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Understanding Methane Aromatization on a Zn-Modified High-Silica Zeolite[**]

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Methane is the principle constituent of natural gas and also the most inert of the saturated hydrocarbons. Its conversion into more commercially useful chemicals and liquid fuels represents one of the most important challenges in modern catalysis.[1] Coaromatization of methane and light hydrocarbons (paraffins and olefins) at 700–800 K is one of the alternative methods for the conversion of methane. It has been reported recently that the conversion of methane during coaromatization with higher alkanes or alkenes (C_2–C_6) at 670–870 K in the presence of bifunctional catalysts (mainly, high-silica ZSM-5 or ZSM-11 zeolites, modified with gallium or zinc) may reach 20–40 %.[2–4] However, previous experiments in which ^{13}C-labeled methane was used did not confirm the presence of the ^{13}C-labeled atoms from the methane in the aromatization products.[5] This result gave rise to scepticism as to whether methane-involved aromatization occurred at all.[5] Herein we report that transfer of isotopically ^{13}C-labeled atoms from methane into the aromatic products does occur to a high degree during the co-conversion of methane and propane on the Zn-modified high-silica zeolite BEA. We have identified the nature of the intermediates formed during the activation of methane and established how the conversion of methane into aromatic compounds occurs.

Figure 1 shows the ^{13}C CP/MAS NMR spectra[6] of the products (in their adsorbed state on the zeolite catalyst) which are formed from methane and propane at 823–873 K. The spectrum of the products formed from unlabeled CH_4 and C_3H_8 exhibits only a weak signal at $\delta = -8.5$ ppm from methane (Figure 1 a). When unlabeled CH_4 was replaced with $^{13}CH_4$, the spectrum of the reaction products showed two new signals, which undoubtedly belong to hydrocarbons containing the ^{13}C labels from the $^{13}CH_4$ (Figure 1 b). The carbon atoms of the ^{13}C-labeled methane molecules are incorporated into both methyl groups (signal at $\delta = 20$ ppm) and aromatic rings ($\delta = 130$ ppm) of the methyl-substituted aromatic compounds[7] (Figure 1 b,c).

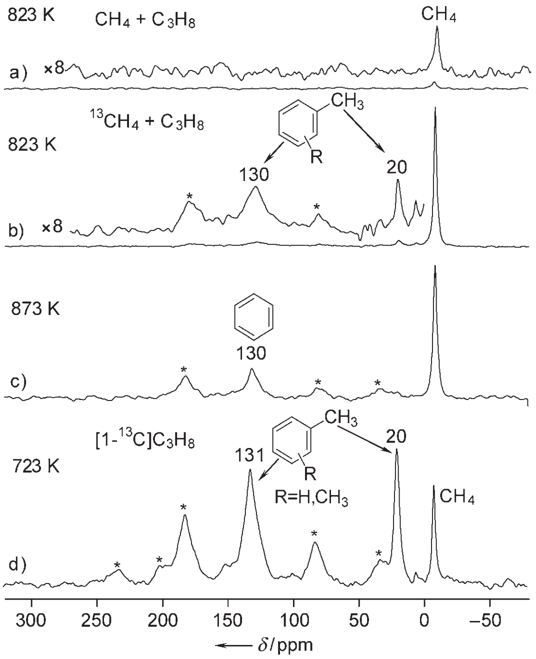
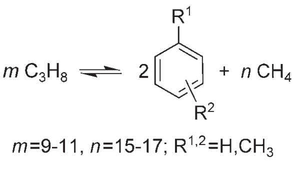


Figure 1. ^{13}C CP/MAS NMR spectra of products in the adsorbed state formed from methane and propane on zeolite Zn/H-BEA: a) from CH_4 and C_3H_8 at 823 K for 15 min; b,c) from $^{13}CH_4$ and C_3H_8 at 823 K for 15 min (b) and at 873 K for 15 min (c); d) from $[1\text{-}^{13}C]C_3H_8$ at 723 K for 15 min. Asterisks (*) in Figures 1, 3, and 4 denote the spinning side bands.

According to GC-MS analysis of the products extracted from the zeolite, a mixture of benzene and toluene, as well as *m*- and *p*-xylenes (BTX) with ^{13}C enrichment is formed from $^{13}CH_4$ and unlabeled propane at 773–823 K (Figure 2). The presence of singly ($^{13}C_1$), doubly ($^{13}C_2$), and triply ($^{13}C_3$) labeled molecules of BTX (Figure 2 b) provides proof for the incorporation of ^{13}C-labeled methane into both the methyl groups and the carbon atoms of the aromatic rings of BTX.

