A New Mechanism for the First Carbon−Carbon Bond Formation in the MTG Process: A Theoretical Study

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Abstract: The formation of the first carbon−carbon bond in the methanol to gasoline (MTG) process has been examined with density functional theory. Two reaction pathways survive. One is the CO-catalyzed mechanism and the other is the new mechanism that involves the reaction of methane and formaldehyde. The new mechanism is one of the most energetically favorable and is consistent with available experiments.

1. Introduction

The methanol to gasoline (MTG) process is a zeolite-catalyzed route for the conversion of methanol to hydrocarbons in the gasoline boiling range (300−470 K). The mechanism of this process has attracted considerable interest because zeolite is a unique catalyst that selectively yields hydrocarbons of C_2 $-C_{10}$. Experimental studies have established that this process goes through three reaction steps: (i) the dehydration of methanol to dimethyl ether (DME), (ii) the conversion of an equilibrium mixture of methanol and DME to olefins, and (iii) the bond chain polymerization of olefins and isomerization. A number of theoretical studies have already been reported for the process preceding carbon−carbon (C−C) bond formation.[1−3] However, the mechanism for the first C−C bond formation of step (ii) is not fully understood.

Recently, Blaszkowski and van Santen[1] have theoretically investigated two main different pathways for step (i):

(a) methanol is adsorbed on the active site of zeolite H−Z to form surface methoxy CH_3-Z, and then another methanol approaches this surface-bonded methyl group to form DME (called the Rideal-Eley mechanism),

$$CH_3OH + H\text{-}Z \rightarrow (CH_3^+\cdots OH_2\cdots Z^-)^{\ddagger} \rightarrow CH_3\text{-}Z + H_2O \quad (1a)$$

$$CH_3OH + CH_3\text{-}Z \rightarrow (CH_3OH\cdots CH_3^+\cdots Z^-)^{\ddagger} \rightarrow CH_3OCH_3 + H\text{-}Z \quad (1b)$$

(b) two methanol molecules are adsorbed simultaneously on the active site and are then dehydrated to form DME directly,

$$2CH_3OH + H\text{-}Z \rightarrow (CH_3OH\cdots CH_3^+\cdots OH_2\cdots Z^-)^{\ddagger} \rightarrow CH_3OCH_3 + H\text{-}Z + H_2O \quad (2)$$

By analyzing the calculated energy diagrams using a cluster model of the active site, they concluded that path (b) is preferable to path (a). The calculated low activation barriers in path (b) support the experimentally observed rapid creation of DME in the initial step of the MTG process. It is also suggested that two methanol molecules rapidly attain an equilibrium with DME on the active site.

According to calculated results, the Rideal-Eley mechanism is not the most preferable pathway for step (i), but this mechanism is noteworthy since the surface methoxy appears to be an important intermediate in step (ii). Ono and Mori[4] exposed H-ZSM-5 to deuterated methanol CD_3 OH, then evacuated the specimen at 423 K. In the associated infrared spectra, they assigned two new bands at 2220 and 2070 cm^{-1} to the antisymmetric and symmetric vibrations of C−D bonds in the CD_3 group of surface methoxy. They also found that these new bands disappeared at 512 K as hydrocarbons were formed,

$$CD_3OH + H\text{-}Z \rightarrow CD_3\text{-}Z + H_2O \quad (\text{at } 423\text{ K}), \quad (3a)$$

$$CD_3\text{-}Z \rightarrow D\text{-}Z + \text{hydrocarbons} \quad (\text{at } 512\text{ K}) \quad (3b)$$

These results suggest that surface methoxy is an intermediate in C−C bond formation. The remaining question is by what route the first C−C bond is formed from the surface methoxy intermediate.

In this study, we propose a new mechanism for step (ii) called "the methane−formaldehyde mechanism", where methane and formaldehyde are formed from the surface methoxy intermediate and react to form ethanol. This mechanism is a modification of the carbonium ion mechanism where methanol attaches to the carbenium ion CH_3^+ from surface methoxy to form ethanol,

$$CH_3OH + CH_3\text{-}Z \rightarrow (HOCH_3\cdots CH_3^+\cdots Z^-)^{\ddagger} \rightarrow CH_3CH_2OH + H\text{-}Z \quad (4)$$

The carbonium ion mechanism was proposed by Ono and Mori[4] and Kagi[5] in an analogy of this type of hydrocarbon formation under superacidic conditions.[6] However, we found that the methyl group of the surface methoxy attaches to the hydrogen atom in the methyl group of methanol in place of the carbon

