Methylation of Alkenes and Methylbenzenes by Dimethyl Ether or Methanol on Acidic Zeolites

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Received: March 4, 2005; In Final Form: April 24, 2005

The methylation of propene and toluene with dimethyl ether has been studied using both experimental and theoretical methods, and the results are compared with results obtained for methylation with methanol. The results indicate that the nature of the methylation reaction mechanisms is very similar for both methylation agents. Both experiment and theory show that dimethyl ether is a slightly more reactive methylating agent than methanol.

1. Introduction

The conversion of methanol to hydrocarbons over acidic zeolite catalysts has been the subject of widespread research since the reaction was discovered at Mobil in the 1970s. Depending on the choice of catalyst and reaction conditions, methanol may be transformed into a gasoline fraction rich in aromatics or into light alkenes, predominantly ethene and propene.[1–3] The reaction mechanism of the methanol to hydrocarbons reaction has been the subject of considerable debate, and more than 20 different mechanistic proposals may be discerned in the vast literature covering the subject.[2]

However, during the past decade, our understanding of the reaction steps comprising the mechanism during steady-state conversion has been greatly enhanced, as the *hydrocarbon pool* mechanism has gained increasing acceptance.[4–6] This is an indirect mechanism, believed to proceed via repeated methylations and dealkylations of organic reaction centers trapped inside the zeolite voids. The exact chemical nature of the hydrocarbon pool might depend on both reaction conditions and catalyst type. However, methylbenzenes, and in particular the higher homologues, have been identified as key intermediates during methanol conversion over both SAPO-34 and H-*β* catalysts.[7–20]

To elucidate the complex hydrocarbon pool mechanism, it has been particularly useful to investigate the reactivity of the compounds known to be present inside the catalyst voids during the methanol-to-hydrocarbons reaction (MTH). Both experimental and computational reports on the coupling methanol with alkenes or arenes, alkenes with arenes, and alkenes with alkenes have been presented previously.[21–24] Also, the loss of alkenes from the methylbenzene intermediates mentioned above has been examined with experimental and computational techniques.[25]

In the present report, we address a less-explored issue and compare the reactivity of dimethyl ether and methanol as methylating agents toward alkenes and arenes. The dehydration of two methanol molecules into dimethyl ether and water is

the fastest reaction in the MTH system, and methanol and dimethyl ether are typically present simultaneously when the conversion of methanol is less than 100%. Methanol or dimethyl ether and propene have been co-reacted at very high feed rates in order to isolate the methylation step and to minimize product formation via other routes, such as the above-mentioned hydrocarbon pool mechanism. These experimental observations are compared with results obtained with computational techniques, and it has hence been possible to assess the reactivity of the two methylating agents individually.

2. Methods

2.1. Computational Details. All calculations were done using the Gaussian 98 program package.[26] The B3LYP hybrid density functional combined with 6-31G(d) basis sets was employed for all geometry optimizations. No geometric constraints were used in the optimizations. Additionally, single-point electronic energies were calculated for the optimized geometries using B3LYP and MP2 combined with larger basis sets, i.e., B3LYP/cc-pVTZ and MP2/6-311G(d,p). This methodological approach has been thoroughly evaluated for related systems and found to be adequate for our purposes.[21–24]

The zeolite catalyst has been modeled by a widely used cluster consisting of four tetrahedral atoms (4T), i.e., three silicon and one aluminum atom in order to generate the acidic site, as detailed in ref 22. The three silicon atoms surround aluminum, thus creating a small surface area. These silicon atoms and the oxygen atom bonded to aluminum on the underside of the cluster are saturated with hydrogen atoms. Quite often, there are several possible orientations of the reacting molecules on the cluster. For instance, a methyl group substituent may point away from or toward the surface. Care was taken to ensure that reactants and products were coordinated similarly to the cluster for all reactions, thereby making the calculation of reliable energy trends easier, but not otherwise influencing the results.

