and adsorption complexes of reactants, intermediates, and products as well as the corresponding activation barriers and adsorption energies of the numerous reactions involved in such a process. Brønsted acid catalyzed methanol dehydration to dimethyl ether is the first step of the MTG process. Two different mechanisms are possible. One proceeds via an associative interaction between two methanol molecules, generating directly dimethyl ether, while the other proceeds via a methoxy surface species intermediate. The presence of water lowers the activation barrier of the last mechanism by more than 50 kJ/mol. Our calculations suggest that ethanol and ethyl methyl ether are the first formed species with a C–C bond. Several different mechanisms for those reactions have been studied. The activation barriers involved in such reactions are of the order of 300 kJ/mol for both ethanol and ethyl methyl ether. Without coadsorbed water, the activation barriers are 60 kJ/mol higher. In a following step ethylene is formed from alcohol or ether. Those reactions are very fast due to a very low activation barrier. Trimethyloxonium, proposed to be an intermediate in the formation of ethyl methyl ether, can be excluded as an intermediate for the C–C bond formation. Although it can be formed, its further reaction to ethanol or ethyl methyl ether involves activation barriers that are over 80–150 kJ/mol higher than their formation directly from dimethyl ether and methanol. Reaction paths for the formation of methane and formaldehyde, which are observed in reactions for very low methanol coverages, have also been studied.

1. Introduction

The methanol-to-gasoline, MTG, process¹ has attracted a great deal of attention in the last 20 years since it is one of the most successful routes for the acid zeolite catalyzed conversion of methanol to synthetic fuels. A large variety of different experiments (ref 2–14 and references therein) established that

methanol is first dehydrated to dimethyl ether (DME) and that an equilibrium mixture of methanol and DME is then converted to olefins, aliphatics, and aromatics up to C10. The mechanism of those reactions, especially the formation of the first C–C bond and the nature of the intermediates involved, is a matter of significant debate.

Several different mechanisms have been proposed for C–C bond formation. The formation of free carbene radicals,³ formation of trimethyloxonium and ylide intermediates^{4,5} carbocations,⁶ and mechanisms involving ketene intermediate and CO as the active catalyst⁷ have been proposed. Intermediate surface methoxy species formation has also been suggested⁸ as a possible route for C–C bond formation, as well as being essential to some of the mechanisms mentioned above.^{3b,5,6} The free carbene route is very unlikely, since it involves very high activation barriers. Trimethyloxonium (TMO) formation was observed in NMR experiments from dimethyl ether on HZSM5.⁹ Nevertheless, because those ions decompose back to ethers at lower temperatures compared to those needed for hydrocarbon

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synthesis and also because they are not observed when methanol is coadsorbed, the mechanistic significance of the observation of oxonium ions has been considered uncertain.⁹ Lewis-basic sites,¹⁰ NMR,⁹ and mass spectroscopy¹¹ studies show that CO and ketene play no intermediary or catalytic role in the MTG chemistry on HZSM5.

It is generally agreed that propylene and especially ethylene are the initial products. By performing NMR experiments of methanol activation on HZSM5 at concentrations between 50 and 100% of maximum adsorption capability of the zeolite, Munson et al.⁹ were able to identify ethylene and ethyl methyl ether in between the intermediary products. They suggest that ethanol also plays an important intermediary role. Another important feature in the MTG process is the role of water. Munson et al.⁹ have observed that water modifies the acidity of the zeolite. This affects profoundly the chemistry of olefin formation and retards coke formation. The residual water has a significant effect on the kinetics of hydrocarbon synthesis, and even at temperatures greater than 723 K it is observed to evolve from the zeolite.¹⁵

The interaction of methanol with acidic zeolites is a subject that has attracted considerable interest of theoreticians.^{16–19} Even simple questions such as (i) how methanol at low (one methanol molecule) and higher coverages (two and three methanol molecules) adsorbs to the acidic-basic sites of the zeolite, (ii) the heat of adsorption, and (iii) methoxonium formation are still subjects of debate. Computations^{16–19} using various different methods and cluster size predict the heat of adsorption of one single methanol with the acidic zeolite to be in the range of –64 and –83.0 kJ/mol (all for HZSM5). Two methanol molecules can adsorb in many different ways to the zeolitic Brønsted acid–Lewis base sites. The heat of adsorption for the second methanol molecule is less than that for the first, and was calculated to be –55^{21,22} and –35^{16g} kJ/mol. The third question whether methanol is protonated or not receives different answers according to the technique used. In cluster calculations^{17,18,23} the ion pair ($\text{H}_3\text{COH}_2^+\cdots\text{OZ}^-$) is not a minimum in the potential energy surface but a first-order saddle point. This implies a transition state. On the other hand, first-principle studies performed on a periodic zeolite model using a plane wave basis set (core electrons are represented by pseudopotentials) have shown that when a single methanol adsorbs at a

zeolitic eight-ring pore opening of chabazite, it forms a methoxonium ion.^{19,24} Protonation was, nevertheless, not observed when the proton–methanol interaction was analyzed in sodalite^{19,24,25} where large open cages are linked by six- and four-ring windows. Nevertheless, the energy differences between protonated and hydrogen bonded methanol are just a few kilojoules per mole.^{17–19,23–25}

