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# Methane Activation and Transformation on Ag/H-ZSM-5 Zeolite Studied with Solid-State NMR

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ABSTRACT: With regard to a general interest in methane utilization in a rational way the activation and transformation of methane on Ag-modified zeolite ZSM-5 (Ag/H-ZSM-5) have been studied with solid-state NMR. The activation of methane occurs by dissociation of the C–H bond on silver cations via the "carbenium" pathway: methane C–H bond cleavage results in the methoxy groups (O–CH$_3$) and possibly silver-hydride species (Ag–H). The formation of surface methoxy groups on Ag/H-ZSM-5 has been detected experimentally with ^{13}C CP/MAS NMR at 508–623 K for the first time. A comparative analysis of the kinetics of the H/D exchange between methane and acid hydroxyl groups for H-ZSM-5 and Ag/H-ZSM-5 zeolites reveals a significant promoting effect of silver cations on the H/D exchange reaction and therefore on methane activation. This effect has been rationalized in terms of reversible methane dissociation on the surface of Ag/H-ZSM-5 zeolite and further involvement in the exchange of the methoxy groups and the silver-hydride species. Ethane represents the first intermediate product of methoxy group transformation. It is formed by the reaction of a methoxy group with methane. Further, dehydrogenation of ethane offers ethene, producing immediately π-complexes with Ag$^+$ cations, which are stable at temperature as high as 673 K. At 823 K π-complexes decompose and ethene undergoes oligomerization, cyclization, dehydrogenation, and aromatization to give benzene. In the presence of methane, ethene π-complexes decompose and become involved in oligomerization and aromatization reaction at lower temperature, already at 673 K. Methane is also involved in the reaction of coaromatization with ethene. This involvement occurs by the alkylation of aromatics, formed from ethene, with methane. Further demethanation of methylbenzenes in the presence of dihydrogen evolved at the stages of ethene transformation to aromatics produces benzene as the main reaction product.
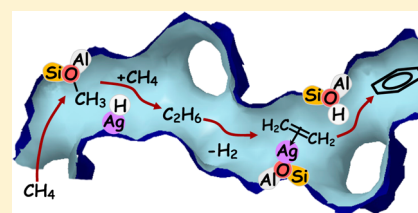
1. INTRODUCTION

Methane is an abundant and readily accessible natural resource, and its utilization in a rational way is of essential commercial importance. There is a growing interest in methane conversion to more useful chemical intermediates and products.[1] In particular, the catalytic conversion of methane to methanol[2−4] and higher hydrocarbons[4,5] has received much attention in the last decades.

The main problem of methane utilization lies in its chemical inertness, therefore the possible paths of its catalytic conversion are restricted. In general, the need for a suitable coreactant to be used with methane in order to overcome thermodynamic limitations has been recognized,[5] and several successful attempts for methane coconversion with light hydrocarbons on the metal-containing zeolite catalysts have been reported. The joint conversion of methane with C$_3$–C$_6$ paraffins[6−11] or C$_2$–C$_4$ olefins[7] on Zn- or Ga-modified ZSM-type zeolites, with methanol[12] on Zn–Mo/H-ZSM-5, and with ethene[13−16] or benzene[13,14] on Ag/H-ZSM-5 is the promising basement for future development of the processes related to methane conversion to more valuable chemicals and fuels.

Understanding the pathways for methane activation and transformation is the key to develop the approaches for improvement of catalyst activity and selectivity. The conversion of methane to aromatics in the presence of higher hydrocarbons has been proved with ^{13}C MAS NMR and GC-MS,[17−19] and the mechanism of methane activation on Zn- and Ga-containing zeolites has been proposed.[17−25] Several attempts have been made to inquire into the methane activation on Ag-modified zeolite catalysts.[13−16,26,27] The activation is considered to occur on silver cationic species by dissociation of the methane C–H bond with the formation of silver-hydride species and surface methoxy groups. However, the experimental data obtained[13,14,16,26] provided only indirect evidence for this activation mechanism. The formation of silver-hydride species has been observed only for methane dissociation on Ag-FAU zeolite,[26] but not on Ag-ZSM-5. The formation of methoxy groups was not detected at all. Moreover, the "alkyl" pathway is considered to be the preferential initial

Table 1. Concentration of Different OH Groups and Composition of Zeolite Unit Cell for ZSM-5 Zeolite Samples

| zeolite sample	concn of OH groups (μmol·g^{-1})			zeolite unit cell
	SiOH, 1.8 ppm	AlOH, 2.4 ppm	SiOHAl, 4.0–6.0 ppm	
H-ZSM-5	100		1200	$H_{6.9}Al^{tetr}_{6.9}Si_{89.1}O_{192}$
Ag/H-ZSM-5	100	200	500	$Al^{oct}_{0.1}Ag_{1.1}H_{3.1}Ag^+_{3.7}Al^{tetr}_{6.8}Si_{89.1}O_{192}$

step for methane activation over Ag-ZSM-5 in comparison with the "carbenium" pathway according to the theoretical calculations by Ding et al.[28] In other words, methane dissociation is expected to result in formation of the Ag—CH$_3$ and O—H species, rather than O—CH$_3$ and Ag—H species. So, the reliable experimental identification of the primary intermediates of methane activation on Ag-ZSM-5 zeolite is of importance for clarifying the mechanism of methane conversion to higher hydrocarbons on Ag-modified zeolite catalysts.

In the present paper we report on the results of our study of both pure methane activation and conversion and methane coconversion with ethene on Ag/H-ZSM-5 catalyst with solid-state NMR spectroscopy. We have analyzed the kinetics of H/D exchange between CD$_4$ and Brønsted acid sites (BAS) of the pure acid form and Ag-modified zeolite H-ZSM-5 with ^{1}H MAS NMR in situ. This allowed us to clarify the role of Brønsted acid sites and silver cations in the methane activation step. ^{13}C MAS NMR provided identification of the primary and secondary intermediates of methane transformation to aromatics. The role of methane in ethene transformation to aromatics on Ag/H-ZSM-5 zeolite was also established.

2. EXPERIMENTAL SECTION

2.1. Materials Characterization and Samples Preparation. The template-free synthesized NH$_4$-ZSM-5 (Si/Al = 13) zeolite was kindly provided by Tricat Zeolites. The parent ammonium form of the zeolite was transformed into the hydrogen form (H-ZSM-5) by calcination at 773 K for 5 h. The silicon-to-aluminum ratio of 13 was estimated for H-ZSM-5 zeolite based on ^{29}Si MAS NMR analysis[29] and confirmed by chemical analysis data. No extra framework aluminum atoms were observed in the ^{27}Al MAS NMR spectrum of the hydrated H-ZSM-5 zeolite. The Ag-modified zeolite (Ag/H-ZSM-5) was prepared by ion-exchange of 2.5 g of H-ZSM-5 with 25 mL of 0.15 M AgNO$_3$ aqueous solution overnight at 25 °C in the dark with subsequent filtration, washing with distilled water, drying at 393 K for 14 h, and further calcination at 673 K for 4 h in a flow of air. The silver-to-aluminum ratio 0.7 (8.2 wt % Ag) in the final sample of Ag/H-ZSM-5 zeolite was obtained by chemical analysis. Concentrations of bridged SiOHAl and silanol SiOH groups were estimated by ^{1}H MAS NMR with methane as internal standard. The detailed composition of the unit cell for the used zeolite samples has been established in terms of Si/Al, Ag/Al ratios and SiOHAl groups concentration (Table 1).

Silver mainly exists as an exchanged ion (Ag$^+$) in Ag-ZSM-5 zeolite.[27,30−32] The silver cations are considered to be symmetrically bidentated to two oxygen atoms of zeolite [AlO$_4$]$^-$ tetrahedron and the interaction is of ionic character.[27,31]
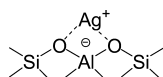
We have supposed that unexchanged silver exists as metallic species formed by thermal decomposition of AgNO$_3$ during calcination.[33] Indeed, the silver atoms (Ag^0) or the metallic clusters (Ag$_n^0$) are formed in Ag/H-ZSM-5 zeolite samples with high silver loading (10−15 wt %) according to Miao et al.[27,32] So, we believe that in our Ag/H-ZSM-5 zeolite sample silver exists in a form of the exchanged ion (Ag$^+$) and the metallic species (Ag), the former being the prevailing species (Table 1).

Methane-^{13}C (90% ^{13}C), ethene-^{13}C$_1$ (99% ^{13}C), ethane-^{13}C$_1$ (99% ^{13}C), methane (≥99.0% purity), ethene (≥99.0% purity), benzene (≥99.0% purity), and methane-d_4 (99% D) were purchased from Aldrich Chemical Co. Inc. (ACC inc.) and were used without further purification.

The NMR measurements of the H/D exchange kinetics, as well as the analysis of the reaction products for methane and ethene conversion on Ag/H-ZSM-5 zeolite, have been performed in a glass closed batch microreactor. It represents an axially high symmetrical sealed glass tube of 3 or 5.5 mm outer diameter and 10 mm length containing hydrocarbons adsorbed on Ag/H-ZSM-5 zeolite powder. This reactor could be tightly inserted in NMR zirconia rotor (4 or 7 mm outer diameter) for in situ analysis of the reaction products. The sample of Ag/H-ZSM-5 (25 or 80 mg) in a glass tube was activated at 673 K for 24 h under vacuum with the residual pressure less than 10^{-3} Pa. A 100−300 μmol g^{-1} sample of a hydrocarbon was adsorbed on the sample under vacuum at the temperature of liquid nitrogen and then sealed by flame keeping the sample in liquid nitrogen to prevent its heating by the flame.

Some additional experiments were performed to probe the reactivity of the particular intermediate surface species formed on Ag/H-ZSM-5 zeolite. In these experiments, after the reaction performed at a specific temperature, the sealed glass tube, containing the zeolite sample with hydrocarbons, was opened under argon atmosphere, and the zeolite powder was transferred to a new glass tube followed by evacuation, adsorption of additional reagent, and sealing the tube by flame.

2.2. NMR Measurements. NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer equipped with broad-band double-resonance-MAS probe. Zirconia rotors with the inserted sealed glass tubes were spun at 3−15 kHz by dried compressed air.

^{1}H MAS NMR spectra were recorded by the Hahn-echo pulse sequence ($\pi/2−\tau−\pi−\tau−$acquisition), where τ equals one rotor period (100−333 μs). The excitation pulse length was 5.0 μs ($\pi/2$), and typically 8−32 scans were accumulated with a 4−60 s delay.

