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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

Mikhail V. Luzgin, Anton A. Gabrienko, Vladimir A. Rogov, Alexander V. Toktarev, Valentin N. Parmon, and Alexander G. Stepanov*

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia

By using 13C solid-state NMR spectroscopy and GC-MS analysis, the activation of methane and coaromatization of methane and propane have been monitored on gallium-modified zeolite BEA at 573–823 K. A noticeable degree involvement of the 13C-label from methane-13C into the aromatic reaction products (benzene, toluene) has been demonstrated. The major intermediate of the methane activation represents gallium-methyl species, which are formed by methane dissociative adsorption on Ga_2O_3 species of the zeolite. The minor species of methane activation, Ga-methoxy groups, provide the involvement of methane into aromatics by the methylation of aromatic molecules, which are generated exclusively from propane, by the mechanism of electrophilic substitution. Ga-methyl species can serve as methylating nucleophilic agent for the reaction of nucleophilic substitution with participation of aromatic molecules, which contain the electron-withdrawing substitutes.

Introduction

Conversion of small alkanes catalyzed by bifunctional zeolites modified with gallium represents a very significant object from both industrial and fundamental aspects. Of essential commercial importance is the transformation of natural saturated hydrocarbons to aromatic compounds (Cyclar process[1]), which are valuable chemicals themselves, and they represent also the raw materials for further organic syntheses.

Two concepts of high aromatization performance of such catalysts are usually considered. According to the first concept, high activity and selectivity of Ga-modified zeolites to aromatic products in comparison with unpromoted catalysts are due to the strong hydrogen back-spillover effects of gallium additive. Ga species increase the rate of recombinative hydrogen desorption and deplete the surface hydrogen pool available for the hydrogenation, which is reverse to the initial stage of the reaction, thus favoring the aromatization.[2–7] Another concept of high aromatization activity of Ga-modified zeolites considers metal species to be the centers of both alkane activation by dissociative adsorption and alkane dehydrogenation.[8–12] The nature of the intermediates (alkoxy or Ga-alkyl groups), which could be initially formed on interaction of alkane with Ga species on the zeolite surface, is still under debate.[13–15] So, the mechanism of the activation of very stable C–H bonds and the nature of surface species formed under alkane activation on Ga-modified zeolites are of great academic interest.[2–7,12,13,15–24]

Among all small alkanes, special attention is focused on methane, the most abundant but the least reactive and the most underused hydrocarbon for the purposes of the chemical industry. Direct aromatization of neat methane is unfavorable from the standpoint of thermodynamics.[25–27] No wonder therefore that for the last decades essential efforts have been focused on the joint conversion of methane with higher hydrocarbons (alkanes or olefins) to aromatic products. Such methane-involved

aromatization could overcome the thermodynamic limitations associated with the conversion of neat methane.[25–27] Several results for coaromatization of methane with light hydrocarbons have been reported for Ga- and Zn-modified zeolites.[25,27–35] The achieved conversion of methane was 20–40%.

Since the first publication devoted to the coaromatization of methane with higher hydrocarbons, the hypothesis on the "carbenium" pathway of methane activation on Ga(or Zn-)-modified zeolites has been commonly supposed. It assumes the formation of methyl cation stabilized by the surface of zeolite.[25,33–35] In the case of Zn-modified high-silica zeolites BEA, this hypothesis has been confirmed by the direct observation of zinc-methoxy species (as stabilized methyl cation), resulting from the dissociative adsorption of methane on ZnO species located in the intracrystalline void of zeolite.[36,37]

In the case of zeolites modified with Ga only indirect evidence for dissociative adsorption of methane has been reported,[38] the nature of intermediates formed from methane on metal-containing active center being unclear. The lack of any experimental results, which could throw some light on the mechanism of the initial activation of methane on zeolites modified with gallium, has promoted theoretical studies of the dissociative adsorption of methane on Ga-loaded zeolites.[39,40] Two alternative pathways of methane activation have been considered in dependence on the direction of C–H bond polarization by [Ga=O]$^+$ species. "Alkyl" pathway presumes $C^{\delta-}–H^{\delta+}$ polarization and alkyl abstraction by Ga with the formation of methyl-gallium species, Ga-CH$_3$. The alternative "carbenium" mechanism of methane activation implies $C^{\delta+}–H^{\delta-}$ polarization and hydride abstraction by gallium to form the methoxy group, Ga-O-CH$_3$. Theoretical calculations indicated that the "alkyl" pathway was energetically more favorable.[39] Also, based on the quantum-chemical calculations, a similar conclusion on the pathway of methane activation has been made for Ag$^+$-exchanged zeolites.[41]

* To whom correspondence should be addressed. Phone: +7 383 326 9437. Fax: +7 383 330 8056. E-mail: stepanov@catalysis.ru.