Surface methoxy species formation by dehydration of methanol and dimethyl ether is generally considered to be the initial step in the methanol-to-gasoline process. Theoretical calculations have shown that methoxy groups can be formed from dissociative adsorption of a single methanol molecule^{17,18} or from the adsorbed methanol dimer.^{21,28,29} In the first case the C and O atoms of methanol will form a six-member ring with the –OAlOH– lattice atoms. The ring formed has a considerably strained geometry. This results in a very high activation barrier for the dehydration process. If a second methanol is allowed to assist the reaction an eight-membered ring will be formed. The system now has a much more relaxed geometry resulting in a lowering of the activation barrier by over 50 kJ/mol. The ring is now composed of the –OAlOH– lattice atoms, C and O of the reacting methanol and the OH group of the “assisting” methanol molecule. The function of the second methanol molecule is to allow a relaxation of the geometrical parameters of the transition state acting as a bridge between the zeolite and the reacting methanol. The reaction produces the transfer of the proton from the zeolite to the OH group of the first methanol yielding water. This and analogous reactions will be discussed, elucidating further the function of the second methanol molecule (or water) in stabilizing transition states.

We have shown^{21,28} that dimethyl ether can be formed via two different kinds of mechanisms. The first is an associative mechanism and involves the simultaneous adsorption and reaction of two methanol molecules, with formation of dimethyl ether and water in one step. The second is a methoxy-mediated mechanism. It involves initial dehydration of one methanol molecule generating a surface methoxy (CH_3) group. This methoxy group will then react with the second methanol molecule yielding DME. Just as for methoxy, DME can be formed with or without coadsorbed water or methanol. The presence of water lowers the activation barrier by ~50 kJ/mol.

In the present study we show how ethanol, ethyl methyl ether, trimethyloxonium, and ethylene can be formed by starting with methanol, DME, and surface methoxy groups. Additionally we propose a path for methane and formaldehyde formation, which are observed in reactions with very low methanol concentrations. Carbenium-like transition states (TS) are the intermediates proposed here for all reactions. We will first analyze reaction paths to primary reaction products such as ethanol and methyl ether and then decomposition of these molecules to ethylene.

We have used density functional theory (DFT) to calculate reactants, adsorption complexes, transition states, and products involved in several different paths of formation of each one of the compounds mentioned above. The cluster approach has been used to represent the acidic zeolite. Adsorption energies and activation barriers make a comparison between all the studied paths possible.

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2. Method

The calculations are based on density functional theory (DFT)³⁰ as implemented in the program de Dgauss (versions 2.1 and 3.0).³¹ Nonlocal exchange and correlation corrections (NL) due to Becke³² and Perdew,³³ respectively, are included in the final energy obtained within the local density approximation (due to Vosko et al.).³⁴ This level of accuracy is found to be excellent for the description of binding energies.^{17,27} For systems involving strong hydrogen bridges (as in the methanol:zeolite system) the computation of properties that strongly depend on the geometry of the structure, such as infrared spectrum and protonation, requires inclusion of nonlocal corrections during the optimization, self-consistently (NLSCF). We have shown earlier that the energies obtained with use of the NL or NLSCF corrections differ only by a few kilojoules per mole.^{17,21,27} The purpose of the present study is not to discuss infrared spectra or to analyze the small energy differences between protonated and ground state complexes. We intend to analyze the large energy changes along the various reaction paths. Since optimizing structures including self-consistent nonlocal corrections involves a large computational cost, we did not go beyond the NL correction. It is important to notice that the geometry of transition states, where the interaction is purely ionic, is not affected significantly whether the NL or NLSCF corrections are included.^{17,21,27}

The basis sets used are the double- ζ quality and include polarization functions for all non-hydrogen atoms (DZPV).³⁵ They were optimized for use in density functional calculations in order to minimize the basis set superposition error (BSSE).³⁶ A second set of basis functions, the fitting basis set,³⁷ is used to expand the electron density in a set of single-particle Gaussian-type functions. Geometry optimization calculations are carried out to a minimum for reactants, adsorption complexes, and products and to a saddle point for transition states (TS). All TS's shown in this study have only one imaginary mode, while the structures optimized to a minimum presented no imaginary modes. The frequencies are obtained from analytic second derivatives.³⁸ Zero-point energy (ZPE) corrections have been included for all optimized structures.

The various molecular systems chosen depended on the particular reaction studied, consisting of methanol, dimethyl ether, water, methanol, ethyl methyl ether, ethylene, and/or trimethyloxonium. It has been shown earlier^{21,26} that differences not larger than 10 kJ/mol are obtained for the adsorption energies and activation barriers by using clusters of different size (up to 5T atoms). Even though the deprotonation energies of the various clusters vary (~ 30 kJ/mol),²¹ due to the stabilization effects of the adsorbed molecules, binding energies are much less affected by the cluster size. Since the present study involves a large number of structures we decided to use the small HOHAl-(OH)₂OH and HO(CH₃)Al(OH)₂OH clusters to represent the acidic zeolite and methoxy surface, respectively. No geometry constraints have been imposed in any of the studied structures. In the only case where the small cluster used failed to correctly describe the molecular system under study (one methanol molecule adsorbed at the methoxy surface), results from use of a larger cluster were taken.^{17,28} One has to keep in mind that the use of larger cluster systems would enable us to study in detail changes in the activation barriers as well as heat of adsorption of the different systems as a function of zeolite composition and/or acidity. It has been shown earlier^{27,39} how small clusters can be used to analyze the consequences of zeolites structure effects on acidity.