For all stationary points, vibrational spectra were calculated to ensure that the correct number of imaginary frequencies was at hand, i.e., one imaginary frequency for transition states and zero for energy minima. The correctness of the transition states was investigated by perturbing the geometries very slightly along the reaction coordinate corresponding to the negative eigenvalue

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in the Hessian and using the geometries thus produced as starting points for energy minimizations. This is a convenient method for locating the energy minima connected by a given transition state. It was confirmed that the transition states that were found involve the rupture and formation of the required bonds, thus properly describing the desired reactions.

In the following, when energies are discussed, we refer to the B3LYP/6-31G(d) + ZPE values, unless otherwise stated.

2.2. Experimental Procedure. The methylation of propene over an H−ZSM-5 catalyst was selected as a test reaction to evaluate the reactivity of methanol and dimethyl ether as methylating agents. The experimental setup has been described in detail previously.[27,28] The experiments were carried out in a fixed bed microreactor. Propene and dimethyl ether were fed as gases, whereas methanol was introduced by passing part of the carrier gas (nitrogen) through an evaporation saturator. Total gas flow through the reactor was held constant at 100 mL/min. The propene partial pressure was fixed at 20 mbar, and the methanol and dimethyl ether partial pressures were varied from 25 to 75 mbar for methanol and to 100 mbar for dimethyl ether. The resulting feed rates (WHSV) are in the ranges 161−317 and 195−531 h^{-1} for methanol + propene and dimethyl ether + propene, respectively.

The H−ZSM-5 catalyst used was a gift from Süd-Chemie. The Si/Al ratio is 45, and the crystal size is very small, about 50 nm. The catalyst activity was stabilized by reacting neat methanol for some hours prior to the actual methylation experiments. Control experiments where ^{13}C-methanol and ^{12}C-alkenes were co-reacted were performed, and the pretreatment with neat methanol does not have significant effect on the isotopic distribution of the methylation products. This shows that the reaction mechanism does not depend on the stabilizing procedure. The pretreatment combined with the small crystal size makes the catalyst resistant toward further deactivation and diffusion limitations and thus ideally suited for kinetic measurements.

Product analysis was performed using standard gas chromatography (GC-FID). Previous experiments with isotopically labeled methanol have shown that, at the reaction conditions outlined above, more than 80% of the linear butenes are formed via methylation.[27,28] Hence, the total yield of linear butenes constitutes a good measure of the rate of propene methylation and has been used to calculate the rates in the current set of experiments.

3. Results and Discussion

3.1. Calculations. The computational results presented here are derived from a fairly simple, but well-validated, cluster model.[21−24] Quite clearly, such cluster calculations severely overestimate barrier heights. This is caused mainly by the omission of the larger part of the catalyst framework surrounding the active site and limitations of the computational scheme employed. As a consequence, steric effects are poorly described as arbitrarily large molecules or assemblages of molecules may be adsorbed onto the cluster. Moreover, the limited description of the electrostatic field that is present inside the zeolite pores combined with the poor ability of density functional theory (DFT) methods to model weak dispersion forces lead to a considerable destabilization of charged species and transition states with considerable charge separation relative to neutral molecules physisorbed onto the cluster. This is amply discussed elsewhere.[21−24] Despite these complications, it is possible to perform qualitative explorations of general reaction mechanisms of reactions that occur locally on one single active site.[29] Further,

comparisons of the energy profiles for similar chemical rearrangements that are unaffected by steric limitations appear to be valid, and this approach has led to a fair amount of insight on several different systems.[21−24,30−34]

