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Methane aromatization on Zn-modified zeolite in the presence of a co-reactant higher alkane: How does it occur?

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ABSTRACT

By using ^{13}C solid-state NMR and GC–MS, the analysis of the ^{13}C-label transfer from methane-^{13}C into the products of methane and propane co-aromatization on Zn/H-BEA zeolite at 823–873 K has been performed. A high degree involvement of ^{13}C-carbon atoms of methane into aromatic products (benzene, toluene, xylenes) has been demonstrated. The main pathway of methane conversion into aromatics has been determined to consist in the methylation of aromatics, which is produced exclusively from propane, by methane. The methoxy species formed by the dissociative adsorption of methane on ZnO species of the zeolite is responsible for the methylation.

1. Introduction

Methane is the most abundant among naturally available hydrocarbons. Simultaneously it is the least reactive among alkanes. For this reason the methane conversion into more valuable chemicals is much more difficult to perform than the other saturated hydrocarbons. Commonly accepted methods of methane utilization are indirect and include usually an intermediate stage of syngas, $CO + H_2$, production which requires a consumption of either huge amounts of energy or expensive pure dioxygen [1].

Over last decades, there were numerous attempts to develop alternative methods for the conversion of methane into higher hydrocarbons, the special attention being focused on the search for direct non-oxidative processes of methane aromatization. Due to thermodynamic limitations, direct conversion of neat methane into aromatic compounds with a considerable yield can be expected only at extremely high ($>$1000 K) temperatures [2]. Various Mo- or Re-modified zeolites have been reported to catalyze aromatization of neat methane [3–5] with the conversion no higher than 10%.

From the standpoint of thermodynamics, a transformation of methane in the presence of co-reactants should be more preferable since it could proceed at much lower temperatures [2,6,7]. Co-aromatization of methane and light hydrocarbons, paraffins or olefins, at 700–800 K is among such promising processes. The experiments on co-aromatization of methane with propane, propene and butene were first provided for Ga-modified zeolite H-ZSM-5 [6]. Other examples of such co-conversion of methane and higher alkanes have been offered for zeolite catalysts modified with Zn: for Zn/H-ZSM-11 in the presence of ethane [8,9] and light gasoline (C_5–C_6) [10–12]; for Mo–Zn/H-ZSM-5 in the presence of propane or isobutane [2]; for Mo–Zn/H-ZSM-5, Cu–Zn/HZSM-5, and La–Zn/HZSM-5 in the presence of propane [13–15]. The reported conversion of methane during such co-aromatization reached 20–40 wt.%.

The appropriate preceding isotope tracing experiments with the use of methane-^{13}C did not confirm the embedding of methane ^{13}C-carbon atoms into the aromatic products on metal-promoted high-silica zeolite [16]. A lack of reliable confirmation with isotopically labeled molecules of methane and higher hydrocarbon co-conversion, as well as the absence of reliably justified mechanism, rationalizing a transfer of ^{13}C-label from methane into the reaction products, caused the essential doubts as to whether methane-involved co-aromatization occurred at all [16].

In this paper we present a careful analysis of a transfer of isotopically ^{13}C-labeled carbon from methane into the reaction products, aromatic hydrocarbons, at co-conversion of methane and propane on Zn-modified high-silica zeolite BEA. Combined monitoring of this reaction with solid-state NMR and GC–MS

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[17] enable us to demonstrate a high degree involvement of ^{13}C-labeled methane into aromatic hydrocarbons. We have identified the intermediate formed under methane activation and determined the main pathway of methane to aromatics conversion.

2. Experimental

2.1. Materials characterization and samples preparation

The initial acidic form of zeolite beta (H-BEA) was synthesized by the procedure described in ref. [18] using tetra-ethylammonium hydroxide as a template with the subsequent calcination at 823 K in the air flow for 6 h. Zinc-modified zeolite beta (Zn/H-BEA) was prepared by the impregnation of a H-BEA sample with the saturated solution of zinc formate, its subsequent drying at 473 K for 14 h and calcination at 673 K for 4 h in the flow air. The Zn content in the final Zn/H-BEA zeolite was 7.7 wt.%. The materials were characterized with ^{1}H, ^{27}Al, ^{29}Si MAS NMR, as well as with XRD, UV–vis and IR diffuse reflectance spectroscopy. Si/Al = 15 ratio in the zeolite was estimated on the basis of chemical analysis and confirmed by the ^{29}Si MAS NMR spectrum analysis.

As to the state of the zinc atoms in Zn/H-BEA, the XRD analysis revealed the presence of a “bulk” ZnO phase. The UV–vis diffuse reflectance spectrum of the Zn/H-BEA sample has shown a band at 265 nm from sub-nanometric ZnO clusters and a band at 370 nm from macrocrystalline particles of ZnO on the extra surface of the zeolite [19]. More detailed characteristics of the used zeolite are provided elsewhere [20].

Methane (≥99.0% purity), methane-^{13}C, ^{13}CH$_4$ (90% ^{13}C), propane (≥98% purity), propane-1-^{13}C (99% ^{13}C), toluene-α-^{13}C (99% ^{13}C) and benzene (≥99.0% purity) were purchased from Aldrich Chemical Company Inc. and used without further purification. The reaction was carried out in a sealed glass tube of 5.5 mm outer diameter and 10 mm length, which could be tightly inserted into the 7 mm o.d. zirconia rotor for subsequent in situ NMR analysis of the reaction products. The samples (80–100 mg) were activated first in air by the increase of temperature from 300 to 673 K with the rate of 1 K min^{-1}. Further, the samples were maintained at 673 K for 20 h under vacuum with the residual pressure less than 10^{-2} Pa. The co-adsorption of methane and propane (*ca.* 320 μmol g^{-1} of each alkane), or methane (*ca.* 320 μmol g^{-1}) and benzene (*ca.* 75 μmol g^{-1}), or toluene-α-^{13}C (*ca.* 200 μmol g^{-1}) was performed at the temperature of liquid nitrogen. The glass tube with the sample was then sealed off from the vacuum system at the temperature of liquid nitrogen. Further, the sample was warmed to room temperature and heated at 523–873 K for 15 min–3 h for the reaction to proceed. The reaction products were analyzed in an adsorbed state with both ^{13}C and ^{1}H MAS NMR. In addition, the products were extracted from the zeolite with diethyl ether and analyzed with GC–MS.