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Table 1. Carbon–Carbon Bond Formation Activation Energies (direct reaction paths)

$$\Delta E = E_{TS} - E_{IS}$$

initial state	product state	ΔE (kJ/mol)
1. CH ₃ ⁺ _{ads} + CH ₃ OH _{ads} (2 Os atoms)	CH ₃ CH ₂ OH _{ads}	319
2. CH ₃ ⁺ _{ads} + H ₂ O _{ads} + CH ₃ OH _{ads} (3 Os atoms)	CH ₃ CH ₂ OH _{ads} + H ₂ O _{ads}	251
3. CH ₃ OH _{ads} + CH ₃ OH _{ads} (2 Os atoms)	CH ₃ CH ₂ OH _{ads}	310
4. CH ₃ ⁺ _{ads} + CH ₃ OCH ₃ _{ads} (2 Os atoms)	CH ₃ OCH ₂ CH ₃ _{ads}	270
5. CH ₃ ⁺ _{ads} + H ₂ O _{ads} + CH ₃ OCH ₃ _{ads} (3 Os atoms)	CH ₃ OCH ₂ CH ₃ _{ads} + H ₂ O _{ads}	211
6. CH ₃ OH _{ads} + CH ₃ OCH ₃ _{ads} (3 Os atoms)	CH ₃ OCH ₂ CH ₃ _{ads} + H ₂ O _{ads}	265

In the future, when larger systems containing T-site rings become computationally accessible, the transition states and adsorption complexes reported here can be used as starting points to analyze in detail the consequences of an embedded system. At the moment, although they are being tested,^{19,24,25} they are exceptionally demanding in terms of computational resources being thus far from the daily "routine" calculations.

3. Results

1. Ethanol and Methyl Ethyl Ether Formation. Two main paths for carbon-carbon bond formation are considered. The direct reaction path without formation of intermediates such as oxonium ions and reaction paths that proceed via intermediate oxonium ion formation. The activation energies and reaction paths have been summarized in Tables 1 and 2 respectively. In the table for each initial state the number of surface oxygen atoms (O_s) required to make reactions possible is indicated. In the zeolite it implies a site requirement, since not each zeolite T-site can offer three oxygen atoms for coordination. A total of six direct carbon-carbon formation routes and three indirect routes have been considered.

Primary products from the direct as well as indirect mechanism are ethanol or methyl ethyl ether. Figures 1–3 show three different reaction paths for ethanol formation. The first two are methoxy-mediated reactions while the last involves an associative mechanism. For clarity, the hydride termination of the lattice oxygens and one hydroxyl termination of the aluminum atom are not shown. The first path, depicted in Figure 1, starts with a surface methoxy species. A methanol molecule reacts with this methoxy group to produce adsorbed ethanol.

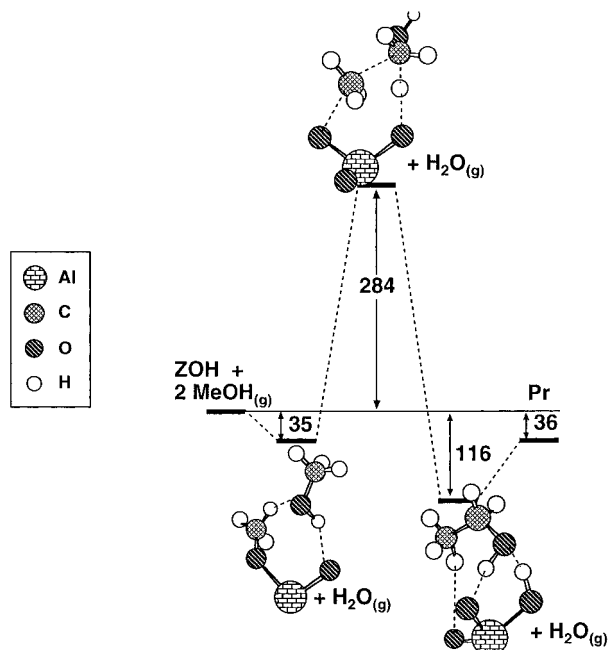
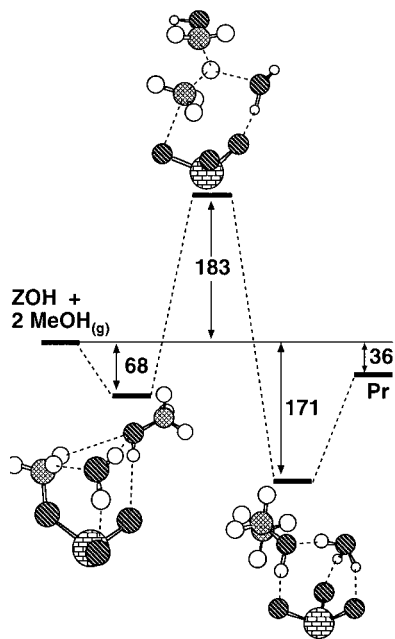
Since the use of the small cluster would produce an incorrect extra bond between the OH of methanol with the OH termination of the cluster, we have used a cluster with silicon terminations in this case. The high transition state energy for this reaction of 319 kJ/mol is due to the need to stretch the methoxy CO bond and the highly covalent CH bond in methanol. The methanol molecule becomes rotated in the transition state such that the weak methanol hydrogen bond is broken and is replaced by an interaction between the basic cluster oxygen atom and the methanol CH₃ group. In the final state one of the methyl hydrogen atoms is back-donated as a proton to the cluster oxygen atom. As discussed earlier, a methoxy intermediate can be formed from a single as well as two adsorbed methanol molecules.^{21,28,29}

