

## Reactivity of Surface Alkoxy Species on Acidic Zeolite Catalysts

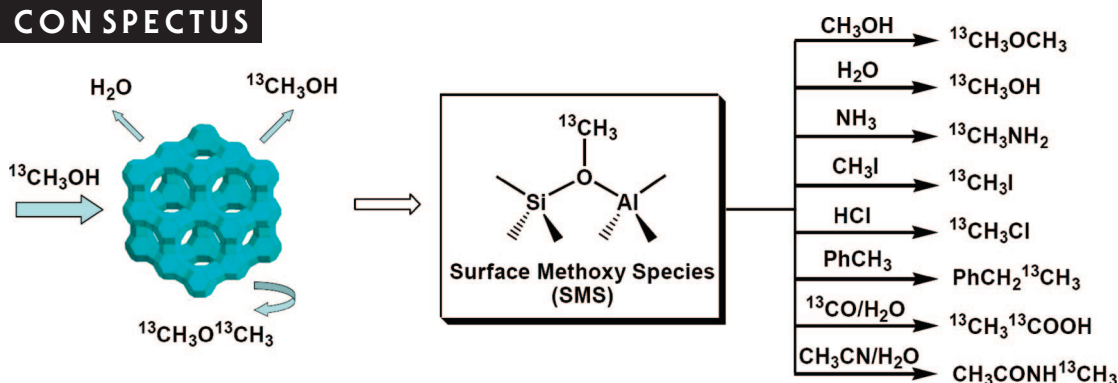
WEI WANG\*<sup>†</sup> AND MICHAEL HUNGER<sup>‡</sup>

<sup>†</sup>State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Gansu 730000, P. R. China,

<sup>‡</sup>Institute of Chemical Technology, University of Stuttgart, Stuttgart 70550, Germany

RECEIVED ON SEPTEMBER 19, 2007

### CON SPECTUS



A solid understanding of the mechanisms involved in heterogeneously catalyzed reactions is of fundamental interest for modern chemistry. This information can help to refine modern theories of catalysis and, in a very practical way, can help researchers to optimize existing industrial processes and develop new ones. To understand the mechanisms of heterogeneous catalysis, we need to observe and identify reaction intermediates on a working catalyst. Motivated by this goal, we have monitored the catalytic events in heterogeneous systems using in situ magic-angle-spinning (MAS) NMR under flow conditions. In this Account, we describe the reactivity and possible intermediate role of surface alkoxy species in a variety of zeolite-catalyzed reactions.

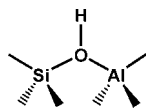
First, we isolate the surface alkoxy species on a working zeolite catalyst and then investigate the chemical reactivity with different probe molecules under reaction conditions. Finally, we investigate reaction mechanisms facilitated by these intermediate surface alkoxy species.

We examined the reactivity of surface methoxy species (SMS) in terms of C–O bond and C–H bond activation. SMS on acidic zeolite catalysts act as an effective methylating agent when reacted with different probe molecules (including methanol, water, ammonia, alkyl halides, hydrochlorides, aromatics, carbon monoxide, and acetonitrile) through C–O bond activation. At higher reaction temperatures (ca. 523 K and above), the C–H bond activation of SMS may occur. Under these conditions, intermediates such as surface-stabilized carbenes or ylides are probably formed. This C–H bond activation is directly related to the initiation mechanism of the methanol-to-olefin (MTO) process and invites further investigation. Based on our experimental results, we also discuss the reactivity and the carbenium-ion-like nature of surface alkoxy species and recent theoretical investigations in this area.

### Introduction

Understanding of the mechanisms in heterogeneously catalyzed reactions is not only of fundamental interest for refinement of theories in modern chemistry, but also of practical importance for optimization of existing industrial processes

and development of new ones. The reaction pathway in heterogeneous catalysis, in principle, goes through the following stages: (i) adsorption of the reactant molecules onto the surface of the solid catalyst at active sites; (ii) activation of the adsorption complex being formed between the catalyst

**SCHEME 1.** Schematic Representation of Zeolite Brønsted Acid Sites

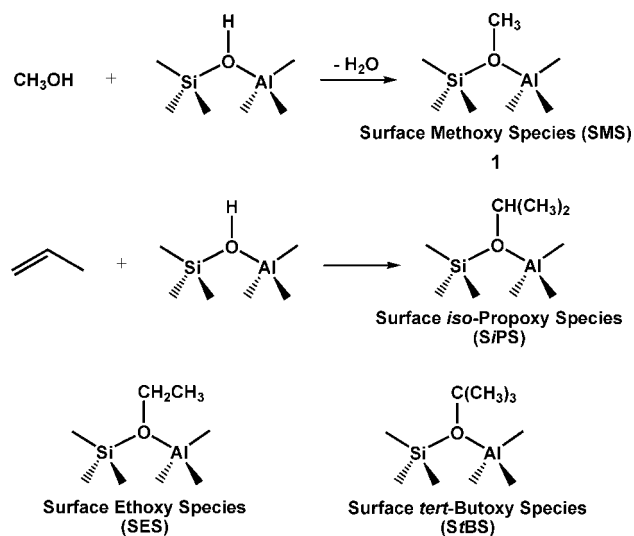
surface and the reactant molecules; (iii) occurrence of possible reaction intermediates and, subsequently, formation of reaction products; (iv) desorption of the product molecules from the catalyst surface and recycle of the active sites. In order to elucidate more explicitly the mechanisms involved in heterogeneous catalysis, knowledge of the structures and the nature of ground, reactant, intermediate (if any), and product states is an important prerequisite. Moreover, proper description of each maximum of the potential energy along the reaction coordinate between reactants and products, which refers to the corresponding transition state or activated complex, is highly desirable.

The starting point to approach the mechanistic issues of heterogeneous catalysis is, therefore, the structure of the heterogeneous catalyst itself and the nature of the active sites that catalyze the reaction under investigation. Crystalline aluminosilicate zeolites<sup>1</sup> are important heterogeneous catalysts and have been widely utilized in petroleum-refining chemistry, such as cracking, isomerization, and alkylation processes. The framework structure of zeolites consists of connected  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  coordination tetrahedra. By sharing of one oxygen atom between each two tetrahedra, a three-dimensional network containing channels, cages, or both is formed with a certain topology. The well-defined microporous structure of zeolite crystals dramatically affects the size- and shape-dependent adsorption and diffusion processes of the reactants and products in heterogeneous catalysis and greatly influences the reaction pathways through steric constraints on reaction intermediates and transition states. In the case of acidic zeolites, the hydroxyl protons, which act as Brønsted acid sites, are located on oxygen bridges connecting tetrahedrally coordinated silicon and aluminum atoms (Scheme 1). These hydroxyl protons are well accepted as catalytic active sites in acidic zeolites. Characterization of the Brønsted acidity of zeolites includes at least the identification of the strength, density, and accessibility of these hydroxyl protons, which is essential to understand their nature and reactivity in zeolite-catalyzed reactions. This topic has stimulated intensive research carried out both experimentally and theoretically. For detailed discussion, the reader is referred to excellent reviews previously published.<sup>2-4</sup> Lewis acid sites may also exist in zeolites as extraframework aluminum species or framework defects. Their nature and role in catalysis is still a

matter of discussion, the topic of which is, however, beyond the scope of this Account.