^{13}C MAS NMR spectra were recorded at room temperature using either only a high power proton decoupling or in combination with the cross-polarization (CP) technique (^{13}C CP/MAS NMR). The following conditions were used for recording the spectra with CP: the proton high power decoupling field strength was 11.7 G (5.0 μs length of 90° ^{1}H pulse), contact time was 2 ms at the Hartmann−Hahn matching condition of 50 kHz, and the delay time between scans was 2 s. A few tens of thousands of scans were collected for each ^{13}C NMR spectrum.
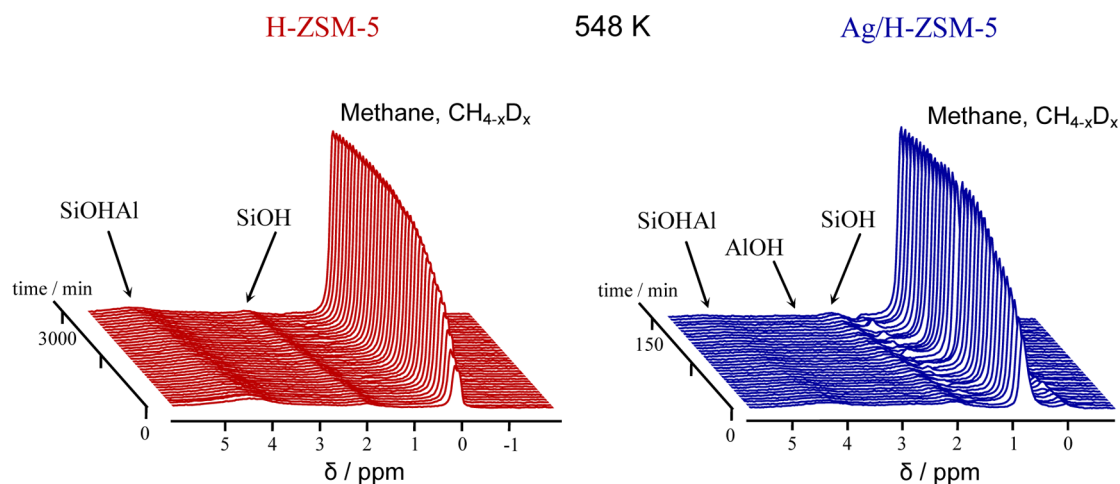
Figure 1. Stack plot of the ^{1}H MAS NMR spectra at 548 K of methane-d_4 adsorbed on H-ZSM-5 or Ag/H-ZSM-5 zeolite.
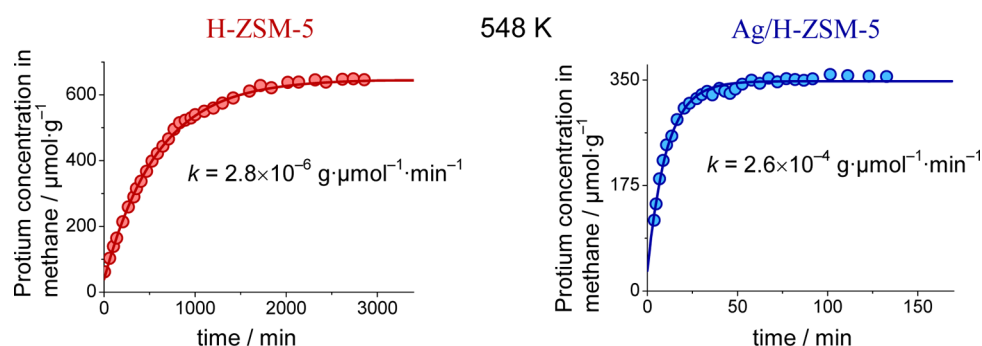

Figure 2. Experimental and simulated (solid curves) kinetics of the H/D exchange for methane-d_4 on H-ZSM-5 and Ag/H-ZSM-5 zeolites. The rate constants k derived from kinetics simulation at 478−563 K are presented in Figure 3. Accuracy of the rate constants determination was 10−15%.

^{27}Al MAS NMR spectra were acquired with a short $\pi/12$ radio frequency pulse (0.6 μs), and about 1000 scans were accumulated with a 0.5 s recycle delay. ^{29}Si MAS NMR spectra were recorded with a $\pi/2$ excitation pulse of 5.0 μs duration and 20 s repetition time, and 1000 scans were acquired for signal accumulation. Both ^{27}Al and ^{29}Si NMR spectra were recorded with use of 4 mm rotors and a spinning rate of 10−15 kHz.

The chemical shift was referenced to TMS for ^{1}H, ^{13}C, and ^{29}Si NMR and to 0.1 M Al(NO$_3$)$_3$ solution for ^{27}Al NMR with accuracy ±0.5 ppm.

The sample temperature was controlled by the Bruker BVT-2000 variable-temperature unit. For in situ kinetics measurements, the calibration of the temperature (373−573 K) inside the rotor was performed (accuracy of ±1 K) by using lead nitrate, located inside the rotor, as a ^{207}Pb MAS NMR chemical shift thermometer.[34]

2.3. Kinetics Model. A consecutive scheme of H/D exchange has been used for the analysis of the H/D exchange kinetics. In this scheme, all the deuterium atoms in methane-d_4 exchange consecutively by the protium of the SiOHAl groups. SiOH and AlOH groups were not considered to be involved in the exchange with methane. The details of the kinetics model and the protocol used for the rate constants determination were similar to that described previously in refs 22, 24, 35, and 36.

3. RESULTS

3.1. The H/D Exchange of Methane-d_4 on H-ZSM-5 and Ag/H-ZSM-5 Zeolites. The H/D exchange reaction between methane-d_4 and acid bridged hydroxyl groups (SiOHAl) of H-ZSM-5 and Ag/H-ZSM-5 zeolites has been followed with ^{1}H MAS NMR in situ at 478−563 K. Figure 1 shows the change with time of ^{1}H MAS NMR spectra of methane-d_4 adsorbed on H-ZSM-5 and Ag/H-ZSM-5 zeolites. The intensity of the signals at 0.1 ppm from methane (CH$_{4-x}$D$_x$, $x = 0/3$) formed on H-ZSM-5 and at 0.9 ppm from CH$_{4-x}$D$_x$ formed on Ag/H-ZSM-5 increases, whereas the intensity of the broad signal at 4.2 ppm from SiOHAl groups decreases in the course of the reaction. This points to a transfer of protium from the zeolite SiOHAl group to the methane-d_4 molecule to form CH$_{4-x}$D$_x$ and a reverse transfer of deuterium from CD$_4$ to the zeolite acid OH group, i.e. on occurrence of the H/D exchange between methane-d_4 and SiOHAl groups of the zeolites. The comparative analysis of the rate of the H/D exchange, derived from the kinetic curves (Figure 2), reveals that modification of the zeolite with silver results in the significant increase of the H/D exchange rate by 2 orders of magnitude. The activation energy of the exchange decreases from 113 kJ·mol^{-1} for H-ZSM-5 to 94 kJ·mol^{-1} for Ag/H-ZSM-5 (Figure 3).

3.2. The Transformation of Methane on Ag/H-ZSM-5 Zeolite. Figure 4 shows ^{13}C NMR spectra of methane-^{13}C adsorbed on Ag/H-ZSM-5 zeolite after successive heating of the sample at 298−823 K. Only the signal at −16 ppm from the initial methane-^{13}C is observed at room temperature both in ^{13}C MAS and ^{13}C CP/MAS NMR spectra (Figure 4a,b). The signal at 59 ppm appears in ^{13}C NMR spectra after the sample heating at 573 K (Figure 4c,d). This signal is still observed in
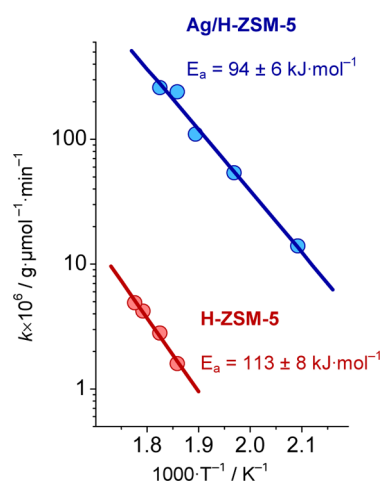
Figure 3. Arrhenius plots for the H/D exchange reaction of methane-d_4: on H-ZSM-5 (red circles) and Ag/H-ZSM-5 (blue circles) zeolites.

^{13}C NMR spectra at 623 K (Figure 4e,f). The chemical shift of this signal is typical for the methyl group of O−CH$_3$ methoxide species formed on the surface of zeolites[17−19,37−39] and heteropolyacids.[40,41] So, the formation of methoxy groups from methane is detected on Ag/H-ZSM-5 at 573−623 K with both ^{13}C MAS and ^{13}C CP/MAS NMR.