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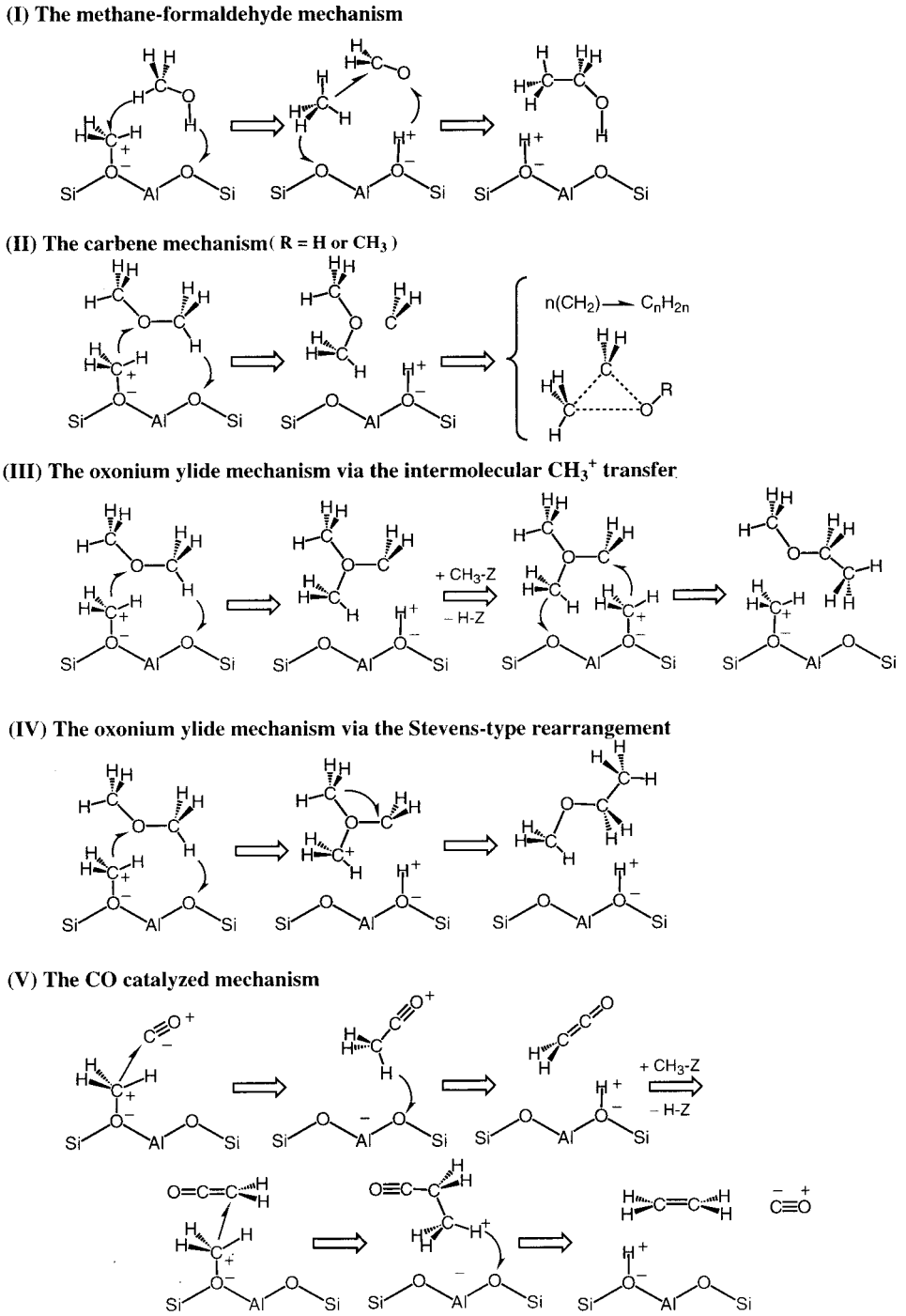

Figure 1. Schematic illustrations of reaction schemes proposed for the first C−C bond formation in the MTG process. Surface methoxy CH_3-Z is assumed as the only methylating agent.

atom to form methane and formaldehyde, and subsequently, the methane reacts with the formaldehyde to form ethanol as illustrated in Figure 1. By measurements in a flow reactor, Hutchings et al.[7] observed that methane is formed in the initial conversion of methanol at 543 K and methane decreases as hydrocarbon increases. Nováková et al.[8] revealed the equivalent production of methane and formaldehyde above 630 K under low-pressure conditions. Moreover, Blaszkowski et al.[9] have theoretically found a transition state for hydride transfer between methanol and surface methoxy to form methane. Since methane is very slow to react, almost all conventional experimental and theoretical studies have supposed methane to be independent of the first C−C bond formation.[8]

In addition to the new mechanism, a variety of other mechanisms have been suggested for the first C−C bond formation in the MTG process. Typical mechanisms are illustrated in Figure 1.

Mechanism (II) is called "the carbene mechanism" where the C−C bond is formed through methylene CH_2 production.[11] In this mechanism, methylene reacts with methanol or DME on

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the active site through a carbenoid species that is easily converted to ethanol or methyl ethyl ether, respectively. Lee and Wu[12] demonstrated hydrocarbon formation from diazomethane, CH_2N_2, which is a good carbene donor, over H-ZSM-5 at 470 K and confirmed the participation of methylene as a source of the C−C bond. No direct evidence, however, has been reported for the existence of methylene in the process, because methylene may be too labile to exist independently in these conditions. Sinclair et al.[13] have recently proposed theoretically that the carbene mechanism proceeds through a surface-stabilized carbene.

In oxonium ylide mechanisms (III) and (IV), the C−C bond is formed by an intermolecular transfer of the CH_3 group from surface methoxy to methylenedimethyloxonium ylide, $(CH_3)_2OCH_2$, and an intramolecular rearrangement within the oxonium ylide (called the Stevens-type rearrangement mechanism), respectively. These mechanisms were suggested in the experiment by Olah et al.[14] where hydrocarbons are formed from trimethyloxonium (TMO) salt in the presence of strong bases. However, Sommer et al.[15] have proposed that this mechanism cannot be applied to the MTG process, and Munsen et al.[16] have reported on an in situ solid-state NMR study which showed that little methyl ethyl ether is formed from methanol over H-ZSM-5 zeolite, although it is the initial product of the first C−C bond formation according to this mechanism. Moreover, Shah et al.[3] have recently found theoretically that no local minimum for the ylide species exists within the microporous environment.

Mechanism (V), which is called "the CO-catalyzed mechanism", has been proposed by Jackson and Bertsch[17] from the high cation affinity of carbon monoxide, CO. In this mechanism, CO associates with protonated methanol, DME, or surface methoxy to form ketene (the first step), and then ethylene is constituted from the reaction of ketene and another methanol (the second step). CO acts only as a catalyst in this mechanism. Jackson and Bertsch calculated the energy diagram leaving the active site of zeolite, and estimated the highest energy barrier as only 15.0 kcal/mol. However, NMR studies[18] suggest that the further addition of CO results in a slight decrease in the conversion of methanol and no increase in the initial reaction rate. Hutchings et al.[19] have reported that ketene reacts with potent methylating agents to yield only the expected products for the methylation of the oxygen atom of ketene.

We also investigate the possibilities of these mechanisms by examining the energy variations along the corresponding reaction paths, using theoretical calculations.