One of the key steps to understand the mechanisms of heterogeneous catalysis is, of course, the observation and identification of reaction intermediates being formed on a working catalyst. Motivated by this, many in situ spectroscopic methods have been developed in the past decades to monitor the catalytic events in heterogeneous systems under real reaction conditions.<sup>5-7</sup> Since 1995, for example, an in situ magic-angle-spinning (MAS) NMR technique under continuous-flow (CF) conditions<sup>8</sup> has been applied for direct NMR investigations of the formation and transformation of reaction intermediates in zeolite-catalyzed reactions under steady-state conditions. On the basis of the in situ CF MAS NMR spectroscopy, a stopped-flow (SF) protocol<sup>9</sup> was further introduced to distinguish reactive intermediates from spectator species, which allows a safer identification of the reaction mechanisms involved. Recently, the in situ MAS NMR technique under flow conditions was directly coupled with UV/vis spectroscopy.<sup>10</sup> The high sensitivity gained by UV/vis spectroscopy facilitates the in situ observation of aromatic compounds and unsaturated carbenium ions formed in zeolite-catalyzed reactions. The above-mentioned NMR techniques, which we developed, prove successful in observation and identification of possible intermediates in several important zeolite-catalyzed reactions. Experimental details of these techniques and interpretation of the resulting spectra have been the subjects of review papers<sup>11,12</sup> and, therefore, will not be duplicated herein. In this Account, we will only focus on the mechanistic information of heterogeneous systems obtained by these techniques. More specifically, our recent results on the reactivity and possible intermediate role of surface alkoxy species in a variety of zeolite-catalyzed reactions will be summarized and discussed.

In addition to observation and identification of reaction intermediates, description of the transition states that connect reactants, intermediates, and products is the main task for mechanism elucidation. In comparison with direct detection of reaction intermediates in heterogeneous catalysis, however, the only measurable property of the transition states is their energies relative to reactant or product states, the values of which may sometimes be derived from kinetics study or from product distribution analysis. Many experimental techniques applied in mechanistic investigations of solution systems, for example, isotopic labeling, trapping, and stereochemical analysis, may also give additional hints on the structure and nature of the transition states in heterogeneous catalysis. On the other hand, quantum chemistry is of great power to predict the structure, nature, and relative stability of the transi-

**SCHEME 2.** Formation of Surface Alkoxy Species upon Dehydration of Alcohols or Adsorption of Olefins on Zeolite Brønsted Acid Sites

tion states involved in zeolite-catalyzed reactions.<sup>1,2,13</sup> On the basis of our experimental results and recent theoretical investigations on the carbenium-ion-like transition states in zeolite-catalyzed reactions, the reactivity of surface alkoxy species ( $>\text{C}_1$  species) will be discussed in comparison with that of surface methoxy species (SMS) in this Account.

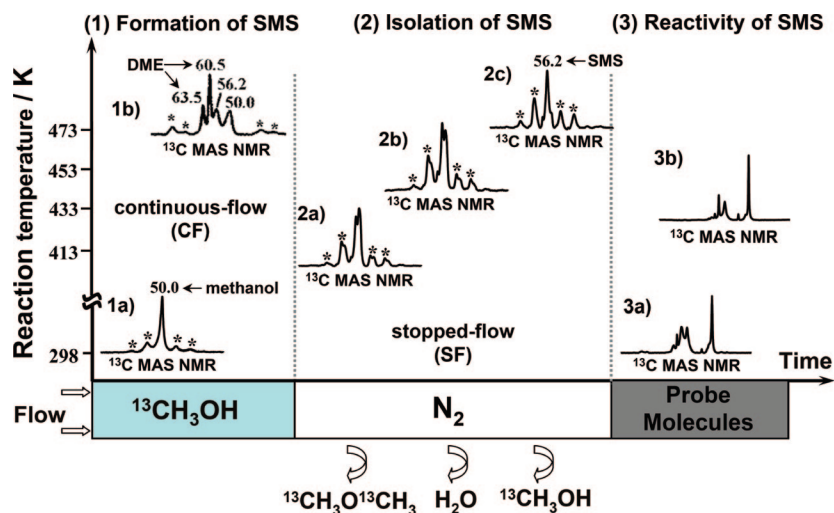
Although, as mentioned above, many basic principles in physical organic chemistry for solution systems are applicable for elucidating the mechanisms in heterogeneous catalysis, one must be always aware of the unique nature of heterogeneous systems under investigation. For example, it has been well established that carbenium ions are key intermediates involved in a variety of acid-catalyzed reactions in solution. However, simple carbenium ions have never been identified as long-lived intermediates on acidic zeolite catalysts. Instead, covalent alkoxy species are experimentally observed as stable surface species upon dehydration of alcohols or adsorption of olefins on acidic zeolites (Scheme 2). The stability and the formation mechanism of surface alkoxy species on zeolite Brønsted acid sites have been intensively investigated by quantum chemical calculations. It was also suggested that surface alkoxy species that possess carbenium-ion-like nature may act as catalytic intermediates in zeolite chemistry.<sup>2,3,14</sup> However, convincing experimental evidence for this hypothesis can hardly be obtained due to the occurrence of rapid secondary reactions on zeolite catalysts, which severely hinders the observation of primary intermediates and complicates the interpretation of spectroscopic results. We approached this issue by isolating the surface alkoxy species on a working zeolite catalyst first and investigating their chemical reactivity with different probe molecules under reaction

conditions thereafter (Figure 1). This strategy allows us to investigate the intermediate role of surface alkoxy species in certain zeolite-catalyzed reactions in which the corresponding alcohols (or olefins) are reacted with the probe molecules. In this Account, accordingly, we will present our research results in the following sequence: (i) in situ observation and isolation of surface alkoxy species on acidic zeolite catalysts; (ii) possible intermediate role of surface alkoxy species evidenced by the reactions of surface alkoxy species (mainly, SMS **1**) with probe molecules; (iii) discussion on mechanism issues in zeolite-catalyzed reactions involving surface alkoxy species as possible reaction intermediates.