The signals at 4 and 109 ppm appear in ^{13}C NMR spectra of methane-^{13}C adsorbed on Ag/H-ZSM-5 zeolite after heating at 623 K (Figure 4e,f) and 673 K (Figure 4g,h). The intensity of the signal at 4 ppm decreases, whereas the intensity of the signal at 109 ppm increases in the temperature range of 623−673 K (Figure 4e−h). This observation is the evidence for ethane and ethene formation as the first products of methane conversion. Ethane and ethene have been previously observed by gas chromatography as the reaction products of methane conversion on Ag/H-ZSM-5 catalysts.[27,30] A chemical shift of the signal at 4 ppm is similar to that of ethane adsorbed on different zeolites.[42−44] The signal at 109 ppm from ethene has an unusual chemical shift in comparison with that from gaseous
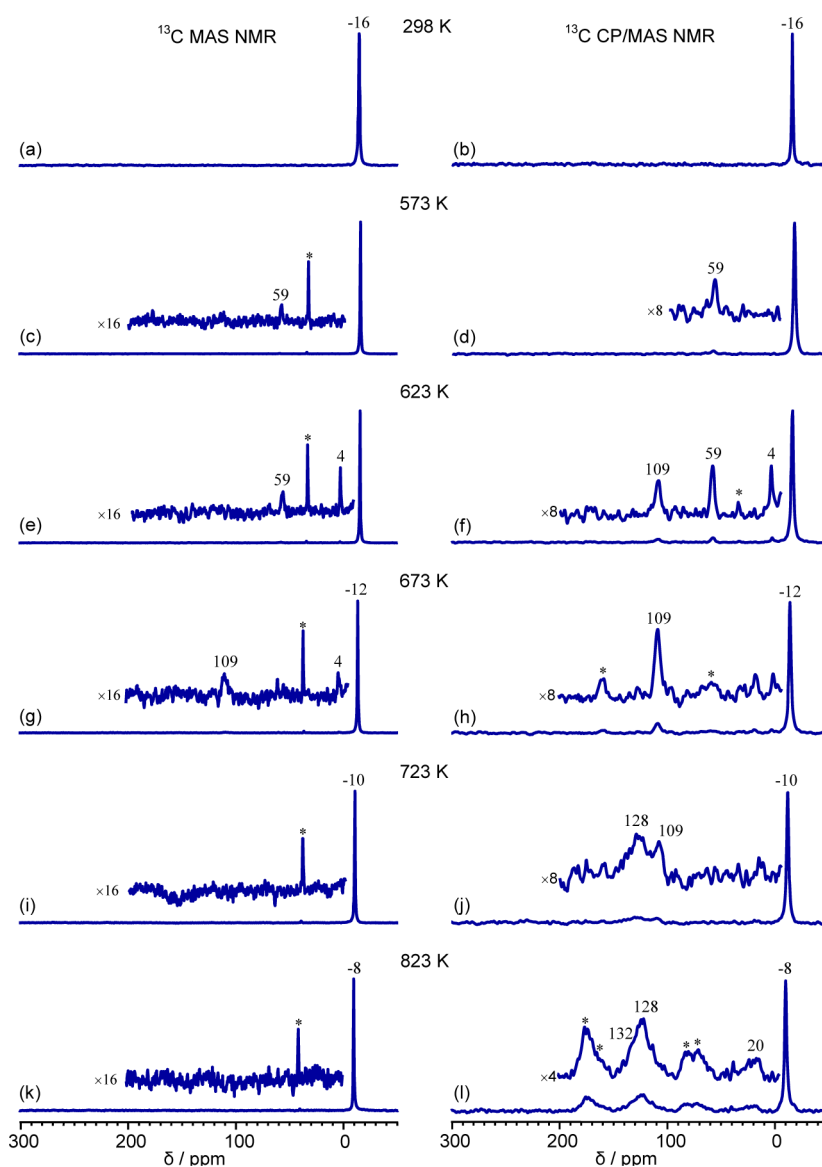

Figure 4. ^{13}C MAS and ^{13}C CP/MAS NMR spectra of methane-^{13}C adsorbed on Ag/H-ZSM-5 at room temperature (a, b), and after heating the sample for 1 h at 573 (c, d), 623 (e, f), 673 (g, h), 723 (i, j), and 823 K (k, l). Asterisks denote the spinning side bands.

ethene at 122 ppm.[45] This points to the formation of ethene π-complexes with silver cations of Ag/H-ZSM-5 zeolite. The formation of such π-complexes has been observed earlier with ^{13}C MAS NMR for ethene adsorption on Ag/SiO$_2$[45] and Ag/Al$_2$O$_3$.[46]

The broad signal at 128 ppm nearby the signal at 109 ppm is detected in the ^{13}C CP/MAS NMR spectrum after the methane-^{13}C reaction on Ag/H-ZSM-5 at 723 K (Figure 4j). [13]C chemical shifts of 125−135 ppm are typical for benzene rings of simple alkyl-substituted aromatics adsorbed on zeolite catalysts.[17,19,47] The broad signals at 128−134 ppm and around 20 ppm are evident in the ^{13}C CP/MAS NMR spectrum at 823 K (Figure 4l). This points to the formation of methyl-substituted aromatic hydrocarbons such as toluene and xylenes.[47] These data show that pure methane transforms to aromatic hydrocarbons on Ag/H-ZSM-5 zeolite at temperatures above 723 K. Only the formation of C$_2$-hydrocarbons was reported in previous works.[27,30] Thus, at the increase of the reaction temperature methane is successively transformed to aromatics through the stage of intermediate formation of methoxy species, which further transforms to ethane and ethene. Which of them, ethane or ethene, is the primary product of methoxy group transformation is not clear from the performed experiment. To clarify this issue we have further carried out the monitoring of ethane transformation with temperature.

3.3. Ethane Transformation on Ag/H-ZSM-5 Zeolite. Only the signal at 4 ppm from ethane-[13]C$_1$ is observed in the ^{13}C CP/MAS NMR spectrum at room temperature (Figure 5a). The signal at 109 ppm from the ethene π-complexes appears in the spectrum after the sample heating at 523 K (Figure 5b). The intensity of the signal at 109 ppm increases at 573 K (Figure 5c). The broad signals at 126−145 and 20 ppm from ethene oligomers or methyl substituted aromatics are observed in the ^{13}C CP/MAS NMR spectrum after heating at 673 K (Figure 5d).[47−51] Thus, ethene (or rather π-complexes of ethene) is formed from ethane on Ag/H-ZSM-5 followed by the formation of the olefin oligomers and aromatics (Figure 5b−d).

3.4. Ethene Transformation on Ag/H-ZSM-5 Zeolite. Ethene-[13]C$_1$ adsorption on Ag/H-ZSM-5 results in a formation of ethene π-complex with silver cations as could be concluded from the observed signal at 109 ppm (Figure 6a). This prevents fast ethene oligomerization, which usually proceeds on acid sites of this type of zeolite even at room temperature.[48−52] The ethene π-complex formed is persistent at temperatures as high as 673 K. Indeed, the signal at 109 ppm from the π-complex is still observed in the ^{13}C CP/MAS NMR spectrum after sample heating at 673 K (Figure 6b). The transformation of the ethene π-complex to aromatic hydrocarbons has been detected at temperatures above 723 K. This transformation was very fast at such a relatively high temperature and we failed to detect any intermediate products, e.g., ethene oligomers. Observation of the signal at 128 ppm and the absence of the signal at 20 ppm, which would be evidence for methyl-substituted aromatics formation, indicate that benzene is formed as the main aromatic product (Figure 6c).

3.5. Methane and Ethene Coconversion on Ag/H-ZSM-5 Zeolite. To inquire into the possibility of methane and ethene joint conversion into aromatics on Ag/H-ZSM-5 zeolite the transformation of ethene-[13]C$_1$/methane (Figure 6d−f), methane-^{13}C/ethene (Figure 6g−i), and methane/ethene

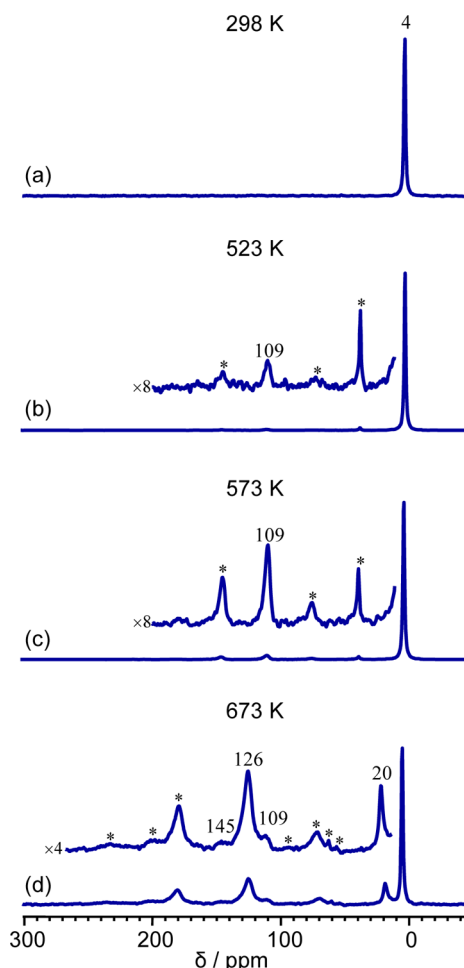**Figure 5.** ^{13}C CP/MAS NMR spectra of ethane-[13]C$_1$ adsorbed on Ag/H-ZSM-5: (a) room temperature; (b−d) heating for 1 h at 523 (b), 573 (c), and 673 K (d). Asterisks denote the spinning side bands.

(Figure 6j−l) has been monitored with ^{13}C CP/MAS NMR. Similar to pure ethene the formation of the ethene π-complex is detected for coadsorbed ethene and methane (Figure 6d,g,j). Two signals at −7 and −13 ppm for methane-^{13}C are observed in ^{13}C CP/MAS NMR spectra of methane-^{13}C/ethene (Figure 6g) at room temperature. The adsorbed ethene molecules seem to influence the centers of methane adsorption, i.e., silver cations[30] and the zeolite Brønsted acid sites,[53] resulting in the observation of two signals from adsorbed methane.