The combination of two methanol molecules to form dimethyl ether and water has been the subject of several computational studies.[35−37] Blaszkowski and van Santen investigated three different reaction paths relying on a 3T cluster model combined with an NLSCF/DZPV computational scheme and concluded that a concerted, single-step mechanism is favored over mechanisms involving a surface bound methoxide intermediate.[37] A barrier of 145 kJ/mol was found. We recalculated the energy profile for concerted dimethyl ether formation with our cluster and found an activation energy relative to the adsorbed reactants of 134 kJ/mol at the B3LYP/6-31G(d) + ZPE level, 132 kJ/mol without ZPE correction, and 144 and 140 kJ/mol at the B3LYP/cc-pVTZ//B3LYP/6-31G(d) and MP2/6-311G(d,p)//B3LYP/6-31G(d) levels, respectively. Additional details are given in the Supporting Information. The slightly lower barrier found here can be attributed to the somewhat larger cluster model and the use of a different computational scheme. For comparison, Bandiera and Naccache have reported an experimentally determined true activation barrier of 80 kJ/mol for dimethyl ether formation on H-mordenite.[38]
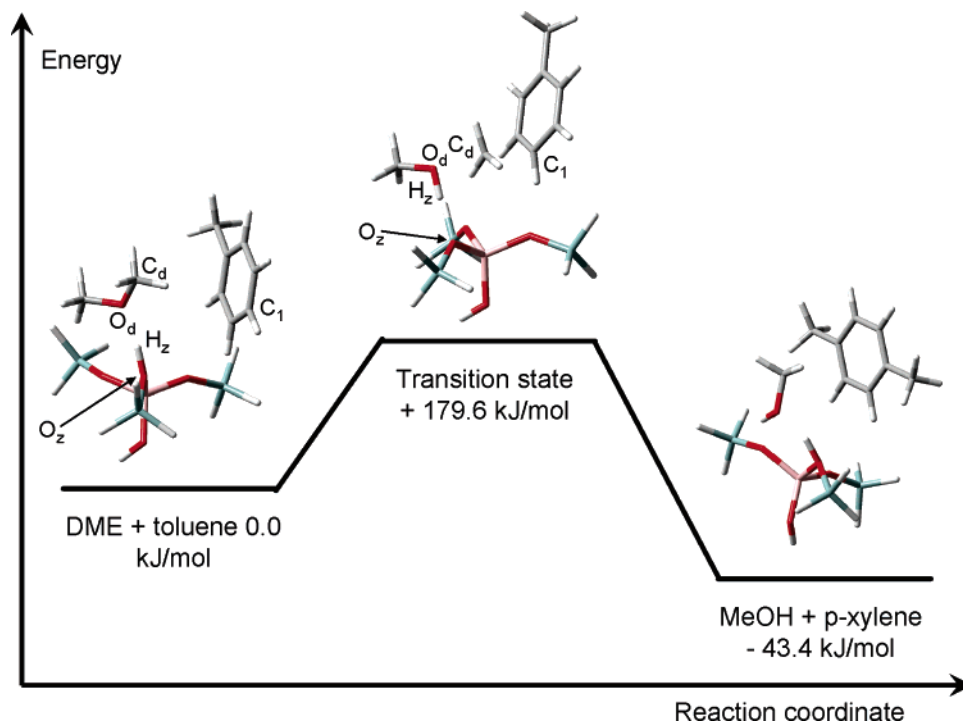
The energy profiles for the methylation of propene and toluene with dimethyl ether are displayed in Figures 1 and 2, respectively. Calculated energies are shown in Table 1, and relevant geometric parameters are given in Table 2. We have previously studied the methylation of alkenes[21] and arenes[22] with methanol, and some data are included in Tables 1 and 2 for comparison. An associative methylation mechanism has been assumed, where initially both reactants are loosely bound (physisorbed) to the cluster. Carbon−carbon bond formation then occurs in a single-step fashion and does not involve a methoxide intermediate. Vos et al. have shown that this single step, associative methylation mechanism is at least as likely as a two-step, dissociative mechanism involving a surface bound intermediate when methanol is the methylating agent.[33]

The starting point for both methylations is dimethyl ether and the hydrocarbon coadsorbed on the cluster. Dimethyl ether is located on the acidic site, as a hydrogen bond is formed between the dimethyl ether oxygen atom and the acidic proton. This is indicated by the H_zO_d distances in Table 2. The hydrocarbons are loosely bound and located next to dimethyl ether on the cluster. The coadsorption energies are slightly smaller than those previously reported for methanol and propene or toluene,[21,22] indicating that dimethyl ether is somewhat less strongly adsorbed than methanol.