### In Situ MAS NMR Observation and Isolation of Surface Alkoxy Species on Acidic Zeolite Catalysts

In 2000, we confirmed by in situ MAS NMR spectroscopy the existence of SMS during methanol conversion under CF conditions on solid acid catalysts such as zeolites H-Y, H-ZSM-5, and zeotype catalyst, silicoaluminophosphate H-SAPO-34 (step 1 in Figure 1).<sup>15</sup> In agreement with previous NMR studies under batch conditions, the  $^{13}\text{C}$  chemical shift for SMS that we observed is ca. 56.2 ppm on H-Y, 59.4 ppm on H-ZSM-5, and 56.6 ppm on H-SAPO-34. In Scheme 2 is shown the formation of SMS upon dehydration of methanol on acidic zeolite catalysts. As indicated in spectrum 1b in Figure 1, however, dimethyl ether (DME,  $^{13}\text{C}$  chemical shifts of 63.5 and 60.5 ppm) is also formed as the reaction product during the conversion of methanol ( $^{13}\text{C}$  chemical shift of 50.0 ppm) at reaction temperature of ca. 473 K. It, therefore, comes to the question concerning the reactivity of SMS: are SMS the reaction intermediates for the formation of dimethyl ether from methanol, or they are only spectator species on the working catalyst? This issue may be tackled<sup>15</sup> by isolation of SMS on the working catalyst with a SF protocol (step 2 in Figure 1), followed by further investigation on the reaction of SMS with methanol as probe molecules (similar to step 3 in Figure 1). The SF protocol realizes a purge of the working catalyst with dry nitrogen at elevated temperatures, which progressively removes DME, water, and the surplus of methanol.<sup>16</sup> With the use of SF protocol, SMS are selectively retained on the working catalyst, which give the dominating signal at 56.2 ppm together with spinning sidebands (denoted by asterisks) in spectrum 2c in Figure 1. Following a similar procedure, we successfully isolated surface ethoxy species (SES) upon dehydration of ethanol on acidic zeolite H-Y.<sup>17</sup>

It is worth noting that surface alkoxy species are not easy to detect by solid-state NMR spectroscopy. In the case of ole-



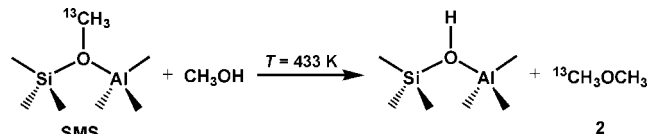
**FIGURE 1.** Protocol of the in situ continuous-flow (CF) and stopped-flow (SF) MAS NMR experiments applied to investigate the reactivity of surface methoxy species (SMS) on acid zeolite catalysts: (1) recording of  $^{13}\text{C}$  MAS NMR spectra under CF conditions at elevated reaction temperatures during conversion of methanol ( $^{13}\text{C}$ -enriched methanol is used to facilitate the  $^{13}\text{C}$  NMR detection), which indicates the formation of SMS ( $^{13}\text{C}$  chemical shift of 56.2 ppm) on acid zeolite catalysts; (2) recording of  $^{13}\text{C}$  MAS NMR spectra under SF conditions during purging the catalyst with dry carrier gas ( $\text{N}_2$ ) only, which achieves the isolation of SMS from water, dimethyl ether (DME,  $^{13}\text{C}$  chemical shifts of 63.5 and 60.5 ppm), and methanol ( $^{13}\text{C}$  chemical shift of 50.0 ppm); (3) recording of  $^{13}\text{C}$  MAS NMR spectra during the reaction of SMS with additional probe molecules (in most case,  $^{13}\text{C}$ -nonenriched reagents are used to only trace the transformation of  $^{13}\text{C}$ -enriched SMS), which reveals the reactivity and possible intermediate role of SMS. This step can be performed under either flow conditions or batch conditions. The  $^{13}\text{C}$  chemical shifts are all in the unit of ppm. Asterisks denote the spinning sidebands. Zeolite H-Y was used as the solid acid catalyst and ammonia as probe molecules in the figure.

fin adsorption on acidic zeolites, fast oligomerization of olefins takes place even at ambient temperature, which may mask the initial formation of surface alkoxy species. In the case of alcohol dehydration, on the other hand, removal of water from the working catalyst is crucial because hydration of surface alkoxy species back to the corresponding alcohol is ready to occur (*vide infra*). Most solid-state NMR investigations are, however, performed under batch conditions in fused glass ampoules or in gastight rotors, where removal of water and isolation of surface alkoxy species can hardly be achieved. Additionally, once being formed, surface alkoxy species may participate in further reactions with other reactants coexisting in the heterogeneous systems. The in situ SF protocol we applied not only facilitates the detection of surface alkoxy species by removal of water (step 2 in Figure 1) but also makes it possible to further investigate the reactivity of surface alkoxy species with different probe molecules (step 3 in Figure 1).

## Reactivity of SMS on Acidic Zeolite Catalysts: C–O Bond Activation

The intermediate role of SMS in zeolite catalysis has been a matter of debate, largely due to the lack of experimental evidence for identifying both the formation and further transformation of SMS in the same reaction. By in situ SF MAS NMR spectroscopy, we are able to study the chemical transformation of SMS with different reactants (probe molecules) under reaction conditions (step

**SCHEME 3**



3 in Figure 1) after the isolation of SMS formed on a working catalyst. The reactivity of SMS revealed by our research may be better described in terms of C–O bond and C–H bond activation, respectively. In this section, the results of C–O bond activation of SMS are summarized.

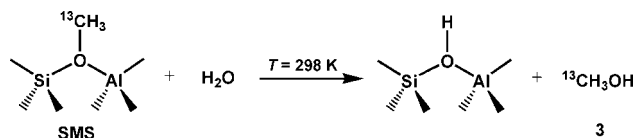
**Reaction of SMS and Methanol.** DME **2** was observed as the reaction product of SMS and methanol at 433 K on zeolite H-Y (Scheme 3).<sup>15</sup> Note that non- $^{13}\text{C}$ -enriched methanol was chosen to react with  $^{13}\text{C}$ -enriched SMS, which facilitates the interpretation of the NMR spectra. The result indicates that SMS may play an intermediate role in the formation of DME by conversion of methanol on acidic zeolite catalysts. However, the direct formation of DME from two methanol molecules on Brønsted acid sites<sup>18,19</sup> cannot be excluded as a competition pathway.

**Reaction of SMS and Water.** SMS react with water at ambient temperature, leading to the formation of methanol **3** on zeolites H-Y and H-ZSM-5 and silicoaluminophosphate H-SAPO-34 (Scheme 4).<sup>20</sup>

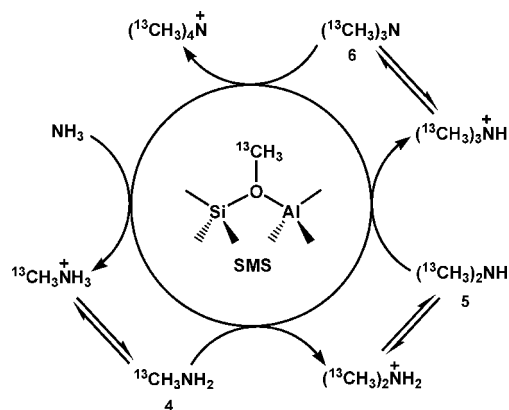
**Reaction of SMS and Ammonia.** SMS react readily with ammonia on zeolite H-Y and silicoaluminophosphate