We have also established that the stability of the ethene π-complex is significantly lowered in the presence of methane. Indeed, while the signal at 109 ppm from the ethene π-complex is detected in the spectrum of adsorbed ethene (Figure 6b) at 673 K, this signal disappears in the presence of coadsorbed methane (Figure 6e). Instead, the signals at 126−142 ppm from unsaturated carbon atoms and at 15−30 ppm from the methyl and methylene groups of ethene oligomers are observed in spectra at 673 K (Figure 6e,h,k).[48−52] Also, the weak signal at 88 ppm has been detected in the ^{13}C CP/MAS NMR spectrum of ethene-[13]C$_1$ and methane (Figure 6e). The signals with the similar chemical shifts of 87−89 ppm have been earlier observed for olefins adsorbed on H-ZSM-5 or HY zeolites.[51,54] These signals have been attributed to the surface alkoxy species formed from olefin oligomers by protonation with Brønsted acid sites of zeolites. Further, the oligomeric olefins formed from the ethene π-complex convert to aromatic hydrocarbons,
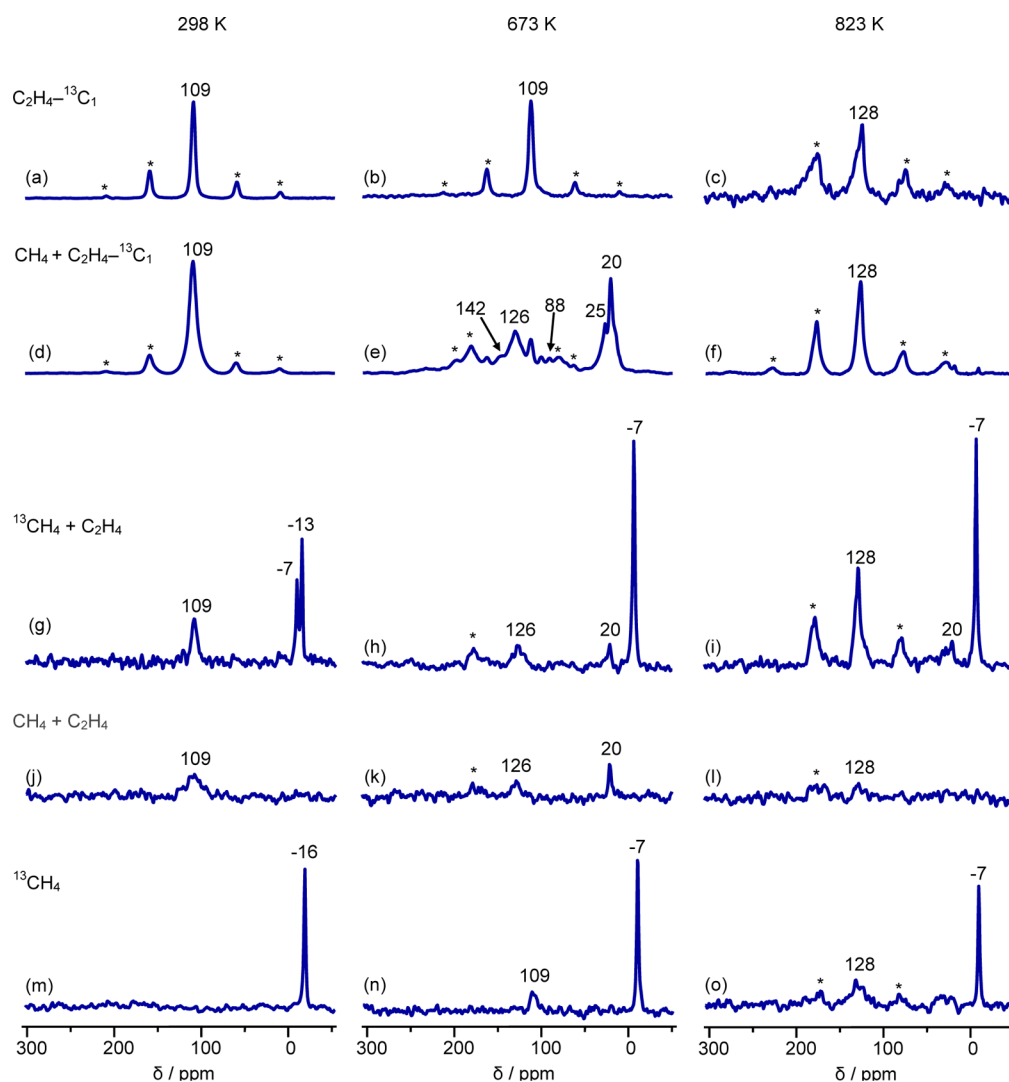
Figure 6. ^{13}C CP/MAS NMR spectra of methane and ethene adsorbed on Ag/H-ZSM-5 at room temperature and heated for 15 min at 673–823 K. Ethene-^{13}C$_1$ was heated at 298 (a), 673 (b), and 823 K (c). Methane and ethene-^{13}C$_1$ were heated at 298 (d), 673 (e), and 823 K (f). Methane-^{13}C and ethene were heated at 298 (g), 673 (h), and 823 K (i). Methane and ethene were heated at 298 (j), 673 (k), and 823 K (l). Methane was heated at 298 (m), 673 (n), and 823 K (o). Spectra g–o were acquired under identical conditions, with 3000 scans and a repetition time of 2 s. Asterisks denote the spinning side bands.

preferentially to benzene, because mainly signals at 128 ppm are detected in spectra after reaction at 823 K (Figure 6f,i,l).[47] So, in the presence of methane, ethene starts converting to aromatic hydrocarbons with the oligomeric olefins as intermediates at temperatures 100−150 K lower, compared to the temperature of ethene conversion in the absence of coadsorbed methane. The reason could be the competition of methane with ethene for centers of adsorption, Ag$^+$ cations. Indeed, the formation of strong adsorption complexes of Ag$^+$ cations with methane was earlier reported.[30] Rather notable upfield chemical shift of adsorbed methane (−16 ppm, Figure 4a), compared to that on H-ZSM-5 (−7 ppm),[55] supports this suggestion. Expulsion of ethene by methane from the centers of adsorption, Ag$^+$ cations, allows involvement of ethene in the reaction on Brønsted acid sites by oligomerization and further aromatization.

On the basis of these experiments performed, it was not possible to establish whether methane was involved in the reaction with ethene as far as methane was not labeled with ^{13}C isotope. To clarify this we have further performed the reaction

of methane-^{13}C/ethene (Figure 6g−i), methane/ethene (Figure 6j−l) and methane-^{13}C (Figure 6m−o) at 298−823 K and recorded the spectra of the reaction products under identical conditions. The results point to the methane conversion to aromatic hydrocarbons in the presence of ethene. There is no difference in the intensities of the signals of ethene oligomers at 126 and 20 ppm in spectra at 673 K of methane-^{13}C/ethene (Figure 6h) and methane/ethene (Figure 6k). This indicates that methane is not involved in the reaction at 673 K, only ethene converts to oligomeric products. However, the intensity of the signal from aromatic products at 128 ppm is significantly higher in the spectrum of methane-^{13}C/ethene (Figure 6i) than in the spectrum of methane/ethene (Figure 6l) at 823 K. This shows that ^{13}C atoms from methane-^{13}C are transferred to aromatic products. So, we conclude that methane converts to aromatic products at temperature 823 K in the presence of ethene. We have already established that pure methane converts to aromatic hydrocarbons on Ag/H-ZSM-5 zeolite without any coreactants (Figure 4j,l). But the conversion of pure methane-^{13}C is too

Scheme 1. The Mechanism of the H/D Exchange between Methane and Brønsted Acid Sites on Ag/H-ZSM-5 Zeolite
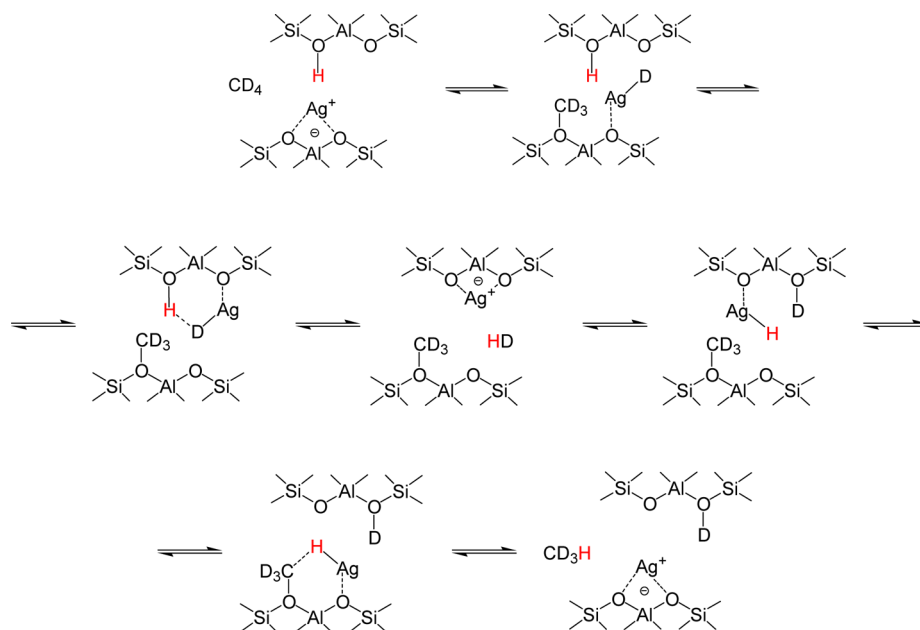
low to account for the high intensity of the signal at 128 ppm from aromatic products of methane-^{13}C/ethene coconversion (cf. Figure 6o,i).

4. DISCUSSION

Mechanism of H/D Exchange for Methane on Ag/H-ZSM-5. The kinetics parameters of the H/D exchange reaction between methane and acid hydroxyl groups (SiOHAl) of the pure acid-form H-ZSM-5 zeolite obtained in the present work are in good accordance with the experimental[21,56−60] and theoretical[61−64] data published earlier. The H/D exchange occurs by synchronous mechanism with simultaneous transfer of methane deuterium to the oxygen of the zeolite framework and the proton of the zeolite SiOHAl group to the methane molecule involving a penta-coordinated carbon atom in a transition state.[56,59,61−64]

Modification of the zeolite with silver results in notable changes of the H/D exchange kinetic parameters. The rate constant is 2 orders of magnitude higher and the activation energy is 19 kJ·mol^{-1} lower for Ag/H-ZSM-5 as compared to H-ZSM-5 zeolite. These changes of the kinetic parameters point to a promoting effect of silver on the H/D exchange reaction. The mechanism of the H/D exchange should be different from that for the pure acid-form zeolites. Both Brønsted acid sites and silver cations should be involved in the H/D exchange reaction and therefore in methane activation.

A promoting effect of metal species loaded in zeolites on the H/D exchange reaction between small alkanes and Brønsted acid sites has been observed for Zn- and Ga-modified zeolites.[21,22,24] The strong influence of zinc or gallium on the H/D exchange was considered to be achieved by involvement in the exchange of Zn- or Ga-alkyl species formed by dissociative adsorption on metal cationic sites or oxide species.[21,22,24,65]

Our data show the formation of methoxy groups from methane on the surface of Ag/H-ZSM-5 zeolite at elevated temperatures, the signal at 59 ppm from the surface methoxy groups is clearly detected (Figures 4d,f). No signals that could be assigned to the Ag-methyl species at −5/−15 ppm[66] were

detected in our ^{13}C NMR spectra. So, we experimentally prove the suggestion of Baba et al.[13−16,26] on the formation of methoxy species at methane activation on Ag/H-ZSM-5. Therefore, we can conclude that methane dissociation on Ag/H-ZSM-5 zeolite occurs via the "carbenium" pathway: C−H bond cleavage on silver cationic species results in the surface methoxy groups and possibly silver-hydride species (Ag−H). The expected signal at −0.1 ppm from Ag−H species[67] was not detected in our ^{1}H MAS NMR spectra, presumably due to low quantity of the formed hydride species and/or its large signal width.

Having a positive charge on a carbon atom, the methoxy group is unlikely to interact with the SiOHAl group directly to provide an exchange reaction similar to that of the metal−alkyl species. Therefore, we suppose the following mechanism of the H/D reaction between methane and Brønsted acid sites (BAS) of Ag/H-ZSM-5 zeolite (Scheme 1). The first step is deuterated methane dissociation on silver cation with surface methoxy groups and silver-deuteride (Ag−D) species formation. The second step is the interaction of Ag−D with BAS to form dihydrogen (HD). Further, dissociative adsorption of HD on Ag$^+$ cations gives silver-hydride species (Ag−H). The final step is the reverse interaction of Ag−H with deuterated methoxy groups to give methane, containing protium (CD$_3$H), and silver cations. This mechanism could account for the substantial difference between the kinetic parameters for the H/D exchange on Ag/H-ZSM-5 and H-ZSM-5 zeolites.