Neat propane converts on Zn/H-BEA into a mixture of aromatic products and methane at lower temperature (573–723 K; Figure 1 d). According to the ^{1}H MAS NMR spectra, approximately 1.6–1.7 methane molecules are produced per reacted propane molecule. The possible overall reaction which describe the aromatization of propane can be described by Equation (1).



(1)

m=9-11, n=15-17; $R^{1,2}$=H,CH_3

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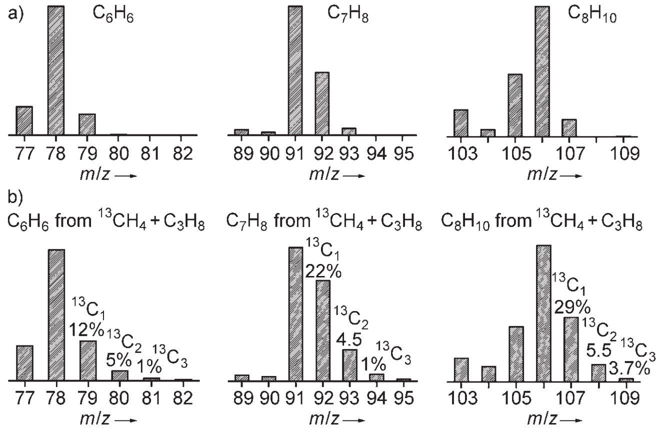
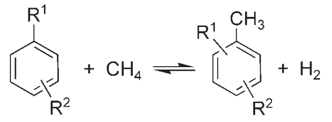


Figure 2. Mass-spectra of benzene, toluene, and *p*-xylene: a) with the natural abundance of ^{13}C and b) formed from ^{13}C-labeled methane and propane at 823 K (15 min) on zeolite Zn/H-BEA with the estimated isotopic composition (mol %).

The embedding of the carbon atoms of $^{13}CH_4$ into the aromatic compounds is observed for samples heated at 823–873 K (Figure 1 b,c) and for those which were preheated at lower temperatures of 573–723 K. In the latter case, the complete conversion of propane into aromatic compounds occurs (Figure 1 d) prior to the transfer of the ^{13}C atom from methane into the aromatic molecules, which begins at 823 K. Thus, a possible pathway for the conversion of methane may represent the interaction of CH_4 with the aromatic molecules formed exclusively from propane [Eq. (2)].



(2)

Both unlabeled methane formed in reaction (1) and $^{13}CH_4$ introduced as the co-reactant can participate in the alkylation reaction. Taking into account both the stoichiometry of reaction (1) and the methane/propane ratio in the initial reactant mixture (1:1), the expected $^{12}CH_4/^{13}CH_4$ alkylating mixture should contain about 38 mol % $^{13}CH_4$. This value is highly consistent with the amount of ^{13}C label in aromatic compounds formed from $^{13}CH_4$ and C_3H_8 if converted into singly ^{13}C-labeled molecules (25–51 % for 15 min reaction at 823 K, see Figure 2 b). This fact, as well as the finding that the mole fraction of the singly ^{13}C-labeled molecules of toluene and xylene appreciably exceeds that of benzene (Figure 2 b), provides additional evidence that the transfer of the ^{13}C atoms from methane into the BTX molecules starts with the methanation of aromatic compounds formed from propane [Eq. (2)].

The conversion of neat methane as well as the co-conversion of methane and benzene has been further studied to gain insight into the mechanisms of both the activation and conversion of methane into aromatic compounds. The activation of methane on Zn-containing zeolites was earlier presumed[2,4] to proceed with the formation of a methyl cation by transfer of a hydride ion from the methane molecule, which was preactivated on the metal oxide species, to the carbenium ion formed from higher hydrocarbons. Our data show that the activation of methane on Zn/H-BEA indeed occurs at 523 K through the formation of a surface methoxy species (a "stabilized methyl cation") ($\delta = 58$ ppm[8] in the ^{13}C CP/MAS NMR spectrum, Figure 3 a). The initial activation of methane also gives a Zn-CH_3 species ($\delta = -21$ ppm[9]). We have not detected any surface methyl species during the reaction of methane on the unpromoted acidic form of the zeolite. Thus, both the methoxy and zinc-methyl species may be formed by heterolytic dissociative adsorption of methane on nanosized ZnO clusters located inside the channels of the Zn/H-BEA zeolite[9] (Scheme 1 a). The dissociation of meth-

