On the Reactivity of Surface Methoxy Species in Acidic Zeolites

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Abstract: The in situ preparation and isolation of surface methoxy species on acidic zeolites are followed by further investigations of their reactivity in heterogeneously catalyzed reactions. For the first time, the following solid-state NMR evidence for the high reactivity of surface methoxy species has been obtained: (i) Surface methoxy species react readily with ammonia on acidic zeolites at room temperature, by which methylamines and methylammonium cations are formed. (ii) The transformation of surface methoxy species to other alkoxo species can be achieved by the reaction of surface methoxy species and corresponding alkyl halides on acidic zeolites. (iii) Surface methoxy species react readily with hydrochloride, giving methyl chloride as the sole product. (iv) The classic Koch carboxylation reaction and Ritter reaction in solution can be performed with surface methoxy species on acidic zeolites. (v) Carbon monoxide and carbon dioxide are produced by the oxidation of surface methoxy species in the presence of oxygen. The stability and reactivity of surface methoxy species are discussed in comparison with other surface alkoxo species (> C, species).

Introduction

Knowledge of the mechanisms involved in heterogeneously catalyzed reactions is of fundamental interest and may also be of value for the optimization of existing industrial processes and for the development of new ones. Carbenium ions were considered as likely intermediates involved in a variety of reactions catalyzed by acidic zeolites. However, the efforts to experimentally verify the long-lived existence of simple alkyl cations, e.g., isopropyl or tert-butyl cations, in acidic zeolites have been in vain so far.3–6 It was suggested by Kazansky7 that free carbenium cations mostly exist as transition states rather than as persistent intermediates in acid-catalyzed reactions performed on acidic zeolites. Instead, the surface alkoxo (alkoxide) species with carbenium-ion-like properties4 may act as catalytic intermediates in zeolite chemistry.7 This topic has been stimulating extensive research interest, and important progress has recently been made by using theoretical calculations.8–13 Due to the complexity of the heterogeneous system under study, however, experimental evidence for the existence and reactivity of surface alkoxo species 3–6,14–16 is still lacking or ambiguous.

By an in situ stop-flow MAS NMR technique, we have been able to observe the formation of surface methoxy species...
from methanol\textsuperscript{17} and surface ethoxy species from ethanol\textsuperscript{14} on acidic zeolites. Furthermore, the intermediary role of surface methoxy species in the methanol-to-olefin (MTO) process was demonstrated.\textsuperscript{13} On acidic zeolites at reaction temperatures lower than 473 K, surface methoxy species act as reactive methylating agents, which can react with methanol to form dimethyl ether (DME)\textsuperscript{12b} and with toluene to form xylenes.\textsuperscript{14c} At reaction temperatures higher than 523 K, the decompositions of surface methoxy species takes place as a result of dissociation of the C–H bond of the methyl group, which is further responsible for the first C–C coupling and, therefore, for the formation of primary hydrocarbons in the MTO process.\textsuperscript{17c,d}

The approach we developed\textsuperscript{17} for the in situ preparation of surface methoxy species allows us to further investigate the reactivity of surface methoxy species in heterogeneously catalyzed reactions. In this contribution, \textsuperscript{13}C MAS NMR spectroscopy is utilized to study the reactions of surface methoxy species with ammonia, alkyl halides, hydrochloride, carbon monoxide, acetonitrile, and oxygen on solid acid catalysts. On the basis of these experimental findings, the reactivity of surface methoxy species is discussed in terms of C–O bond and C–H bond activation, respectively. By benefit of recent theoretical investigations, the relative stability and reactivity of surface alkoxy species in acidic zeolites are further compared.

Experimental Section

Materials. Zeolite Na–Y ($n_{Na}/n_{Al} = 2.7$) was purchased from Degussa AG, Hanau, Germany. The NH$_4$–Y zeolite was prepared by a four-fold ion exchange of zeolite Na–Y at 353 K in a 1.0 M aqueous solution of NH$_4$NO$_3$. After an ion-exchange degree of 90% was reached, the material was washed in demineralized water and dried at room temperature. Subsequently, the NH$_4$–Y zeolite was heated in a vacuum with a rate of 20 K/h up to the final temperature of 723 K. There, the material was calcined at a pressure below $10^{-2}$ mbar for 12 h leading to zeolite H–Y. The silicoaluminophosphates H–SAPO-34 with an $n_{Si}/n_{Al} + n_{P} + n_{Si}$ of 0.11 was prepared according to the recipe described in ref 18 for the synthesis of Ni–SAPO-34, but omitting the nickel salt. To remove the template, the as-synthesized material was heated at a rate of 60 K/h to 873 K in dry nitrogen and calcined at this temperature for 6 h in synthetic air (20 vol % oxygen, 60 L/h). Subsequently, the sample was subjected to additional calcination in a vacuum with a heating rate of 20 K/h up to the final temperature of 673 K. At this temperature, the material was calcined at a pressure below $10^{-2}$ mbar for 12 h leading to silicoaluminophosphate H–SAPO-34. The dehydrated catalysts were sealed in glass tubes until their further use. All catalysts were characterized by AES-ICP, XRD, and solid-state \textsuperscript{1}H, \textsuperscript{27}Al, and \textsuperscript{29}Si MAS NMR spectroscopy. The results indicated that the material obtained after cation exchange and calcination was neither damaged nor dealuminated. \textsuperscript{13}C-Enriched methanol (\textsuperscript{13}C-enrichment of 99%), \textsuperscript{13}C-enriched methyl iodide (\textsuperscript{13}C-enrichment of 99%), and \textsuperscript{13}C-1-ethyl ethyl iodide (\textsuperscript{13}C-1-ethoxy of 99%) were purchased from Cambridge Isotopes. \textsuperscript{13}C-Enriched carbon monoxide (\textsuperscript{13}C-enrichment of 99%) was purchased from Aldrich.