2. Calculations

We determine the reaction paths illustrated in Figure 1 by optimizing equilibrium and transition state structures as well as the active site structures of H-Z and CH_3-Z. Surface methoxy is assumed as the methylating agent of all mechanisms.

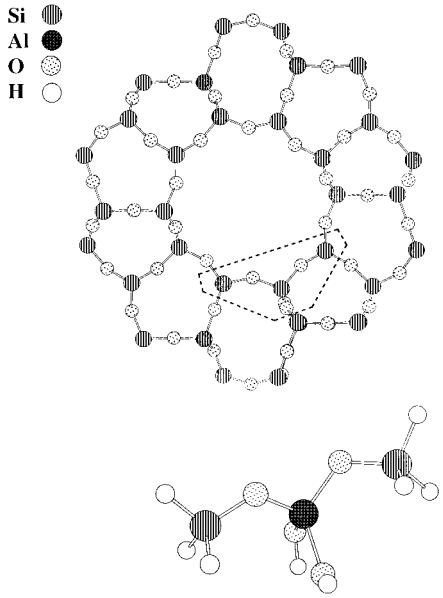

Figure 2. The 10-ring structure of zeolite H-ZSM-5 and the equilibrium structure of the atom cluster. The central Si atom of the cluster is replaced by an Al atom and the terminal bonds are capped by H atoms. The Si and hydroxyl O atoms are fixed at the experimental atomic positions in all calculations.

The active site of H-ZSM-5 is approximated by an atom cluster[20] $(SiH_3)-O-Al(OH)_2-O-(SiH_3)^-$ as shown in Figure 2. This cluster is picked out from the 10-ring structure of the siliciferous zeolite ZSM-5[21]. In the cluster, the central Si atom is replaced by an Al atom and the terminal bonds are capped by H atoms. The Si and hydroxyl O atoms are fixed at the experimental atomic positions in the following calculations.

Geometry optimizations of the cluster and the complexes are carried out by the Hartree−Fock method employing the 3-21G[22] basis set for all atoms except the STO-6G[23] basis set for the H atoms in the zeolite cluster. No symmetry constraints were assumed in any procedure. Energy diagrams are calculated by using the density functional method with nonlocal exchange-correlation corrections due to Becke[24] and Lee, Yang, and Parr[25] (BLYP), employing the Hay-Wadt effective core potential[26] plus the valence double-ζ basis set for Al and Si atoms and the cc-pVDZ[27] for H, C, and O atoms, and the STO-6G[23] for the H atoms in the cluster. It should be noted here that we have already confirmed for several significant states that the use of inexpensive basis set in geometry optimizations has little effect on reaction energy diagrams within a few kilocalories per mole. All calculations are performed with the GAUSSIAN 94 program package.[28]

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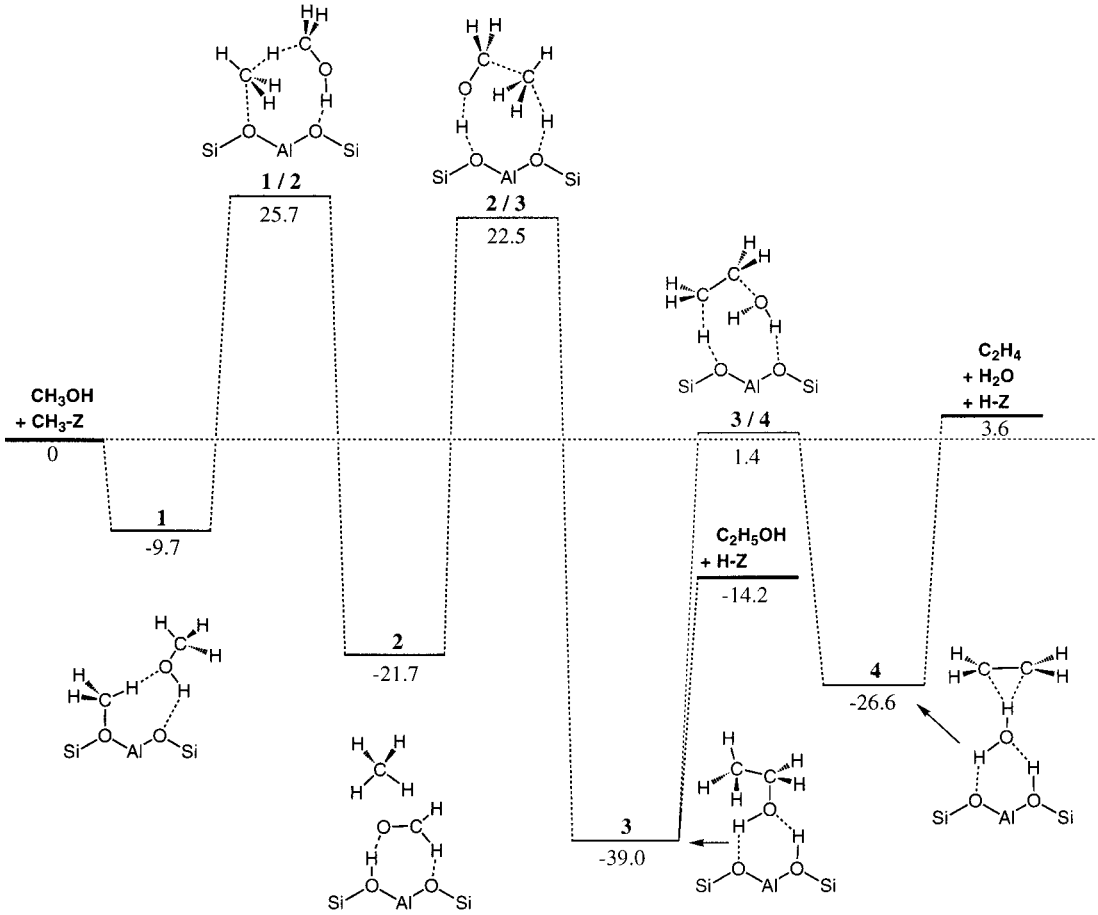

Figure 3. Calculated energy diagram for mechanism I called the methane−formaldehyde mechanism. Relative energy values to the dissociation limit of methanol and CH_3-Z are calculated by the BLYP method (kcal/mol). For detailed geometries, see Figure 4.