What Is the First Intermediate of Methane Transformation to Aromatics: Methoxy Species or Ethane? Methane activation under oxidative conditions is considered to occur via abstraction of a hydrogen atom from methane molecule by specific surface oxygen species.[68,69] The resulting methyl radicals may either dimerize to ethane in the gas phase or react further on the surface. Analysis of the ^{13}C NMR spectra after heating methane on Ag/H-ZSM-5 at different temperatures shows that the signal from the methoxy species appears in the spectrum at 573 K, whereas the signal of ethane becomes visible in the spectrum only at 623 K (cf. Figure 4, parts c,d and e,f). This fact indicates that the methoxy group is the first

Scheme 2. The Mechanism of the Ethane Formation during Methane Conversion on Ag/H-ZSM-5 Zeolite
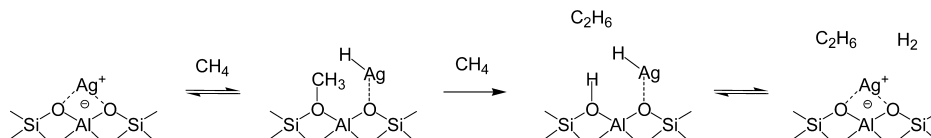
intermediate of methane transformation to aromatics. Ethane can be the product of further methoxy group transformation.

Which of Them, Ethane or Ethene, Is the Prime Product of Methoxy Group Transformation? We have observed simultaneously the formation of ethane and ethene from the methoxy species (Figure 4e,f). In fact, it is not clear which of them is the first product of the carbon–carbon coupling reaction. According to Yoshida et al.[30] ethane is the main product of methane conversion on Ag/H-ZSM-5 catalyst under photoirradiation during the reaction. The data of the present work (Figure 4e–h) point to the transformation of ethane to ethene in the course of methane conversion. Really, the intensity of the signal from ethane that appeared in ^{13}C MAS NMR spectra at 623 K (Figure 4e,f) significantly decreases in the spectra at 673 K, whereas the intensity of the signal from the ethene π-complexes increases. To prove that ethane does transform to ethene we have monitored the ethane-$^{13}C_1$ conversion on Ag/H-ZSM-5 zeolite with ^{13}C CP/MAS NMR (Figure 5). The formation of the ethene π-complexes from ethane has been observed. So, we claim that Ag/H-ZSM-5 zeolite is capable of performing dehydrogenation of ethane to ethene and ethane is the first product of the carbon–carbon coupling reaction during methane conversion on Ag/H-ZSM-5 zeolite. But the question about the pathway of ethane formation from the methoxy group is still unclear.

How Does Ethane Form from Methane? Transformation of methane into ethane at 623–673 K by the reaction $2CH_4 = C_2H_6 + H_2$ is thermodynamically unfavorable, $\Delta_r G^0_{673} = +71.8$ kJ/mol and $K_p = 2.7 \times 10^{-6}$. The equilibrium concentration of ethane at 673 K estimated from K_p (at 673 K) under conditions of our experiment should be 1.0 μmol/g. This is in accordance with our estimate (from ^{13}C MAS NMR spectrum, Figure 4e) of the quantity of the formed ethane, ca. 1.4 μmol/g. So, the observed quantity of ethane formed from methane is in good accordance with that predicted by thermodynamics.

A possible pathway of ethane formation from methane requires discussion. We have established that the methoxy group is the primary product of methane activation. The surface methoxy groups are highly polarized species and therefore should be very reactive.[38,70] There are two pathways for ethane formation from the methoxy group: (1) dimerization of methyl radicals formed from methoxy groups by the reaction: $2CH_3–O + 2Ag–H \rightarrow CH_3CH_3 + 2OH + 2Ag^0$, and (2) the interaction of methoxy species with methane by Scheme 2.

We have performed two experiments to verify these alternative hypotheses. We generated methoxy species from methane by heating methane-^{13}C on Ag/H-ZSM-5 at 573 K. Further, two samples were prepared. In the first sample, unreacted methane was fully pumped out (353 K, 16 h), so only the signal from methoxy groups was detected in the spectrum (Figure 7a). The second sample was evacuated for a short time (several minutes at room temperature) that led to the presence of some residual amount of methane along with the surface methoxy species in the spectrum (Figure 7c). Further, both samples were heated at 623 K for 5 min. In the
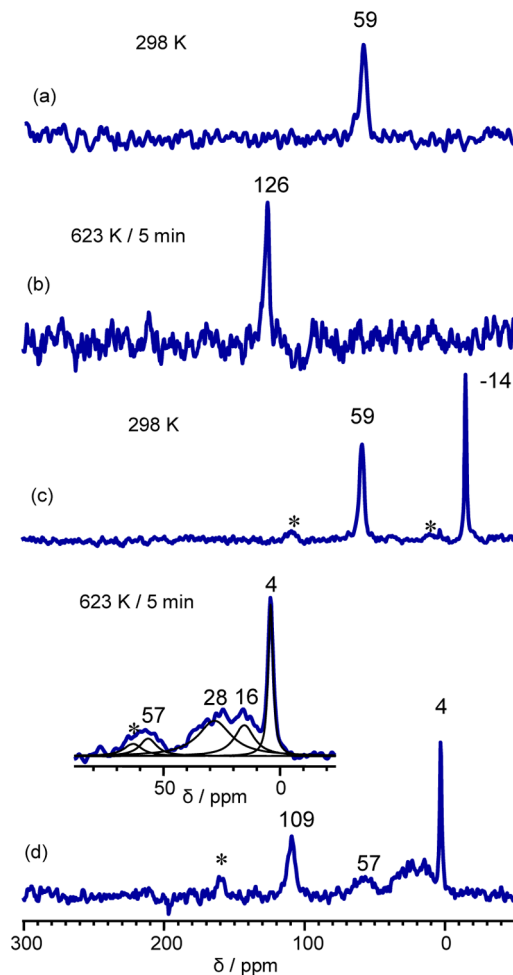

Figure 7. ^{13}C CP/MAS NMR spectra of methoxy species generated from methane-^{13}C on Ag/H-ZSM-5 (a, c) and after subsequent heating at 623 K for 5 min (b, d). (a) The residue of methane was completely pumped out after the methoxy was generated at 573 K; (b) ^{13}C MAS NMR spectrum; (c) methane was removed only partially, so the signal is also present in the spectrum at −14 ppm. The insert above part d shows the extension of the spectra in (d) at −20/+80 ppm. Asterisks denote the spinning side bands.

first sample, the signal from the methoxy species disappeared, but the expected signal from ethane did not appear. Instead, the signal at 126 ppm becomes detectable (Figure 7b), indicative of CO_2 formation. This points to the oxidation of the methoxy species to carbon dioxide, possibly by some residual oxygen in the sample or by silver cations with assistance of the zeolite framework oxygen. In the second sample, the signals from both methoxy species and methane disappeared in the spectrum and the signal from ethane at 4 ppm became detectable (Figure 7d), together with the signals from ethene (109 ppm) and ethene oligomers, exhibiting broad signals at 16 and 28 ppm. These data provide the evidence for the formation of ethane by Scheme 2, via the reaction between methoxy species and

Scheme 3. The Possible Mechanism of the Ethane Dehydrogenation on Ag/H-ZSM-5 Zeolite
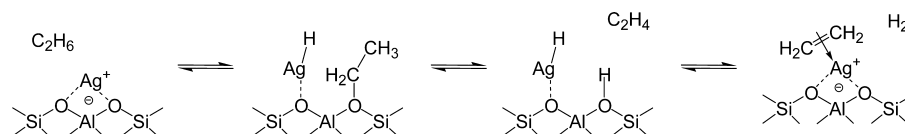
methane. The acid proton and the silver-hydride species formed at ethane formation may interact to regenerate the initial active center $[AlO_4]^-Ag^+$ and give molecular hydrogen. The latter reaction is plausible due to well-known reversibility of the hydrogen chemisorption on Ag-modified zeolites.[26,67]

Observation of the signals from ethene and its oligomers could point to further dehydrogenation of ethane to ethene and oligomerization of the latter that occurs within 5 min of the reaction at 623 K.

Possible Pathway of Ethane to Ethene Transformation. The next stage of methane transformation on Ag/H-ZSM-5 is ethene formation from ethane. This stage has been separately monitored in the case of pure ethane conversion on Ag/H-ZSM-5 zeolite (Figure 5). One can suggest that the activation of ethane occurs by the same way as the methane activation, i.e., via dissociation of the alkane on silver cations with the surface ethoxy groups and the silver-hydride species formation (Scheme 3). The surface ethoxy groups should exhibit two signals in the ^{13}C MAS NMR spectrum at 59−61 from the $O-CH_2-$ fragment and at 14−16 from the $-CH_3$ group.[71,72] However, we have not detected any signals with such chemical shifts for either ethane-$^{13}C_1$ or methane-^{13}C conversion on Ag/H-ZSM-5 zeolite (Figures 4−6). Although, the signals at 16 and 57 ppm detected at methoxy group and methane interaction to form ethane (Figure 7d) could be the evidence for ethoxy species formation as intermediate at ethane transformation to ethene. The ethoxy group represents a state of ethene adsorption on the Brønsted acid site of the zeolite and can be in equilibrium with ethene. Deprotonation of the ethoxy groups results in ethene desorption followed by π-complexes formation between ethene and silver cations (Scheme 3). The formation of such π-complexes may be the driving force of ethane-to-ethene conversion, probably due to their lesser reactivity and therefore higher stability in comparison with the ethoxy groups. This might be the reason that we observe only the π-complex of ethene (Figures 4−6), and the surface ethoxy group was never reliably identified.

The Pathways of Ethene and Ethene/Methane Transformation to Aromatics. Our data show that ethene itself, or formed as intermediate from methane, transforms on Ag/H-ZSM-5 to aromatic hydrocarbons with intermediate formation of ethene oligomers (Figures 4−6). Due to formation of the strong adsorption complex of ethene with Ag^+ cations, ethene oligomerization starts only at 723 K, contrary to pure H-ZSM-5, where oligomerization occurs already at room temperature.[49−52] In the presence of methane, the oligomerization of ethene begins at 673 K due to possible expulsion of ethene from Ag^+ adsorption centers by methane. The signal at 88 ppm which is observed for ethene-$^{13}C_1$ and methane coadsorbed on Ag/H-ZSM-5 zeolite at 673 K (Figure 6e) is the evidence for intermediate oligomeric surface alkoxides formation from ethene oligomers[51] on Ag/H-ZSM-5 zeolite, which finally transform to aromatics.