In the present paper we provide the direct spectroscopic evidence that Ga-methyl species represent the prevailing intermediates formed under the methane activation on Ga-modified zeolite BEA. Methoxy groups Ga-O-CH₃ are generated as minor species; however, they are responsible for involving methane in coaromatization with propane on this catalyst.

Experimental Methods

The initial acidic form of zeolite β (H-BEA) was synthesized by the procedure described in ref 42 using tetraethylammonium hydroxide as a template. Ga-modified zeolite β sample (Ga/H-BEA) was prepared by incipient wetness impregnation of the parent sample of zeolite H-BEA with an aqueous solution of gallium nitrate, subsequent drying at 473 K for 14 h, and further calcination at 673 K for 4 h in a flow of air. The Ga content in the final Ga/H-BEA zeolite was 1.26 wt %, and the Si/Al ratio was 18. Detailed characterization of the zeolite is presented in ref 43.

Methane ($\geq$99.0% purity), methane-^{13}C ($^{13}CH_4$, 90% ^{13}C), propane ($\geq$98% purity), propane-1-^{13}C (99% ^{13}C), toluene-α-^{13}C (99% ^{13}C), benzene (of $\geq$99.0% purity), and chlorobenzene (of $\geq$99.0% purity) were purchased from Aldrich Chemical Co. Inc. and were used without further purification.

The activation of methane as well as the reaction of methane and propane coaromatization on Ga/H-BEA zeolite were studied in a glass closed batch microreactor of 0.05 cm³ (axially high symmetrical sealed glass tube of 3 mm outer diameter and 10 mm length with coadsorbed on zeolite methane and propane (1:1)) at 573−823 K. The sample of Ga/H-BEA zeolite (ca. 25 mg) in a glass tube was activated at 673 K for 20 h under vacuum with the residual pressure less than 10^{-2} Pa. A 75 μmol of each alkane (or methane alone) was coadsorbed on the zeolite sample under vacuum at the temperature of liquid nitrogen and then sealed. After the reaction performance at 523−823 K, the reactor was cooled to room temperature and transferred to a 4 mm zirconia rotor for the ^{13}C MAS NMR analysis. After NMR analysis the sealed reactor was opened, reaction products were extracted with diethyl ether, and GC-MS analysis was performed.

NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer at room temperature. ^{13}C MAS NMR spectra with the high power proton decoupling were recorded with cross-polarization (CP) denoted below as ^{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 4 ms at the Hartmann−Hahn matching condition of 50 kHz, and the delay time between scans was 3 s. A few thousand scans were collected for each ^{13}C NMR spectrum. The spinning rate was 5−8 kHz. ^{13}C chemical shifts of adsorbed organic species were measured with respect to TMS as an external reference with accuracy ±0.5 ppm.

The GS-MC analysis of the products extracted with diethyl ether from the catalyst after the reactions was performed on a Varian CP-3800 gas chromatograph. For the product separation a PLOT fused silica capillary column with the length of 30 m and the inner diameter of 0.32 mm was used. The column was filled with CP-PoraPLOT Q-HT as a stationary phase. The temperature program started at 313 K with the heating rate of 10 deg min^{-1}. The detector was a mass-spectrometer Varian Saturn-2000, which scanned from m/z 10 to 650 with a cycle time of 0.5 s.

Results and Discussion

Activation of Methane on Ga/H-BEA Zeolite. Figure 1 shows ^{13}C CP/MAS NMR spectra of the products of methane
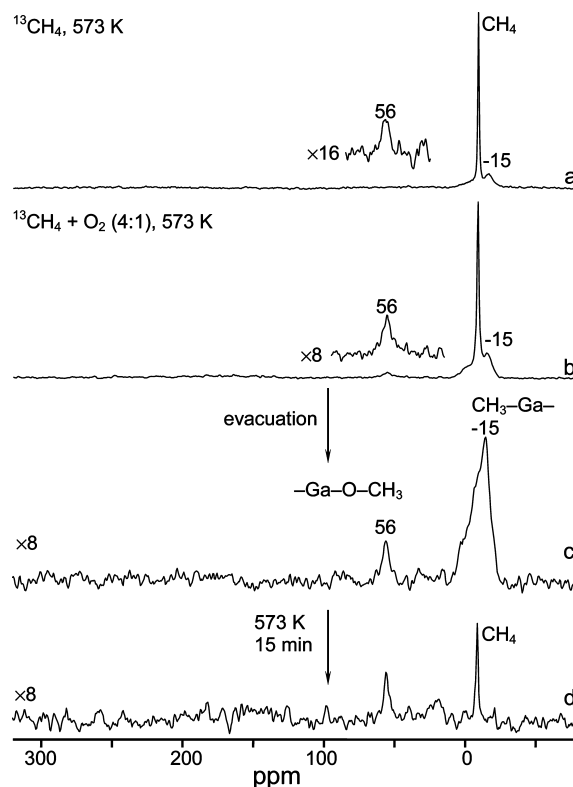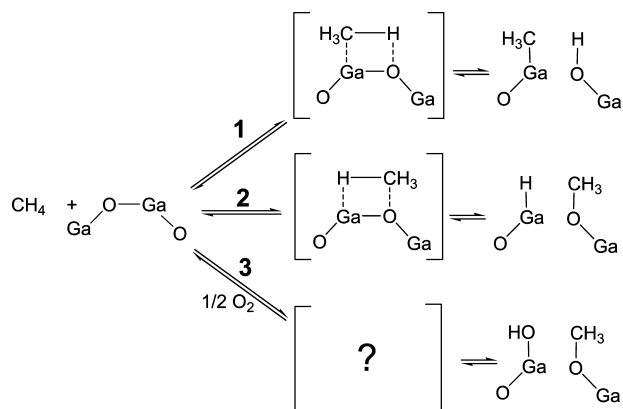