3. Calculated Results

The energy diagrams for the calculated reaction paths and the detailed geometries are given in Figures 3−8 with BLYP energies.

A. The Methane−Formaldehyde Mechanism (I). The energy diagram for the methane-formaldehyde mechanism is shown in Figure 3. The C−C bond formation proceeds in two elementary steps. The first step is the formation of methane and formaldehyde through H^- transfer from methanol to CH_3-Z. The second step is the formation of ethanol through the decomposition of methane into H^+ and CH_3^- followed by their transfers to the basic oxygen atom of H-Z and the carbon atom of formaldehyde, respectively. Ethanol is dehydrated to ethylene through the transition state of the ethyl cation, $C_2H_5^+$. As mentioned in the Introduction, the carbonium ion, $CH_4CH_2OH^+$, type intermediate does not appear in this mechanism, instead, methane is identified as a product assisting the exchange of H^+ and CH_3^+ between methanol and H-Z. The rate-determining energy barrier for this mechanism is in the formation of methane and formaldehyde. The transition state lies 25.7 kcal/mol above the dissociation limit of methanol and surface methoxy. This energy can be compared to the activation energy of about 30 kcal/mol reported by Blaszkowski and van Santen for the formation of surface methoxy from methanol through the Rideal-Eley mechanism, which certainly occurs in the primary stage of the MTG process. Hence this energy barrier seems accessible in this process. The low activation barriers in this mechanism are due to the hydrogen bond that is formed in every transition state.

The energy barrier of the methane consumption step is lower than that of the methane formation step by 3.2 kcal/mol, indicating that methane and formaldehyde are converted more easily than formed. The low energy barrier seems curious in view of the poor reactivity of methane. However, it can be understood in view of the high reactivity of formaldehyde because the nucleophilic addition of anionic species to the carbon atom of formaldehyde is a typical reaction under acidic conditions. The active site also seems to contribute to this step by offering the proton on the acidic oxygen atom and assisting the cleavage of the C−H bond of methane on the basic oxygen atom.

B. The Carbene Mechanism(II) and the Oxonium Ylide Mechanism (III) via the Stevens-Type Rearrangement. Energy diagrams for mechanisms (II) and (III) in Figure 5 show that the formation of methylene CH_2 and methylenedimethyl-oxonium ylide, $CH_2O(CH_3)_2$, from DME adsorbed on CH_3-Z is highly endothermic; the formation energies are 86.5 and 77.2 kcal/mol, respectively. These values are comparable to the dissociation energies of ordinary chemical bonds. The CH_2−O bond length of the ylide is calculated to be 1.757 Å. Thus, the oxonium ylide is a weakly bound complex of methylene and DME. The formation of the ylide requires a large amount of energy due to its structural characteristics. The reaction of free methylene and oxonium ylide is thus found to be unlikely even on H-Z. There may be a surface-stabilized carbene[13] in the carbene mechanism. However, we consider that it may not essentially affect this argument, since we have calculated the reaction energy barrier as 45.9 kcal/mol from the dissociation

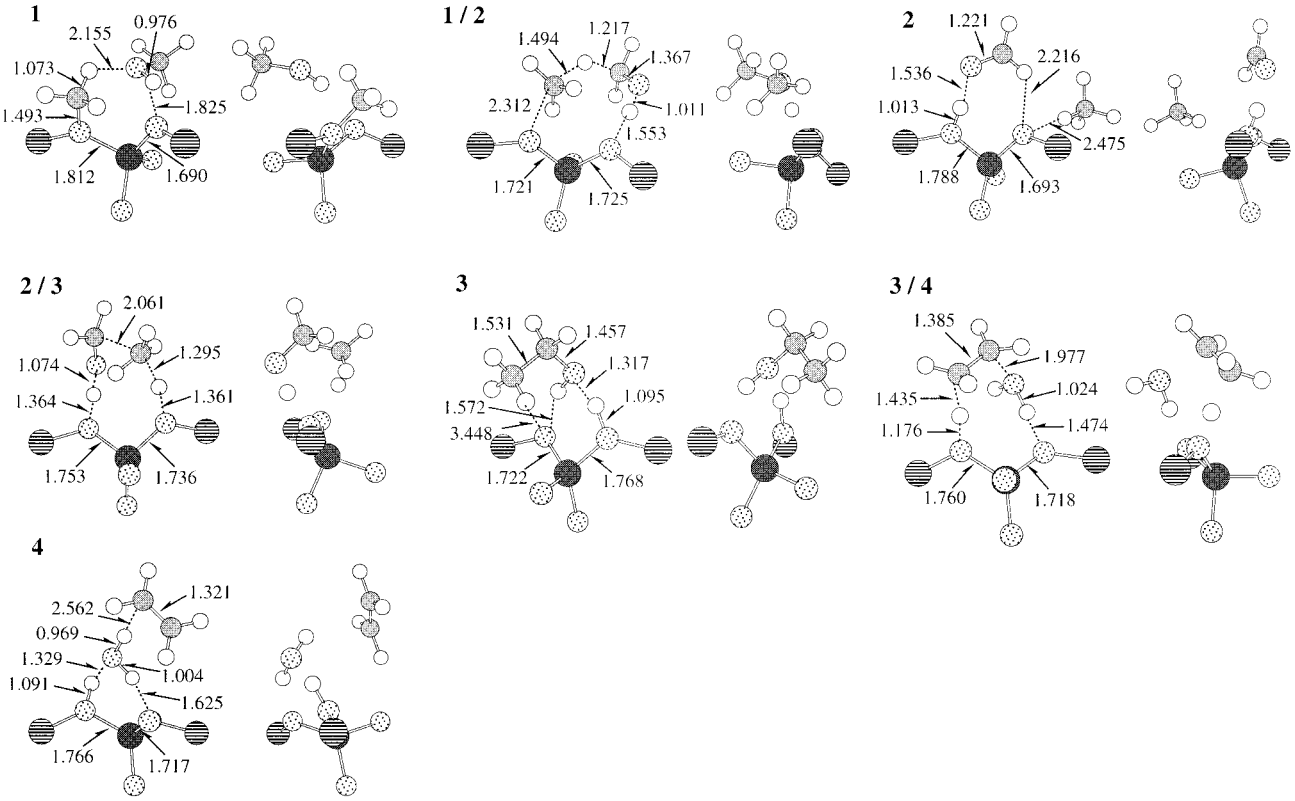

Figure 4. Calculated geometries of equilibrium and transition state structures for mechanism I. For structure numbers, see Figure 3.

limit of H_2O and surface methoxy to the product, H_2O adsorbed on a surface-stabilized carbene.