2.2. NMR experiments

All the NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer at room temperature. ^{1}H NMR spectra with the magic angle spinning (^{1}H MAS NMR) were recorded by the Hahn-echo pulse sequence ($\pi/2$–τ–π–τ-acquisition), where τ was equal to the one rotor period (200 μs). The excitation pulse length was 5 μs ($\pi/2$), and 64 scans were accumulated with a 5-s delay. ^{13}C MAS NMR spectra with the high power proton decoupling were recorded with or without cross-polarization (CP) denoted below as ^{13}C CP/MAS NMR and ^{13}C 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, the delay time between scans was 3 s. The single pulse excitation ^{13}C MAS NMR spectra were recorded with 45° flip angle ^{13}C pulses of the 2.5 μs duration and 10 s recycle delay, which satisfied the 10T_1 condition. High power proton decoupling in these experiments was used only during the acquisition time. This eliminates the Nuclear Overhauser Enhancement of the signal areas and allows quantitative assessment of the signals [21]. A few thousand scans were collected for each ^{13}C NMR spectrum. The spinning rate was 5 kHz. ^{13}C and ^{1}H chemical shifts of adsorbed organic species were measured with respect to TMS as an external reference with accuracy ±0.5 ppm. The precision in determination of the relative line position was 0.1–0.15 ppm for ^{13}C NMR and 0.05 ppm for ^{1}H NMR.

2.3. GC–MS analysis

The GS–MS analysis of the products extracted 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 K min^{-1}. The detector was a mass-spectrometer Varian Saturn-2000, which scanned from m/z = 10 to m/z = 650 with the cycle time of 0.5 s.

3. Results and discussion

We first verified the occurrence of the reaction of methane conversion into aromatics on Zn-modified zeolite BEA by monitoring the transformation of ^{13}C-labeled methane (^{13}CH$_4$) in the presence and absence of the co-reactant propane. Solid state NMR has provided the analysis of the reaction products in situ, i.e., directly on the catalyst surface, whereas GC–MS gave us information on the products extracted from the zeolite.

3.1. Co-conversion of methane and propane

Fig. 1 shows the ^{13}C CP/MAS NMR spectra for the adsorbed products formed from methane and propane. To make a comparative analysis of the spectra possible, all of them were accumulated under identical conditions with the similar CP parameters, rotation speed and number of scans. No doubt that in case of using CH$_4$, labeled with ^{13}C isotope (90% of ^{13}C isotope enrichment), the signals in the spectra should arise mainly from the ^{13}C-label of methane after it has been transferred into the products. The spectrum of the products formed at 823 K from unlabeled CH$_4$ and C$_3$H$_8$ (natural abundance of ^{13}C isotope is 1.07%) exhibits only a weak signal at −8.5 ppm from un-reacted methane (Fig. 1a). When unlabeled CH$_4$ was substituted with ^{13}CH$_4$, two new signals, at 20 and 130 ppm, appear in the spectrum of the products (Fig. 1b). These two signals undoubtedly belong to the hydrocarbons, containing the ^{13}C–labels, coming from the initial ^{13}CH$_4$ (cf. Fig. 1a and b). According to their characteristic chemical shift, the signal at 130 ppm belongs to carbon atoms of aromatic ring and the one at 20 ppm is due to the methyl groups attached to aromatic ring of aromatic molecules [22] formed in the reaction.

Analysis of the spectra in Fig. 1 allows us to conclude that the carbon atoms of methane convert into both the methyl groups and the carbon atoms of aromatic rings of the methyl-substituted aromatic compounds. Further increase of either the temperature (up to 873 K) or the reaction time (up to 3 h at 823 K) leads to a noticeable growth of the signal at 130 ppm from aromatic ring carbons. Simultaneously, the signal of the methyl groups at 20 ppm disappears from the spectrum (Fig. 1c). The disappearance of the

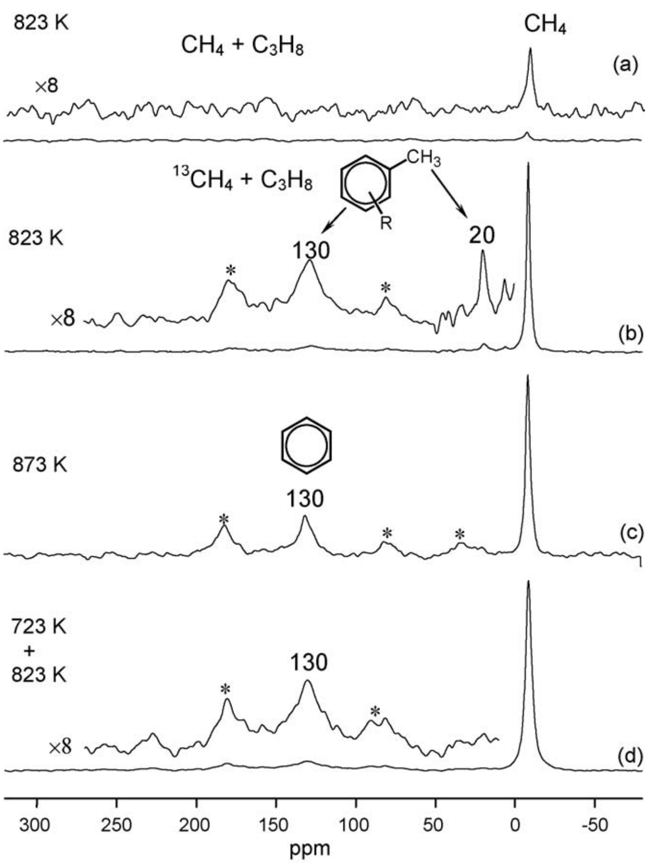


Fig. 1. ^{13}C CP/MAS NMR spectra of products formed from methane and propane on zeolite Zn/H-BEA: (a) from CH_4 at 823 K for 15 min; (b) from $^{13}CH_4$ and C_3H_8 at 823 K for 15 min; (c) from $^{13}CH_4$ and C_3H_8 at 873 K for 15 min; (d) as (b) but the sample was preheated at 723 K for 15 min. (*) Denote the spinning side-bands.