Figure 1. ^{13}C CP/MAS NMR spectra of the products of the methane-^{13}C conversion on zeolite Ga/H-BEA: (a) at 573 K; (b) at 573 K in the presence of O_2 (CH₄:O_2 (mol) = 4:1); (c) after evacuation of sample in b at room temperature; and (d) after heating of sample c at 573 K.

activation on Ga/H-BEA in the absence and the presence of molecular oxygen at 573 K. In the absence of O_2, the signal at −15 ppm is clearly visible in the spectrum in addition to the signal from unreacted methane at −8.3 ppm (Figure 1a). Since for unpromoted zeolite H-BEA no conversion of methane is detected under the same conditions, gallium, which exists in Ga/H-BEA as the highly dispersed Ga_2O_3 species,[43] is responsible for the observed resonance at −15 ppm. The negative chemical shift of this signal is indicative of a partial negative charge at the carbon atom. This testifies for the formation of a metal-methyl bond. For the methyl group attached to gallium in organometallic compounds, Ga-CH₃, the chemical shift of 0−10 ppm is typical.[44,45] Therefore, we attribute the broad signal centered at −15 ppm to gallium-methyl species, formed at dissociative adsorption of methane on gallium oxide species[46] (Scheme 1, pathway 1).

Ga-CH₃ groups proved to be the main species that have been detected on the surface of Ga/H-BEA by ^{13}C solid-state NMR after activation in a wide range of temperatures from 573 to 823 K. However, the 16-fold enhancement of the spectrum of Figure 1a allows one to detect one more signal of weak intensity at 56 ppm. Such a chemical shift is typical for the methyl group bound to the oxygen atom in methoxides on the surface of solid acid catalysts such as zeolites[47−49] or heteropolyacids.[50,51] Therefore, this signal belongs to the methoxy group attached to the gallium atom, Ga-O-CH₃. The addition of a small fraction of molecular oxygen (CH₄:O_2 = 4:1) results in enhancement of the intensity of the signal at 56 ppm. This may indicate that gallium methoxide can be formed by two pathways, dissociative adsorption of methane on the Ga−O bond of gallium(III) oxide or/and partial oxidation of methane on the gallium oxide species (see Scheme 1, pathways 2 and 3).

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SCHEME 1: Different Pathways of the Methane Activation on Ga/H-BEA Zeolite According to the ^{13}C Solid-State NMR Data

Figure 2. ^{13}C CP/MAS NMR spectra of products formed from methane and propane on zeolite Ga/H-BEA at 823 K for 15 min: (a) from CH_4 and C_3H_8 and (b) from $^{13}CH_4$ and C_3H_8. Unreacted methane was removed from the sample by evacuation to provide more detailed observation of the signals from the reaction products. For the correct comparison of the spectra the identical conditions (CP parameters, rotation speeds, and number of scans) were used. Asterisks (∗) denote the spinning side bands.

On the basis of the relative intensities of the signals from gallium-methyl and gallium-methoxy species we can conclude that the activation of methane on Ga-modified zeolite H-BEA proceeds predominantly via "alkyl" pathway with the formation of the gallium-methyl species. Nevertheless, the alternative "carbenium" mechanism of initial methane conversion, which gives rise to Ga-methoxide, is also realized, although to a lesser extent (Scheme 1). This is in a good accordance with theoretical calculations of the relative stabilities of gallium-methyl and gallium-methoxy species.[39] In the presence of molecular oxygen the "carbenium" pathway of methane activation occurs to a larger extent.

Ga-Me and Ga-O-Me intermediate species, if formed, proved to be persistent species even in the absence of atmosphere of initial methane. Indeed, when we removed methane from the sample by evacuation at room temperature, the signals at −15 and 56 ppm do not disappear (Figure 1c). Heating of the sample containing only the intermediates of the methane activation results in complete disappearance of the Ga-methyl species, whereas methoxy groups remain on the surface of the catalyst (Figure 1d). At the same time, the signal at −8.6 ppm from methane appears in the spectrum (Figure 1d) in place of gallium-methyls. Thus, at 573 K in the absence of methane atmosphere Ga-methyl species decompose producing methane in accordance with the reversible process of their formation−destruction as shown in Scheme 1 (pathway 1). The intensity of the signal from methane is smaller than that of Ga-CH₃ species from which methane was formed (cf. Figure 1, spectra d and c). This is due to the peculiarities of the spectra registration with cross-polarization, which enhances the resonances from more rigid species, adsorbed or bound to the surface, in contrast to that from mobile molecules, e.g., weakly adsorbed or gaseous methane.