The adsorption structure of the oxonium ylide was optimized in relation to the mechanism for the formation of free methylene and oxonium ylide. The expected structure, however, was not found as an energy minimum, instead, an adsorption structure of TMO was obtained as a result of proton donation from the acidic oxygen atom in H-Z to the carbon side of the oxonium ylide (Figure 5). This implies that the basicity of the active site is not strong enough to cleave the C−H bond of TMO. Calculations with optimized isolated geometries for oxonium ylide and H-Z lead to a hypothetical adsorption structure of 43.3 kcal/mol, which is 33.9 kcal/mol lower than the dissociation limit. The energy barrier is much higher than that of the rate-determining step in the methane−formaldehyde mechanism.

C. The Oxonium Ylide Mechanism (IV) via the Intermolecular CH_3^+ Transfer. For mechanism (IV), the calculated transition state structure of the intramolecular CH_3^+ transfer is quite different from the expected structure given in Figure 1. In this mechanism, the CH_2 group of the oxonium ylide changes into CH_3^+ by abstracting H^+ from H-Z, and then the CH_3-O bond of the ylide is completely broken to form CH_3^+ (Figure 5). Through geometrical optimization from a transition state structure, we found that two carbon atoms do not bind directly to form ethanol; instead, the CH_3^+ abstracts H^- from the methyl group of DME to form methane and surface bonding ether, $Z\text{-}CH_2OCH_3$, that might be converted into formaldehyde on H-Z. Backward optimization of this transition state leads to the adsorption structure of DME, but it does not go through the oxonium ylide type adsorption structure mentioned in the previous section. These results show that the mechanism does not follow the proposed pathway of the Stevens-type rearrangement shown in Figure 1, but passes through the intermediate of methane and formaldehyde. As to the origin of the C−C bond, Hutchings et al.[19] have concluded from D/H isotope labeling experiments that the Stevens-type rearrangement may be a small contribution. The calculated mechanism seems to be consistent with their conclusion. The energy barrier was calculated as 35.3 kcal/mol, which indicates that methane formation from DME also may be an energetically favorable process.

D. The CO-Catalyzed Mechanism (V). Mechanism (V) proceeds through five elementary steps, as shown in Figure 7. The methylation of CO and ketene proceeds in the same way as the expected route in Figure 1, and is followed by two additional steps of the formation of surface ethoxy $CH_3CH_2\text{-}Z$ from methylketene and the CH_2-H bond cleavage through ethyl cation to form ethylene. Jackson and Bertsch[17] have suggested this mechanism on the basis of model calculations of $CO + CH_3\,OH_2^+$ and $CH_2CO + CH_3OH_2^+$, that is, the CH_3^+ transfer from $CH_3OH_2^+$ to CO and ketene. The energy diagram in Figure 7 shows an energetically favorable route for this mechanism taking the active site of zeolite into consideration. It also includes the C−H bond cleavage of acylium ion $CH_3\text{-}CO^+$ and the dissociation of CO. The rate-determining step is the formation of ketene and methylketene where the energy barriers are 28.7 and 25.6 kcal/mol, respectively. The highest energy barrier is almost the same as that of the methane−formaldehyde mechanism with the difference of 3.0 kcal/mol.

4. Discussion

As a result of the calculated energy profiles of the mechanism for the first C−C bond formation, we found that the methane−formaldehyde mechanism (I) and the CO-catalyzed mechanism (V) are possible candidates. We investigate the possibility of these two mechanisms by a comparison with experimental results.

The most striking characteristic of mechanism (I) is the formation of methane and formaldehyde. Methane formation