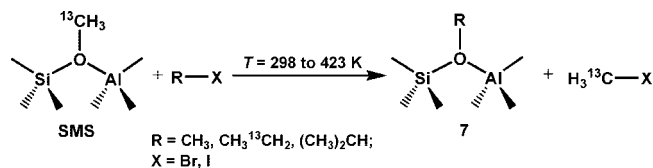
SCHEME 4



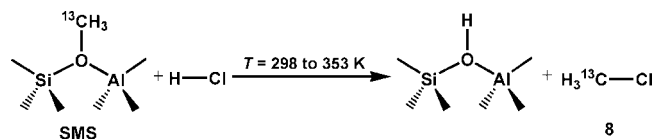
SCHEME 5



SCHEME 6



SCHEME 7

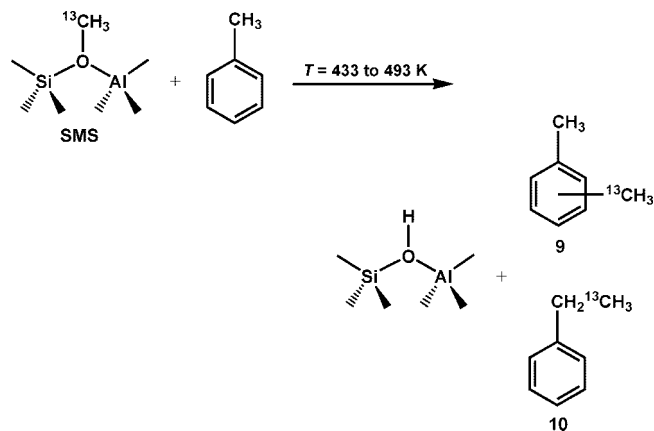


H-SAPO-34 at ambient temperature, by which methylamines and the corresponding methylammonium cations are formed (Scheme 5).<sup>21</sup> The selectivity toward monomethylamine **4**, dimethylamine **5**, and trimethylamine **6** largely depends on the concentration of ammonia and the reaction temperature.<sup>22</sup>

**Reaction of SMS and Alkyl Halides.** The reaction of SMS and ethyl iodide indicates the transformation of SMS to surface ethoxy species (SES) on zeolite H-Y and silicoaluminophosphate H-SAPO-34. SMS also react with other alkyl halides, such as methyl iodide, isopropyl iodide, and ethyl bromide, by which the corresponding alkoxy species **7** are expected to form (Scheme 6).<sup>21</sup>

**Reaction of SMS and Hydrochloride.** Scheme 7 describes the reaction of SMS and hydrochloride on zeolite H-Y, by which methyl chloride **8** is formed together with the recovery of zeolite Brønsted acidity.<sup>21</sup>

SCHEME 8



**Reaction of SMS and Aromatic Compounds.** Xylenes **9** and ethylbenzene **10** are formed as main products in the reaction of SMS with toluene on zeolite H-Y (Scheme 8).<sup>20</sup>

**Koch-Type Carbonylation Reaction.** The classic Koch carbonylation reaction of olefins and carbon monoxide involves carbenium ions as reaction intermediates in superacidic solutions. Transient existence of unstable acylium cation **11** in the reaction of SMS and carbon monoxide on zeolite H-Y was evidenced by our trapping experiments with water and ammonia, in which acetic acid **12** and acetamide **13** are formed, respectively (Scheme 9).<sup>21</sup>

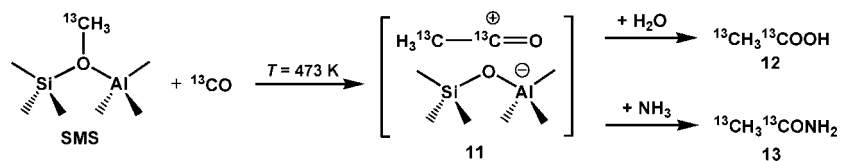
**Ritter-Type Reaction.** SMS react with acetonitrile on zeolite H-Y to produce the *N*-alkylnitrilium cation **14**, which can be further hydrolyzed to form *N*-methyl acetamide **15** as the final product (Scheme 10). The mechanism was rationalized in accordance with the classic Ritter reaction in solution media.<sup>21</sup>

As summarized above, SMS act as effective methylating agents when reacting with different probe molecules through C–O bond activation on acidic zeolite catalysts. Other evidence concerning C–O bond activation includes the reactions of SMS with aniline to form *N*-methylanilinium cations,<sup>23,24</sup> with benzene to form alkyl-substituted aromatics,<sup>25–28</sup> and with ethene or propene to start oligomerization of olefins.<sup>25,29</sup> Therefore, SMS may play an important intermediate role in a variety of zeolite-catalyzed reactions: methylation of amines, olefins, aromatics, carbon monoxide, acetonitrile, and so on.

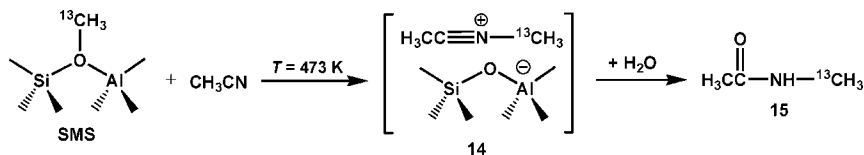
### C–H Bond Activation of SMS on Acidic Zeolite Catalysts: Debates on the Initiation Mechanism of the Methanol-to-Olefin (MTO) Process

In the absence of other reactants, however, isolated SMS on acidic zeolite catalysts show a high thermal stability at temperatures below 473 K.<sup>16</sup> When the reaction temperatures are further increased to ca. 523 K and above, SMS are decom-

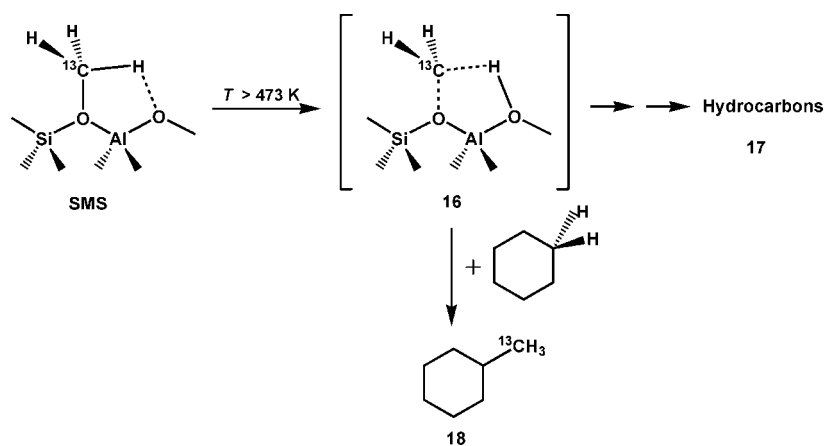
## SCHEME 9



## SCHEME 10



## SCHEME 11



posed on zeolites H-Y and H-ZSM-5, and silicoaluminophosphate H-SAPO-34, leading to the formation of hydrocarbons **17**, such as propane, isobutane, and aromatics (Scheme 11).<sup>20,30</sup> In addition to the weakening of C–O bond, the C–H bond activation of SMS may be assisted by the adjacent basic oxygen atoms of the zeolite framework at high temperatures. As a result, surface-stabilized intermediates **16** with carbene or ylide nature are likely formed. Indirect evidence for the existence of transient carbene-like species was obtained by trapping experiments with cyclohexane.<sup>20</sup> The formation of methylcyclohexane **18** implies the typical insertion reaction of carbene into the  $sp^3$  C–H bond of cyclohexane. Oxidation of SMS to carbon monoxide and carbon dioxide might be looked upon as additional evidence for the carbene mechanism.<sup>21</sup>