Figure 2 shows the second reaction path that, similar to the first, starts with the surface methoxy species. This will be followed by ethanol formation. Now the importance of coad-

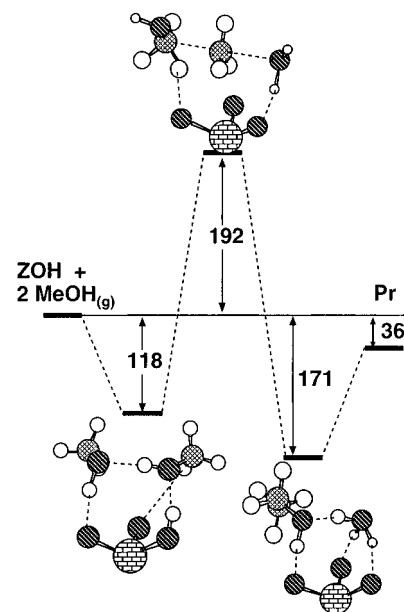
Table 2. Carbon–Carbon Bond Formation Activation Energies (via trimethyloxonium); Decomposition of Trimethyloxonium

$$\Delta E^I = E_{\text{TS}}^I - E_{\text{IS}}; \quad \Delta E^A = E_{\text{TS}}^A - E_{\text{AS}}; \quad \Delta E^T = E_{\text{TS}}^A - E_{\text{IS}}$$

initial state	intermediate	ΔE^I (kJ/mol)	adsorption complex	product	ΔE^A (kJ/mol)	ΔE^T (kJ/mol)
1. $\text{CH}_3^+_{\text{ads}} + \text{CH}_3\text{OCH}_3_{\text{ads}}$ (3 O_s)	$\text{O}(\text{CH}_3)_3_{\text{ads}}$	143	$\text{O}(\text{CH}_3)_3_{\text{ads}}$	$\text{CH}_3\text{OCH}_2\text{CH}_3_{\text{ads}}$	220	336
2. $\text{CH}_3\text{OCH}_3_{\text{ads}} + \text{CH}_3\text{OCH}_3_{\text{ads}}$ (3 O_s)	$\text{O}(\text{CH}_3)_3_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$	173	$\text{O}(\text{CH}_3)_3_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$	$\text{CH}_3\text{OCH}_2\text{CH}_3_{\text{ads}}$	215	348
3. $\text{CH}_3^+ + \text{CH}_3\text{OCH}_3_{\text{ads}}$ (3 O_s)	$\text{O}(\text{CH}_3)_3_{\text{ads}} + \text{CH}_3\text{OH}_{\text{ads}}$	143	$\text{O}(\text{CH}_3)_3_{\text{ads}} + \text{CH}_3\text{OH}_{\text{ads}}$	$\text{C}_2\text{H}_5\text{OH}_{\text{ads}} + \text{CH}_3\text{OCH}_3_{\text{ads}}$	205	269
4.			$\text{O}(\text{CH}_3)_3_{\text{ads}} + \text{CH}_3\text{OH}_{\text{ads}}$	$2\text{CH}_3\text{OH}_{\text{ads}}$	52	

**Figure 1.** Ethanol formation via a methoxy-mediated mechanism. Energies in kJ/mol.**Figure 2.** Ethanol formation via a methoxy/water-mediated mechanism. Energies in kJ/mol.

sorbed water is studied. The transition state becomes rather different from the one in the previous path. In the diagram the

**Figure 3.** Ethanol formation via an associative mechanism. Energies in kJ/mol.

most stable mode of adsorption for methanol and water at the methoxy surface is shown.

Note that now the initial state requires at least three oxygen surface O_s atoms.

The activation energy was lower by 68 kJ/mol compared to the complex without the water molecule. This demonstrates the importance of an “assisting” molecule in cases where the reaction proceeds via a methoxy intermediate.^{21,28,29}

The reason for such a lower activation barrier is partially because of the less strained geometry of the transition state. Comparing the $\text{C}-\text{C}-\text{O}_L$ angle ($L = \text{lattice}$) of the transition state without water (153°) with the one including water (172°), one sees an increase of 20° for this angle. The larger angle allows the carbenium-like ion in the transition state to become as close as possible to the trigonal planar geometry, its most stable configuration. Since this is an $\text{S}_{\text{N}}2$ type reaction, inversion of the hydrogens of the carbenium-like ion leaving the surface in the direction of the methanol molecule occurs. An angle of 180° will produce the least distorted geometry for the carbenium ion, and thus a more stable transition state as discussed before.^{18,29} In addition the polarizable adsorbed molecule (water of methanol) will help in the stabilization of the polar transition states.