The role of different surface species, formed on Ga/H-BEA zeolite from methane, will be further discussed for the target reaction of the methane and higher alkane coaromatization.

Coconversion of Methane and Propane. In a contradiction to the first report on the successful coaromatization of methane with higher alkane or alkene on Ga-modified zeolite,[25] the successive isotope-tracer experiments with the use of mass-spectrometry analysis did not confirm the fact of embedding methane into aromatic products at the joint conversion of methane and higher hydrocarbon on Ga-modified zeolite.[52] In this paper we have found that the involvement of methane into the process of coaromatization with higher alkane (propane) does occur on zeolite Ga/H-BEA.
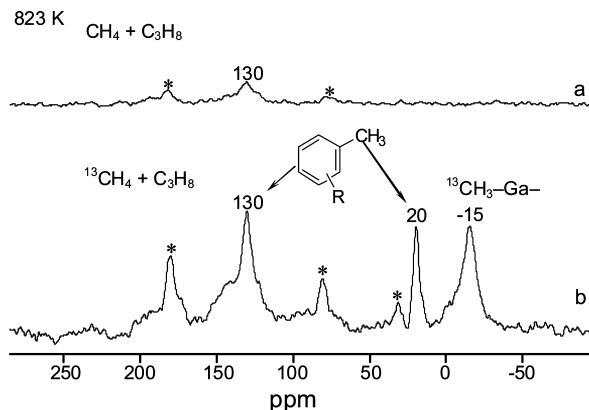
Figure 2 shows ^{13}C CP/MAS NMR spectra of the products formed from methane and propane on zeolite Ga/H-BEA at 823 K. When unlabeled CH_4 and propane were used for the reaction, the weak signal at 130 ppm appeared in the spectrum (Figure 2a). It belongs to carbon atoms of the aromatic ring[53] in the products formed in the reaction. However, it is not clear from this spectrum whether the aromatics formed from methane or propane. When unlabeled CH_4 was replaced with methane enriched with ^{13}C, $^{13}CH_4$ (99% ^{13}C), the signal at 130 ppm from aromatic rings increased notably (cf. Figure 2a,b). At the same time two new signals appeared in the spectrum at −15 ppm from Ga-methyl species and at 20 ppm. The latter resonance is assigned to the methyl groups attached to the aromatic ring.[53]

So, a considerable enrichment with ^{13}C-carbon atoms of the aromatic products, formed during coaromatization of methane-^{13}C and propane on Ga/H-BEA catalyst, is observed. $^{13}CH_4$ is converted into both the aromatic carbons and the methyl groups bound to the aromatic ring. Thus, methane is indeed involved in the aromatization process during its coconversion with propane on Ga/H-BEA zeolite at 823 K.

To clarify the composition of the products formed at methane and propane coconversion on Ga/H-BEA, as well as to estimate the degree of the methane involvement into the aromatization process, the extracted products were analyzed by gas chromatography with mass-spectrometric detection (GC-MS). The GC-MS analysis revealed that benzene and toluene are formed as the main products of methane and propane coconversion on Ga/H-BEA. Figure 3 shows the quantitative estimation of methane-originated ^{13}C-isotope content in aromatic molecules, based on the comparison of the mass spectra of the products formed in the presence of $^{13}CH_4$ with those of aromatic molecules (benzene and toluene) with natural abundance of ^{13}C isotope. According to these data, ca. 7% of benzene and 12% of toluene contain one ^{13}C-carbon atom per molecule, which originates from methane. The portion of the double-^{13}C-labeled molecules ($^{13}C_2$) is 3−3.5% for both aromatic products (Figure 3). On the basis of these data, we have estimated the average content of ^{13}C-carbons of methane-^{13}C in aromatic products. About 2.2 mol % of carbon atoms of benzene and 2.7 mol % of carbon atoms of toluene originate from $^{13}CH_4$. Thus, the fact that the methane is involved in the process of aromatization with higher alkane on Ga/H-BEA zeolite is confirmed by two independent methods, ^{13}C NMR and GC-MS.
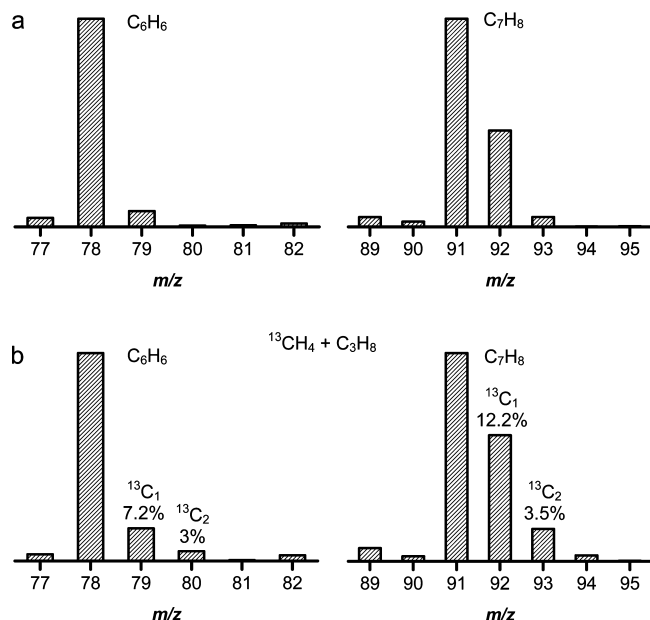
Figure 3. Mass spectra of benzene and toluene: (a) with the natural abundance of ^{13}C and (b) formed from ^{13}C-labeled methane and propane at 823 K (15 min) on zeolite Ga/H-BEA, with the estimated isotopic composition (mol %).