Although it has been well accepted that the methanol-to-olefin (MTO) process is dominated by a “hydrocarbon pool” mechanism under steady-state conditions, the first C–C bond formation in the induction period is still a matter of debate, which is directly related to the issue of C–H bond activation of SMS.<sup>31–42</sup> Experimental evidence from IR and NMR investigations indicates that C–H bond cleavage of SMS is responsible for the formation of first hydrocarbons in the MTO

process (see, for example, research papers cited in refs 20 and 21). It has also been proposed<sup>31,32</sup> that SMS may act as precursors of surface-stabilized carbene or ylide, though the detailed mechanism for the first C–C bond formation from SMS is still a matter of research. Theoretical investigation showed that surface-stabilized carbene could be produced by deprotonation of SMS on acidic zeolites with an activation barrier of 215–232  $\text{kJ mol}^{-1}$ .<sup>35</sup> A higher value of 242  $\text{kJ mol}^{-1}$  for this step was recently reported, which, however, energetically disfavors the mechanism for the C–H bond activation of SMS.<sup>36</sup>

An experimental argument against the C–H bond activation of SMS was also raised in 2002.<sup>37</sup> The initiation of the MTO process was explained by a few ppm of organic impurities instead of any direct route from pure methanol and DME.<sup>37</sup> The conclusion is based on GC analyses of the product streams after a series of pulses of fractionally distilled methanol onto the solid acid catalysts. The experimental data reasonably indicate that the yield of volatile products increases with the growth of the “hydrocarbon pool” on the working catalyst, which offers further evidence for the “hydrocarbon pool” mechanism. However, these results may not nec-

essarily prove that organic impurities would create the primary hydrocarbon pool on the working catalyst; neither may they prove that trace impurities would govern the duration of the kinetic induction period in the MTO process: in comparison with trace impurities on the working catalyst, SMS indisputably coexist in large quantities, which proved to be further converted to hydrocarbons by different research groups (*vide supra*). Our investigation by the combined  $^{13}\text{C}$  MAS NMR-UV/vis spectroscopy further indicates that traces of organic impurities (from 30 to 1000 ppm) present in the methanol do not affect the formation of primary hydrocarbons from SMS.<sup>30</sup>

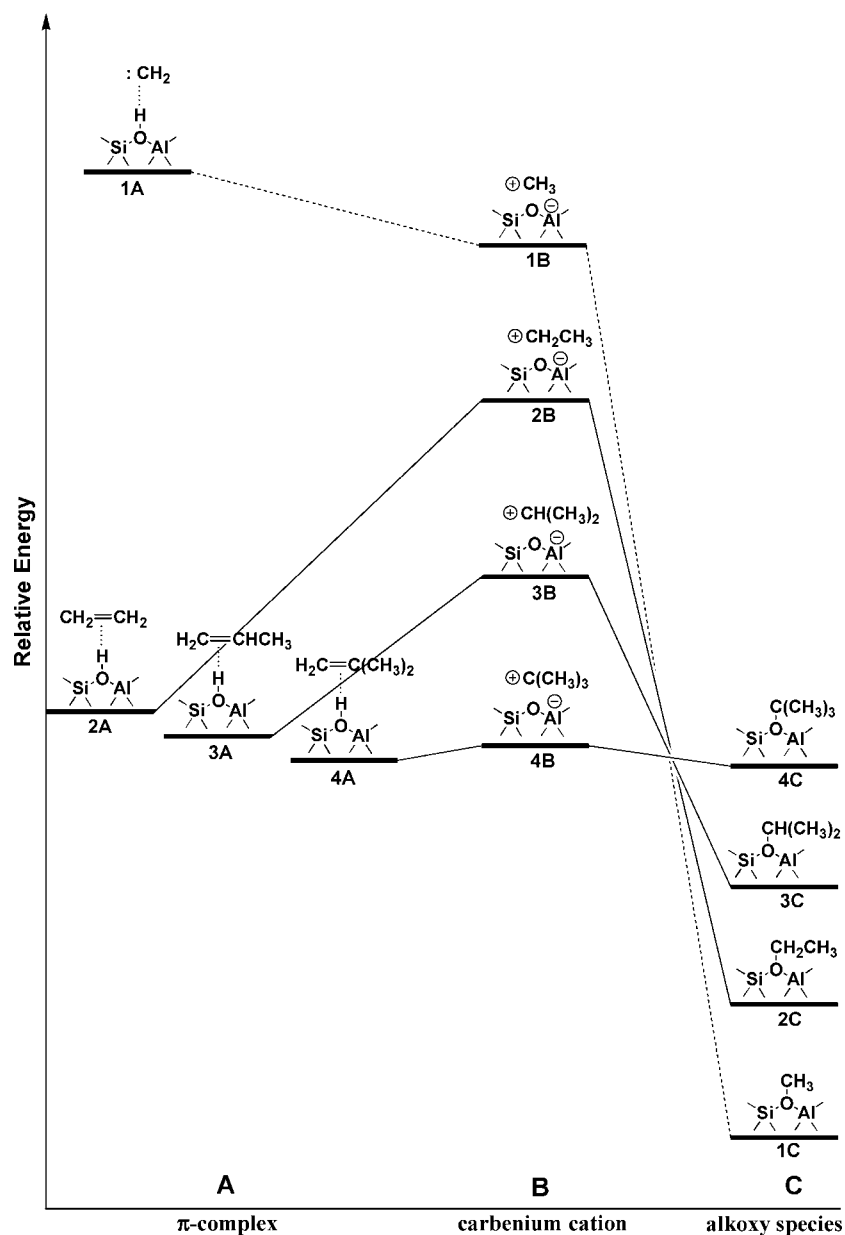
In contradiction to a number of previous investigations, it was recently reported<sup>38</sup> that the C–H bonds of SMS are not broken at temperatures between 573 and 623 K on silicoaluminophosphate H-SAPO-34 evidenced by H/D exchange studies. Once formed from the decomposition of SMS via C–H bond activation, **16** would undergo secondary reactions to form hydrocarbons (Scheme 11). As a result, the reverse reaction from **16** to form SMS should be disfavored. Therefore, it is very reasonable to have only observed the absence of H/D exchange<sup>38</sup> between the residual  $\text{CH}_3$ -SAPO-34 and  $\text{CD}_3$ -SAPO-34 on the catalyst. However, C–H bond activation of SMS may not be excluded because the yields and the H/D distribution of olefin products from SMS were not analyzed.<sup>38</sup> The discrepancy in experimental results concerning the C–H bond activation of SMS may also arise from different methods, catalysts, and experimental conditions being used.<sup>39,40</sup> For example, IR and NMR results, which favor the C–H bond activation of SMS, were obtained from the working catalysts, while GC and GC/MS analyses, which disfavor the C–H bond activation, came from the volatile products. No C–H bond activation of SMS was observed on zeolite H-ZSM-22,<sup>41,42</sup> which may be responsible for the failure of zeolite H-ZSM-22 to convert methanol into olefins under normal MTO conditions.