Sample Preparation. In the in situ preparation of surface methoxy species from \textsuperscript{13}C-enriched methanol on acidic catalysts H–Y and H–SAPO-34 was described elsewhere.\textsuperscript{17} By \textsuperscript{13}C spin-counting experiments, the coverage of surface methoxy species was determined as ca. 0.44 per acid site on acidic zeolite H–Y, which agrees well with our previous results.\textsuperscript{17d} The methylated catalyst (ca. 300 mg) was then loaded with a volatile reactant on a vacuum line and fused in a glass tube (outer diameter of ca. 6 mm and length of ca. 180 mm) for further thermal treatment. After heating, the glass tube was opened in a glovebox, and the catalyst was transferred into a 7 mm MAS NMR rotor for solid-state MAS NMR measurements. In the case of oxidation reaction, the methylated catalyst was transferred into an MAS NMR insert (Wilmad, 5.6 mm o.d. with constrictions) inside a glovebox, and loaded with ca. 5 mbar of oxygen and, subsequently, sealed. The sealed glass inserts were heated to the reaction temperature for 20 min.

\textsuperscript{13}C MAS NMR Experiments. All \textsuperscript{13}C MAS NMR investigations were performed with a 7 mm Bruker MAS NMR probe on a Bruker MSL-400 spectrometer at a \textsuperscript{13}C resonance frequency of 100.6 MHz. \textsuperscript{13}C high-power proton decoupling (HPDEC) MAS NMR spectra were recorded after an excitation with a $\pi/2$ pulse and with a repetition time of 5 s. For \textsuperscript{13}C spin-counting experiments, a repetition time of 30 s was performed, and an external intensity standard (dehydrated zeolite H–Y loaded with \textsuperscript{13}C(CH$_3$OH) was applied. \textsuperscript{13}C cross-polarization (CP) MAS NMR spectra were performed with a contact time of 5 ms and with a repetition time of 2 s. The sample spinning rates of ca. 3.5 to 4.5 kHz were applied. All \textsuperscript{13}C MAS NMR spectra were referenced to tetramethylsilane (TMS).

Results

Reaction of Surface Methoxy Species and Ammonia at Room Temperature. Heterogeneously catalyzed alkylation of amines by alcohols, for example, the methylation of ammonia by methanol on zeolite catalysts,\textsuperscript{19–22} has attracted significant interest in recent years. Different mechanisms have been proposed for the reaction of methanol and ammonia on acidic zeolites.\textsuperscript{20} It has been suggested that ammonia and methylamines are preferentially adsorbed on Bronsted acid sites, due to their higher proton affinities in the gas phase than that of methanol.\textsuperscript{20} Therefore, most of the proposed mechanisms assume that the reaction does not involve surface methoxy species.\textsuperscript{20} However, the existence of surface methoxy species has been experimentally observed by in situ IR spectroscopy during the reaction of methanol and ammonia on acidic zeolite H–Y.\textsuperscript{20,21} In addition, the formation of surface methoxy species during aniline methylation on acidic zeolite H–Y has been shown with the application of in situ MAS NMR spectroscopy.\textsuperscript{23,24} In this contribution, the reaction of surface methoxy species and ammonia was, therefore, studied by \textsuperscript{13}C MAS NMR spectroscopy. It was found that surface methoxy species react readily with ammonia on acidic zeolite H–Y and silicoaluminophosphate H–SAPO-34 at room temperature, by which methylamines and methylammonium cations are formed.

For convenience of comparison, Figure 1a shows again the \textsuperscript{13}C MAS NMR spectrum recorded after the in situ preparation of surface methoxy species (\textsuperscript{13}CH$_3$–Y) on zeolite H–Y from the \textsuperscript{13}C-enriched methanol.\textsuperscript{17} The dominating signal at 56 ppm with spinning sidebands is due to surface methoxy species.\textsuperscript{17}
The signal at 63 ppm is originated from side-on adsorbed DME, while the broad signal at 50 ppm is caused by terminal methoxy species (SiOCH₃). Upon loading of 200 mbar of ammonia on the methylated zeolite Y (approximately 1.5 NH₃ per surface methoxy species) at room temperature, new signals appear at 26 and 24 ppm which are assigned to methylamine, CH₃ NH₂, and protonated methylamine, CH₃ NH₃⁺, respectively. Upon loading of 500 mbar of ammonia on the methylated zeolite Y (approximately 3.5 NH₃ per surface methoxy species) at room temperature, additional signals at 34 and 56 ppm become evident (Figure 1c). The signal at 34 ppm is due to the protonated dimethylamine, (CH₃)₂NH⁺. In comparison with the signal of surface methoxy species (Figure 1a), the signal at 56 ppm in Figure 1c is much narrower and, therefore, assigned to the tetramethylammonium cation, (CH₃)₄N⁺, according to the literature. The assignments are further supported by the ¹³C MAS NMR spectrum in Figure 1d, which was recorded after the catalyst sample (c) was fully hydrated at room temperature. As indicated in Figure 1d, the broad signal at 50 ppm (25) Thursfield, A.; Anderson, M. W.; Dwyer, J.; Hutchings, G. J.; Lee, D. J. Chem. Soc., Faraday Trans. 1998, 94, 1119–1122.