In the transition states, the acidic proton is completely transferred to dimethyl ether and a new hydrogen−oxygen bond is formed, as seen from the H_zO_d distances. Consequently, one of the methyl groups is departing, and it is about halfway between the hydrocarbon and the O_d atom. This methyl group undergoes an S_N2 type umbrella inversion and has just passed beyond the planar inversion point at the transition state, as seen from the small $O_dC_1C_2C_d$ dihedral angles. Geometrically, the transition states are very similar to those previously reported for the methanol cases, but the O_zH_z distances are shorter for dimethyl ether, indicating a stronger interaction. However, when methanol is the methylating agent, a water molecule is formed, and this water molecule forms two hydrogen bonds, as opposed to only one hydrogen bond when dimethyl ether is investigated.
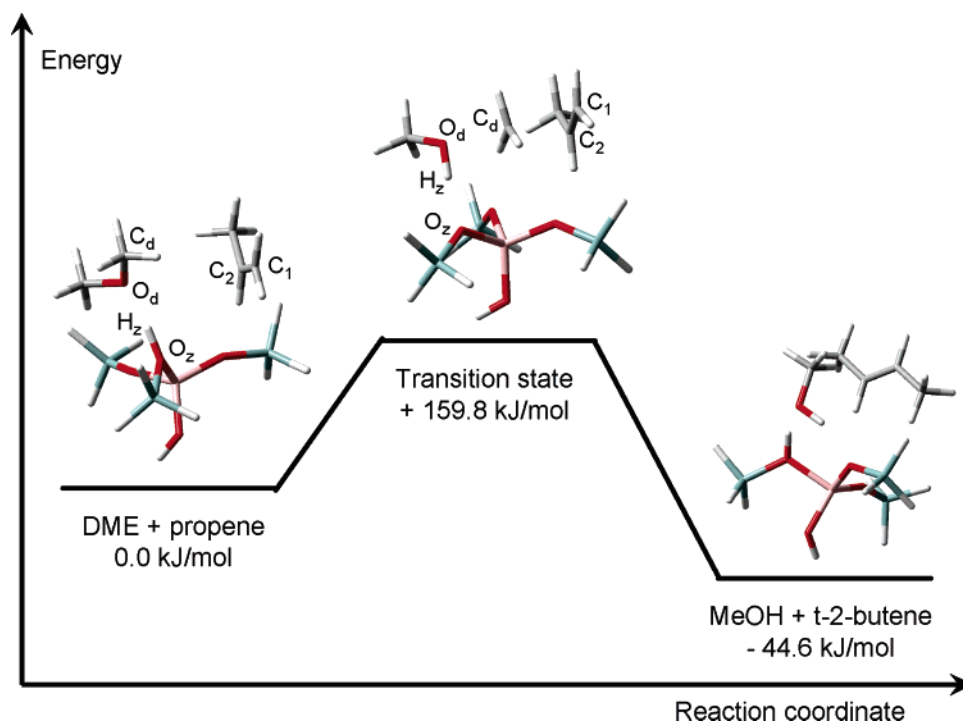
Figure 1. Energy profile for the methylation of propene with dimethyl ether. B3LYP/6-31G(d) + ZPE energies. Atom-type assignment: Grey, carbon; white, hydrogen; red, oxygen; light blue, silicon; aluminum, pink.

Figure 2. Energy profile for the methylation of toluene with dimethyl ether. B3LYP/6-31G(d) + ZPE energies. For atom-type assignments, see Figure 1.

The calculated barrier heights are slightly lower for dimethyl ether than for methanol. This is reproduced at every level of theory investigated and for both hydrocarbons. On average, the barriers are 8 kJ/mol lower for dimethyl ether, corresponding to a factor of 5 in reaction rate at 350 °C, if the preexponentials are assumed equal.