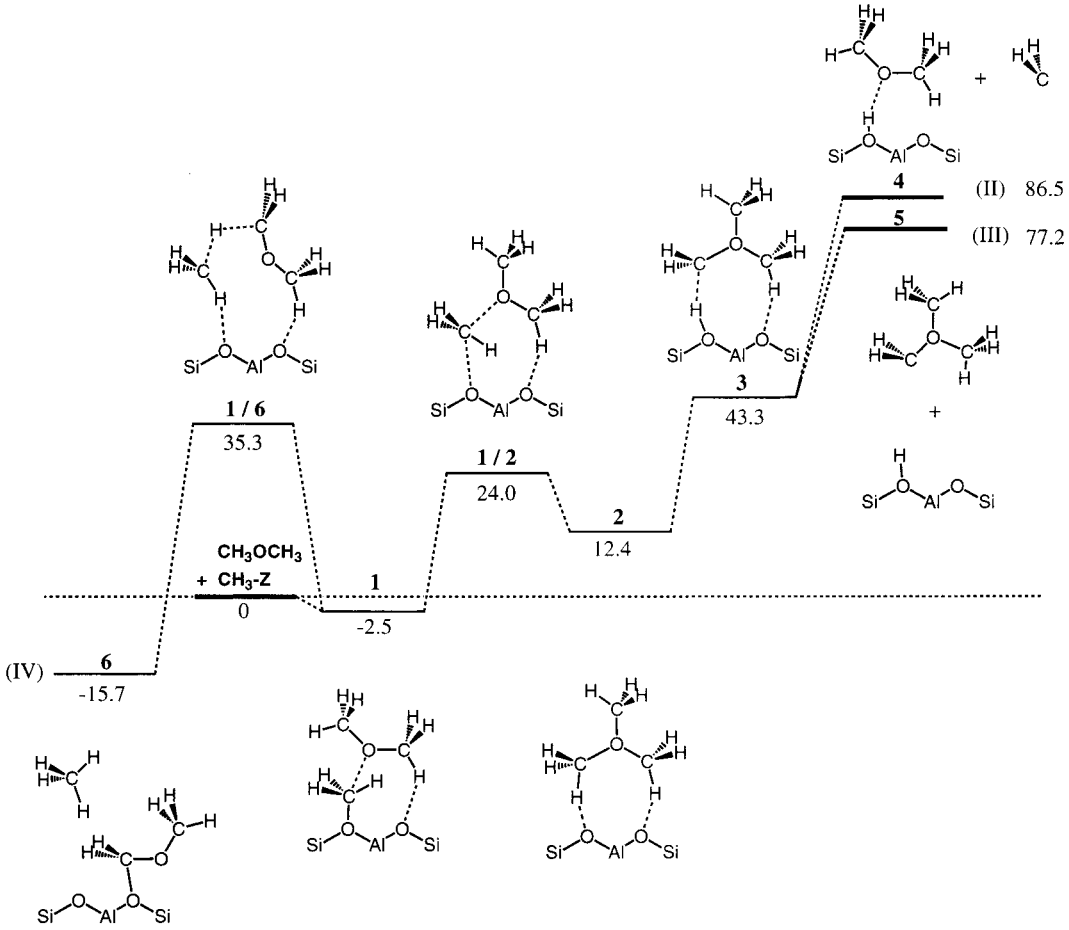

Figure 5. Calculated energy diagrams for mechanisms II−IV. Relative energy values to the dissociation limit of DME and CH_3-Z are calculated by the BLYP method (kcal/mol). For detailed geometries, see Figure 6.

has been reported in many experimental studies. In addition, the equivalent formation of formaldehyde has been reported by Nováková et al.[8] However, these formations have been regarded as a reaction of methanol under acidic conditions. The key feature is the presence of the relatively weak $O-CH_3^+$ bond of surface methoxy, that is, the CH_3^+ group receives H^- from the methyl group of the neighboring methanol to form methane. Ono and Mori[4] and others[8] have shown that methane is formed simultaneously with the appearance of surface methoxy as well as the C−C bond species. Ono and Mori have also found from infrared analysis that adsorption spectra due to surface methoxy disappear with the formation of hydrocarbons. These experiments give direct evidence for the consumption of surface methoxy as a source of methane. Experimentally detected methane must be supplied through the first step of mechanism (I).

In previously proposed mechanisms, methane has never been considered as a source of the first C−C bond in the MTG process because of its poor reactivity. However, the energy diagram of mechanism (I) shows that once methane is formed through the reaction of methanol and surface methoxy, the C−C bond is easily formed by the reaction of methane and formaldehyde because the energy barrier of C−C bond formation is lower than that of methane formation. There is experimental evidence that methane decreases as hydrocarbons increase.[7] From the experimental point of view, mechanism (I) seems to be one of the most favorable routes.

There are possibly two relevant D/H labeling studies against the new mechanism. One is the study on CH_3OD conversion by Hutchings et al.[19] and the other is the study on CH_3OH/D_2O conversion by Mole and Whiteside.[29] These studies show that deuterium is incorporated in ethylene and methane about twice as much as in DME, while in the new mechanism there is no process for proton transfer from the hydroxy groups of methanol or water into methane and ethylene. These results can be interpreted by assuming that hydrogen atoms in the methyl group of surface methoxy are exchanged with deuterium atoms under this condition. Note that the second plausible route in the methanol-to-DME process, the Rideal-Eley mechanism, also proceeds through the surface methoxy intermediate, as mentioned in the Introduction. We will wait for further experimental evidence that supports this hypothesis.

Another possible experimental result against this mechanism is the appearance of DME prior to the hydrocarbon formation. It seems to imply that the first C−C bond should be formed from DME, although DME does not participate in mechanism (I). The most likely explanation is that C−C bond formation reaches detectable amounts after the equilibrium of methanol and DME is reached. According to this explanation, DME formation is a side reaction. It is also interesting to note that DME adsorbed on H-Z is converted to form methanol adsorbed on surface methoxy that corresponds to state 1 in mechanism (I) (Figure 3), in the energy diagram for the Rideal-Eley mechanism proposed by Blaszkowski and van Santen.[1]

The only inconsistency with mechanism (I) is that ethanol is the initial product of the first C−C bond formation while it has never been explicitly reported as a product except in the