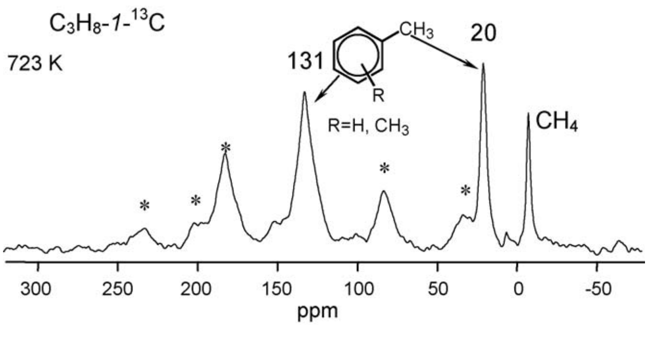
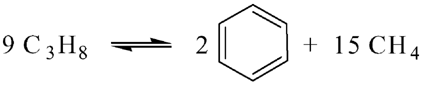
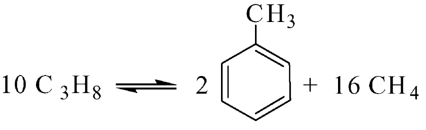


Fig. 2. ^{13}C CP/MAS NMR spectra of products formed from C_3H_8-1-^{13}C on zeolite Zn/H-BEA at 723 K for 15 min. (*) Denote the spinning side-bands.

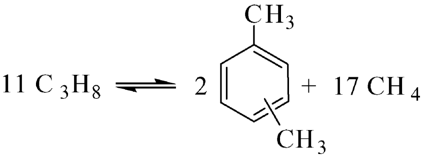
signal of the methyl groups may indicate that the ^{13}C-labeled carbon atoms are further transferred into aromatic rings and/or demethylation of the aromatics occurs. Thus, at 823–873 K a noticeable quantity of methane-^{13}C transforms to aromatic hydrocarbons by the reaction of methane and propane co-conversion on zeolite Zn/H-BEA. No conversion of $^{13}CH_4$ to aromatics in the presence of propane was observed at lower reaction temperatures, $T < 773$ K. At the same time, neat propane converts to a mixture of aromatic products with similar NMR characteristics already at 573–723 K (Fig. 2). The absence of signals from un-reacted propane at 17–18 ppm [17,23] in Fig. 2 is indicative of complete conversion of propane for 15 min of the reaction at 723 K. Methane is formed as a by-product of propane aromatization (cf. Figs. 1b and 2). According to the quantitative ^{1}H MAS NMR spectra, *ca.* 1.6–1.7 methane molecules are produced per one propane molecule reacted. The overall reactions, which describe propane aromatization under conditions of our experiment, could be the following:



(1)



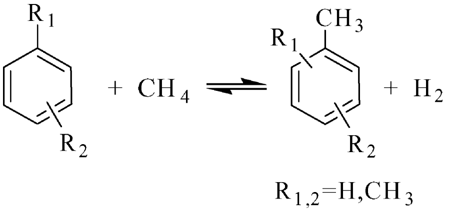
(2)



(3)

The reactions (1)–(3) are extremely favorable in terms of thermodynamics, e.g., $\Delta_r G^\circ_{823} = -800\ \mathrm{kJ\ mol^{-1}}$ for the reaction (1). This provides a complete conversion of propane to aromatic molecules (see Fig. 2).

The embedding of the carbon atoms of methane-^{13}C into aromatics is observed for the samples heated at 823–873 K (Fig. 1b and c) and for those which were preheated at lower reaction temperatures of 573–723 K (Fig. 1d). For the latter case, a complete conversion of propane into aromatics occurred (Fig. 2) prior a transfer of methane-^{13}C carbon atoms into aromatic molecules to begin at 823 K. Thus, a possible pathway of the methane conversion into aromatics could be the interaction of CH_4 with the aromatic molecules formed exclusively from propane:



(4)

For the direct methylation of aromatics with methane, positive values of standard Gibbs potential of the reaction are typical at the temperature range used in the present study (e.g., $\Delta_r G^\circ_{823} = +41\ \mathrm{kJ\ mol^{-1}}$ for the benzene methylation). However, a great negative magnitude of $\Delta_r G^\circ$ for the reactions (1)–(3) can stimulate the alkylation stage (4) in case the processes are considered as thermodynamically coupled ones [2].

To have a complementary to NMR evidence of methane-^{13}C conversion into aromatics as well as to specify a composition of the reaction products and the distribution of ^{13}C-labels over the aromatic molecules, the GC–MS analysis of the products formed from methane-^{13}C and propane has been performed. The analysis of the products extracted with diethyl ether from the zeolite has confirmed that a mixture of benzene (29 mol%), toluene (51 mol%), *m*- and *p*-xylenes (20 mol%) (BTX) is formed from methane and propane at 823 K (Table 1). Fig. 3b shows the molecular ion region of the mass-spectra of this BTX mixture. For comparison, the mass-spectra of corresponding aromatic compounds with the natural ^{13}C-abundance are presented in Fig. 3a. Preliminary analysis of these spectra brings us to a conclusion that singly ($^{13}C_1$), doubly ($^{13}C_2$) and even triply ($^{13}C_3$) labeled aromatic molecules are

Table 1
The composition of the products formed under co-aromatization of methane and propane (*ca.* 320 μmol g^{-1} of each alkane reacted) on zeolite Zn/H-BEA (15 min at 823 K).

Product concentration (μmol g^{-1})	
Benzene	17
Toluene	29
Xylenes	11
Methane	880

formed. On the basis of the signal pattern of unlabeled molecules, the observed experimental mass-spectra of aromatic molecules formed from $^{13}CH_4$ and propane were simulated and the mole fraction of each labeled molecule was estimated (Fig. 3c). Mass-spectrometry analysis confirms the presence of the ^{13}C-labeled carbon atoms of initial methane-^{13}C in both the methyl groups and the aromatic ring of BTX formed from methane and propane. About 6% of ^{13}C-labeled methane carbons are transferred to aromatic molecules at 823 K.