## Discussion on the Reactivity of Surface Alkoxy Species on Acidic Zeolite Catalysts

In contrast to the case in homogeneous systems, solvation effects are largely absent on zeolite catalysts and simple carbenium ions are, therefore, less stabilized by zeolite framework.<sup>2</sup> Indeed, simple carbenium ions have never been experimentally observed as stable intermediates in acid-catalyzed reactions performed on acidic zeolites so far. They may exist as highly activated and short-lived transition states and, therefore, only represent saddle points on the potential energy surface. On the other hand, covalent alkoxy species are consistently identified as persistent species upon the adsorption of olefins or dehydration of alcohols on acidic zeolites. The rel-

ative stability of surface alkoxy species and the activation energies for their formation via carbenium-ion-like transition states can be deduced from theoretical investigations of olefin adsorption on acidic zeolites. As depicted in Figure 2, the activation of olefins on acidic zeolites starts with the formation of  $\pi$ -complex (**2A** for ethene, **3A** for propene and **4A** for isobutene), and through a carbenium-ion-like transition state (**2B**, **3B**, and **4B**), the corresponding surface alkoxy species ( $\sigma$ -complex, **2C**, **3C**, and **4C**) are formed. The relative stability of surface alkoxy species follows the order ethoxy **2C** > isopropoxy **3C** > *tert*-butoxy **4C**, while the energy levels of carbenium-ion-like transition states follow the order **2B** > **3B** > **4B**.<sup>43</sup> Moreover, the energy differences among  $\pi$ -complex of isobutene **4A**, *tert*-butyl cation **4B**, and *tert*-butoxy species **4C** are quite small.<sup>44–46</sup> SMS **1C** can be further added in Figure 2 as the most stable alkoxy species and, accordingly, methyl cations **1B** as the most highly activated transition state.

The C–O bond reactivity of surface alkoxy species with different probe molecules can be, therefore, discussed by analyzing the energy differences from **C** to **B** in Figure 2. The following results may be derived: (i) According to the Hammond postulate, surface *tert*-butoxy species would possess more carbenium-ion-like nature than other alkoxy species presented in Figure 2. In contrast, the covalent-bond nature should be profound in the case of SMS. (ii) The nucleophilic substitution reaction with SMS is more  $\text{S}_{\text{N}}2$ -mechanism oriented, in which both nucleophile (probe molecules) and SMS simultaneously take part in the transition state. The involvement of probe molecules in the transition state will, more or less, decrease the activation energy in comparison with the energy difference between **1C** and **1B** in Figure 2. This explains that the reactions of SMS with probe molecules having high nucleophilicity (water, ammonia, or methylamines) take place at room temperature, while for those with low nucleophilicity (hydrochloride, carbon monoxide, or acetonitrile), higher reaction temperatures are required. (iii) The  $\text{S}_{\text{N}}1$ -mechanism may dominate the nucleophilic substitution reactions of the bulky *tert*-butoxy species on acidic zeolites. In this case, the presence of probe molecules does not contribute significantly in the rate-determining step in which the transition state largely resembles the corresponding carbenium ions, and therefore, the activation energy in this step should be close to the energy difference between **4C** and **4B** shown in Figure 2.



**FIGURE 2.** Energy profiles for the formation of surface alkoxy species (**A** → **B** → **C**) on acidic zeolite catalysts, adapted from ref 21. Discussion on the reactivity of surface alkoxy species with additional probe molecules is based on the reverse route (**C** → **B**).

## Conclusions and Perspectives

Elucidation of the reaction mechanisms in heterogeneous catalysis is a complicated issue. Direct observation of reaction intermediates and detailed investigation of their reactivity on the working catalysts offer important mechanistic information, which may be realized by in situ spectroscopic methods. The reaction intermediates involved in heterogeneous catalysis can vary in nature from highly reactive species to relatively stable ones. The in situ spectroscopic method being applied could only detect possible intermediates that possess long enough lifetime. It is also feasible to further isolate the long-lived intermediates formed in some heteroge-

neously catalyzed systems and investigate their nature and chemical reactivity thereafter. This strategy has been exploited in our investigations of the SMS reactivity by in situ SF MAS NMR spectroscopy. Through this approach, the possible intermediate role of SMS in a variety of zeolite-catalyzed reactions has been revealed. The reactivity of SMS can be discussed in terms of C–O bond and C–H bond activation, respectively. SMS on acidic zeolite catalysts act as an effective methylating agent in the reactions with different probe molecules through C–O bond activation. At higher reaction temperatures, C–H bond activation of SMS may further occur, by which intermediates with surface-stabilized carbene or ylide



nature are likely formed. The latter issue is directly related to the mechanistic elucidation of the MTO process and invites further investigations.

In order to properly understand the reaction mechanisms in heterogeneous catalysis, one needs to know the nature of the transition states that connect reactants, intermediates, and products. Ingenious experiments should be designed to obtain the rate constants of the elementary reaction steps in the catalytic cycle. Isotopic labeling, trapping, and stereochemical analysis may offer additional information on the structure and nature of the transition states in heterogeneous catalysis. On the other hand, quantum chemistry<sup>2</sup> can be very useful to address these issues. The reactivity and the carbenium-ion-like nature of surface alkoxy intermediates ( $>C_1$  species) on acidic zeolite catalysts are briefly discussed in this Account in combination with recent theoretical investigations. Further experimental efforts are expected to obtain detailed information on the reactivity of these surface alkoxy species ( $>C_1$  species). In addition to  $^{13}C$  MAS NMR,  $^{15}N$  MAS NMR<sup>47</sup> may also be utilized for mechanistic investigations on some zeolite-catalyzed reactions. The combination of several in situ spectroscopic methods can provide complementary information about the working catalysts. Structure–reactivity relationship in heterogeneous systems<sup>48</sup> is an important issue for mechanism elucidation. The adsorption and diffusion effects should be also taken into account to correlate with the overall catalytic performance on acidic zeolite catalysts.