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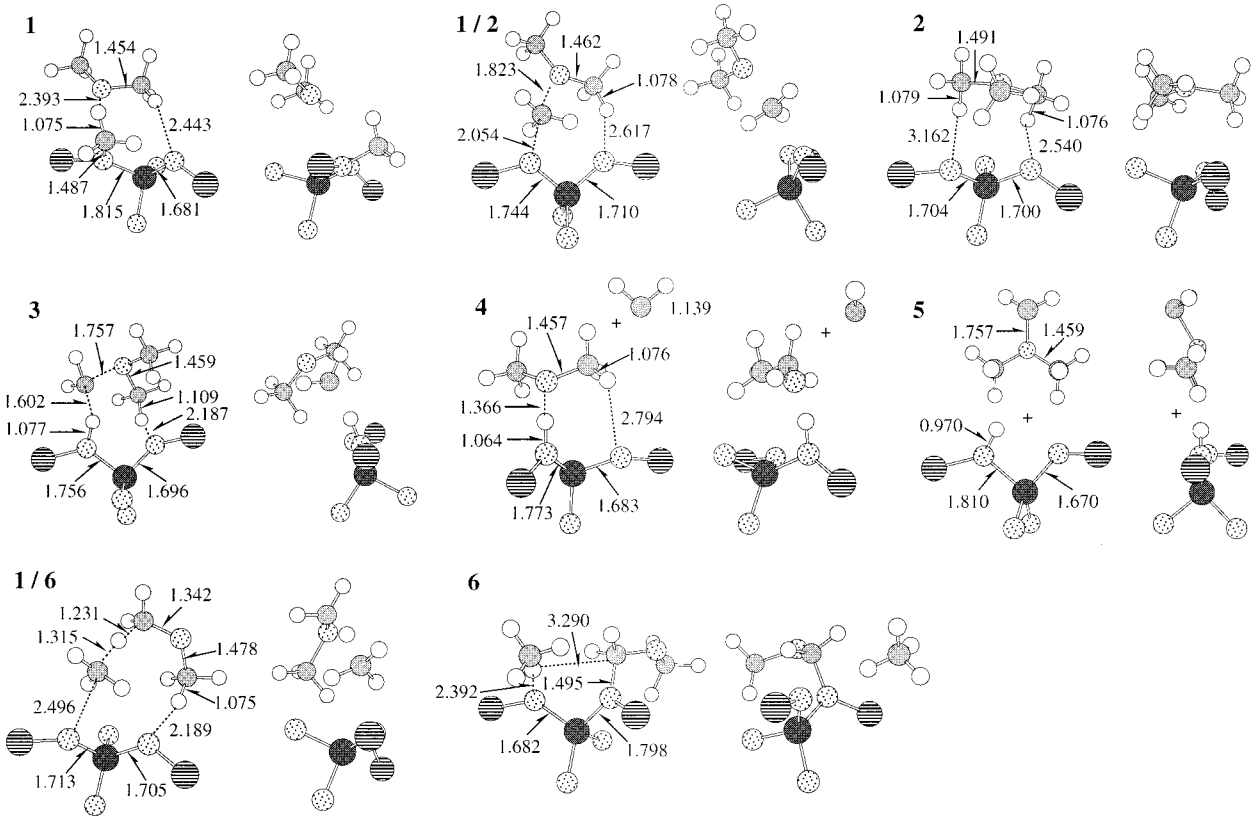

Figure 6. Calculated geometries of equilibrium and transition state structures for mechanisms II−IV. For structure numbers, see Figure 5.

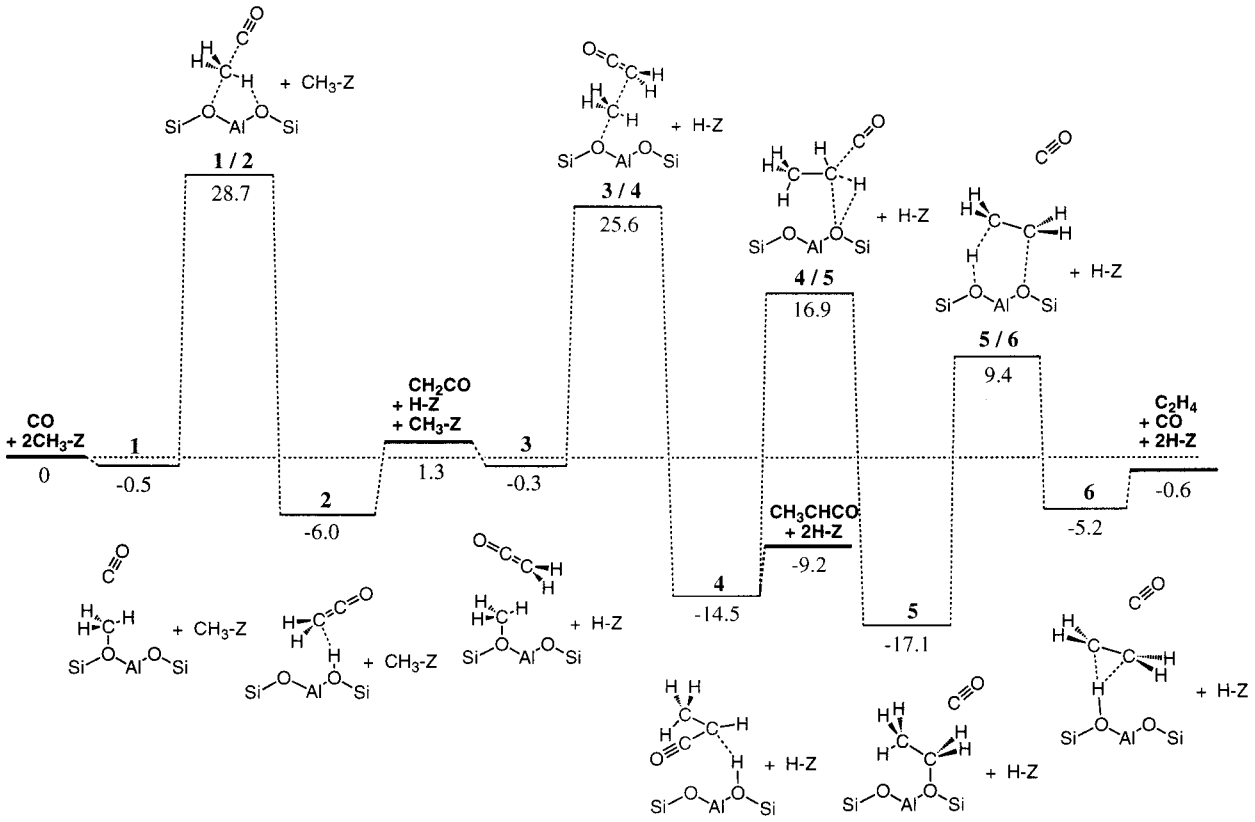

Figure 7. Calculated energy diagram for mechanism V called the CO-catalyzed mechanism. Relative energy values to the dissociation limit of CO and CH_3-Z are calculated by the BLYP method (kcal/mol). For detailed geometries, see Figure 8.

experiment by Nováková et al.[8] Since the calculated energy diagram shows that ethanol is converted to ethylene more easily than it is formed from methane and formaldehyde, the absence of ethanol may be due to the rapid conversion into ethylene in this condition. This could be verified by further experimental analysis.