The third path (Figure 3) circumvents formation of intermediate methoxy from methanol. Elsewhere^{21,28} we discussed the associative path for dimethyl ether formation and methoxy formation, with transition state energies of respectively 145 and 100 kJ/mol, starting from a similar initial state. Here we find that the transition state for alcohol formation requires 310 kJ/

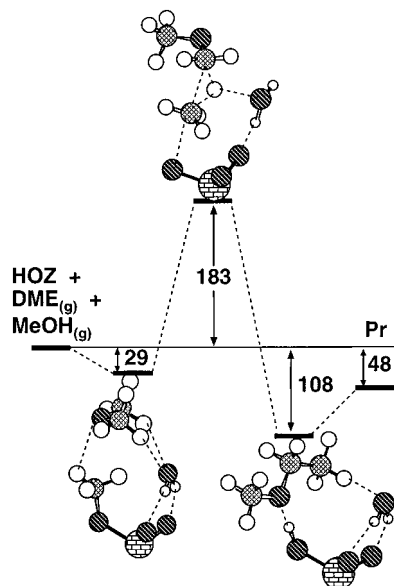


Figure 4. Ethyl methyl ether formation via a methoxy/water-mediated mechanism. Energies in kJ/mol.

mol, only slightly less than the methoxy intermediated reaction path. Note how in all three transition states the surface methoxy is converted to a planar carbenium ion in the transition state.

The transition states for the reaction of dimethyl ether to methyl ethyl ether are quite analogous to the transition states discussed for reaction with methanol. The main difference is the considerably reduced barrier energy. For the reaction of dimethyl ether in the presence of a water molecule a barrier as low as 211 kJ/mol is found. The corresponding structures are shown in Figure 4. Interestingly, Jamamurthy et al.⁴⁰ deduced for Temperature Programmed Desorption experiments with pre-adsorbed methanol an activation energy of 195 kJ/mol. Whereas for dimethyl ether formation we found earlier^{21,20} that methoxy formation is not a necessary step, here we find for the formation of methyl ethyl ether that the methoxy species is an essential surface intermediate.

Trimethyloxonium (TMO) can be formed from DME by reaction with a methoxy surface intermediate (methoxy mediated, shown in Figure 5) or by reaction with methanol (associative path, Figure 6). Table 2 summarizes the results obtained. The transition state energies for trimethyloxonium ion formation as well as the consecutive carbon-carbon bond formation step are given. Also the overall transition state energy ΔE^{\ddagger} with respect to the initial state can be found in the table. Comparison of these values with those in Table 1 shows immediately that the reaction path via trimethyloxonium has to be considered unfavorable compared to the direct C-C bond formation path (reaction path 5, Table 1). Formation of the trimethyloxonium ion appears to be relatively easy. However, formation of a carbon-carbon bond from this intermediate is highly activated. The lowest reaction path corresponds to intermolecular methylation of trimethyloxonium, a reaction also considered by Olah et al.⁴¹ (Table 2, reaction 3, Figure 7).

According to the mechanism proposed by Van den Berg⁴ and Olah et al.,⁵ TMO could be involved in C-C bond formation by first donating one of the hydrogens to the lattice with formation of an ylide [dimethyloxonium methylide, $(\text{CH}_3)_2\text{O}^+\text{CH}_2^-$], which by (i) Stevens rearrangement⁴ would result in methyl ethyl ether or (ii) by reaction with methanol or DME⁵

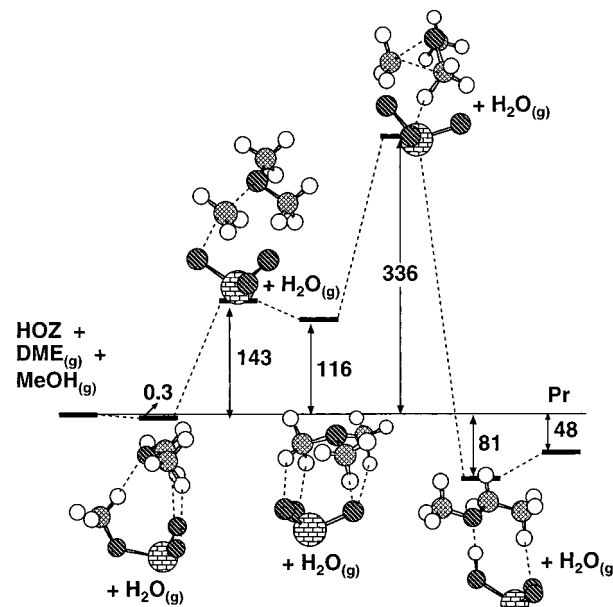


Figure 5. Trimethyloxonium formation from a surface methoxy species and DME followed by ethyl methyl ether formation. Energies in kJ/mol.