It is generally accepted that aromatization of olefins on acid zeolite catalysts includes the steps of oligomerization, dehydrogenation, hydrogen transfer, and cyclization.[73−78] All

stages are complex acid catalyzed reactions proceeding via carbenium ion mechanism. So, we can suppose that the acid catalyzed aromatization of ethene is also realized on Ag/H-ZSM-5 zeolite. But we should not exclude either the silver cations from dehydrogenation steps similar to a possible involvement of Ag^+ cations in ethane dehydrogenation to ethene (Scheme 3).

The pure methane conversion at 673−823 K is relatively low (Figure 4g,i,k). Therefore, we have performed a joint methane and ethene conversion to aromatics. The data show that methane is indeed involved in the reaction at $T > 673$ K. This is evidenced by intense signal from aromatics at methane-^{13}C/ethene coconversion at 823 K (Figure 6i).

The joint conversion of methane and ethene on Ag/H-ZSM-5 zeolite has been studied previously,[13−16] with propene being the main product of the reaction under flow conditions. With the use of ^{13}C-labeled methane Baba et al.[13] showed that propene resulted from interaction of ethene with methane-^{13}C. The surface methoxy groups formed from methane were supposed to interact with ethene to give propene. We have performed an additional experiment to verify this possible pathway for propene formation. First, the methoxy species was generated by heating methane-^{13}C on Ag/H-ZSM-5 at 573 K. Then, unreacted methane was pumped out from the sample and the unlabeled ethene was adsorbed. In the case of the reaction between methoxy species and ethene, the signal from the ^{13}C-labeled methyl group of propene at 19 ppm[47] would be observed in the spectrum. However, 5 min heating of the sample at 673 K resulted in disappearance of the signal from the methoxy groups, decrease of the intensity of the signal from ethene π-complexes, and appearance of weak and broad signals from ethene oligomers (the spectrum was very similar to that shown in Figure 7d, except the presence of the signal from ethane). No expected signal at 19 ppm from the methyl group of propene was detected. These results show that no evident interaction between the methoxy groups and ethene occurs to form propene under conditions of our experiment, despite the evidence for this reaction provided by Baba et al.[13]

In case of propene formation from ethene and methane, we could suggest that involvement of methane in coaromatization with ethene occurs at the stage of propene formation. Further dimerization and dehydrogenation of propene would give benzene, the main reaction product detected at 823 K. Another mechanism of methane involvement in aromatization could be alternatively realized on Ag/H-ZSM-5 under conditions of our experiment. The incorporation of methane into aromatic products can be realized by the reaction of methane with aromatics formed from ethene oligomers, similar to involvement of methane into coaromatization with propane on Zn/H-BEA or Ga/H-BEA.[17−19] To check the possibility of aromatics alkylation with methane on Ag/H-ZSM-5 under our conditions, methane was reacted with benzene.

Figure 8 shows ^{13}C CP/MAS NMR spectra of methane-^{13}C and benzene adsorbed on Ag/H-ZSM-5 zeolite. Two signals at −8, −15 ppm from methane-^{13}C and at 128 ppm from benzene are observed in the spectrum at room temperature (Figure 8a).
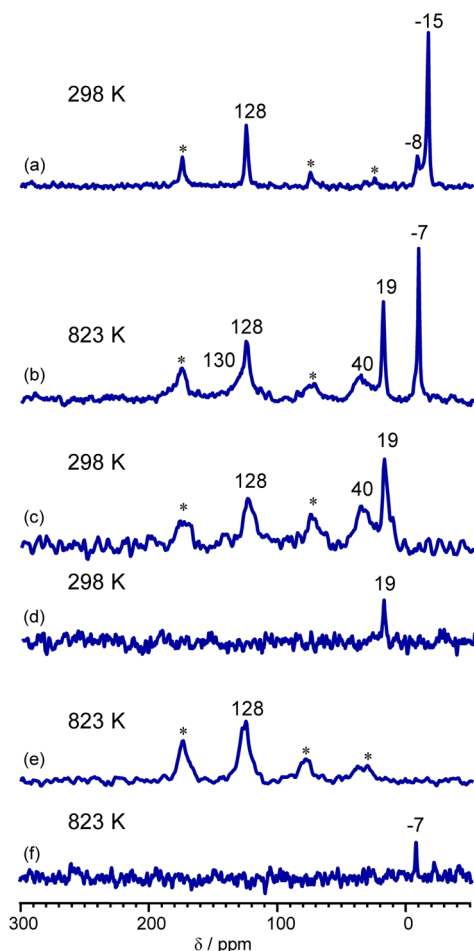
Figure 8. ^{13}C CP/MAS (a, b, c, e) and ^{13}C MAS (d, f) NMR spectra of methane-^{13}C and benzene coadsorbed on Ag/H-ZSM-5: (a) at room temperature; (b) reacted at 823 K for 15 min; (c, d) after methane evacuation under vacuum at 423 K for 3 h; (e, f) after molecular hydrogen adsorption on the sample (c, d) and further heating at 823 K for 15 min. Asterisks denote the spinning side bands.

The signals at 19, 40, and 130 ppm (visible as a shoulder to the signal at 128 ppm) appear in the spectrum after heating at 773–823 K (Figure 8b). The signals at 19 and 130 ppm belong to the methyl groups and aromatics ring of methylbenzenes,[47] respectively. The signal at 40 ppm is assigned to diphenyl-methane and its methyl substituted derivatives.[47] So, we conclude that alkylation of benzene with methane occurs at 823 K and ^{13}C atoms from methane-^{13}C convert to the methyl groups of aromatic hydrocarbons (toluene, xylenes) followed by scrambling to aromatic rings, resulting in signals in the vicinity of 130 ppm. Methyl substituted aromatic products seem to interact with initial benzene to form diphenylmethane, giving the signal at 40 ppm from the —CH$_2$— group.

Thus, with these experiments we confirm the earlier conclusion by Baba et al.[13,14] on the possibility of benzene alkylation with methane on Ag/H-ZSM-5.

Note, however, that the final product of methane and ethene coaromatization, benzene, contains ^{13}C-label in the benzene ring, while the aromatic products formed by interaction of methane-^{13}C with aromatics formed exclusively from ethene should be methyl-substituted aromatics and contain ^{13}C-label in the methyl group. We can suggest that ^{13}C-label penetrates to the aromatic ring by the scrambling of the ^{13}C atoms from the

methyl groups to the aromatic ring. Further, methyl benzenes undergo demethanation in the excess of hydrogen formed at the ethene aromatization stage to offer ^{13}C-labeled benzene as the final product. This ^{13}C-label scrambling is considered to occur via the ring expansion/contraction mechanism with the phenylmethyl cation as an intermediate or a transition state.[17−19] One of the pieces of evidence for this mechanism is the diphenylmethane formation. Indeed, the phenylmethyl cation, if formed, possesses the reactivity toward aromatic ring, i.e., it can alkylate aromatic molecules.[79] So, the observation of the signal from diphenylmethane is in favor of phenylmethyl cation formation and the possibility of the ^{13}C-label scrambling through this cation intermediate.

To verify a possibility of methyl benzenes demethanation, the following experiment was performed. Methane was pumped out from the sample containing methylaromatics (Figure 8c,d). As a result the ^{13}C CP/MAS spectrum of the sample exhibits only the signals at 19 and 128 ppm (Figure 8c) and the corresponding ^{13}C MAS spectrum shows only the signal at 19 ppm (Figure 8d) from the more mobile methyl groups of methyl benzenes. Further molecular hydrogen adsorption and heating at 823 K result in the disappearance of the signal at 19 ppm (Figure 8e) and the appearance of the signal from methane at −7 ppm (Figure 8f). This experiment confirms that benzene forms in excess of hydrogen from methyl benzenes that primarily formed at methane and ethene coaromatization.

Thus, the reason for enhanced intensity of the signal from benzene, detected at coaromatization of methane-^{13}C and ethene at 823 K (Figure 6i), is clear now. This is due to the formation of ^{13}C-labeled benzene. It is produced by the reaction of methane-^{13}C with aromatics formed from ethene, further ^{13}C-label scrambling from the methyl group of aromatics into its aromatic ring, and subsequent methyl aromatics demethanation in the presence of hydrogen.

5. CONCLUSION

Application of ^{1}H and ^{13}C MAS NMR to the characterization of methane conversion pathways on silver loaded ZSM-5 zeolite allowed us to make the following conclusions about the mechanism of methane activation and transformation on this zeolite at 573−823 K.

The activation of methane occurs by dissociation of the C−H bond on silver cations via the "carbenium" pathway: methane C−H bond cleavage results in the methoxy groups (O−CH$_3$) and possibly the silver-hydride species (Ag−H). The formation of surface methoxy groups on Ag/H-ZSM-5 has been detected experimentally with ^{13}C CP/MAS NMR at 508−623 K for the first time. A comparative analysis of the H/D exchange kinetics between methane and acid hydroxyl groups of H-ZSM-5 and Ag/H-ZSM-5 zeolites reveals a significant promoting effect of silver cations on the H/D exchange reaction and therefore on methane activation. This effect has been rationalized in terms of reversible methane dissociation on the surface of Ag/H-ZSM-5 zeolite and further involvement in the exchange of the methoxy groups and the silver-hydride species.

Ethane represents the first intermediate product of methoxy group transformation. It is formed by the reaction of the methoxy group with methane. Further dehydrogenation of ethane provides ethene, which offers immediately π-complexes with Ag$^+$ cations. The latter species are stable at temperatures as high as 673 K. At 823 K π-complexes decompose and ethene undergoes oligomerization, cyclization, dehydrogenation, and aromatization to give benzene. In the presence of methane

ethene π-complexes decompose and become involved in oligomerization and aromatization reaction at lower temperature, already at 673K.

Methane is also involved in the reaction of coaromatization with ethene. The involvement of methane in aromatization reaction occurs by the alkylation with methane of aromatics formed from ethene. Further demethanation of methylbenzenes in the presence of dihydrogen evolved at the stages of ethene transformation to aromatics produces benzene as the main reaction product.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Schwarz, H. Chemistry with Methane: Concepts Rather than Recipes. *Angew. Chem., Int. Ed.* **2011**, *50*, 10096−10115.