Figure 1. ¹³C HPDEC MAS NMR spectra of methylated zeolites Y (¹³CH₃–Y), recorded before loading of ammonia (a), after loading of 200 mbar of ammonia at room temperature (b), after loading of 500 mbar of ammonia at room temperature (c). Spectrum d was recorded after the catalyst sample (c) was fully hydrated at room temperature. As a control experiment, spectrum e shows the ¹³C MAS NMR spectrum of acidic zeolite H–Y after loading of methanol and ammonia at room temperature, in which the ¹³C signal of methanol (49 ppm) is 1 ppm high-field shifted due to the coexistence of ammonia on the acidic zeolite H–Y. Asterisks denote spinning sidebands.
The reaction of terminal surface methoxy species with water to methanol,\textsuperscript{13} has a $^{13}$C chemical shift of ca. 48 ppm, \textsuperscript{24} the $^{13}$C MAS NMR which includes the methylation/demethylation (or disproportionation) reaction rate may be governed by further transfer of these atoms of the reactant, CH$_3$CH$_2$I. A weak signal appears at 23 ppm, which is assigned to methyl iodide $^{13}$CH$_3$I.\textsuperscript{15b} The reaction of surface methoxy species and ethyl iodide becomes more evident at 373 and 423 K, as indicated in Figure 2b and 2c, respectively. A new signal at 73 ppm occurred with spinning sidebands in Figure 2b, left, and dominates the spectrum in Figure 2c, left. In agreement with our recent findings,\textsuperscript{14} the signal at 73 ppm is assigned to the methylene carbon atoms of the reactants, CH$_3$CH$_2$I. The above-mentioned assignments are further supported by the $^{13}$C CP/MAS NMR spectrum shown in Figure 2d, left, which was recorded after the catalyst was hydrated at room temperature. The formation of CH$_3$CH$_2$OH at 60 ppm and $^{13}$CH$_3$OH at 50 ppm indicates the hydrolysis of surface ethoxy species\textsuperscript{14} and surface methoxy species\textsuperscript{17} by water. The $^{13}$C HPDEC MAS NMR spectra simultaneously recorded for each sample are shown in Figure 2, right. The same signals occur in each $^{13}$C HPDEC MAS NMR spectrum as those in the corresponding $^{13}$C CP/MAS NMR spectrum, although with different relative intensities.

The reaction of surface methoxy species and ethyl iodide is depicted in Scheme 2, which shows the transformation of surface methoxy species to surface ethoxy species on the catalyst. A similar reaction was found for surface methoxy species reacting with other alkyl halides, by which the corresponding alkoxy species are expected to form. Figure 3 shows some representative $^{13}$C HPDEC MAS NMR spectra recorded after the reaction of $^{13}$C-enriched surface methoxy species and nonenriched alkyl halides on zeolite H–Y and silicoaluminophosphate H–SAPO-34. The formation of $^{13}$C-enriched methyl iodide $^{13}$CH$_3$I (Figures 3a to 3d) or methyl bromide $^{13}$CH$_3$Br (Figure 3e) indicates that the reaction of surface methoxy species and alkyl halides takes place in a similar manner as that described in Scheme 2. For example, after the reaction of $^{13}$C-enriched surface methoxy species ($^{13}$CH$_3$–Y) and nonenriched isopropyl iodide [(CH$_3$)$_2$CH–I] at room temperature, the signal of $^{13}$C-enriched methyl iodide $^{13}$CH$_3$I occurs at 23 ppm in the $^{13}$C HPDEC MAS NMR spectrum (Figure 3c). This signal dominates the $^{13}$C HPDEC MAS NMR spectrum after the reaction at 373 K (Figure 3d). Another example is the reaction of $^{13}$C-enriched surface methoxy species and nonenriched ethyl bromide on zeolite H–Y. Figure 3e shows the $^{13}$C HPDEC MAS NMR spectrum recorded after the reaction at 423 K. The reaction of terminal surface methoxy species with water to methanol,\textsuperscript{13} the $^{13}$C MAS NMR spectroscopy was first applied to investigate the reaction of surface methoxy species ($^{13}$CH$_3$–Y) and $^{13}$C-1-enriched ethyl iodide (CH$_3$$^{13}$CH$_2$I). Figure 2a, left, shows the $^{13}$C CP/MAS NMR spectrum recorded after loading of CH$_3$$^{13}$CH$_2$I on the methylated zeolite Y, $^{13}$CH$_3$–Y, at room temperature. The signal at 4 ppm is due to the methylene carbon atoms of the reactant, CH$_3$CH$_2$I. A weak signal appears at 23 ppm, which is assigned to methyl iodide $^{13}$CH$_3$I.\textsuperscript{15b} The reaction of surface methoxy species and ethyl iodide becomes more evident at 373 and 423 K, as indicated in Figure 2b and 2c, respectively. A new signal at 73 ppm occurred with spinning sidebands in Figure 2b, left, and dominates the spectrum in Figure 2c, left. In agreement with our recent findings,\textsuperscript{14} the signal at 73 ppm is assigned to the methylene carbon atoms of the reactants, CH$_3$CH$_2$I. The above-mentioned assignments are further supported by the $^{13}$C CP/MAS NMR spectrum shown in Figure 2d, left, which was recorded after the catalyst was hydrated at room temperature. The formation of CH$_3$CH$_2$OH at 60 ppm and $^{13}$CH$_3$OH at 50 ppm indicates the hydrolysis of surface ethoxy species\textsuperscript{14} and surface methoxy species\textsuperscript{17} by water. The $^{13}$C HPDEC MAS NMR spectra simultaneously recorded for each sample are shown in Figure 2, right. The same signals occur in each $^{13}$C HPDEC MAS NMR spectrum as those in the corresponding $^{13}$C CP/MAS NMR spectrum, although with different relative intensities.

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A dominating signal at 11 ppm, which is due to the $^{13}$C-enriched methyl bromide ($^{13}$CH$_3$Br), indicates the transformation of surface methoxy species to surface ethoxy species by the reaction of surface methoxy species and ethyl bromide on zeolite H-Y. We cannot, however, figure out the detailed mechanism for the reaction of surface methoxy species and alkyl halides. For example, the reaction depicted in Scheme 2 can take place either in one step or in sequential steps which start from the formation of surface ethoxy species and HI, followed by the subsequent reaction of HI with surface methoxy species.

