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The Mechanism of Dimethyl Ether Formation from Methanol Catalyzed by Zeolitic Protons

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The methanol-to-gasoline (MTG) process is one of the most successful routes for the catalytic conversion of methanol to hydrocarbons in the gasoline boiling range (30–200 °C). A large variety of different experiments established that methanol catalyzed by an acidic zeolite 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 methanol adsorption, dehydration, and silylation, formation of the first C–C bond and the nature of the intermediates involved are still not fully understood. Concerning DME formation, different mechanisms have been proposed in the literature. Bandiera and Naccache proposed the reaction of methanol occurs at the Brønsted acid and its adjacent Lewis basic sites with formation of the two surface species $[\text{CH}_3\text{OH}]^+$ and $[\text{CH}_3\text{O}]^-$ which, upon condensation, give DME and water. Kubelková et al. proposed that methanol is initially adsorbed at the zeolite. With transference of the zeolitic proton the methoxonium ion, $\text{CH}_3\text{OH}^+$, is formed. This dehydrates leaving a methyl group bonded to the zeolitic surface. Later on, those surface methoxy groups can react with another species $[\text{CH}_3\text{O}]^-$ to be a stable intermediate species in the dehydration process, which upon condensation also used in its methoxy form, where the acidic proton was replaced by a methyl $(\text{CH}_3)$ group.

Two different pathways were studied for the DME formation. The first path (Path I) involves two different elementary steps, as shown in Figure 1. The AIOH cluster has been used, but the hydride termination of the silicon atoms are not shown in the pictures. The first step is associated with the initial adsorption of one methanol molecule at the zeolite acidic site which is then dehydrated, leaving a methyl group attached to the basic oxygen of the zeolite. This step was discussed earlier in more detail. Activation barrier taken with respect to the most stable mode of adsorption of one methanol molecule at the acidic site (PI-ads$_{\text{meth}}$) is rather high, plus 215 kJ/mol. Using Hartree–Fock plus MP2 correction this barrier was found to be plus 231 kJ/mol. The methoxonium ion $(\text{CH}_3\text{OH}^+)$, proposed to be a stable intermediate species in the dehydration process, was found to be a transition state for the reaction of hydrogen exchange. The dehydration process is followed by the reaction of the surface methoxy species with a second methanol molecule. The adsorption of the second methanol to the surface methoxy (PI-ads$_1$) is exothermic with an adsorption energy of $-37$ kJ/mol. With respect to this state, the true activation barrier for DME formation (the energy difference between PI-ads$_1$ and PI-ts$_1$) was calculated to be plus 160 kJ/mol. The rate-limiting step for DME formation according to this first pathway is, thus, the dehydrogenation of the first methanol molecule, plus 215 kJ/mol. The $\text{CH}_3$ group of the transition state PI-ts$_1$ has characteristics of a carbenium ion with a trigonal planar geometry. It is similar to the TS for the dehydration process, PI-ts$_{\text{Sal}}$. For both TS's, the acidic and basic sites of the zeolite are involved.

The reaction energy diagram for the second reaction path of methanol dehydration (Path II) using the AIOH cluster is shown in Figure 2. In this second path two methanol molecules are adsorbed in the acidic/basic sites of the zeolite (PII-ads$_1$ in the figure). The heat of adsorption of two methanol molecules at the acidic site is rather strong, $-130$ kJ/mol (or $-65$ kJ/mol per methanol molecule). Note that the experimental adsorption energy is given in terms of "kilojoules per mole of methanol". As expected, the last value ($-65$ kJ/mol) is slightly lower than the one calculated earlier for a single methanol molecule ($-73$ kJ/mol for the AIOH cluster). This result agrees with one of the experimental heats of adsorption for methanol in H-ZSM5 zeolite reported in the literature, $-63$ kJ/mol, but is lower than the other, $-115$ kJ/mol. The adsorption is followed by the rotation of the methyl group of the right-side methanol molecule in such a way that the methyl group is now free to interact with the hydroxyl group of the left-side methanol molecule (PII-ads$_2$). The last is $\approx 55$ kJ/mol less stable than PII-ads$_1$. Via a rather complex transition state (PII-ts$_2$) water and DME can be directly formed. In the transition state the zeolitic proton is transferred to the right-side methanol, forming a water molecule. The C–O bond stretches, and the methyl group is now much closer to the left-side methanol. The central methyl group assumes sp2 hybridization, characteristic of an imaginary mode. No symmetry constraints have been used in the optimization of any of the studied structures. The clusters $\text{H}_3\text{SiOHAH}_2\text{OSiH}_3$ (AIOH) and $\text{H}_3\text{SiOAIH}_2\text{OSiH}_3$ (AIIH) were used to represent the acidic zeolite. The AIIH cluster was also used in its methoxy form, where the acidic proton was replaced by a methyl $(\text{CH}_3)$ group.
carbenium ion. The proton of the second methanol molecule is transferred back to the zeolite regenerating the acidic site, and simultaneously, DME is formed. In the resulting adsorption complex (PII-ads3) water and DME are strongly adsorbed to the acidic site. Nearly 80 kJ/mol is necessary to desorb them. As it can be seen in the figure, the activation barrier with respect to the reactants is very low, only +15 kJ/mol. With respect to the adsorption complex of the two methanol molecules (PII-ads1), the true activation barrier for this path becomes +145 kJ/mol. This should be compared to the experimental true activation barrier for methanol dehydration to DME for dealuminated H-mordenite, reported to be +80 kJ/mol. The experimental barrier is rather low and not consistent with one of the heat of adsorption for methanol reported in the literature, −115 kJ/mol. With respect to the mechanism proposed by Bandiera and Naccache, although the general idea is the same as for Path II, the details of the mechanism are different. In between the intermediates proposed CH$_3$OH and CH$_3$O$^-$, the first is a TS and the second was not obtained in the calculations. In the Path II we propose that two methanol molecules adsorb at the Lewis basic and Brønsted acid sites, which then undergo the reaction via a complex carbenium-like TS.

The activation barrier obtained for Path II is 70 kJ/mol lower than the limiting step found for the other pathway involving the intermediate surface methoxy species (+215 kJ/mol). Thus, Path II will have preference over Path I. One concludes that DME is formed according to an associative mechanism without formation of an intermediate methoxy species. The reaction mechanism is of the SN$_2$ (backside) type, similar as expected in the homogeneous phase.

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