One should pay attention to the appreciable exceeding of the mole fraction of the $^{13}C_1$ singly labeled molecules for toluene (22%) and xylenes (29%) in comparison with that of benzene (12%). At the same time, the proportions of the doubly and triply labeled molecules do not change practically for these aromatic compounds (Fig. 3c). These observations provide a supplementary confirmation that a transfer of methane-^{13}C carbon atoms into the BTX molecules begins with the methylation of aromatics formed from propane. $^{13}CH_4$ converts initially into methyl group of methylbenzenes.

Both unlabeled methane formed by the reactions (1)–(3) and $^{13}CH_4$ introduced as the initial co-reactant can participate in the alkylation reaction (4). Taking into account both the stoichiometry of reactions (1)–(3) and methane:propane molar ratio in the initial reactant mixture (1:1), the expected $^{12}CH_4$–$^{13}CH_4$ alkylating mixture should contain *ca.* 38 mol% of $^{13}CH_4$. Based on data of Fig. 3 and Table 1 we have estimated the content of ^{13}C-labels in aromatic products formed from $^{13}CH_4$ and C_3H_8. We found that 35 mol% of BTX on average contained ^{13}C labels, if converted into singly ^{13}C-labeled molecules. This value is consistent with the composition of $^{12}CH_4$–$^{13}CH_4$ alkylating mixture, provided that all aromatics formed from propane is methylated by $^{12}CH_4$–$^{13}CH_4$ mixture. This fact provides one more confirmation that the alkylation of aromatics, formed from propane, by methane molecules represents the main pathway of methane-^{13}C conversion into aromatics. The ^{13}C-enrichment observed for carbon atoms of aromatic rings of BTX could be rationalized by a transfer of the ^{13}C-label from methyl groups of methylbenzenes into their aromatic rings [24] (vide infra, Section 3.2).

After reaction performance at 873 K, benzene represents a sole reaction product, extracted from the zeolite. This is consistent with the disappearance of the signal from methyl groups observed in ^{13}C NMR spectra (Fig. 1c). The ^{13}C-content in benzene molecules estimated from the mass-spectra increases notably (see Fig. 4). This indicates that demethylation of toluene and xylenes occurs at 873 K, in accordance to reversible reaction (4), the equilibrium is shifted towards benzene. Thus, the parallel processes of the ^{13}C-label scrambling in toluene and xylenes and a demethylation by the reaction (4), provide a notable enrichment of benzene with ^{13}C-isotope.

One should note that more methane ($^{13}CH_4$ + $^{12}CH_4$) is formed than consumed during the co-conversion of $^{13}CH_4$ and propane

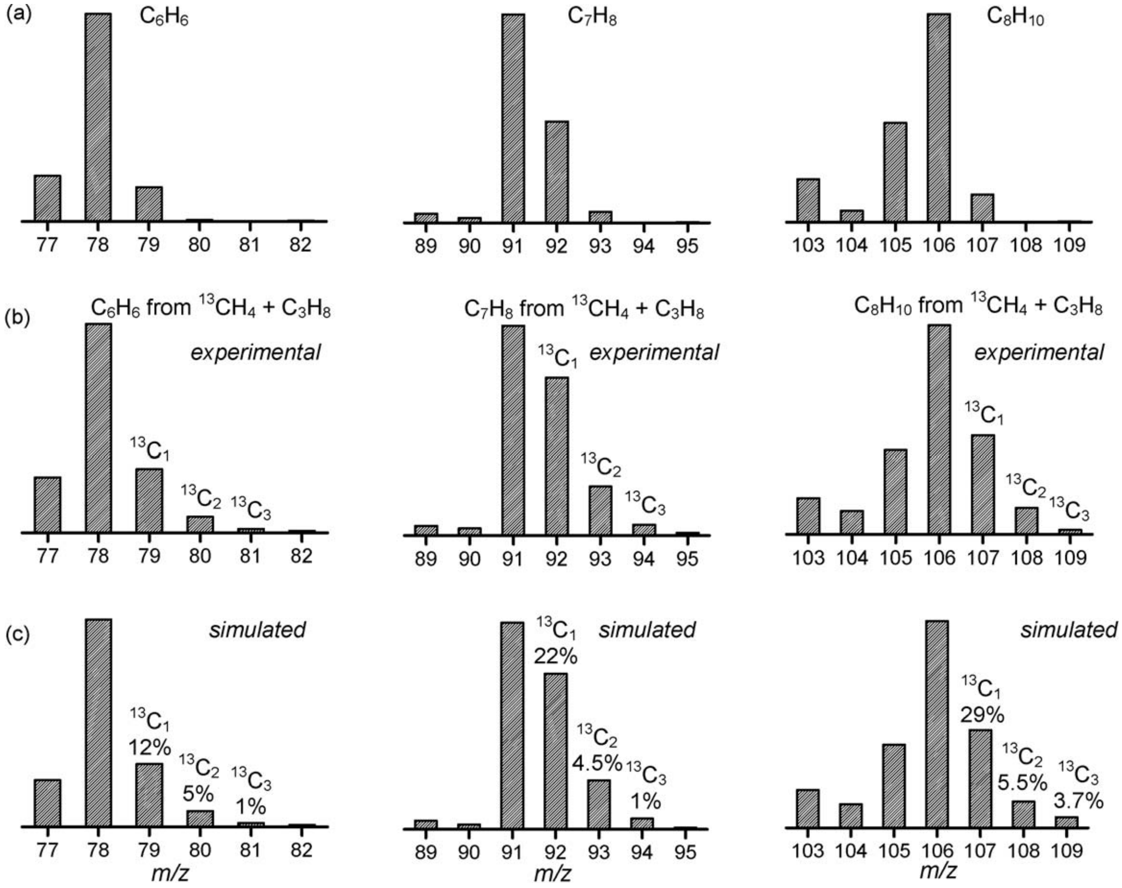


Fig. 3. (a) Mass-spectra of benzene, toluene, and *p*-xylene with the natural abundance of ^{13}C; (b) mass-spectra of BTX formed from ^{13}C-labeled methane and propane on zeolite Zn/H-BEA (823 K, 15 min); (c) simulated spectra for (b) with the estimated isotopic composition (mol%).