It should be noted that observable conversion of methane into aromatic molecules is detected only at $T \geq 823$ K. The complete aromatization of neat propane on this catalyst occurs already at 723 K (spectrum not shown) and gives rise to the mixture of benzene, toluene, and methane. The sample, containing $^{13}CH_4$ and C_3H_8 and preheated at 723 K, gives similar spectrum after the reaction at 823 K as that shown in Figure 2b, i.e. as the sample heated immediately at 823 K. Thus, the embedding of methane-^{13}C to aromatics at 823 K presumably occurs by the reaction of methane-^{13}C with aromatic molecules, formed from propane already at 723 K. Probably this embedding occurs by methylation of the products of propane aromatization with the methane molecule:
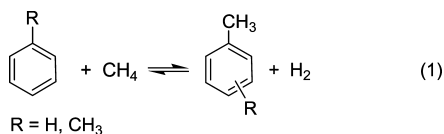
This supposition finds confirmation by the ^{13}C-isotopic distribution in aromatic molecules formed from $^{13}CH_4$ and C_3H_8 (Figure 3), which is characterized by the evident domination of the single-$^{13}C_1$-labeled toluene molecules over the other products enriched with ^{13}C. This could be the result of the methane primary conversion into methyl groups adjacent to aromatic rings according to the scheme of methylation mentioned above.

In principle, both gallium-methyl and gallium-methoxy species can serve as intermediates of the methylation stage. Let us consider these alternatives.

What Is the Key Intermediate of Methane Embedding to Aromatics: Ga-CH$_3$ or Ga-O-CH$_3$ Species? To clarify the role of the observed intermediates, Ga-CH$_3$ and Ga-O-CH$_3$ species, in methane embedding to aromatics, the conversion of Ga-methyl and gallium-methoxy species in the presence of benzene has been studied. For this purpose the samples analogous to that of spectra a and b in Figure 1 were evacuated and benzene
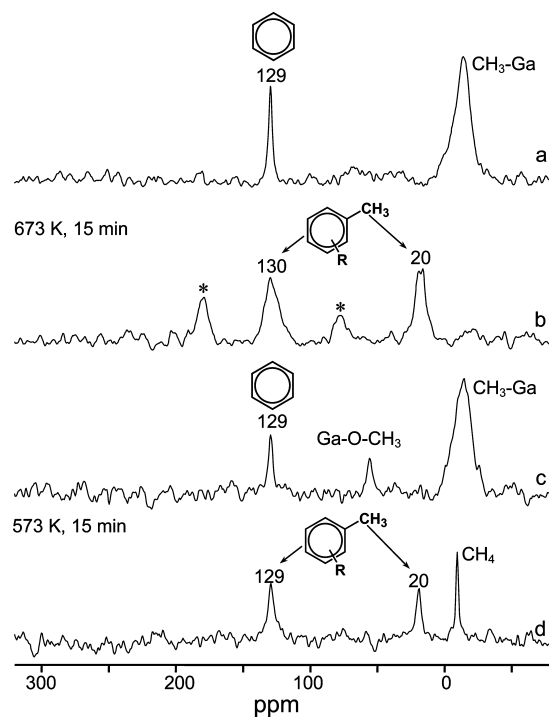

Figure 4. ^{13}C CP/MAS NMR monitoring the reactivity of gallium-methyl and gallium-methoxy species toward benzene on zeolite Ga/H-BEA: (a) the spectrum of $^{13}CH_4$-originated gallium-methyl group, formed in the absence of oxygen additive, with coadsorbed benzene; (b) after heating of a sample at 673 K for 15 min; (c) the spectrum of $^{13}CH_4$-originated gallium-methyl and gallium-methoxy groups, generated in the presence of oxygen additive, with coadsorbed benzene; and (d) after heating of sample c at 573 K for 15 min. Asterisks (∗) denote the spinning side bands.