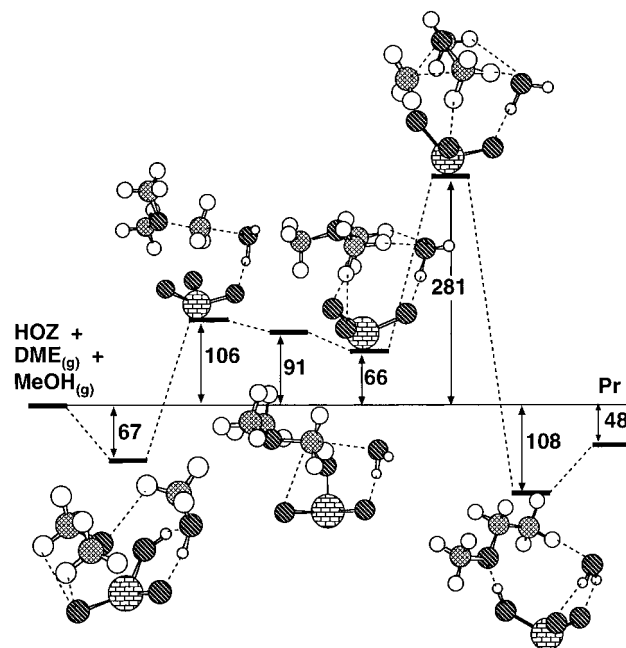


Figure 6. Trimethyloxonium formation via an associative mechanism from methanol and DME followed by ethyl methyl ether formation in the presence of water. Energies in kJ/mol.

would give ethyldimethyl oxonium. This last compound would result in ethylene and DME formation. In trying to optimize the ylide, the proton was found to return to TMO. Several different initial geometries have been used, but in no case was ylide obtained. The only situation where the proton did stay attached to the lattice, resulting in the ylide was the one where the system was optimized with the MNDO (PM3) method. However, this cannot be considered a reliable result. We have optimized the transition state for the methyl ethyl ether formation (Stevens rearrangement) directly from TMO.

Additionally, we have considered the formation of two DME molecules and water from TMO and MeOH (Table 2, reaction 4). The reaction path is depicted in Figure 8. The TS involved is an associative type TS. The barrier is ~ 150 kJ/mol lower than that of the previous cases. The conclusion is that formation

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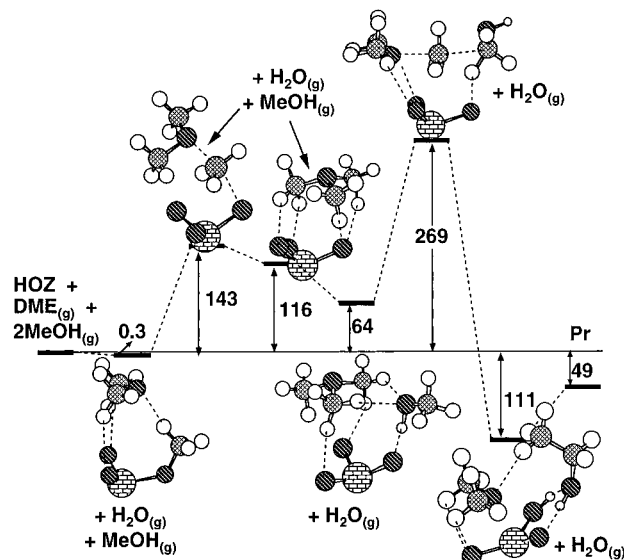


Figure 7. Ethanol formation from trimethyloxonium and methanol. Energies in kJ/mol.

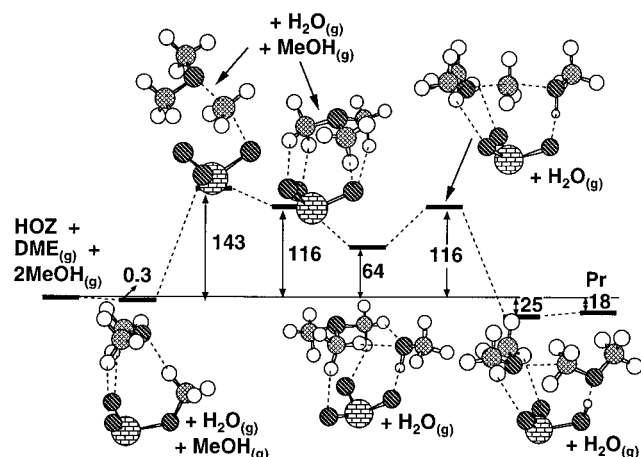


Figure 8. DME formation from trimethyloxonium and methanol. Energies in kJ/mol.

Table 3. Activation Energies for Ethylene Formation (direct reaction paths)

$$\Delta E = E_{\text{TS}} - E_{\text{IS}}$$

initial state	product state	ΔE (kJ/mol)
1. $\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}$	$\text{CH}_2\text{CH}_2_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$	171
2. $\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$ (3 Os atoms)	$\text{CH}_2\text{CH}_2_{\text{ads}} + 2\text{H}_2\text{O}_{\text{ads}}$	182
3. $\text{CH}_3\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O}_{\text{ads}}$ (2 Os atoms)	$\text{CH}_2\text{CH}_2_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}} + \text{CH}_3\text{OH}_{\text{ads}}$	134

of compounds with a C–C bond from TMO is very difficult, and decomposition of trimethyloxonium to two dimethyl ether molecules by reaction with methanol is relatively easy. This has also been observed experimentally.⁹

2. Ethylene Formation. Ethylene and propene have been reported as important intermediates.⁴² Therefore a study of the dehydration of ethanol and acid catalyzed methyl ethyl ether formation is also of interest. Paths without (Table 3) and with (Table 4) intermediate ethoxy formation have been compared. The lowest reaction path is found for protolysis of the methyl ethyl ether bond to produce ethylene and methanol. This is a reaction that proceeds via intermediate ethoxy formation.