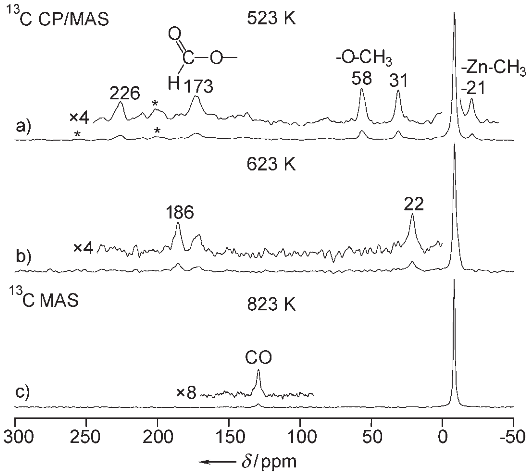
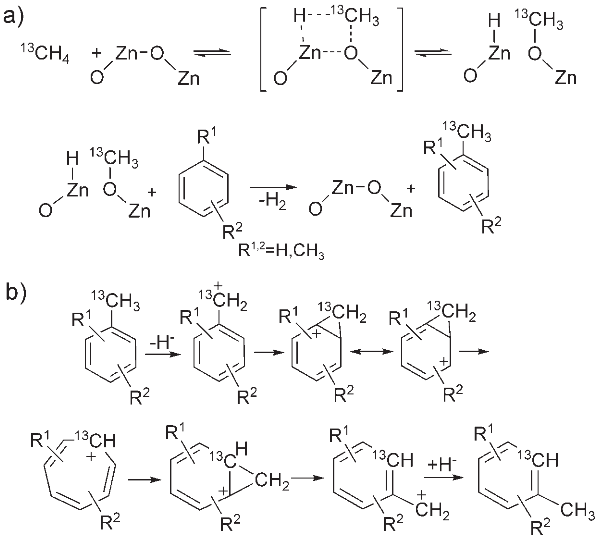


Figure 3. ^{13}C NMR spectra of $^{13}CH_4$ heated on zeolite Zn/H-BEA: a) at 523 K (^{13}C CP/MAS spectrum); b) at 623 K (^{13}C CP/MAS spectrum); c) at 823 K (^{13}C MAS spectrum).



Scheme 1. The mechanism of the ^{13}C-label transfer from $^{13}CH_4$ into aromatic compounds during methane and propane co-conversion on zeolite Zn/H-BEA.

ane on ZnO species may be facilitated by neighboring acidic sites of the zeolite.[2b]

In the absence of a co-reactant, the methoxy group is further partially oxidized at 523 K into the surface formate Zn-O-CH=O ($\delta = 173$ ppm[10]). The latter species interacts with Zn-CH_3 to produce acetaldehyde ($\delta = 31$ ppm for CH_3 and $\delta = 226$ ppm for the carbonyl group,[7] Figure 3 a). At higher reaction temperatures, acetic acid ($\delta = 22$ ppm for CH_3 and $\delta = 186$ ppm for COOH[11]) is formed as the result of the further oxidation of acetaldehyde (Figure 3 b). Finally, at 823 K, which is used for the co-conversion of propane and methane, the only ^{13}C-labeled product observed is carbon dioxide ($\delta = 127$ ppm, Figure 3 c) which is formed by decarboxylation of acetic acid.[12] Aromatic compounds were not detected in either the ^{13}C or ^{1}H MAS NMR spectra in the conversion of neat methane under these conditions.

In contrast to neat methane, the methoxy species ($\delta =$ 58 ppm, Figure 4 a) represents the only intermediate formed at 523 K from $^{13}CH_4$ in the presence of benzene. At 573 K, the surface methoxy species converts quantitatively into the methyl group of methylbenzenes ($\delta = 20$ ppm, Figure 4 b). At 823 K, both a broadening of the signal at $\delta = 130$ ppm and a decrease in the intensity of the signal corresponding to the methyl groups occur, which points to a transfer of the ^{13}C-label from the methyl groups to the aromatic ring of the methylbenzenes, which exhibit a variety of chemical shifts (from $\delta = 125$ to 135 ppm,[7] Figure 4 c). Both the methylation stage at 573 K and further transfer of the ^{13}C-label into the aromatic rings of the methylbenzenes at 823 K are also evident in the mass spectra (not shown).

