In situ high temperature MAS NMR study of the mechanisms of catalysis. Ethane aromatization on Zn-modified zeolite BEA

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ABSTRACT

Ethane conversion into aromatic hydrocarbons over Zn-modified zeolite BEA has been analyzed by high-temperature MAS NMR spectroscopy. Information about intermediates (Zn-ethyl species) and reaction products (mainly toluene and methane), which were formed under the conditions of a batch reactor, was obtained by $^{13}$C MAS NMR. Kinetics of the reaction, which was monitored by $^1$H MAS NMR in situ at the temperature of 573 K, provided information about the reaction mechanism. Simulation of the experimental kinetics within the frames of the possible kinetic schemes of the reaction demonstrates that a large amount of methane evolved under ethane aromatization arises from the stage of direct ethane hydrogenolysis.

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1. Introduction

Since the end of 1980s a high resolution solid state NMR spectroscopy has been demonstrating its efficiency for characterization of chemical reactions on surface of solid acid catalysts [1–9]. Much information has been obtained on the products and intermediates formed on the catalysts surface but never earlier detected at the reactors outlet [1,2,9–13]. The nature and the structure of some important intermediates were elucidated [1,9–11,13–16]. Nowadays, high-temperature NMR probes make it possible to perform both in situ analysis of the reaction products at 573–673 K [17] and to monitor the kinetics of the reaction at the temperature of 573 K [18,19].

Aromatization of light alkanes into more valuable aromatic hydrocarbons over zeolite catalysts has attracted much attention in the past decades [20–23]. It has been unequivocally demonstrated that modification of zeolites with Zn or Ga results to the essential enhancement of light alkane conversion to aromatics. However, a notable amount of undesired saturated hydrocarbons (mainly methane) is still produced [24,25]. The higher aromatizing ability of these catalysts is generally assigned to an increase in the rates of the initial alkane and subsequent olefin oligomers dehydrogenation [20,22,23]. It has been also concluded that the role of Zn (or Ga) species consists of promoting the recombinative desorption of hydrogen atoms as H$_2$ which leads to increasing the formation of unsaturated intermediates as prerequisite for cyclization [21,25].

In this paper we monitor the products and intermediates with $^{13}$C MAS NMR and analyze the kinetics of ethane aromatization with $^1$H MAS NMR in situ on Zn/H-BEA with the aim to clarify the mechanism of this aromatization reaction and to shed some light on the routes of a notable formation of undesirable by-product, methane.

2. Experimental

2.1. Material characterization and sample preparation

Acidic zeolite beta (H-BEA) was synthesized by the procedure described in Ref. [26] using tetra-ethyl-ammonium hydroxide as template with subsequent calcination at 823 K in an air flow for 6 h. Zinc form (Zn/H-BEA) was prepared by impregnation of H-BEA with saturated solution of zinc formate, subsequent drying at 473 K for 14 h, and further calcination at 673 K for 4 h in a flow of air. The Zn content in a final Zn/H-BEA zeolite was 7.7 wt%.

Materials were characterized by XRD, SEM, TEM, UV–vis and IR diffuse reflectance spectroscopy, $^1$H, $^{27}$Al, and $^{29}$Si MAS NMR.
spectroscopy. The silicon-to-aluminum ratio of 15 was obtained by both chemical analysis and $^{29}$Si MAS NMR spectrum analysis [27]. It was proved by $^{27}$Al MAS NMR that the synthesized Zn/H-BEA contained no extra-framework aluminum atoms. Only one signal appeared at 54 ppm due to tetra-coordinated aluminum atoms. However, a small quantity of extra-framework aluminum was created during the process of sample activation. The activation offered a weak signal at 5 ppm (ca. 2% of intensity with regards to the signal at 54 ppm) in $^{27}$Al MAS NMR spectrum. A residual quantity of 320 $\mu$mol g$^{-1}$ for the acidic SiOHAI groups in Zn/H-BEA was estimated by $^1$H MAS NMR with adsorbed methane as internal standard.

XRD analysis demonstrated the presence of a bulk ZnO phase in Zn/H-BEA. Additionally UV–vis diffuse reflectance spectrum of Zn/H-BEA sample showed a band at 265 nm from sub-nanometric ZnO clusters and a band at 370 nm from macromolecular particles of ZnO on the extra surface of the zeolite [28].

Ethane $C_2H_6$ (purity $\geqslant 99\%$) and ethane $C_2H_6-1-^{13}C$ (99% $^{13}C$ enrichment) were purchased from Aldrich Chemical Company Inc. and used without further purification. The samples for NMR measurements were prepared by heating 80 mg of the zeolite sample in the glass tubes of 5.5 mm outer diameter. The samples were activated by an increase in the temperature from 300 to 673 K at the rate of 10 K h$^{-1}$ under vacuum. Further, the samples were maintained at 673 K for 24 h under vacuum (less than $10^{-2}$ Pa). The loading with alkane was performed at room temperature with a quantity of 320 $\mu$mol g$^{-1}$ of ethane, and each sample was then sealed off (length of the glass tube = 10 mm). This glass tube could be tightly inserted into the 7 mm rotor. The NMR probe with the sample was preheated for 20 min at the temperature at which the conversion of ethane did not yet occur at a notable rate. Then the temperature was increased by 100 K up to the reaction temperature within 8 min, equilibrated for 2–5 min, and then the acquisition of NMR signal started.