*Our research work summarized in this Account has been entirely performed at University of Stuttgart, and we gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft. W.W. also grateful for the research grants (Nos. 20621091 and 20602016) from National Natural Science Foundation of China.*

#### BIOGRAPHICAL INFORMATION

**Wei Wang** was born in 1972 in Xinjiang, P. R. China. He received his Ph.D. (physical organic chemistry, 1998) from Lanzhou University under the supervision of Prof. You-Cheng Liu. After his postdoctoral research at University of Stuttgart (2000–2001, with Prof. Michael Hunger) and at University of Southern California (2001–2002, with Prof. James F. Haw), he joined Prof. Hunger's Laboratory where he worked for four years on the applications of in situ NMR techniques in mechanistic studies of heterogeneous catalysis. In 2006, he was promoted as Professor at Lanzhou University. He is the recipient of the Cheung Kong Professorship awarded in 2006 by the Ministry of Education of China.

**Michael Hunger** was born in 1955 in Leipzig, Germany. He studied physics at the University of Leipzig and obtained his Ph.D. in 1984 at the Department of Physics. After his Habilitation and a

number of periods abroad, he moved to the Institute of Chemical Technology at University of Stuttgart in 1992, and was appointed Professor at the Faculty of Chemistry in 1999. His research interests are focused on the development of new techniques of solid-state NMR and UV/vis spectroscopy for the characterization of microporous and mesoporous solid catalysts and in situ spectroscopy of heterogeneous catalytic reactions. He received the CSIR-Humboldt Research Award in 2005.

#### FOOTNOTES

\* To whom correspondence should be addressed. E-mail: wang\_wei@lzu.edu.cn. Tel: +86 931 8912282. Fax: +86 931 8915557.

#### REFERENCES

- Cejka, J.; van Bekkum, H.; Corma, A.; Schueth, F. *Introduction to Zeolite Molecular Sieves*, 3rd ed.; Elsevier: Amsterdam, 2007; pp 1–1094.
- van Santen, R. A.; Kramer, G. J. Reactivity Theory of Zeolitic Brønsted Acidic Sites. *Chem. Rev.* **1995**, *95*, 637–660.
- Farneth, W. E.; Gorte, R. J. Methods for Characterizing Zeolite Acidity. *Chem. Rev.* **1995**, *95*, 615–635.
- Corma, A. Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions. *Chem. Rev.* **1995**, *95*, 559–614.
- Haw, J. F. *In-Situ Spectroscopy in Heterogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 2002; pp 1–288.
- Weckhuysen, B. M. *In-Situ Spectroscopy of Catalysts*; American Scientific Publishers: Stevenson Ranch, CA, 2004; pp 1–332.
- Hunger, M.; Weitkamp, J. *In situ* IR, NMR, EPR and UV/Vis Spectroscopy: Tools for New Insight into the Mechanisms of Heterogeneous Catalysis. *Angew. Chem.* **2001**, *113*, 3040–3059; *Angew. Chem., Int. Ed.* **2001**, *40*, 2954–2971.
- Hunger, M.; Horvath, T. A New MAS NMR Probe for In situ Investigations of Hydrocarbon Conversion on Solid Catalysts under Continuous-Flow Conditions. *J. Chem. Soc., Chem. Commun.* **1995**, 1423–1424.
- Wang, W.; Seiler, M.; Ivanova, I. I.; Weitkamp, J.; Hunger, M. In situ Stopped-Flow (SF) MAS NMR Spectroscopy: A Novel NMR Technique Applied for the Study of Aniline Methylation on a Solid Base Catalyst. *Chem. Commun.* **2001**, 1362–1363.
- Hunger, M.; Wang, W. Formation of Cyclic Compounds and Carbenium Ions by Conversion of Methanol on Weakly Dealuminated Zeolite H-ZSM-5 Investigated via a Novel In situ CF MAS NMR/UV-Vis Technique. *Chem. Commun.* **2004**, 584–585.
- Hunger, M.; Wang, W. Characterization of Solid Catalysts in the Functioning State by Nuclear Magnetic Resonance Spectroscopy. *Adv. Catal.* **2006**, *50*, 149–225.
- Hunger, M. In situ Flow MAS NMR Spectroscopy: State of the Art and Applications in Heterogeneous Catalysis. *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, in press, doi: 10.1016/j.pnmrs.2007.08.001.
- van Santen, R. A.; Neurock, M. Reactivity Index Relations in Theoretical Heterogeneous Catalysis. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knoezinger, H., Schueth, F., Weitkamp, J., Eds.; Wiley VCH: Weinheim, Germany, 2008, pp 1415–1445.
- Kazansky, V. B. The Nature of Adsorbed Carbenium Ions as Active Intermediates in Catalysis by Solid Acids. *Acc. Chem. Res.* **1991**, *24*, 379–383.
- Wang, W.; Seiler, M.; Hunger, M. Role of SMS in the Conversion of Methanol to Dimethyl Ether on Acidic Zeolites Investigated by In Situ Stopped-Flow MAS NMR Spectroscopy. *J. Phys. Chem. B* **2001**, *105*, 12553–12558.
- Wang, W.; Buchholz, A.; Arnold, A.; Xu, M.; Hunger, M. Effect of Surface Methoxy Groups on the  $^{27}Al$  Quadrupole Parameters of Framework Aluminum Atoms in Calcined Zeolite H-Y. *Chem. Phys. Lett.* **2003**, *370*, 88–93.
- Wang, W.; Jiao, J.; Jiang, Y.; Ray, S. S.; Hunger, M. Formation and Decomposition of Surface Ethoxy Species on Acidic Zeolite Y. *ChemPhysChem* **2005**, *6*, 1467–1469.
- Blaszowski, S. R.; van Santen, R. A. The Mechanism of Dimethyl Ether Formation from Methanol Catalyzed by Zeolitic Protons. *J. Am. Chem. Soc.* **1996**, *118*, 5152–5153.
- Blaszowski, S. R.; van Santen, R. A. Theoretical study of C–C bond formation in the methanol-to-gasoline process. *J. Am. Chem. Soc.* **1997**, *119*, 5020–5027.
- Wang, W.; Buchholz, A.; Seiler, M.; Hunger, M. Evidence for an Initiation of the Methanol-to-Olefin Process by Reactive Surface Methoxy Groups on Acidic Zeolite Catalysts. *J. Am. Chem. Soc.* **2003**, *125*, 15260–15267.
- Jiang, Y.; Hunger, M.; Wang, W. On the Reactivity of Surface Methoxy Species in Acidic Zeolites. *J. Am. Chem. Soc.* **2006**, *128*, 11679–11692.