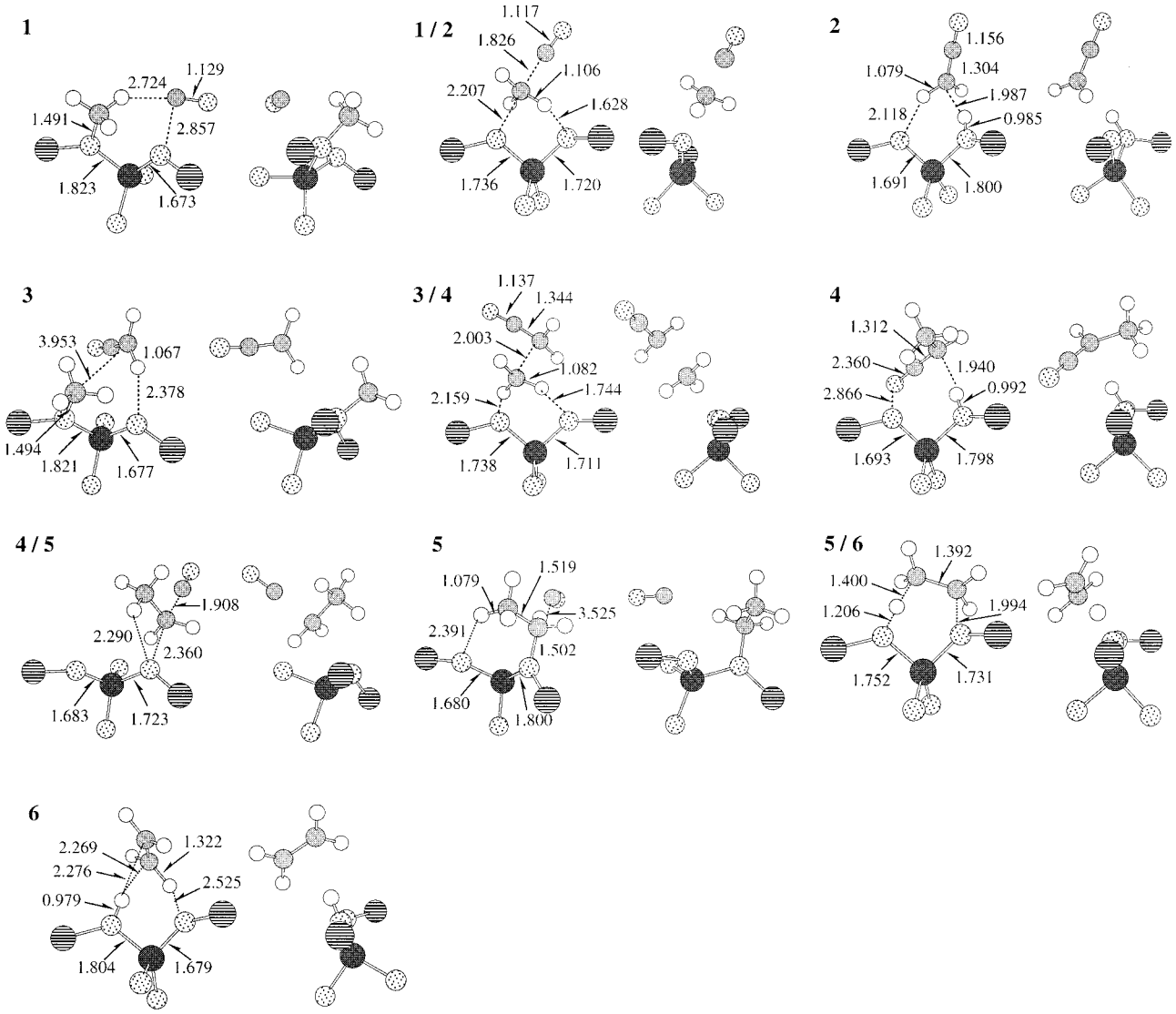

Figure 8. Calculated geometries of equilibrium and transition state structures for mechanism V. For structure numbers, see Figure 7.

For the participation of CO, several negative experimental results have been reported. By a ^{13}C NMR shift analysis, Nagy et al.[18] found that additional CO has little effect on the conversion rate of methanol. Hutchings et al.[19] concluded from mass spectra analysis that further addition of CO does not change either the conversion rate or the product distribution. These observations imply that the CO-catalyzed mechanism (V) is not involved in hydrocarbon formation despite an energy profile competitive with the methane−formaldehyde mechanism. There are three probable interpretations as to why the CO-catalyzed mechanism does not participate in the process. (1) As seen in Figure 7, the adsorption energy of methanol molecule to surface methoxy, 9.7 kcal/mol, is much larger than that of the CO molecule to surface methoxy, 0.5 kcal/mol. Although we have no definite information on the difference in reactivity between the strongly adsorbed and weakly adsorbed states, it is clear that there are many more adsorption states of methanol than of CO in the initial step of this process. (2) CO may react with molecules other than methanol and surface methoxy at low temperature, and after all, CO may be consumed without participating in forming hydrocarbons. (3) Even if CO reacts with methanol or surface methoxy to form ketene, we expect that no ketene may be concerned with the hydrocarbon formation because Hutchings et al.[19] observed that ketene reacts with potent methylating agents to yield only the expected products for the methylation of the oxygen atom of ketene.

5. Conclusions

We have proposed a new mechanism for the first C−C bond formation in the MTG process that proceeds through the reaction of methane and formaldehyde. Energy diagrams were calculated for five mechanisms of the first C−C bond formation from the surface methoxy intermediate. As a result, we found that the new mechanism is the most energetically preferable route of all mechanisms. The new mechanism is consistent with all available experiments. This mechanism also indicates that methane is not a byproduct in the MTG process and ethanol is the initial product in the first C−C bond formation.

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