Direct dehydration of ethanol is slightly favored over ethoxy-mediated dehydration. The latter is significantly influenced by

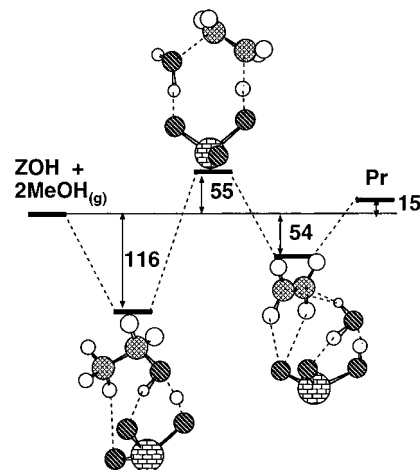


Figure 9. Direct ethylene formation from ethanol. Energies in kJ/mol.

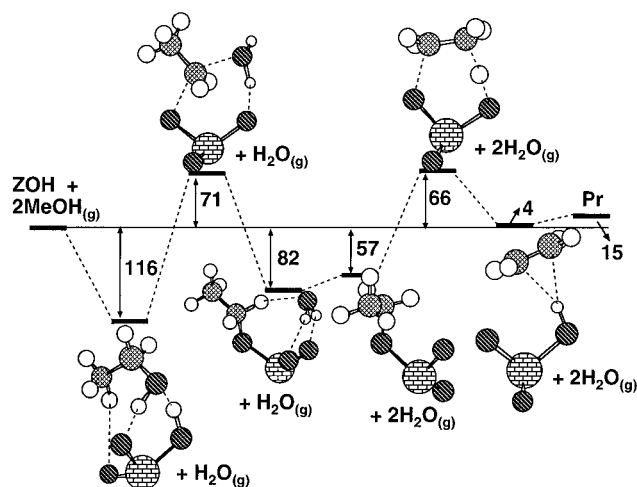
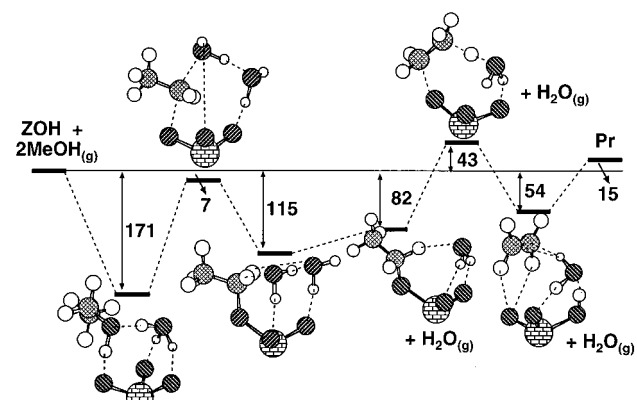
coadsorbed H_2O . Details on reaction energies and transition state structures for these reactions are given respectively in Figures 9, 10, 11, and 12. In order to compare these results with other studies in Figure 10, we have included a reaction energy diagram for the ethoxy-mediated ethylene formation from ethanol.

Ethoxy surface species formation from ethylene has been the subject of earlier studies.^{43,44} Using the Hartree–Fock method (HF), a 1T atom, and a 3-21G basis set, Kazansky et al.⁴⁴ found an activation barrier with respect to the gas-phase ethylene and the zeolitic cluster of 36 kJ/mol. With the same method and cluster, the barrier found by Evleth et al.⁴³ was 66 kJ/mol. Using a 1T atom cluster and a MP2/6-31G* optimized structure, Evleth et al.⁴³ have found an activation barrier with respect to ethylene adsorbed to the zeolitic surface of 100 kJ/mol. The heat of adsorption in this case was calculated to be 30 kJ/mol, which gives an activation barrier with respect to the gas-phase reactants of 70 kJ/mol. Using the same basis set but the DFT/BLYP method, Evleth et al. have calculated a true barrier of 59 kJ/mol, which is close to that obtained in the present work (62 kJ/mol). This shows the tendency of DFT to underestimate adsorption energies and activation barriers, especially for systems involving weak van der Waals interactions.

3. Methane Formation. In experiments performed by Kubelková et al.¹⁴ at a low methanol concentration (0.25–0.7 molecules per zeolite acidic site), DME, methane, and formaldehyde are observed before aromatics formation. When the amount of methanol is increased to two molecules per site, no more CH_4 is observed, but now alkene and alkane formation occur. In the case of very low methanol coverages, formation of methoxy groups from a single methanol should be considered. Figure 13 shows the energy diagram on CH_4 formation from methanol and a surface methoxy. If the CH_3 group of the methanol molecule approaches the methoxy group, hydride transfer to the methoxy group generates CH_4 . Simultaneously, the transfer of the H of the methanol's OH group to the zeolitic surface will regenerate the acidic site with formation of a formaldehyde molecule. The barrier for this process is just a few kilojoules per mole higher than the methoxy mediated DME formation, 210 kJ/mol.¹⁷ In previous work²⁷ we have calculated the transition state for hydride transfer and formation of a surface $-\text{CH}_2\text{OH}$ group from CH_3OH . The true barrier found was much higher, on the order of +275 kJ/mol (or +200 kJ/mol with respect to the gas-phase reactants). The direct path discussed here is clearly the preferred route to CH_4 formation from methoxy and methanol. This does not imply that in