- 22 Jiang, Y.; Huang, J.; Wang, W.; Hunger, M. Formation of Methylamines by the Reaction of Ammonia with Surface Methoxy Species on Zeolite H-Y and the Silicoaluminophosphate H-SAPO-34. *Stud. Surf. Sci. Catal.* **2007**, *170*, 1331–337.
- 23 Ivanova, I. I.; Pomakhina, E. B.; Rebrov, A. I.; Hunger, M.; Kolyagin, Y. G.; Weitkamp, J. Surface Species Formed during Aniline Methylation on Zeolite H-Y Investigated by In Situ MAS NMR Spectroscopy. *J. Catal.* **2001**, *203*, 375–381.
- 24 Wang, W.; Seiler, M.; Ivanova, I. I.; Sternberg, U.; Weitkamp, J.; Hunger, M. Formation and Decomposition of *N,N,N*-Trimethylanilinium Cations on Zeolite H-Y Investigated by In Situ Stopped-Flow MAS NMR Spectroscopy. *J. Am. Chem. Soc.* **2002**, *124*, 7548–7554.
- 25 Forester, T. R.; Howe, R. F. In Situ FTIR Studies of Methanol and Dimethyl Ether in ZSM-5. *J. Am. Chem. Soc.* **1987**, *109*, 5076–5082.
- 26 Datka, J.; Rakoczy, J.; Zadrozna, G. The Properties of Alkoxy Groups in Zeolites Studied by IR Spectroscopy. In *Proceedings of the 12th International Zeolite Conference*, Treacy, M. M. J., Marcus, B. K., Bisher, M. E., Higgins, J. B., Eds.; Materials Research Society: Warrendale, PA, 1999; pp 2601–2608.
- 27 Ono, Y.; Mori, T. Mechanism of Methanol Conversion into Hydrocarbons over ZSM-5 Zeolite. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2209–2221.
- 28 Rakoczy, J.; Romotowski, T. Alkylation of Benzene with Methanol on Zeolites: Infrared Spectroscopy Studies. *Zeolites* **1993**, *13*, 256–260.
- 29 Salehirad, F.; Anderson, M. W. Solid-State  $^{13}\text{C}$  MAS NMR Study of Methanol-to-Hydrocarbon Chemistry over H-SAPO-34. *J. Catal.* **1996**, *164*, 301–314.
- 30 Jiang, Y.; Wang, W.; Marthala, V. R. R.; Huang, J.; Sulikowski, B.; Hunger, M. Effect of Organic Impurities on the Hydrocarbon Formation via the Decomposition of Surface Methoxy Groups on Acidic Zeolite Catalysts. *J. Catal.* **2006**, *238*, 21–27.
- 31 Hutchings, G. J.; Hunter, R. Hydrocarbon Formation from Methanol and Dimethyl Ether: A Review of the Experimental Observations Concerning the Mechanism of Formation of the Primary Products. *Catal. Today* **1990**, *6*, 279–306.
- 32 Stöcker, M. Methanol-to-Hydrocarbons: Catalytic Materials and Their Behavior. *Microporous Mesoporous Mater.* **1999**, *29*, 3–48.
- 33 Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B. The Mechanism of Methanol to Hydrocarbon Catalysis. *Acc. Chem. Res.* **2003**, *36*, 317–326.
- 34 Wang, W.; Jiang, Y.; Hunger, M. Mechanistic Investigations of the Methanol-to-Olefin (MTO) Process on Acidic Zeolite Catalysts by In Situ Solid-State NMR Spectroscopy. *Catal. Today* **2006**, *113*, 102–114.
- 35 Sinclair, P. E.; Catlow, C. R. A. Generation of Carbenes during Methanol Conversion over Brønsted Acidic Aluminosilicates. A Computational Study. *J. Phys. Chem. B* **1997**, *101*, 295–298.
- 36 Lesthaeghe, D.; van Speybroeck, V.; Marin, G.; Waroquier, M. Understanding the Failure of direct C-C Coupling in the Zeolite-Catalyzed Methanol-to-Olefin Process. *Angew. Chem., Int. Ed.* **2006**, *45*, 3133–3136.
- 37 Song, W.; Marcus, D. M.; Fu, H.; Ehresmann, J. O.; Haw, J. F. An Oft-Studied Reaction That May Never Have Been: Direct Catalytic Conversion of Methanol or Dimethyl Ether to Hydrocarbons on the Solid Acids HZSM-5 or HSAPO-34. *J. Am. Chem. Soc.* **2002**, *124*, 3844–3845.
- 38 Marcus, D. M.; McLachlan, K. A.; Wildman, M. A.; Ehresmann, J. O.; Kletnieks, P. W.; Haw, J. F. Experimental Evidence Direct Catalytic Conversion of Methanol or Dimethyl Ether to Hydrocarbons on the Solid Acids HZSM-5 or HSAPO-34. *Angew. Chem., Int. Ed.* **2006**, *45*, 3133–3136.
- 39 Haw, J. F.; Marcus, D. M.; Kletnieks, P. W. Effect of Organic Impurities on the Hydrocarbon Formation via the Decomposition of Surface Methoxy Groups on Acidic Zeolite Catalysts. Comment. *J. Catal.* **2006**, *244*, 130–133.
- 40 Jiang, Y.; Wang, W.; Marthala, V. R. R.; Huang, J.; Sulikowski, B.; Hunger, M. Response to Comments on the Paper: Effect of Organic Impurities on the Hydrocarbon Formation via the Decomposition of Surface Methoxy groups on Acidic Zeolite Catalysts. *J. Catal.* **2006**, *244*, 134–136.
- 41 Cui, Z.-M.; Liu, Q.; Song, W.-G.; Wan, L. J. Insight into the Mechanism of Methanol-to-Olefin Conversion at Zeolites with Systematically Selected Framework Structures. *Angew. Chem.* **2006**, *118*, 6662–6665.
- 42 Cui, Z.-M.; Liu, Q.; Bain, S.-W.; Ma, Z.; Song, W.-G. The Role of Methoxy Groups in Methanol to Olefin Conversion. *J. Phys. Chem. C* **2008**, *112*, 2685–2688.
- 43 For detailed discussion, see ref 21 and references cited therein.
- 44 Rozanska, X.; van Santen, R. A.; Demuth, T.; Hutschka, F.; Hafner, J. A Periodic DFT Study of Isobutene Chemisorption in Proton-Exchanged Zeolites: Dependence of Reactivity on the Zeolite Framework Structure. *J. Phys. Chem. B* **2003**, *107*, 1309–1315.
- 45 Boronat, M.; Viruela, P.; Corma, A. Reaction Intermediates in Acid Catalysis by Zeolites: Prediction of the Relative Tendency to Form Alkoxides or Carbocations as a Function of Hydrocarbon Nature and Active Site Structure. *J. Am. Chem. Soc.* **2004**, *126*, 3300–3309.
- 46 Tuma, C.; Sauer, J. Protonated Isobutene in Zeolites: *tert*-Butyl Cation or Alkoxide. *Angew. Chem., Int. Ed.* **2005**, *44*, 4769–4771.
- 47 Marthala, V. R. R.; Jiang, Y.; Huang, J.; Wang, W.; Glaser, R.; Hunger, M. Beckmann Rearrangement of  $^{15}\text{N}$ -Cyclohexanone Oxime on Zeolites Silicalite-1, H-ZSM-5, and H-[B]ZSM-5 Studied by Solid-State NMR Spectroscopy. *J. Am. Chem. Soc.* **2006**, *128*, 14812–14813.
- 48 Iglesia, E.; Bhan, A. A Link between Reactivity and Local Structure in Acid Catalysis on Zeolites. *Acc. Chem. Res.* **2008**, *41*, 559–567.