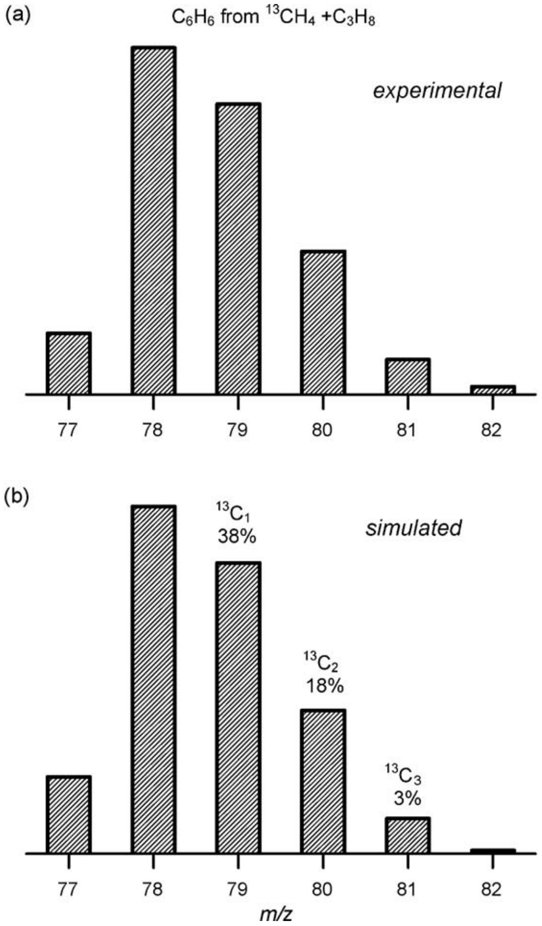


Fig. 4. Mass-spectra of benzene formed from $^{13}CH_4$ and C_3H_8 on zeolite Zn/H-BEA (873 K, 15 min): (a) experimental spectrum; (b) simulated spectrum with the estimated isotopic distribution (mol%).

under conditions of our experiment (see Table 1). This is caused by long contact time, which is a peculiarity for the experiments in the batch reactor in comparison with the flow reactor. Indeed, the experiments under flow conditions revealed that the positive methane consumption during co-aromatization with higher alkane was observed only for optimum contact times, no longer than 10 s [2]. For longer contact times more methane was produced than consumed due to the secondary processes of the demethylation of methylbenzenes formed. Such short contact times are not achievable for our experiments in batch reactor. So, demethylation process can be responsible for both the prevalence of the methane formation in comparison with its consumption and the decrease of the ^{13}C-isotope content of BTX. Nevertheless, we believe that the mechanism of the methane-to-aromatics insertion does not depend on the reaction contact time.

To get an insight into the mechanisms of methane co-conversion to aromatics, the co-conversion of methane and benzene has been further studied.

3.2. Co-conversion of methane and benzene

Fig. 5 shows the ^{13}C CP/MAS NMR spectra of products formed from $^{13}CH_4$ and unlabeled benzene at 523–823 K on zeolite Zn/H-BEA. Adsorbed benzene with the natural abundance of ^{13}C isotope is identified at 130 ppm in these spectra. Heating the sample at 523 K results in appearance of two signals (Fig. 5a): the more intense signal at 58 ppm is attributed to the surface methoxy species [25,26], the signal of less intensity at 20 ppm belongs to the CH_3 groups of methylbenzenes. At 573 K the signal from methoxy species completely disappears from the spectrum, while that from the methyl groups of methyl-substituted aromatic compounds increases conformably in its intensity (Fig. 5b). This clearly indicates that surface methoxy species converts quantitatively into the methyl group of methylbenzenes under the interaction with benzene, i.e., at 573 K the methylation of benzene occurs with methoxy species.

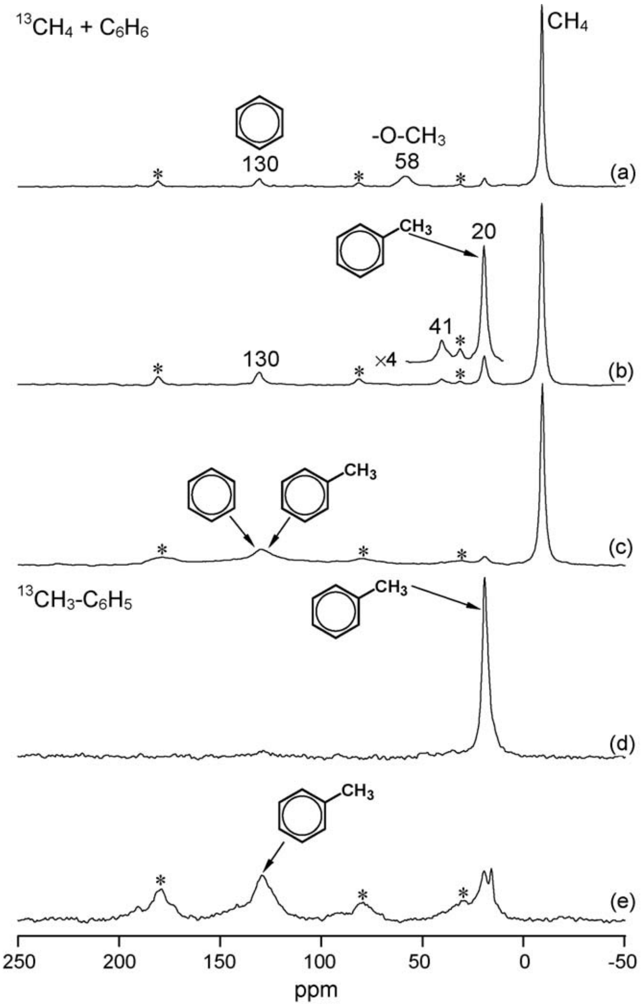


Fig. 5. ^{13}C CP/MAS NMR spectra of products formed on zeolite Zn/H-BEA from: $^{13}CH_4$ and benzene (a–c); toluene-α-^{13}C (d and e). The sample was heated consecutively at 523–823 K: (a) at 523 K, 15 min; (b) at 573 K, 15 min; (c) at 773 and 823 K, 15 min; (d) at 573 K, 15 min; (e) at 823 K, 15 min. (*) Denote the spinning side-bands.