with the natural abundance of ^{13}C isotope was adsorbed on both samples. This allowed one to generate the surface gallium-methyl and gallium-methoxy groups species (Figure 4a,c) in the absence of methane. Note that a weak signal from Ga-O-CH$_3$ species observed in Figure 1a is not visible in Figure 4a, that is after evacuation of unreacted methane and benzene adsorption. This may be rationalized by the relative stabilities of different surface intermediates. Indeed, as we already noted the theoretical calculations showed that the "alkyl" pathway of methane activation with the formation of Ga-CH$_3$ species was energetically more favorable.[39] So, in the absence of the additive of molecular oxygen, Ga-O-CH$_3$ species presumably form in a concentration that is either hardly detectable (Figure 1a) or not detectable by NMR at all (Figure 4a). In the presence of oxygen, the signal from Ga-O-CH$_3$ becomes of notable intensity (Figure 4c).

Heating at 673 K of the sample in which only the signals from Ga-CH$_3$ species and benzene are detectable (Figure 4a) results in a complete disappearance of the signal from gallium-methyl groups at −15 ppm. Simultaneously, a new signal appears at 20 ppm from the methyl groups attached to the aromatic ring (Figure 4b). In addition, the signal at 130 ppm, which belonged initially to unlabeled benzene (Figure 4a), increased in intensity that was expressed in its broadening and an appearance of spinning side bands (cf. Figure 4b,a). At first glance, in the absence of detectable gallium-methoxy groups, the interaction of Ga-methyl species with benzene occurs and Ga-CH$_3$ groups are converted into carbon atoms of aromatic compounds, both methyl groups and aromatic carbons. So, one could conclude from the observed evolution of NMR spectra in Figure 4a,b, that the reaction between Ga-methyl species and

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SCHEME 2: Mechanism of the Carbon Atom Transfer from Methane-^{13}C into Aromatic Products of the Methane and Propane Co-Aromatization on Zeolite Ga/H-BEA[a]
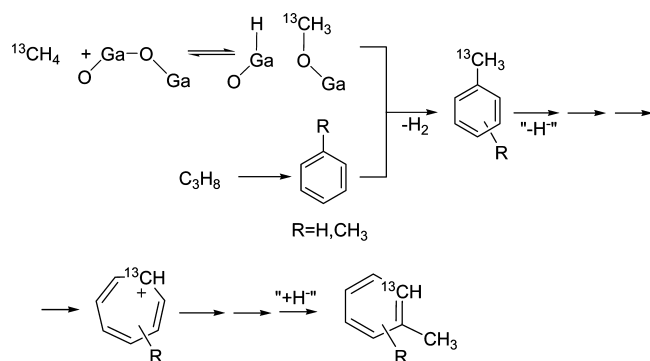
[a] The details of the aromatic ring expansion/contraction mechanism are presented elsewhere.[36,37]

Figure 5. ^{13}C CP/MAS NMR spectra recorded for zeolite Ga/H-BEA: (a) after coadsorption of ^{13}CH$_4$ and benzene; (b) followed by reaction at 673 K; (c) after coadsorption of ^{13}CH$_4$ and chlorobenzene; and (d) followed by reaction at 623 K. Asterisks (∗) denote the spinning side bands.

propane-originated aromatic molecules represents the main pathway of the methane-to-aromatics conversion. However, one should take into account that already at 573 K Ga-methyl species are converted completely back to methane, if the excess of unreacted CH$_4$ has been removed by the evacuation at room temperature (Figures 1d and 4d), while the signal from Ga-O-CH$_3$ at 56 ppm is transformed to the signal at 20 ppm from the methyl group of methyl-substituted aromatics (Figure 4d). Moreover, methyl group of Ga-CH$_3$ species bears a partial negative charge and, thus, can act only as a nucleophilic agent. For the reaction of nucleophilic substitution in aromatic ring, a good leaving group, such as a halide, is usually required at the aromatic ring. This group is substituted by a nucleophile in the course of reaction. So, for benzene and alkylbenzenes, the reaction of nucleophilic substitution cannot be realized and is not mentioned at all in the classical textbooks.[54,55] It also should be emphasized that a notable amount of Ga-methyl groups persists on the surface of the catalysts after the reaction of coaromatization at 823 K (vide supra, Figure 2b).