The progress of reaction beyond the transition states was evaluated by employing the quasi-IRC approach outlined above. The stationary points thus found are designated as "intermediate" in Table 1. For propene, this resulted in formation of methyl-

cyclopropane as one of the protons originating from the propene molecule was returned to the cluster. Methylcyclopropane is not formed during experimental studies, and its predicted formation might be a computational artifact. Similar results have previously been found for alkene dimerization, and this is thoroughly discussed in ref 23. The most stable product arrangement is that shown in Figure 1; methanol is adsorbed on the acidic site and *trans*-2-butene, the thermodynamically most stable linear butene, is located next to methanol. For toluene, the quasi-IRC technique resulted in immediate depro-

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TABLE 1: Energies of the Stationary Points for the Methylation Reactions Relative to the Co-adsorbed Reactants[a]

gas-phase reactants	transition state	intermediate[b]	adsorbed products	gas-phase products	ΔE_a found with methanol	level of theory
			Propene			
67	160	26	−45	43	169	B3LYP/6-31G(d) + ZPE
77	162	22	−44	54	170	B3LYP/6-31G(d)
59	165	13	−54	20	172	B3LYP/cc-pVTZ//B3LYP/6-31G(d)
97	169	−26	−66	46	175	MP2/6-311G(d,p)//B3LYP/6-31G(d)
			Toluene			
69	180	−23	−43	47	190	B3LYP/6-31G(d) + ZPE
78	184	−20	−41	59	195	B3LYP/6-31G(d)
61	186	−33	−49	26	195	B3LYP/cc-pVTZ//B3LYP/6-31G(d)
108	201	−49	−68	56	209	MP2/6-311G(d,p)//B3LYP/6-31G(d)

[a] Data for methylation with methanol taken from refs 21 and 22. [b] For the methylation of propene, methylcyclopropane is formed immediately after the transition state. For the methylation of toluene, the product, *p*-xylene, is first adsorbed onto the acidic site, whereas the most stable product configuration (adsorbed products) involves adsorption of water on the acidic site. See text for additional discussion.

TABLE 2: Geometric Parameters for the Reactions Investigated (Bond Lengths in Å, Angles and Dihedrals in Degrees; Atom Labels Defined in Figures 1 and 2; Some Data Taken from References 21 and 22)

	propene		toluene	
	methanol	dimethyl ether	methanol	dimethyl ether
		Reactants		
O_zH_z	1.03	1.01	1.03	1.01
H_zO_d	1.54	1.61	1.54	1.60
O_dC_d	1.44	1.43	1.44	1.43
C_dC_1	3.94	4.04	4.04	4.09
C_dC_2	4.20	3.78		
		Transition States		
O_zH_z	1.85	1.66	1.87	1.68
H_zO_d	0.99	1.00	0.99	1.00
O_dC_d	2.23	2.17	2.28	2.45
C_dC_1	2.07	2.16	2.00	2.02
C_dC_2	2.35	2.33		
$O_dC_dC_1$			175.1	170.5
$O_dC_1C_2C_d$	3.0	2.1		

TABLE 3: Product Selectivities and Degree of Conversion into Hydrocarbons Other than Propene (Propene 20 mbar Co-reacted with Dimethyl Ether (DME) or Methanol over an H−ZSM-5 Catalyst)

partial pressure (mbar)	*n*-butene (C %)	isobutene (C %)	pentenes (C %)	C_{6+} (C %)	conversion (C %)
		DME			
25	53.3	12.5	18.4	14.3	5.3
50	50.0	11.3	18.7	18.5	4.7
75	48.2	11.0	18.8	20.1	3.9
100	46.6	10.3	18.9	22.2	3.6
		Methanol			
25	59.1	8.6	16.2	10.8	2.5
50	56.7	7.1	17.0	13.5	2.2
75	55.9	6.6	17.2	14.9	1.7

tonation, with *p*-xylene located on the acidic site. A more stable product configuration, however, is found when methanol is interacting with the acidic proton, as shown in Figure 2.