Further increase of the reaction temperature up to 773 K brings no changes in the spectra. At 823 K the signal from aromatic carbons at 130 ppm becomes considerably broader, whereas that from the CH_3 groups decreases (Fig. 5c). These observations can be rationalized in terms of embedding the ^{13}C-labeled carbon atoms into the aromatic ring of methylbenzenes. Possessing a variety of chemical shifts from 125 to 135 ppm [22], they indeed could be responsible for the observed line broadening.

A transfer of the ^{13}C-label from the methyl groups into aromatic ring was further confirmed by experiments with toluene, labeled initially with ^{13}C-isotope in the methyl group. Adsorbed on Zn/H-BEA and heated at 573 K, un-reacted ^{13}C-labeled toluene exhibits only the signal at 20 ppm from the labeled $^{13}CH_3$ group (Fig. 5d). Heating the sample at 823 K results in the decrease of the signal from methyl group. Simultaneously, the signal at 130 ppm from carbon atoms of aromatic ring appears in the spectrum (Fig. 5e). This indicates that the ^{13}C-label, formerly located in the CH_3 group of toluene, is transferred into aromatic ring of the molecule, i.e., the intramolecular ^{13}C carbon-atom scrambling in toluene occurs on Zn/H-BEA zeolite.

The GC–MS analysis of the products formed from $^{13}CH_4$ and benzene confirms the suggested reaction pathway. The analysis revealed that mainly benzene and toluene were among the products extracted from the zeolite for the sample of Fig. 5b. The mass-spectrum of benzene coincides completely with that of the unlabeled benzene (cf. Fig. 6a and b). The molecular-ion region spectrum of toluene (Fig. 6e) resembles the one of ordinary toluene (Fig. 3), except for being shifted by one mass unit upward. The spectrum in Fig. 6e proved to be well simulated with the spectrum of the mixture of 90% $^{13}C_1$ and 10% $^{13}C_0$-toluenes (Fig. 6d). This means that isotopic composition of toluene is close to that of initial $^{13}CH_4$ (90% enrichment with ^{13}C), the proportion of $^{13}C_{\geq 1}$ molecules being negligible. Thus, at 573 K the ^{13}C-labeled carbon atom of the initial $^{13}CH_4$ converts exactly into the methyl group of toluene, no ^{13}C-label insertion into the aromatic ring occurs at this reaction temperature.

At higher reaction temperatures (823 K), an appreciable ^{13}C-label enrichment was also detected in aromatic rings of benzene and toluene as indicated by the presence of $^{13}C_1$ and $^{13}C_2$ fractions for benzene, and $^{13}C_2$ fraction for toluene (Fig. 6c and f). This enrichment is rationalized by occurrence of reversible reaction (4) of demethylation of toluene and with ^{13}C-labels in the aromatics rings.

The above data confirm our assumption that the main pathway of the methane conversion to aromatics in the course of the methane and propane co-conversion represents the alkylation of aromatic molecules, formed from propane, by $^{13}CH_4$. The methoxy species formed from methane on the surface of Zn/H-BEA zeolite serves as the intermediate of the reaction (Scheme 1). The methylbenzenes formed by alkylation of aromatics with the ^{13}C-labeled methane contain initially the ^{13}C-labeles in the methyl groups. Further, ^{13}C-label is transferred from the methyl groups into aromatics ring. Such intramolecular ^{13}C-label scrambling in the methylbenzenes was observed previously on other solid acid catalysts [24].

The scrambling was assumed to proceed via the ring expansion/contraction mechanism [24]. This mechanism supposed the rearrangements in the intermediate protonated methylbenzenes

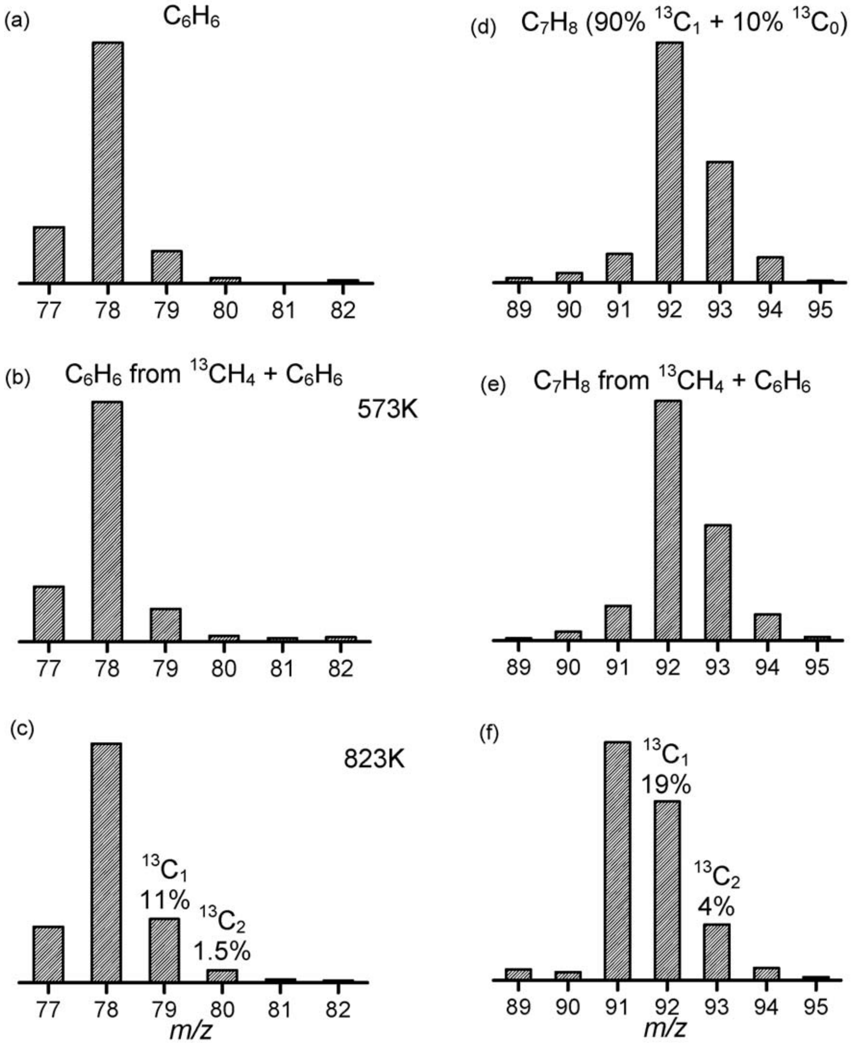
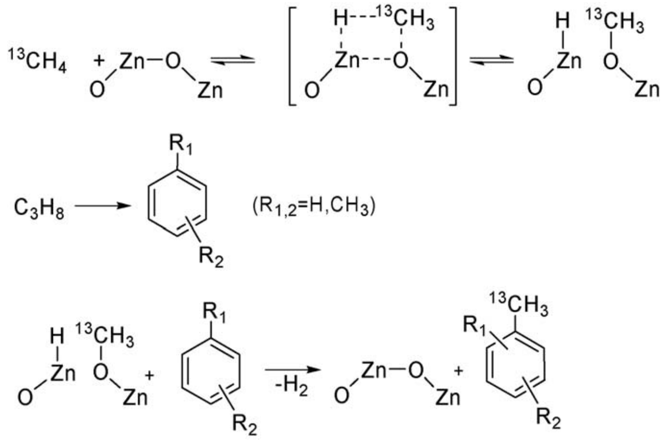
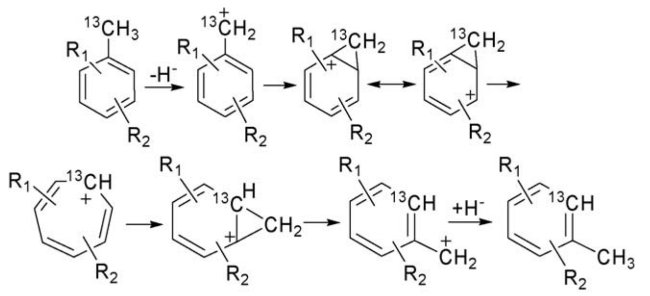