On the basis of the observed transformation of Ga-O-CH$_3$ species in the presence of benzene to the methyl groups bound to the aromatic ring (Figure 4b,d), we conclude that the methylation of aromatic compounds formed from propane by methane-originated methoxy species represents the key stage of the involvement of methane into the coaromatization process (Scheme 2). This reaction represents the electrophilic aromatic substitution, which is typical for benzene and its alkyl derivatives.[54,55] In the absence of molecular oxygen, the concentration of gallium-methoxy species, formed by the dissociative adsorption of methane on gallium oxide species according to pathway 2 of Scheme 1, seems to be insufficient for their reliable observation by solid-state NMR. In the absence of gaseous methane above the sample and when the methylating Ga-O-CH$_3$ species are not detected by NMR, they seem to be formed from Ga-CH$_3$ species: Ga-methyl groups decompose back to methane in accordance with the observed reversibility of the process of their formation by Scheme 1, then the formation of Ga-O-CH$_3$ from methane occurs. The driving force of this process is the presence of aromatic molecules, which can readily trap the Ga-methoxy group by the methylation reaction, thus shifting the equilibrium Ga-CH$_3$ ↔ CH$_4$ ↔ Ga-O-CH$_3$ toward the Ga-methoxy species.

The addition of O$_2$ to the system allows one to enhance the concentration of Ga-O-CH$_3$ intermediates and to reduce temperature of their formation by opening a new channel of
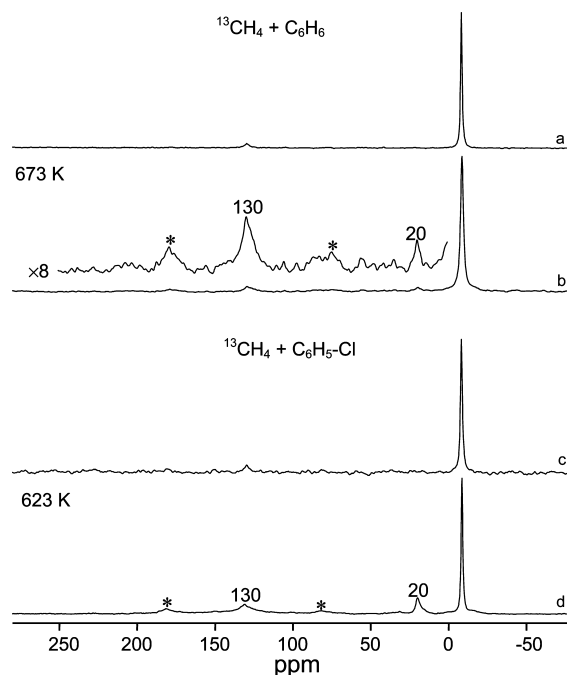
the methane activation on Ga$_2$O$_3$ species via the partial oxidation pathway (Scheme 1, pathway 3). Ga-methyl species seem to represent the dead-end pathway of the methane activation with respect to the reaction of methane and propane coaromatization, but they provide the formation of Ga-O-CH$_3$ as the methylating agent by Scheme 1.

On Zn/H-BEA zeolite ca. 6−18% enrichment with ^{13}C was achieved in the aromatic molecules formed at coaromatization of methane-^{13}C and propane.[36,37] The lower extent of ^{13}C-atoms from methane in the aromatic products formed on Ga/H-BEA (2.2−2.7% under the same reaction conditions) can be explained by the lower ability of the Ga-modified zeolite to generate surface methoxy groups from methane, which are required for methylation of the aromatic compounds formed from propane. Indeed, on Zn/H-BEA zeolite Zn-O-CH$_3$ are easily formed from methane already at 523 K.[36,37] Further studies are needed to rationalize the different behavior of Zn- and Ga-loaded zeolites concerning the methane activation.

Gallium-Methyl Species Can Serve As Nucleophilic Agent for the Reaction of Nucleophilic Substitution in the Aromatic Ring. In spite of the fact that gallium-methyl species are unlikely to participate in methane−propane coaromatization, they could serve as a nucleophilic agent for the reaction of nucleophilic substitution. To check this hypothesis, we have tested the reactivity of methane toward chlorobenzene in comparison with that for unsubstituted benzene (Figure 5).

In the case of benzene, the observable conversion of methane into aromatic carbons, both of the methyl group (20 ppm) and of the aromatic ring (130 ppm), is detected at 673 K. In the case of chlorobenzene the methane-to-aromatic carbon atom conversion occurs already at 623 K, and in a considerably more pronounced extent (cf. Figure 5b,d). This can be rationalized in terms of two factors: (i) different ability of Ga/H-BEA to generate intermediates of different nature, Ga-Me or Ga-O-Me species, from methane, and (ii) the change of the mechanism,
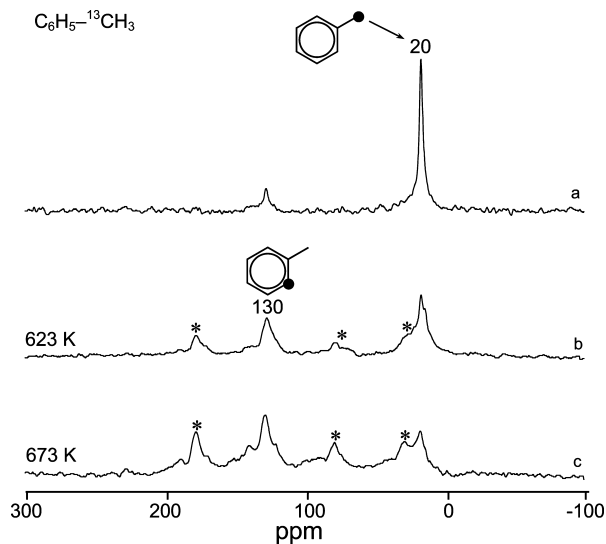
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Figure 6. ^{13}C CP MAS NMR monitoring of the ^{13}C-label scrambling in toluene adsorbed on zeolite Ga/H-BEA: (a) initial C_6H_5-[13]CH_3; (b) after heating sample a at 623 K for 15 min; and (c) after heating sample b at 673 K for 15 min.