**Reaction of Surface Methoxy Species and Hydrochloride.** Methyl chloride, which is used as a general methylating agent and as an intermediate in the manufacture of silicons, synthetic rubber, and methyl cellulose, is commercially produced by two processes: hydrochlorination of methanol and chlorination of methane. The hydrochlorination reaction of methanol and hydrochloride, mainly on alumina-based solid catalysts, is usually preferred in industry. A recent investigation on the interaction of methanol and γ-alumina catalyst shows that chemisorbed methoxy is the only surface species present on the catalyst. Further study indicates that surface methoxy species are involved as a reactive intermediate in hydrochlori-

![Figure 2. $^{13}$C CP/MAS NMR (left) and HPDEC MAS NMR (right) spectra recorded after the reaction of $^{13}$C-1-enriched ethyl iodide (CH$_3^{13}$CH$_2$I, 50 mbar) and surface methoxy species ($^{13}$CH$_3$Y) at 298 K (a), 373 K (b), 423 K (c).](image)

**Scheme 2**

![Scheme](image)
which is due to the formation of methyl chloride, CH\textsubscript{3}Cl. Upon temperature. As can be seen, a new signal appears at 24 ppm, CH\textsubscript{3} Y. Figure 3. 13C HPDEC MAS NMR spectra recorded after the reaction of surface methoxy species and hydrochloride was, therefore, investigated by 13C MAS NMR spectroscopy. Figure 4a, left, shows the 13C HPDEC MAS NMR spectrum recorded after the reaction of methylated zeolite Y (13CH\textsubscript{3}Y) at 298 K (c) and 373 K (d), and ethyl bromide CH\textsubscript{3}CH\textsubscript{2}Br (50 mbar) on methylated zeolite Y (13CH\textsubscript{3}Y) at 423 K (e). Asterisks denote spinning sidebands.

Figure 3. 13C HPDEC MAS NMR spectra recorded after the reaction of methyl iodide (CH\textsubscript{3}I, 45 mbar) on methylated zeolite Y (13CH\textsubscript{3}Y) at 373 K (a), ethyl iodide CH\textsubscript{2}CH\textsubscript{3}I (50 mbar) on methylated silicoaluminophosphate SAPO-34 (13CH\textsubscript{3}SAPO-34) at 423 K (b), isopropyl iodide (CH\textsubscript{3}CH\textsubscript{2}I, 30 mbar) on methylated zeolite Y (13CH\textsubscript{3}Y) at 298 K (c) and 373 K (d), and ethyl bromide CH\textsubscript{3}CH\textsubscript{2}Br (50 mbar) on methylated zeolite Y (13CH\textsubscript{3}Y) at 423 K (e). Asterisks denote spinning sidebands.

Koch-Type Carboxylation Reaction: The Reaction of Surface Methoxy Species and Carbon Monoxide. The classic Koch carbonylation reaction between olefins and carbon monoxide in the presence of water provides evidence for the existence of carbenium ions in superacidic solutions.\(^\text{(32)}\) The first solid-state NMR evidence of the Koch carbonylation reaction on solid acid catalysts was reported in 1995 by Stepanov et al.\(^\text{(33)}\) With the application of 13C MAS NMR spectroscopy, these authors observed the formation of trimethylacetic acid in high yields upon coadsorption of isobutene, carbon monoxide, and water (or coadsorption of tert-butyl alcohol and carbon monoxide) on acidic zeolite H-ZSM-5 under mild conditions.\(^\text{(33)}\) Based on this discovery, high, stable catalytic performance was recently found for the Koch carbonylation reaction on various solid acid catalysts.\(^\text{(34)}\)

Similar to the case in superacidic solutions,\(^\text{(32)}\) the proposed mechanism (Scheme 4) of Koch carbonylation reaction on acidic zeolites\(^\text{(32,33)}\) involves the trapping of an alkyl carbenium ion (R\textsuperscript{+}, transient species, generated from an olefin or alcohol on an acidic zeolite) by carbon monoxide to form an acylium cation, R\textsuperscript{+}=C=O. The latter cation is very unstable and is readily quenched by water to give a carboxylic acid, R--COOH.

As further demonstrated by Stepanov et al.,\(^\text{(36)}\) alkoxys which possess carbenium-ion-like properties may also follow the Koch carbonylation reaction on acidic zeolites. Fujimoto and co-workers\(^\text{(37)}\) are the first who reported the carbonylation of methanol by carbon monoxide at 473 K on acidic zeolites H-Y, H-ZSM-5, and H-Mordenite, the main carbonylated products of which are acetic acid (CH\textsubscript{3}COOH) and methyl acetate (CH\textsubscript{3}COOCH\textsubscript{3}). The carbonylation reaction of methanol describes the reaction of surface methoxy species and hydrochloride on zeolite catalyst, by which the Brønsted acidity of the zeolite would be recovered. As a comparison, the reaction of 13C-enriched methanol and hydrochloride on acidic zeolite H-Y was investigated under the same conditions, and the 13C HPDE MAS NMR results are shown in Figure 4, right. Similar to the cases of surface methoxy species, the reaction of methanol and hydrochloride on acidic zeolite H-Y gives methyl chloride as the product, which is evidenced by the appearance of the 13C MAS NMR signal of methyl chloride at 24 ppm (Figure 4, right). These results indicate that surface methoxy species may also be involved in methanol hydrochlorination on solid catalysts, which is in agreement with the recent work of Lenon and co-workers, who reported their investigation of methanol hydrochlorination on an η-alumina catalyst by means of temperature programmed reaction spectroscopy (TPRS).

To gain mechanistic information of hydrochlorination of methanol on η-alumina catalyst,\(^\text{(30)}\) zeolites also have been suggested as applicable catalysts for the methanol hydrochlorination process.\(^\text{(28,31)}\)

For example, in superacidic solutions,\(^\text{(32)}\) the proposed mechanism (Scheme 4) of Koch carbonylation reaction on acidic zeolites\(^\text{(32,33)}\) involves the trapping of an alkyl carbenium ion (R\textsuperscript{+}, transient species, generated from an olefin or alcohol on an acidic zeolite) by carbon monoxide to form an acylium cation, R\textsuperscript{+}=C=O. The latter cation is very unstable and is readily quenched by water to give a carboxylic acid, R--COOH.