(2) Pitchai, R.; Klier, K. Partial Oxidation of Methane. *Catal. Rev.: Sci. Eng.* **1986**, *28*, 13−88.

(3) Foster, N. R. Direct Catalytic Oxidation of Methane to Methanol − A Review. *Appl. Catal.* **1985**, *19*, 1−11.

(4) Lunsford, J. H. Catalytic Conversion of Methane to More Useful Chemicals and Fuels: A Challenge for the 21st Century. *Catal. Today* **2000**, *63*, 165−174.

(5) Scurrell, M. S. Prospects for The Direct Conversion of Light Alkanes to Petrochemical Feedstocks and Liquid Fuels − A Review. *Appl. Catal.* **1987**, *32*, 1−22.

(6) Echevsky, G. V.; Kodenev, E. G.; Kikhtyanin, O. V.; Parmon, V. N. Direct Insertion of Methane into C₃−C₄ Paraffins over Zeolite Catalysts: A Start to the Development of New One-Step Catalytic Processes for the Gas-to-Liquid Transformation. *Appl. Catal., A* **2004**, *258*, 159−171.

(7) Choudhary, V. R.; Kinage, A. K.; Choudhary, T. V. Low-Temperature Nonoxidative Activation of Methane over H-Galloaluminosilicate (MFI) Zeolite. *Science* **1997**, *275*, 1286−1288.

(8) Anunziata, O. A.; Eimer, G. A.; Pierella, L. B. Catalytic Conversion of Natural Gas with Added Ethane and LPG over Zn-ZSM-11. *Appl. Catal., A* **2000**, *190*, 169−176.

(9) Anunziata, O. A.; Mercado, G. G. Methane Transformation Using Light Gasoline as Co-Reactant over Zn/H-ZSM11. *Catal. Lett.* **2006**, *107*, 111−116.

(10) Anunziata, O. A.; Mercado, G. G.; Pierella, L. B. Improvement of Methane Activation Using n-Hexane as Co-Reactant over Zn/HZSM-11 Zeolite. *Catal. Commun.* **2004**, *5*, 401−405.

(11) Anunziata, O. A.; Mercado, G. V. G.; Pierella, L. B. Catalytic Activation of Methane Using n-Pentane as Co-Reactant over Zn/H-ZSM-11 Zeolite. *Catal. Lett.* **2003**, *87*, 167−171.

(12) Choudhary, V. R.; Mondal, K. C.; Mulla, S. A. R. Simultaneous Conversion of Methane and Methanol into Gasoline over Bifunctional Ga-, Zn-, In-, and/or Mo-Modified ZSM-5 Zeolites. *Angew. Chem., Int. Ed.* **2005**, *44*, 4381−4385.

(13) Baba, T.; Sawada, H. Conversion of Methane into Higher Hydrocarbons in the Presence of Ethylene over H-ZSM-5 Loaded with Silver Cations. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3919−3923.

(14) Baba, T.; Inazu, K. Heterolytic Dissociation of C-H Bond of Methane over Ag⁺-Exchanged Zeolites and Conversion of Methane into Higher Hydrocarbons in the Presence of Ethene or Benzene. *Chem. Lett.* **2006**, *35*, 142−147.

(15) Baba, T.; Abe, Y. Metal Cation-Acidic Proton Bifunctional Catalyst for Methane Activation: Conversion of ¹³CH₄ in the Presence of Ethylene over Metal Cations-Loaded H-ZSM-5. *Appl. Catal., A* **2003**, *250*, 265−270.

(16) Inazu, K.; Koyama, T.; Miyaji, A.; Baba, T. Propene Production from Ethene and Methane Using Silver- and Proton-Exchanged Zeolite Catalysts. *J. Jpn. Pet. Inst.* **2008**, *51*, 205−216.

(17) Luzgin, M. V.; Rogov, V. A.; Arzumanov, S. S.; Toktarev, A. V.; Stepanov, A. G.; Parmon, V. N. Understanding Methane Aromatization on a Zn-Modified High-Silica Zeolite. *Angew. Chem., Int. Ed.* **2008**, *47*, 4559−4562.

(18) Luzgin, M. V.; Rogov, V. A.; Arzumanov, S. S.; Toktarev, A. V.; Stepanov, A. G.; Parmon, V. N. Methane Aromatization on Zn-Modified Zeolite in the Presence of a Co-Reactant Higher Alkane: How Does It Occur? *Catal. Today* **2009**, *144*, 265−272.

(19) Luzgin, M. V.; Gabrienko, A. A.; Rogov, V. A.; Toktarev, A. V.; Parmon, V. N.; Stepanov, A. G. The "Alkyl" and "Carbenium" Pathways of Methane Activation on Ga-Modified Zeolite BEA: ¹³C Solid-State NMR and GC-MS Study of Methane Aromatization in the Presence of Higher Alkane. *J. Phys. Chem. C* **2010**, *114*, 21555−21561.

(20) Kolyagin, Y. G.; Ivanova, I. I.; Ordomsky, V. V.; Gedeon, A.; Pirogov, Y. A. Methane Activation over Zn-Modified MFI Zeolite: NMR Evidence for Zn-Methyl Surface Species Formation. *J. Phys. Chem. C* **2008**, *112*, 20065−20069.

(21) Stepanov, A. G.; Arzumanov, S. S.; Gabrienko, A. A.; Parmon, V. N.; Ivanova, I. I.; Freude, D. Significant Influence of Zn on Activation of the C−H Bonds of Small Alkanes by Bronsted Acid Sites of Zeolite. *Chem. Phys. Chem.* **2008**, *9*, 2559−2563.

(22) Stepanov, A. G.; Arzumanov, S. S.; Gabrienko, A. A.; Toktarev, A. V.; Parmon, V. N.; Freude, D. Zn-Promoted Hydrogen Exchange for Methane and Ethane on Zn/H-BEA Zeolite. In situ ¹H MAS NMR Kinetic Study. *J. Catal.* **2008**, *253*, 11−21.

(23) Wu, J. F.; Wang, W. D.; Xu, J.; Deng, F.; Wang, W. Reactivity of C₁ Surface Species Formed in Methane Activation on Zn-Modified H-ZSM-5 Zeolite. *Chem.− Eur. J.* **2010**, *16*, 14016−14025.

(24) Gabrienko, A. A.; Arzumanov, S. S.; Toktarev, A. V.; Freude, D.; Haase, J.; Stepanov, A. G. Hydrogen H/D Exchange and Activation of C₁-n-C₄ Alkanes on Ga-Modified Zeolite BEA Studied with ¹H Magic Angle Spinning Nuclear Magnetic Resonance in situ. *J. Phys. Chem. C* **2011**, *115*, 13877−13886.

(25) Wang, X. M.; Qi, G. D.; Xu, J.; Li, B. J.; Wang, C.; Deng, F. NMR-Spectroscopic Evidence of Intermediate-Dependent Pathways for Acetic Acid Formation from Methane and Carbon Monoxide over a ZnZSM-5 Zeolite Catalyst. *Angew. Chem., Int. Ed.* **2012**, *51*, 3850−3853.

(26) Baba, T.; Sawada, H.; Takahashi, T.; Abe, M. Chemisorption Study of Hydrogen and Methane by ¹H MAS NMR and Conversion of Methane in the Presence of Ethylene on Ag-Y Zeolite. *Appl. Catal., A* **2002**, *231*, 55−63.

(27) Miao, S.; Wang, Y.; Ma, D.; Zhu, Q.; Zhou, S.; Su, L.; Tan, D.; Bao, X. Effect of Ag⁺ Cations on Nonoxidative Activation of Methane to C₂-Hydrocarbons. *J. Phys. Chem. B* **2004**, *108*, 17866−17871.

(28) Ding, B.; Huang, S.; Wang, W. Methane Activation over Ag-Exchanged ZSM-5 Zeolites: A Theoretical Study. *Appl. Surf. Sci.* **2008**, *254*, 4944−4948.

(29) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; J.Wiley & Sons: Chichester, UK, 1987.

(30) Yoshida, H.; Hamajima, T.; Kato, Y.; Shibata, J.; Satsuma, A.; Hattori, T. Active Ag Species in MFI Zeolite for Direct Methane Conversion in the Light and Dark. *Res. Chem. Intermed.* **2003**, *29*, 897−910.

(31) Bordiga, S.; Turnes Palomino, G.; Arduino, D.; Lamberti, C.; Zecchina, A.; Otero Area, C. Well Defined Carbonyl Complexes in Ag⁺- and Cu⁺-Exchanged ZSM-5 Zeolite: A Comparison with Homogeneous Counterparts. *J. Mol. Catal. A: Chem.* **1999**, *146*, 97−106.

(32) Kuroda, Y.; Mori, T.; Sugiyama, H.; Uozumi, Y.; Ikeda, K.; Itadani, A.; Nagao, M. On the Possibility of AgZSM-5 Zeolite Being a

Partial Oxidation Catalyst for Methane. *J. Colloid Interface Sci.* **2009**, *333*, 294−299.

(33) Newth, G. S. *A Text-book of Inorganic Chemistry*; Longmans, Green, and Co.: London, UK, 1920.

(34) Ferguson, D. B.; Haw, J. F. Transient Methods For in situ NMR of Reactions on Solid Catalysts Using Temperature Jumps. *Anal. Chem.* **1995**, *67*, 3342−3348.

(35) Arzumanov, S. S.; Reshetnikov, S. I.; Stepanov, A. G.; Parmon, V. N.; Freude, D. In situ ^{1}H and ^{13}C MAS NMR Kinetic Study of the Mechanism of H/D Exchange for Propane on Zeolite HZSM-5. *J. Phys. Chem. B* **2005**, *109*, 19748−19757.

(36) Stepanov, A. G.; Arzumanov, S. S.; Luzgin, M. V.; Ernst, H.; Freude, D.; Parmon, V. N. In Situ ^{1}H and ^{13}C MAS NMR Study of the Mechanism of H/D Exchange for Deuterated Propane Adsorbed on HZSM-5. *J. Catal.* **2005**, *235*, 221−228.

(37) Bosacek, V. Formation of Surface-Bonded Methoxy Groups in the Sorption of Methanol and Methyl Iodide on Zeolite Studied by ^{13}C MAS NMR Spectroscopy. *J. Phys. Chem.* **1993**, *97*, 10732−10737.

(38) Jiang, Y.; Hunger, M.; Wang, W. On the Reactivity of Surface Methoxy Species in Acidic Zeolites. *J. Am. Chem. Soc.* **2006**, *128*, 11679−11692.