Fig. 6. Mass-spectra of benzene and toluene after the reaction of ^{13}C-labeled methane and unlabeled benzene on zeolite Zn/H-BEA: (a) standard benzene with natural ^{13}C-abundance; (b) benzene extracted after the reaction at 573 K; (c) benzene extracted after the reaction at 823 K; (d) simulated spectrum for toluene with the composition 90% $^{13}C_1$ + 10% $^{13}C_0$; (e) toluene after the reaction at 573 K; (f) toluene after the reaction at 823 K.



Scheme 1. The mechanism of methane and propane co-aromatization on zeolite Zn/H-BEA and the ^{13}C-label incorporation from methane-^{13}C into aromatics.



Scheme 2. A possible pathway of the ^{13}C-label transfer from the methyl group into the aromatic ring in aromatic molecules formed from methane-^{13}C and propane on zeolite Zn/H-BEA.

formed on Brønsted acid sites [27]. In contrast to that assumption, we believe that ^{13}C-label scrambling in methylbenzenes on Zn/H-BEA catalyst involves the formation of the phenylmethyl cation as an intermediate or transition state (Scheme 2). The well-established dehydrogenating ability of Zn-containing zeolites [28] can facilitate the phenylmethyl cation formation. As well as the methyl cation, the phenylmethyl cation should possess the similar reactivity towards aromatic ring, i.e., it can alkylate aromatic molecules [29]. A small fraction of diphenylmethane is indeed formed from methane-^{13}C and benzene at 573 K as a result of such alkylation. Diphenylmethane is identified by the characteristic signal from ^{13}C-labeled CH_2 group at 41 ppm [30] in ^{13}C CP/MAS NMR spectra (Fig. 5b). 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.

A more detailed conception of the methane activation by the zeolite becomes clear from the analysis of neat methane conversion on Zn/H-BEA.

3.3. Conversion of neat methane

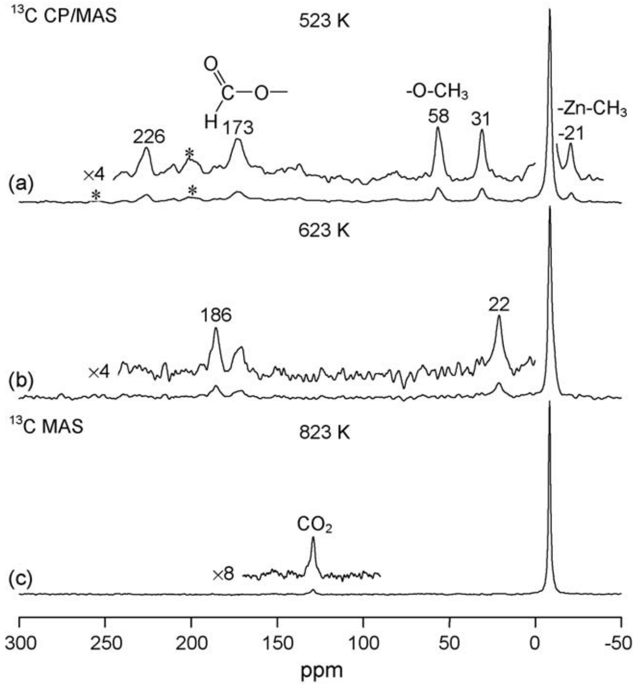
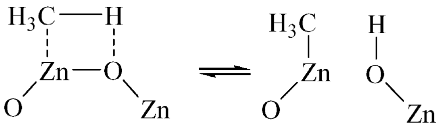


Fig. 7. ^{13}C NMR spectra for $^{13}CH_4$, reacted on zeolite Zn/H-BEA: (a) at 523 K, ^{13}C CP/MAS spectrum; (b) at 623 K, ^{13}C CP/MAS spectrum; (c) at 823 K, ^{13}C MAS spectrum. (*) Denote the spinning side-bands.