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To gain mechanistic information of hydrochlorination of methanol on η-alumina catalyst, the reaction of surface methoxy species and hydrochloride was, therefore, investigated by 13C MAS NMR spectroscopy. Figure 4a, left, shows the 13C HPDE MAS NMR spectrum recorded after the reaction of the methylated catalyst (13CH\textsubscript{3}Y) and hydrochloride (HCl) at room temperature. As can be seen, a new signal appears at 24 ppm, which is due to the formation of methyl chloride, CH\textsubscript{3}Cl. Upon further reaction at 353 K, the signal of methyl chloride at 24 ppm increases, accompanied by the decrease of the signal of surface methoxy species at 56 ppm (Figure 4b, left). Scheme 3 describes the reaction of surface methoxy species and hydrochloride on zeolite catalyst, by which the Brønsted acidity of the zeolite would be recovered. As a comparison, the reaction of 13C-enriched methanol and hydrochloride on acidic zeolite H-Y was investigated under the same conditions, and the 13C HPDE MAS NMR results are shown in Figure 4, right. Similar to the cases of surface methoxy species, the reaction of methanol and hydrochloride on acidic zeolite H-Y gives methyl chloride as the product, which is evidenced by the appearance of the 13C MAS NMR signal of methyl chloride at 24 ppm (Figure 4, right). These results indicate that surface methoxy species may also be involved in methanol hydrochlorination on solid catalysts, which is in agreement with the recent work of Lenon and co-workers, who reported their investigation of methanol hydrochlorination on an η-alumina catalyst by means of temperature programmed reaction spectroscopy (TPRS).
on acid zeolites was proposed to follow the Koch reaction shown in Scheme 4, with the formation of surface methoxy species as the key intermediate. A similar pathway, which involves the reaction of surface methoxy species and carbon monoxide, was also suggested recently by Iglesia and co-workers for the carbonylation reaction of dimethyl ether on acidic zeolites. The suggestion of Iglesia and co-workers is verified by our $^{13}$C MAS NMR investigations presented in this contribution. Figure 5a shows the $^{13}$C CP/MAS NMR spectrum recorded after the reaction of $^{13}$C-enriched carbon monoxide ($^{13}$CO) and nonenriched dimethyl ether (DME, CH$_3$OCH$_3$) on acidic zeolite HY at 473 K. In agreement with previous findings, the $^{13}$C MAS NMR signal at 184 ppm with characteristic spinning sidebands is assigned to the carbonyl carbon of acetic acid, CH$_3$COOH. This assignment was further supported by the adsorption of CH$_3$COOH on zeolite HY. The $^{13}$C CP/MAS NMR recorded thereafter shows the identical chemical shift and very similar spinning sidebands as observed for the signal at 184 ppm in Figure 5a. On the other hand, $^{13}$CO which also has the $^{13}$C chemical shift of ca. 184 ppm is only weakly adsorbed on zeolite HY and does not show any appreciable signal in the $^{13}$C CP/MAS NMR spectrum (not shown). As a control experiment, Figure 5b shows the $^{13}$C CP/MAS NMR spectrum recorded after the reaction of nonenriched DME on acidic zeolite HY at 473 K. The signals at 63 and 60 ppm are due to side-on and end-on adsorbed DME, respectively. The signals appearing at 56 and 50 ppm indicate the reversible formation of surface methoxy species and methanol by the decomposition of DME on acidic zeolites at high temperatures, which agrees well with the work of Iglesia and co-workers and of Forester and Howe. Therefore, the above-mentioned results provide the first $^{13}$C MAS NMR evidence for the mechanism of the carbonylation reaction of DME.
dimethyl ether by carbon monoxide on acidic zeolites, which was originally proposed by Iglesia and co-workers. In agreement with previous work, the formation of an unstable acylium cation, $\text{CH}_3\text{C}^+\text{dO}$, by the reaction of surface methoxy species and CO, was not directly observed by $^{13}$C MAS NMR spectroscopy. However, the transient existence of this cation was further evidenced by our trapping experiment with ammonia, the idea of which was originally presented in the work of Gorte and co-workers. Figure 5c shows the $^{13}$C CP/MAS NMR spectrum recorded after the reaction of $^{13}$C-enriched carbon monoxide, ammonia, and the methylated catalyst, $^{13}\text{CH}_3-Y$, at 473 K. The formation of acetamide, $^{13}\text{CH}_3\text{CONH}_2$, is evidenced by the $^{13}$C signals at 22 ppm for the methyl carbon and 183 ppm for the carbonyl carbon, respectively. This finding indicates the trapping of the unstable acylium cation, $\text{CH}_3\text{C}^+\text{dO}$, with ammonia, by which the stable product acetamide is formed. Our
Figure 6. $^{13}$C HPDEC MAS NMR spectra recorded after thermal treatments of methylated zeolite Y ($^{13}$CH$_3$−Y) in the presence of oxygen (ca. 5 mbar) at elevated temperatures of 393 K (a) to 673 K (e). Asterisks denote spinning sidebands.

result agrees well with the previous work of Gorte and co-workers, who observed the formation of acetylamide from the reaction of ammonia and the acylium cation on zeolite H−ZSM-5 by TPD-TGA measurements.

Ritter-Type Reaction: The Reaction of Surface Methoxy Species and Acetonitrile. Stepanov and Luzgin investigated the reaction of acetonitrile with olefins (1-octene) or alcohols (tert-butyl alcohol) on acidic zeolite H−ZSM-5. In the case of acetonitrile and alcohol coadsorbed on zeolite H−ZSM-5 at room temperature, the intermediate N-alkylnitrilium cation and the final product N-alkylamide are observed simultaneously by room temperature, the intermediate N-alkylnitrilium cation and species and acetonitrile. Stepanov and Luzgin investigated acetonitrile and alcohol coadsorbed on zeolite H−ZSM-5 by $^{13}$C MAS NMR spectroscopy. Figure 5d shows the $^{13}$C HPDEC MAS NMR spectrum recorded after thermal treatments of the methylated catalyst, $^{13}$CH$_3$−Y, in the presence of oxygen (ca. 5 mbar). Carbon monoxide and carbon dioxide are formed at ca. 493 K, which give $^{13}$C MAS NMR signals at 184 and 124 ppm, respectively (Figure 6b to 6e). In agreement with our previous findings, the decomposition of surface methoxy species to hydrocarbons starts at ca. 523 K, as indicated in Figure 6c. The hydrocarbons formed in this case (Figures 6c to 6e) are essentially identical to those in the absence of oxygen (Figure 4 in ref 17c).