3.2. Experiments. The methylation of propene using methanol or dimethyl ether was investigated over an H−ZSM-5 catalyst. Product selectivities are listed in Table 3, and the measured rates of methylation are shown in Figure 3. The experiments were carried out at very high feed rates in order to minimize any side reactions, which inevitably compete with and might even overshadow the methylation step. Previous experiments, where isotopically labeled methanol was used, have shown that the total amount of linear butenes formed during
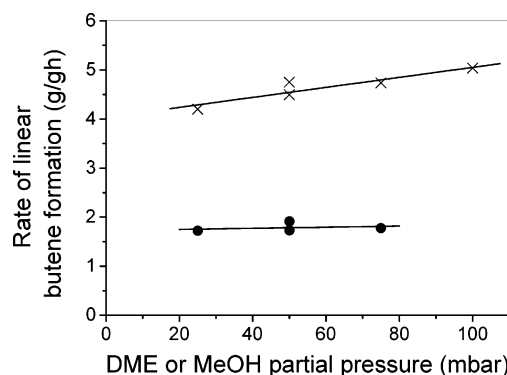
Figure 3. Rate of linear butene formation. Propene (20 mbar) co-reacted with dimethyl ether (DME, crosses) or methanol (MeOH, filled circles) over an H−ZSM-5 catalyst.

the co-reaction constitutes a good estimate of the rate of propene methylation.[27,28]

Linear butenes, which are the expected outcome of a methylation reaction, were always the dominating product in either co-reaction system, with selectivities always close to 50 C % (Table 3). A slightly higher selectivity toward linear butenes was found for methanol, and this is possibly due to the somewhat lower total conversion. In addition to the products listed in Table 3, trace amounts of methane, ethane/ethene, and butanes were observed. The partial pressures of the methylating agents (methanol or dimethyl ether) were varied, and the reaction orders are very close to zero with respect to the methylating agent. This means that the acidic sites are completely covered with either methanol or dimethyl ether and that the data are directly comparable for the two cases. Clearly, the rate of methylation is greater for dimethyl ether than for methanol, with a factor close to 2.5. Assuming equal preexponential factors, this corresponds to a difference in activation energy of 5 kJ/mol at 350 °C.

As a complicating factor, there is some formation of methanol when dimethyl ether is co-reacted with propene. The concentration of methanol at the reactor outlet was close to 4% of the initial dimethyl ether concentration (mole-based), and this corresponds fairly well to the amount of methanol expected if all the *n*-butenes were formed via methylation, the pentenes via double methylation, and the hexenes via triple methylation. Also, there is a prominent formation of dimethyl ether when methanol is co-reacted with propene; the conversion of methanol into dimethyl ether is around 20%. If dimethyl ether is able to compete with methanol for active sites, this might lead to a

slight overestimation of the rate of methylation with methanol, but does not otherwise alter the salient features of Figure 3.

3.3. Concerted versus Stepwise Methylation. We have assumed that the methylation steps occur in a concerted, single-step manner, and the results presented above are fully concurrent with this assumption. However, it should be emphasized that the current data do not allow us to discriminate between a concerted mechanism and a reaction pathway involving surface-bound methoxide intermediates. Even so, some considerations regarding this matter can be made. The methylation was found to be zero order with respect to both methylating agents, and the rate of methylation is greater for dimethyl ether. This zero-order behavior does not imply that there is pseudo-equilibrium between physisorbed methanol/dimethyl ether and methoxide groups. If this were the case, both methylating agents should display identical reactivity, because methylation by the methoxide group, rather than a reaction involving methanol or dimethyl ether, would be the rate-determining step. Hence, *if* the reaction does proceed in a stepwise manner, the methoxide formation must be rate-determining, and the concentration of methoxide groups must be low relative to the concentration of the physisorbed methylating agent.

4. Conclusions

The activity of dimethyl ether and methanol in zeolite-catalyzed methylation reactions has been investigated and compared with both experimental and theoretical methods. The methylation of propene and toluene with dimethyl ether or methanol was investigated using cluster calculations, and the methylation of propene with both methylating agents was examined experimentally. Excellent correlation between experiments and calculations was found. Dimethyl ether is found to be more reactive than methanol, with a factor of 5 as derived from calculations and 2.5 from experiments.

Supporting Information Available: Cartesian coordinates for all reported stationary points and a graphic of the calculated energy profile for the formation of dimethyl ether and water from methanol (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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