Our data on methane interaction with benzene show that the methane activation on Zn/H-BEA proceeds via the formation of a surface methoxy species ("stabilized methyl cation"), which is identified in the ^{13}C CP/MAS NMR spectrum of Fig. 5b. Fig. 7 shows the ^{13}C MAS NMR spectra for neat methane, $^{13}CH_4$, reacted on zeolite Zn/H-BEA at 523–823 K. Surface methoxy species with the signal at 58 ppm is detected for methane reacted at 523 K (Fig. 7a). Additional experiments have also shown that methoxy species does not form from methane on un-promoted pure acidic form of zeolite BEA under the similar reaction conditions. This allows us to conclude that the methoxy species could be formed by a heterolytic dissociative adsorption of methane on ZnO species located inside the channels of Zn/H-BEA zeolite [20] (see Section 2) as depicted in Scheme 1. In addition to the methoxy species, the signals −21, 31, 173, and 226 ppm are also observed for methane reacted at 523 K (Fig. 7a). An essential negative chemical shift of the signal at −21 ppm is typical of the methyl group attached to the metal atom of organo-metallic compounds [31]. So, we have attributed the signal at −21 ppm to the surface Zn–CH_3 species [20], earlier detected by IR spectrosopy on ZnZSM-5 [32]. Similar to Zn–O–CH_3 species, Zn-methyl species can be formed at the heterolytic dissociative adsorption of methane on ZnO species inside the zeolite channels:



According to its position, the signal at 173 ppm belongs to surface formate species [33,34], whereas those at 31 and 226 ppm are assigned to the methyl and carbonyl groups of acetaldehyde [22]. The formation of the surface formate Zn–O–CH═O could be a result of methoxy species oxidation. Acetaldehyde seems to be formed upon the interaction between negatively charged methyl group of Zn–CH_3 and the formate group, which holds a partially positive charge on carbon atom. Heating the sample at the higher temperatures results in the disappearance of Zn–CH_3, Zn–O–CH_3 and acetaldehyde. At the same time, acetic acid (the signals at 22 ppm from CH_3 and 186 ppm from the COOH group [35]) is formed as the result of further acetaldehyde oxidation (Fig. 7b). Finally, at the temperature 823 K, used for the co-conversion of propane and methane, the only ^{13}C-labeled substance observed (besides $^{13}CH_4$) is a small quantity of carbon dioxide formed by decarboxylation of acetic acid [36]. CO_2 is identified in the ^{13}C MAS NMR spectrum by the signal at 127 ppm (Fig. 7c). Aromatic compounds were not detected both in ^{13}C and in considerably more sensitive ^{1}H MAS NMR spectra as the products of neat methane conversion under these conditions.

Thus, methoxy species does not convert to aromatics in the absence of higher hydrocarbon as the co-reactant. It is subsequently oxidized to form finally carbon dioxide.

3.4. Mechanism of methane and propane co-aromatization: final notes

Our results provide a detailed comprehension of both the mechanism of methane activation and the role of higher alkane at its co-conversion with methane on Zn-modified zeolites. Since no conversion of methane is usually observed for the metal unpromoted zeolites and in the absence of a higher hydrocarbon as the co-reactant [2,6], the methane activation was suggested earlier to proceed in a following manner [6,13–15,37]: (i) the formation of carbenium ion from higher hydrocarbon, paraffin or olefin, and pre-activation of methane on metal oxide species; (ii) the hydride ion transfer from pre-activated methane to the carbenium ion with the formation of methyl cation, stabilized by the surface of the zeolite, followed by the conversion of the cation into the CH_2 radical [6,37]. (iii) The dimerization of the CH_2 radical results in ethene. Oligomerization and dehydrocyclization of ethene produce finally aromatic compounds with methane-originated carbons in all positions of the molecules [6,37]. Our data do not confirm this earlier suggested mechanism [6,37].

NMR data show that surface methoxy species (stabilized methyl cation) is formed from methane on Zn/H-BEA even in the absence of any co-reactant. So, a higher hydrocarbon as a source of carbenium ions [6,37] is not required for the methane activation on Zn-modified zeolite. Methane is activated by ZnO species of the zeolite, Brønsted acid sites of the zeolite can also be involved in methane activation [6,20,37].

The role of higher alkane in methane and propane co-conversion consists in producing aromatic compounds. This is evident from the formation of aromatics from propane prior the transfer of ^{13}C-label from methane into aromatics to begin. The aromatics formed by this way interact further with methoxy species generated from methane on ZnO species of the zeolite. This provides a transfer of ^{13}C-label from methane into the aromatic products by the alkylation reaction (Scheme 1). Further transfer of the ^{13}C-label from the methyl group into the aromatics ring is performed in accordance to Scheme 2. Evidently, the oxidative channel of the methoxy species conversion to carbon dioxide is not realized in the presence of aromatics.

Finally, the data obtained unequivocally demonstrate that Zn-modified high silica zeolite catalyst is able to provide the involvement of methane into aromatics in the reaction of methane and higher alkane co-aromatization. These results can be helpful to clarify the chances of co-aromatization of methane in future chemical processes.

4. Conclusions

Analysis with ^{13}C solid state NMR and GC–MS of the pathways of ^{13}C-label transfer from methane-^{13}C into the reaction products of methane and propane co-conversion on Zn-modified high silica zeolite BEA allowed us to draw the following conclusions.

A high degree involvement of methane into the reaction products is observed for methane and propane co-aromatization on Zn/HBEA at 773-873 K, about 35 mol% of the formed aromatics contain ^{13}C-labeled carbons originated from $^{13}CH_4$. Methane-^{13}C carbons are converted into both the methyl groups and the carbon atoms of aromatic rings of methyl-substituted benzenes. The aromatization of neat methane does not occur on Zn-modified zeolite under the conditions used in this study. A transfer of the ^{13}C-labels from methane-^{13}C molecules into the aromatic products is provided by the alkylation reaction with methane of benzene, toluene and xylenes molecules, which are produced exclusively from propane. Surface methoxy species, which are formed at dissociative adsorption of methane at ZnO species of the zeolite, represent the intermediates for the aromatics alkylation reaction. Primarily transferred to the methyl groups by the alkylation reaction, further embedding of the ^{13}C-label of methane-^{13}C into aromatic rings occurs through the scrambling of the carbon atoms in methylbenzenes via ring expansion/contraction mechanism.

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