It is important to note that the formation of carbon monoxide and carbon dioxide (Figure 6b) starts earlier than the onset of the decomposition of surface methoxy species to hydrocarbons. In agreement with Hutchings and co-workers, our NMR results of the oxidation of surface methoxy species by oxygen (Figure 6) are interpreted as the formation of formaldehyde and formic acid which further decompose to carbon monoxide and carbon dioxide. Carbon monoxide is neither an intermediate nor a catalyst during the MTO process, as clarified by Haw and co-workers. Therefore, in the presence of oxygen, the oxidation of surface methoxy species compete with the thermal decomposition of surface methoxy species. However, oxygen may not play an active role to initiate the formation of primary acetylation products.
hydrocarbons in the MTO process, as implied in the previous work of Hutchings and co-workers and in the present study.

Discussion

Intermediates involved in heterogeneously catalyzed reactions can vary in nature from highly reactive species to relatively unreactive ones. In either case, the lifetime of the intermediates must be long enough for successful detection by the spectroscopic method being applied. Similar to the strategy achieved in solution chemistry, it is also possible to further isolate the long-lived intermediates formed in some heterogeneously catalyzed systems and investigate independently their nature and chemical reactivity thereafter. This approach is exemplified in the present contribution where the isolation of surface methoxy species on acidic zeolites can be followed by further investigations of their reactivity with probe molecules. In this section, the stability and reactivity of surface methoxy species are further discussed in comparison with those of other surface alkoxy species (> C1 species).

Carbenium ions are key intermediates involved in a variety of acid-catalyzed reactions performed in solution. Due to the low dielectric constants of acidic zeolites and the absence of solvation effects in zeolites, however, simple carbenium ions may exist as highly activated and short-lived transition states and, therefore, only represent saddle points on the potential energy surface. Indeed, persistent carbenium ions experimentally identified in zeolites are mainly bulky cyclic cations which are charge-delocalized in nature and sterically hindered to the negatively charged zeolite framework. On the other hand, covalent alkoxy species have been consistently observed as long-lived intermediates upon the adsorption of small olefins or dehydration of simple alcohols on acidic zeolites. In 1989, Gorte and co-workers first identified by 13C NMR spectroscopy the formation of surface tert-butoxy species upon the adsorption of tert-butyl alcohol on acidic zeolite H-ZSM-5. Later in the same year, Haw and co-workers reported the 13C CP/MAS NMR evidence for surface isoproxy species formed from the reaction of propene on acidic zeolite H-Y. Subsequently, Stepanov et al. detected by 13C NMR spectroscopy the formation of surface isobutoxy species upon the conversion of isobutanol to the formation of oligomeric alkoxy species upon adsorption of ethene, both on acidic zeolite H-ZSM-5. The IR investigations on the formation of oligomeric alkoxy species upon adsorption of ethene and propene on acidic zeolites H-ZSM-5 and H-Mordenite were reported by Zecchina and co-workers. Adding to the rare evidence for the existence of surface alkoxy species (> C1 species), surface ethoxy species formed from ethanol was recently observed on acidic zeolites H-Mordenite and H-Y.

Nevertheless, knowledge on the reactivity of surface alkoxy species (> C1 species) is still severely lacking so far, largely due to the occurrence of rapid secondary reactions on the solid catalysts which hindered the isolation of primary intermediates and complicates the interpretation of experimental results.

In contrast, surface methoxy species, i.e., the simplest form and probably the most stable form of surface alkoxy species, have been extensively investigated, mostly in connection with mechanistic studies of methanol-to-hydrocarbon conversion on solid acids. Table 1 summarizes typical IR and NMR evidence for the formation of surface methoxy species upon the reactions of methanol on various solid acids. Despite the unequivocal observation of surface methoxy species on solid acids, the role of these surface methoxy species in heterogeneous catalysis has been disputed in a controversial manner. The reactivity of surface methoxy species in acidic zeolites may be better discussed in terms of C=O bond and C-H bond activation, respectively. The C=O bond reactivity of surface methoxy species has been evidenced by reactions with various probe molecules, some of which are included in Table 1. For example, surface methoxy species on acidic zeolites can react with water to produce methanol at room temperature, with methanol to form DME, with aniline to form N-methylamline cations, with benzene or toluene to form alkyl-substituted aromatics (such as, toluene, xylenes, and ethylbenzenes) and react with ethene or propene to reproduce olefins which may undergo further oligomerization reactions. Our results in this contribution further indicate that surface methoxy species can react with ammonia, alkyl halides, hydrochloride, monoxide (Koch-type catalytation reaction), and acetamide (Ritter-type reaction). Therefore, surface methoxy species act as an effective methylaing agent in a variety of reactions with probe molecules on solid acids, in which the C=O bond activation of surface methoxy species is involved.

The relative reactivity of surface alkoxy species in terms of C=O bond activation can be evaluated by benefit of recent theoretical investigations of olefin adsorption on acidic zeolites. As depicted in Figure 7, the adsorption of small olefins on acidic zeolites starts with the formation of a σ-complex (2A for ethene, 3A for propene, and 4A for isobutene in Figure 7), and through a transition state which most probably involves carbenium cations (2B, 3B, and 4B in Figure 7), the corresponding surface alkoxy species (σ-complex, 2C, 3C, and 4C in Figure 7) are formed. Although the energy difference of species in Figure 7 cannot be quantitatively compared, the basic trends for their relative stability are evident. For example, theoretical calculations predict that the relative stability of surface alkoxy species being formed upon adsorption of...
Experimental Observations of Surface Methoxy Species Formed from Methanol on Solid Acid Catalysts