(39) Murray, D. K.; Chang, J. W.; Haw, J. F. Conversion of Methyl Halides to Hydrocarbons on Basic Zeolites. A Discovery by in situ NMR. *J. Am. Chem. Soc.* **1993**, *115*, 4732−4741.

(40) Zhang, H. L.; Zheng, A. M.; Yu, H. G.; Li, S. H.; Lu, X.; Deng, F. Formation, Location, and Photocatalytic Reactivity of Methoxy Species on Keggin 12-$H_3PW_{12}O_{40}$: A Joint Solid-State NMR Spectroscopy and DFT Calculation Study. *J. Phys. Chem. C* **2008**, *112*, 15765−15770.

(41) Luzgin, M. V.; Kazantsev, M. S.; Wang, W.; Stepanov, A. G. Reactivity of Methoxy Species toward CO on Keggin 12-$H_3PW_{12}O_{40}$: A Study with Solid State NMR. *J. Phys. Chem. C* **2009**, *113*, 19639−19644.

(42) Arzumanov, S. S.; Gabrienko, A. A.; Freude, D.; Stepanov, A. G. In situ High Temperature MAS NMR Study of the Mechanisms of Catalysis. Ethane Aromatization on Zn-Modified Zeolite BEA. *Solid State Nucl. Magn. Reson.* **2009**, *35*, 113−119.

(43) Kolyagin, Y. G.; Ivanova, I. I.; Pirogov, Y. A. ^{1}H and ^{13}C MAS NMR Studies of Light Alkanes Activation over MFI Zeolite Modified by Zn Vapour. *Solid State Nucl. Magn. Reson.* **2009**, *35*, 104−112.

(44) Kolyagin, Y. G.; Ordomsky, V. V.; Khimyak, Y. Z.; Rebrov, A. I.; Fajula, F.; Ivanova, I. I. Initial Stages of Propane Activation over Zn/MFI Catalyst Studied by in situ NMR and IR Spectroscopic Techniques. *J. Catal.* **2006**, *238*, 122−133.

(45) Mudrakovskii, I. L.; Mastikhin, V. M.; Bogdanchikova, N. E.; Khasin, A. V. Nature of Ethylene Complexes On the Surface of Ag/SiO$_2$ as Evidenced by ^{13}C NMR Data. *React. Kinet . Catal. Lett.* **1987**, *34*, 185−190.

(46) Plischke, J. K.; Benesi, A. J.; Vannice, M. A. A ^{13}C NMR Study of Ethylene Adsorbed on Reduced and Oxygen-Covered Ag Surfaces. *J. Catal.* **1992**, *138*, 223−239.

(47) Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy, Methods and Applications in Organic Chemistry*; VCH: Weinheim, Germany, 1978.

(48) Derouane, E. G.; Gilson, J.-P.; Nagy, J. B. Adsorption and Conversion of Ethylene on H-ZSM-5 Zeolite Studied by ^{13}C NMR Spectroscopy. *J. Mol. Catal.* **1981**, *10*, 331−340.

(49) van den Berg, J. P.; Wolthuizen, J. P.; Clague, A. D. H.; Hays, G. R.; Huis, R.; van Hoof, J. H. C. Low-Temperature Oligomerization of Small Olefins on Zeolite H-ZSM-5. An Investigation with High-Resolution Solid State ^{13}C NMR. *J. Catal.* **1983**, *80*, 130−138.

(50) Datema, K. P.; Novak, A. K.; van Braam Houckgeest, J.; Wielers, A. F. H. In-situ ^{13}C Magic-Angle-Spinning NMR Measurements of the Conversion of Ethene to Aliphatic Hydrocarbons over Structurally Different Zeolites. *Catal. Lett.* **1991**, *11*, 267−276.

(51) Stepanov, A. G.; Luzgin, M. V.; Romannikov, V. N.; Sidelnikov, V. N.; Paukshtis, E. A. The Nature, Structure, and Composition of Adsorbed Hydrocarbon Products of Ambient Temperature Oligomerization of Ethylene on Acidic zeolite H-ZSM-5. *J. Catal.* **1998**, *178*, 466−477.

(52) Stepanov, A. G.; Zudin, V. N.; Zamaraev, K. I. Two Dimensional J-Resolved ^{13}C Solid-State NMR Analysis of the Products of Ethylene Conversion on Zeolite H-ZSM-5. *Solid State NMR* **1993**, *2*, 89−93.

(53) Chakarova, K.; Drenchev, N.; Hadjiivanov, K. FTIR Evidence of Different Bonding of Methane to OH Groups on H-ZSM-5, HY, and SiO$_2$. *J. Phys. Chem. C* **2012**, *116*, 17101−17109.

(54) Haw, J. F.; Richardson, B. R.; Oshio, I. S.; Lazo, N. D.; Speed, J. A. Reactions of Propene on zeolite HY Catalyst Studied by in situ Variable-Temperature Solid-State Nuclear Magnetic Resonance Spectroscopy. *J. Am. Chem. Soc.* **1989**, *111*, 2052−2058.

(55) Mastikhin, V. M.; Mudrakovskii, I. L.; Pelmenschikov, A. G.; Zamaraev, K. I. Study of Methane Interaction with H-ZSM-5 Zeolites with ^{13}C and ^{1}H NMR. *Khim. Fiz.* **1988**, *7*, 1096−1109.

(56) Schoofs, B.; Martens, J. A.; Jacobs, P. A.; Schoonheydt, R. A. Kinetics of Hydrogen−Deuterium Exchange Reactions of Methane and Deuterated Acid FAU- and MFI-Type Zeolites. *J. Catal.* **1999**, *183*, 355−367.

(57) Kramer, G. J.; Van Santen, R. A. An ab-initio Study of D/H Exchange Between CD$_4$ and the H-Forms of Zeolites FAU and MFI. *J. Am. Chem. Soc.* **1995**, *117*, 1766−1776.

(58) Lee, B.; Kondo, J. N.; Wakabayashi, F.; Domen, K. Infrared Study of H/D Isotope Exchange Reaction of Alkanes and Brønsted Acidic Hydroxyl Groups of FER Zeolite. *Catal. Lett.* **1999**, *59*, 51−54.

(59) Kramer, G. J.; van Santen, R. A.; Emeis, C. A.; Nowak, A. K. Understanding the Acid Behavior of Zeolites from Theory and Experiment. *Nature (London)* **1993**, *363*, 529−531.

(60) Gates, B. C. *Catalytic Chemistry*; Wiley & Sons: New York, NY, 1992.

(61) Blaszkowski, S. R.; Jansen, A. P. J.; Nascimento, M. A. C.; van Santen, R. A. Density Functional Theory Calculations of the Transition States for Hydrogen Exchange and Dehydrogenation of Methane by a Brønsted Zeolitic Proton. *J. Phys. Chem.* **1994**, *98*, 12938−12944.

(62) Blaszkowski, S. R.; Nascimento, M. A. C.; van Santen, R. A. Activation of C−H and C−C Bonds by an Acidic Zeolite: A Density Functional Study. *J. Phys. Chem.* **1996**, *100*, 3463−3472.

(63) Esteves, P. M.; Nascimento, M. A. C.; Mota, C. J. A. Reactivity of Alkanes on Zeolites: A Theoretical ab initio Study of the H/H Exchange. *J. Phys. Chem. B* **1999**, *103*, 10417−10420.

(64) Zheng, X.; Blowers, P. A Computational Study of Alkane Hydrogen-Exchange Reactions on Zeolites. *J. Mol. Catal. A: Chem.* **2005**, *242*, 18−25.

(65) Stepanov, A. G.; Arzumanov, S. S.; Parmon, V. N.; Kolyagin, Y. G.; Ivanova, I. I.; Freude, D. Regioselective H/D Exchange of Propane on Zn/H-MFI Zeolite. *Catal. Lett.* **2007**, *114*, 85−90.

(66) Bergbreiter, D. E.; Lynch, T. J.; Shimazu, S. Nuclear Magnetic Resonance Studies of Methylsilver(I) Complexes. *Organometallics* **1983**, *2*, 1354−1359.

(67) Baba, T.; Komatsu, N.; Sawada, H.; Yamaguchi, Y.; Takahashi, T.; Sugisawa, H.; Ono, Y. ^{1}H Magic Angle Spinning NMR Evidence for Dissociative Adsorption of Hydrogen on Ag$^+$-exchanged A- and Y-zeolites. *Langmuir* **1999**, *15*, 7894−7896.

(68) Lunsford, J. H. The Catalytic Conversion of Methane to Higher Hydrocarbons. *Catal. Today* **1990**, *6*, 235−259.

(69) Bao, X.; Muhler, M.; Schlögl, R.; Ertl, G. Oxidative Coupling of Methane on Silver Catalysts. *Catal. Lett.* **1995**, *32*, 185−194.

(70) Wang, W.; Hunger, M. Reactivity of Surface Alkoxy Species on Acidic Zeolite Catalysts. *Acc. Chem. Res.* **2008**, *41*, 895−904.

(71) Wang, W.; Jiao, J.; Jiang, Y. J.; Ray, S. S.; Hunger, M. Formation and Decomposition of Surface Ethoxy Species on Acidic Zeolite Y. *Chem. Phys. Chem* **2005**, *6*, 1467−1469.

(72) Blümel, J. Reactions of Ethoxysilanes with Silica: A Solid-State NMR Study. *J. Am. Chem. Soc.* **1995**, *117*, 2112−2113.

(73) Haag, W. O. Acid Catalysis with Medium Pore Zeolites; The 6th International Zeolite Conference, 1984, Surrey, UK.

(74) Weisz, P. B. The Remarkable Active Site: Al in SiO$_2$. *Ind. Eng. Chem. Fundam.* **1986**, *25*, 53−58.

(75) Guisnet, M.; Gnep, N. S. Aromatization of short chain alkanes on zeolite catalysts. *Appl. Catal., A* **1992**, *89*, 1−30.

(76) Garwood, W. E. Conversion of C_2–C_{10} to Higher Olefins over Synthetic Zeolite ZSM-5. *ACS Symp. Ser.* **1983**, *218*, 383–396.

(77) Quann, R. J.; Green, L. A.; Tabak, S. A.; Krambeck, F. J. Chemistry of Olefin Oligomerization over ZSM-5 Catalysts. *Ind. Eng. Chem. Res.* **1988**, *27*, 565–570.

(78) Pines, H. *Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: New York, NY, 1981.

(79) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley & Sons: New York, NY, 1973.