by which methane alkylates the aromatic molecule. For chlorobenzene the alkylation by Ga-methyl groups, which can be relatively easily produced from methane, can proceed via nucleophilic substitution of chloride anion in the aromatic ring. For benzene, nucleophilic substitution cannot be realized,[54,55] whereas the reaction of electrophilic substitution demands gallium-methoxy groups, which represents the minor species of the methane activation on Ga/H-BEA zeolite. These factors cause the need to increase the temperature of the reaction for benzene in comparison with chlorobenzene.

These results demonstrate the ability of Ga-CH_3 species to perform the reaction of nucleophilic substitution, which can open up new possibilities of using Ga-loaded zeolites for methane utilization via this type of reaction.

[13]C-Label Transfer from the Methyl Group into the Aromatic Ring: The Intramolecular Scrambling of the Carbon Atom in Methylbenzene. The alkylation reaction 1 provides understanding of the pathway by which methane is converted into the methyl group of the methyl-substituted aromatic molecule. At the same time, according to the present results ^{13}C-carbon atoms of [13]CH_4 are transferred into the aromatic rings of benzene and toluene as well (signal at 130 ppm in Figures 2b and 4b). The transfer of methane carbon atoms to the aromatic ring could proceed via the intramolecular scrambling of ^{13}C label from the methyl group via the ring expansion/contraction mechanism,[56] as occurred in the case of Zn/H-BEA zeolite.[37] To verify this hypothesis, the conversion of toluene, selectively enriched with ^{13}C in the methyl group, C_6H_5-[13]CH_3, on Ga/H-BEA has been further studied (Figure 6). Heating the sample at 623−673 K gives rise to a gradual decrease of the signal at 20 ppm from the [13]CH_3 group of toluene accompanied by simultaneous growth of the signal at 130 ppm from the aromatic moiety (Figure 6b,c). This observation evidently indicates that the intramolecular scrambling of carbon atoms in methylbenzenes takes place on Ga/H-BEA zeolite and it can be responsible for embedding carbon atoms of methane into the aromatic ring during its coaromatization with propane (Scheme 2). The process of toluene demethylation, which is reverse to reaction 1, produces benzene molecules containing ^{13}C-carbons of the initial [13]CH_4.

Conclusions

On the basis of the data of ^{13}C solid-state NMR spectroscopy and GC-MS spectrometry, the following conclusions can be drawn on the methane activation and methane coaromatization with higher alkane on Ga-modified zeolite BEA:

Activation of methane occurs by dissociative adsorption of the alkane on Ga_2O_3 species of the zeolite via the "alkyl" pathway to give rise to gallium-methyl species and via "carbenium" mechanism to offer gallium-methoxy species. Galliummethyls are the major species, while gallium-methoxy groups represent the minor species of the methane activation. The addition of molecular oxygen favors the generation of galliummethoxy species by the reaction of partial oxidation.

A noticeable degree of involvement of methane into the reaction products is observed for methane and propane coaromatization on Ga/HBEA at 823 K. About 2.2−2.7 mol % of carbon atoms of benzene and toluene, both in the aromatic ring and in the methyl groups attached to aromatic ring, originate from [13]CH_4. The main pathway of methane-to-aromatics conversion is the alkylation of aromatic molecules, produced from propane, by the methane molecule. Being the minor species of the methane activation, gallium-methoxy intermediate provides embedding of methane to aromatic products by the mechanism of electrophilic substitution in the aromatic ring. Being initially converted to the methyl groups, ^{13}C-carbons of methane are subsequently incorporated into aromatic rings through the intramolecular scrambling of carbon atoms in the methylbenzenes via the ring expansion/contraction mechanism.

Gallium-methyl species can perform the reaction of nucleophilic substitution in the aromatic ring, thus providing the alternative pathway for methane conversion.

Note Added after ASAP Publication. This manuscript was published on the Web on November 11, 2010, with an error to the Experimental Methods section. The corrected version was reposted on November 16, 2010.

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