<table>
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<th>solid acid</th>
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<th>assignments of surface methoxy species and additional observations</th>
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<tr>
<td>H→ZSM-5 (n_{Si/Al} = 15, 26)</td>
<td>CH₃OH, CD₂OH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>IR bands: 2980, 2868, and 1460 cm⁻¹ (CH₃→ZSM-5); responsible for the methylation of olefins and benzene at 523 K; the onset of significant hydrocarbon formation is accompanied by the cleavage of C–D bonds in CD₂→ZSM-5 above 523 K.</td>
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<td>H→Y (n_{Si/Al} = 1.9, 86% exchange degree)</td>
<td>CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2800–3100 cm⁻¹ (CH₃→Y); secondary reactions take place above 513 K with the formation of hydrocarbons.</td>
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<td>H→ZSM-5 (n_{Si/Al} = 17.8)</td>
<td>CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2220 and 2070 cm⁻¹ (CD₂→ZSM-5); stable up to 512 K; desorption of surface methoxy groups is accompanied by the cleavage of C–D bonds.</td>
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<td>H→Y (n_{Si/Al} = 2.5, 70% exchange degree)</td>
<td>CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2855–3000 and 2855 cm⁻¹; highly reactive above 573 K and readily participate in the formation of C–C bonds at 523–623 K.</td>
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<td>H→ZSM-5 (n_{Si/Al} = 14, 18, 19)</td>
<td>CH₃OH, CD₃OD&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2980 and 2850 cm⁻¹ (CH₃→Y); 2130 and 2070 cm⁻¹ (CD₂→Y); reaction with benzene at 533 K and decomposition above 581 K.</td>
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<td>H→ZSM-5 (n_{Si/Al} = 24, 42, 78, 154)</td>
<td>CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2980, 2959, and 2855 cm⁻¹ (CH₃→ZSM-5); decomposition above 573 K.</td>
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<td>H→ZSM-5 (n_{Si/Al} = 27)</td>
<td>CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2856–2978 cm⁻¹ (CH₃→ZSM-5); involved in the dehydration of methanol to DME at 493 K.</td>
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<td>H→X (n_{Si/Al} = 1.1, 40% exchange degree)</td>
<td>CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>IR bands: 2968 cm⁻¹ (CH₃→X) and 2977 cm⁻¹ (CH₃→Y); responsible for benzene methylation; decomposition at 570 K with the formation of hydrocarbons.</td>
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<td>H→Y (n_{Si/Al} = 2.6, 40% and 77% exchange degree)</td>
<td>CH₃OH + NH₃&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>IR bands: 2957 and 2855 cm⁻¹ (CH₃→ZSM-5).</td>
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<td>H→ZSM-5 (n_{Si/Al} = 35)</td>
<td>¹³CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56 ppm (¹³CH₃→Y), 59.4 pm (¹³CH₃→ZSM-5).</td>
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<td>H→Y (n_{Si/Al} = 2.6)</td>
<td>¹³CH₃OH&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56.2 ppm (¹³CH₃→Y), 59.2 ppm to (¹³CH₃→ZSM-5), 56.6 ppm (¹³CH₃→SAPO-34); react with water to methanol, with methanol to DME, with toluene to xylenes; decomposition at 523 K, responsible for the formation of hydrocarbons and for the methylation of cyclohexane.</td>
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<td>H→ZSM-5 (n_{Si/Al} = 22)</td>
<td>¹³CH₃OH&lt;sup&gt;‡&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56 ppm (¹³CH₃→Y); 59.9 ppm (¹³CH₃→ZSM-5), 60.7 ppm (¹³CH₃→mordenite).</td>
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<td>H→SAPO-34 (n_{Si/Al} + n_{Al} + n_{Fe} = 0.11)</td>
<td>¹³CH₃OH + aniline&lt;sup&gt;b&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56 ppm (¹³CH₃→Y); 52 ppm (¹³CH₃→ZSM-5); 57 ppm (¹³CH₃→SAPO-34).</td>
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<td>H→ZSM-5 (n_{Si/Al} = 19, 26)</td>
<td>¹³CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 53–59 ppm (¹³CH₃→ZSM-5), 57 ppm (¹³CH₃→SAPO-34).</td>
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<td>H→SAPO-34 (n_{Si/Al} = 9)</td>
<td>¹³CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56–62 ppm; form at the onset of hydrocarbon formation.</td>
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<td>H→SAPO-34 (n_{Si/Al} = 0.17)</td>
<td>¹³CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56–62 ppm; form at the onset of hydrocarbon formation.</td>
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<td>H→ZSM-23 (n_{Si/Al} = 28, 36, 40)</td>
<td>¹³CH₃OH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56–62 ppm; form at the onset of hydrocarbon formation.</td>
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<td>H→SAPO-11 (n_{Si/Al} = 0.25)</td>
<td>¹³CH₃OH&lt;sup&gt;d&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 56 ppm (¹³CH₃→SAPO-34); decreases dramatically in the first 30 s during which the initiation reaction of MTO catalysis takes place.</td>
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<td>H→SAPO-34 (1.1 mmol SiOHAl per gram)</td>
<td>¹³CH₃OH&lt;sup&gt;d&lt;/sup&gt;</td>
<td>¹³C MAS NMR signals: 59 ppm; formation of surface methoxy species and hydrocarbons is observed 2 s after methanol injection.</td>
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* In situ IR cell as a pulse microreactor. † Batchlike conditions; adsorption and evacuation. ‡ Flow conditions. ‡ Pulse-quench experiment. † IR bands of surface methoxy species summarized therein.

The formation of methoxy species on acidic zeolites follows the order ethoxy (2C) > isopropoxy (3C) > tert-butoxy (4C). On the other hand, it is well-known that primary carbenium-ion-like transition states present much higher activation energies than tertiary carbenium-ion-like transition states, which results in the relative stability of carbenium ions in the order 4B > 3B > 2B in Figure 7, assuming that the energies for the corresponding π-complex (2A, 3A, and 4A in Figure 7) do not have much difference. In contrast to the cases of alkoxy species (> C₂ species) formed from olefin