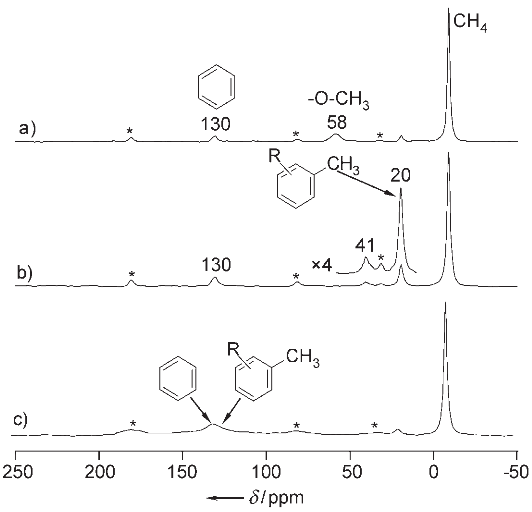


Figure 4. ^{13}C CP/MAS NMR spectra of products formed from $^{13}CH_4$ and benzene (coadsorbed in a ratio of 4:1) on zeolite Zn/H-BEA. The sample was heated consectively for: a) 15 min at 523 K; b) 15 min at 573 K; c) 15 min at 823 K.

Thus, the main pathway for the conversion of methane into aromatic compounds during the course of the methane and propane co-conversion represents the alkylation of propane-originating aromatic molecules by $^{13}CH_4$. A methoxy species is the intermediate of this reaction (Scheme 1 a). The methoxy species, as a stabilized methyl cation, does not convert directly into aromatic compounds in the absence of a higher hydrocarbon as a co-reactant. Therefore, the earlier presumed mechanism[2] of the conversion of methane into aromatic compounds via the formation of a CH_2 radical from the methyl cation, its dimerization to ethene, oligomerization, and dehydrocyclization should be rejected. This mechanism could not be responsible for the ^{13}C enrichment observed in the aromatic rings of BTX in the present study.

The embedding of the ^{13}C atoms from methane into the aromatic ring is a result of a secondary process of intramolecular scrambling of the ^{13}C label in methylbenzenes by a ring-expansion/contraction mechanism.[13] The reversible reaction (2) also provides a notable enrichment of benzene molecules with the ^{13}C isotope. Our proposed scheme of ^{13}C-label scrambling involves the formation of a phenylmethyl cation as the intermediate or transition state (Scheme 1 b) instead of protonated methylbenzenes.[13] This assumption is quite reasonable since a small fraction of diphenylmethane is formed from $^{13}CH_4$ and benzene at 573 K (Figure 4 b, $\delta =$ 41 ppm for the CH_2 group[14]) as a result of the alkylation of benzene with the phenylmethyl cation.[15]

Since the surface methoxy species is even formed from neat methane on Zn/H-BEA, a higher hydrocarbon as a supposed source of carbenium ions[2] is not a requirement for the activation of methane. The role of the higher hydrocarbon consists of producing aromatic compounds, which further serve as a trap for the methoxy species formed from methane on the Zn sites (Scheme 1 a).

In summary, by using isotope-tracing experiments with ^{13}C-labeled methane we have demonstrated a high level of involvement of methane in the aromatization of higher alkanes on Zn-modified zeolites. The mechanism of the aromatization has been established and consists of the alkylation of aromatic compounds, which form exclusively from the higher alkanes. The methoxy species formed by dissociative adsorption of methane on ZnO species is responsible for the alkylation. Further embedding of the ^{13}C-labeled atoms from the methyl groups of methyl-substituted benzene derivatives into their aromatic rings occurs through a ring-expansion/contraction mechanism.

Experimental Section

Methane aromatization was performed in a glass, closed batch microreactor (0.2 cm^3; sealed glass insert for 7 mm zirconia NMR rotors) with coadsorbed $^{13}CH_4$ and propane (1:1) at 573–873 K. The Zn/H-BEA zeolite (Si/Al = 18, 7.2 wt% Zn) sample (ca. 80 mg) was activated at 673 K for 20 h under a vacuum, with the residual pressure less than 10^{-2} Pa. Detailed characteristics of the zeolite used are provided in Ref. [9]. 300 $\mu mol\,g^{-1}$ of each alkane was coadsorbed on the zeolite sample under vacuum and then the reactor sealed. After reaction at 573–873 K, the reactor was cooled down to room temperature for in situ NMR analysis. ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer under magic spinning and with cross-polarization (CP/MAS). Identical conditions (CP parameters, rotation speeds, and number of scans) were used to enable comparison of the spectra in each series of experiments. The products were further extracted from the zeolite sample with diethyl ether and analyzed by GC-MS on a Varian CP-3800 gas chromatograph and Varian Saturn-2000 mass spectrometer.

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