Table 4. Activation Energies for Ethylene Formation (via Ethoxy Intermediates)
$$E^I = E_{TS}^I - E_{IS}; \quad \Delta E^A = E_{TS}^A - E_{AS}; \quad \Delta E^T = E_{TS}^A - E_{IS}$$

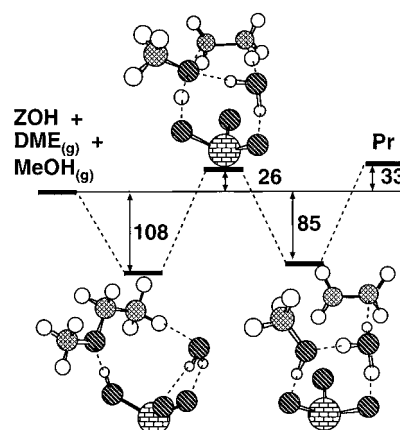
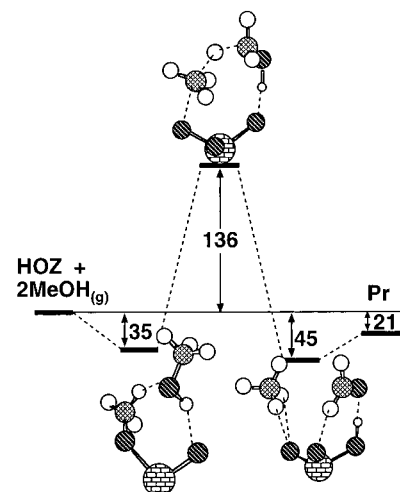
initial state	intermediate	ΔE^I (kJ/mol)	adsorption complex	product	ΔE^A (kJ/mol)	ΔE^T (kJ/mol)
1. $\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}$ (2 O_s)	$\text{CH}_3\text{CH}_2^+_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$	187	$\text{CH}_3\text{CH}_2^+_{\text{ads}}$	$\text{CH}_2\text{CH}_2_{\text{ads}}$	123	182
2. $\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$ (3 O_s)	$\text{CH}_3\text{CH}_2^+_{\text{ads}} + 2\text{H}_2\text{O}_{\text{ads}}$	164	$\text{CH}_3\text{CH}_2^+_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$	$\text{CH}_2\text{OH}_2_{\text{ads}} \text{H}_2\text{O}_{\text{ads}}$	125	214

**Figure 10.** Ethoxy-mediated ethylene formation from ethanol. Energies in kJ/mol.**Figure 11.** Ethoxy-mediated ethylene formation from ethanol in the presence of water. Energies in kJ/mol.

complex reaction mixtures CH_4 formation can also be due to hydride transfer from other molecules.

4. Conclusions

Guided by experimental observations of intermediates formed in studies of the MTG process, several reaction paths for C–C bond formation have been analyzed with DFT. For each reaction several different reaction mechanisms were studied, each one including adsorption complexes of reactants and products as well as transition states. Calculation of heats of adsorption and activation barriers allows for a comparison between different proposed mechanisms and, as a consequence, conclusions can be drawn on the relative importance of the different reaction steps. We propose here that ethanol and ethyl methyl ether are formed from surface methoxy groups, methanol, and/or dimethyl ether. They are the first intermediates containing a C–C bond. The activation barriers involved in their formation are very high being the limiting step for the

**Figure 12.** Direct ethylene formation from ethyl methyl ether and water. Energies in kJ/mol.**Figure 13.** Methoxy-mediated methane and formaldehyde formation. Energies in kJ/mol.

reaction. Ethylene can be easily formed from ethanol and ethyl methyl ether involving much lower activation barriers. The mechanism discussed here operates only for the formation of the very first C–C bonds. In consecutive steps ethylene reacts with oxygenates or other alkenes to give higher olefins, aromatics, alkanes, etc. The reaction chain is maintained by the regeneration of olefins.¹

Formation of trimethyloxonium, proposed to be an intermediate in initial C–C bond formation, is possible. Nevertheless, its further reaction to compounds having a C–C bond, for example, ethyl methyl ether or ethanol, is rather difficult, involving activation barriers that are much too high. Decomposition toward ether involves low activation barriers. The conclusion is that trimethyloxonium can be formed in the MTG

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process, but it plays no important role in forming compounds containing a C–C bond.

For most of the reactions discussed here two different kinds of mechanisms are proposed: one involving an associative interaction of the reactant molecules and another occurring via a surface methoxy species. We have observed that water is very important in stabilizing the transition states involved in alkoxy-mediated reactions where carbenium-type transition states are involved. When water is allowed to assist the reaction, the activation barriers of ethanol or ethyl methyl ether formation can be lowered by 60 kJ/mol. Ethylene formation, on the other hand, does not require extra stabilization provided by water.

The true activation barriers for ethanol and methyl ethyl ether formation are rather high, of the order of +300 kJ/mol (at low surface coverage this implies an apparent activation energy of ~ 180 kJ/mol). These values are not unrealistic. For instance the true activation barrier of the initial cracking reaction of alkanes via carbonium ion type transition states was calculated to be +300 for ethane²⁷ and +240 kJ/mol for isobutane.⁴⁵

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