adsorption on acidic zeolites, theoretical calculations have been dealing with the formation of surface methoxy species from dehydration of methanol only, which makes the systematic comparison complicated. Nevertheless, it is still reasonable to add methoxy species (1C) as the most stable alkoxy species and, accordingly, methyl cations (1B) as the most unstable carbenium cations in Figure 7. The reactivity of surface alkoxy species in terms of C–O bond activation can be, therefore, discussed by looking into the energy differences from C to B in Figure 7, which are directly related to the activation energies being considered. The following results may be derived: (i) According to the Hammond Postulate, the surface tert-butoxy species would possess more carbenium-ion-like nature than other alkoxy species presented in Figure 7. On the contrary, the covalent-bond nature is more profound in the case of surface methoxy species. Indeed, theoretical calculations do indicate that the C–O bond distances decrease in the order tertiary >

of carbene which undergoes the typical sp³ insertion into the C–H bonds.\(^{17c}\) The oxidation reaction of surface methoxy species in this contribution might be looked upon as additional evidence for the carbene mechanism. According to Hutchings and Hunter,\(^{42b}\) the formation of formic acid upon the oxidation of surface methoxy species indicates the existence of carbene which further reacts with oxygen via the Criegee intermediate.\(^{62}\) Furthermore, Sinclair and Catlow\(^{65}\) performed DFT calculations to investigate the decomposition of surface methoxy species on acidic zeolites and showed that surface-stabilized carbene (1A in Figure 7) could be produced with an activation barrier of 215–232 kJ mol\(^{-1}\). The deprotonation step (from 1C to 1A in Figure 7) was, therefore, suggested as the rate-determining step during the conversion of methanol to hydrocarbons. In agreement with the value reported by Sinclair and Catlow,\(^{63}\) Lesthaeghe et al.\(^{64}\) recently calculated a theoretical barrier of 241 kJ mol\(^{-1}\) for the deprotonation of surface methoxy species to carbene. Considering this step as a highly activated one, however, they ruled out the deprotonation of methoxy species to carbene as a possible direct route for the first C–C bond formation during methanol conversion.\(^{64}\) It was recently claimed,\(^{65}\) in contradiction to a number of previous investigations,\(^{66}\) that the C–H bonds of surface methoxy species are not broken at temperatures between 573 and 623 K, supported by the absence of H/D exchange between CH\(_3\)–SAPO-34 and CD\(_3\)–SAPO-34 coexisting on the catalyst. However, direct evidence for the failure of C–C bond formation from these surface methoxy species, i.e., the yields of olefin products and the H/D distribution in these olefins were not disclosed therein,\(^{66}\) although GC and GC–MS were applied to analyze the effluent gases.

**Conclusions**

The in situ stopped-flow protocol we developed\(^{17}\) opens a new approach to the understanding of the nature of surface methoxy species on solid acid catalysts. On the basis of this development, the main focus of this contribution is, therefore, to further investigate the chemical reactivity of surface methoxy species in acidic zeolites. With the application of solid-state \(^{13}\)C MAS NMR spectroscopy, the following evidence for the high reactivity of surface methoxy species are obtained for the first time on solid acid catalysts:

(i) Surface methoxy species react with ammonia on acidic zeolite H–Y and silicoaluminophosphate H–SAPO-34 at room temperature, by which methylamines and methylammonium


(62) For the detailed discussion of Criegee mechanism, through which the carbonyl oxide is formed by the combination of carbene and oxygen, for example, see: Bunnelle, W. H. *Chem. Rev.* 1991, 91, 335–362. One of the referees of this manuscript suggests an alternative mechanistic proposal for the oxidation of surface methoxy species, which consists of a hydride abstraction from gas-phase methanol by surface methoxy species to form methane and formaldehyde. The \(^{13}\)C MAS NMR signal of methane (at ca. –9 ppm) was observed in Figure 6d and 6e upon thermal treatments at 573 and 673 K, respectively. Therefore, the latter possibility cannot be absolutely ruled out, although methane formation is hardly observed at 493 and 523 K (see Figure 6b and 6c).


cations are formed. On the contrary, methanol and ammonia do not react on acidic zeolites at room temperature. The significant difference in reactivity between surface methoxy species and methanol indicates that surface methoxy species are very reactive in methylating amines on acidic zeolites and, if involved, their formation is the rate-determining step during the methylation of amines by methanol on acidic zeolites.

(ii) The transformation of surface methoxy species to surface ethoxy species or other alkoxy species can be achieved by the reaction of surface methoxy species and corresponding alkyl halides on acidic zeolites. This new approach may provide a general method for the preparation of surface alkoxy species from surface methoxy species on solid acid catalysts.

(iii) Surface methoxy species react readily with hydrochloride, by which methyl chloride is produced as the sole product. These results indicate that surface methoxy species may be involved in methanol hydrochlorination on solid catalysts, which agrees well with the recent investigations of methanol hydrochlorination on an \(\eta\)-alumina catalyst by means of TPRS.\textsuperscript{30}

(iv) The classic Koch carbonylation reaction and Ritter reaction in solution can be realized with surface methoxy species on acidic zeolites. In agreement with the recent work of Iglesia and co-workers,\textsuperscript{38} the carbonylation of dimethyl ether by carbon monoxide on acidic zeolites is interpreted as similar to the classic Koch-type reaction in solution, where the unstable acylium cation, CH\(\text{3}-\text{C}^+\text{O}\), is formed by the reaction of surface methoxy species and CO. In accordance with the Ritter-type reaction on solid acid catalysts,\textsuperscript{39} the formation of N-methyl acetamide was interpreted by further hydrolysis of the intermediate, the N-alkynitrilium cation, after the reaction of surface methoxy species and acetonitrile on acidic zeolites.

(v) Carbon monoxide and carbon dioxide can be produced by the oxidation of surface methoxy species on acid zeolites in the presence of oxygen. The oxidation of surface methoxy species may compete with the thermal decomposition of surface methoxy species. However, oxygen may not play an active role to initiate the formation of primary hydrocarbons in the induction period of the MTO process.

Acknowledgment. The Deutsche Forschungsgemeinschaft, the Max-Buchner-Forschungsstiftung, and the Fonds der Chemischen Industrie provided financial support, which the authors gratefully acknowledge. W.W. thanks the Chunhui Project of Education Ministry of P. R. China. We are grateful to the anonymous reviewers for their valuable comments and suggestions.

JA061018Y