2.2. NMR measurements

NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer equipped with high temperature broad-band double-resonance MAS probe. Zirconia rotors (7 mm) with inserted sealed glass tubes were spun at 3–5 kHz by dried compressed air at 300–573 K. $^1$H MAS spectra were recorded at 400.13 MHz by a Hahn-echo pulse sequence $\pi/2-\tau-\pi-\tau$, where $\tau$ equals to one rotor period. The excitation pulse length was 4.5 $\mu$s ($\pi/2$), and 24 scans were accumulated for a spectrum with a 4–6 s delay. $T_1$ for methane and ethane were 420 and 360 ms at 573 K. This made possible a quantitative estimates of signal intensities in $^1$H MAS NMR spectra. The time interval for successive spectra during kinetic measurements was 5–10 min depending on the reaction rate. $^{13}C$ CP MAS NMR spectra with cross-polarization and high-power proton decoupling were recorded at 100.613 MHz at 300 K. A nutation frequency of 50 kHz was used for both Hartmann–Hahn matching and $^1$H decoupling. The contact time was 1–3 ms, and delay between scan was 3 s. About 30,000 scans were accumulated for the $^{13}C$ CP/MAS NMR spectra. $^{27}$Al MAS spectra were acquired with a short $\pi/12$ radio-frequency pulse (0.6 ms), and about 1000 scans were accumulated with a 0.5 s recycle delay. $^{29}$Si MAS spectra were recorded with $\pi/2$ excitation pulse of 5.0 $\mu$s duration, and 20 s repetition time, and 1000 scans for signal accumulation. Both $^{27}$Al and $^{29}$Si NMR spectra were recorded using 4 mm rotor and spinning rate of 10 kHz. The sample temperature was controlled by the Bruker BVT-2000 variable-temperature unit. The calibration of the temperature inside the rotor was performed with an accuracy of $\pm 2$ K by the use of lead nitrate as a $^{203}$Pb MAS NMR chemical shift thermometer [29].

After the reaction inside the sealed glass tube, the products of the ethane conversion were extracted from the catalyst with acetone. Further, we performed a GC-MS analysis of the extracted products. The GC-MS analysis was carried out on a Varian CP-3800 gas chromatograph equipped with a PLOT fused-silica capillary column of 30 m $\times$ 0.32 mm i.d. in a size with CP-PoraPLOT Q-HT as the stationary phase.

2.3. Kinetic analysis

Simulated kinetic curves were calculated by the semi-implicit Runge–Kutta method for integration of sets of stiff equations with an integration step adaptation [30] on the base of reaction kinetic Schemes 2 and 3. Rate constants were determined by fitting of the simulated kinetic curves to the experimentally obtained curves.

3. Results and discussion

3.1. $^{13}C$ NMR analysis of products of ethane conversion

The analysis of the products of ethane conversion was performed by using ethane-1-$^{13}C$. Fig. 1 shows $^{13}C$ CP MAS NMR spectra of the products formed at 573 K. 15 min of reaction results to appearance of weak signals from methane (8.9 ppm) and zinc-ethyl species with two signals at −0.5 (CH$_2$ group) and 12.5 ppm (CH$_3$ group), as expected for ZnEt$_2$ [31]. Several other weak signals at 12–31 ppm can be attributed to olefin oligomers. The signal of

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**Fig. 1.** $^{13}C$ CP MAS NMR spectra of ethane-1-$^{13}C$ on Zn/H-BEA after heating at 573 K during 15 min (a) and 12 h (b). Asterisks (*) denote the spinning sidebands.
the initial ethane at 5.7 ppm almost vanishes at larger reaction time (12 h, Fig. 1b). The main products of ethane conversion are aromatics (toluene with the signals at 130 and 19 ppm) and methane. The signals at 13.4 and 28.7 ppm appear to arise from oligomeric hydrocarbons that precede aromatics formation from ethane. The signal at −21.5 ppm is referred to zinc-methyl species [13]. The characteristic signals at −0.5 ppm (Fig. 1a) and −21.5 ppm (Fig. 1b) never appear in the studies of hydrocarbon conversion on metal-free zeolites. This confirms their assignment to hydrocarbon fragments attached to zinc.

These data show that ethane converts into aromatics at 573 K with formation of significant amounts of methane. The formation of zinc-ethyl species from ethane gives evidence that the early step of alkane conversion involves a dissociative adsorption of ethane on ZnO species, which are located inside the channels of the zeolite (Scheme 1).

The signal from zinc-methyl species at −21.5 ppm (after 12 h) indicates that the methane, which is evolved during the ethane conversion into aromatics, is also subjected to a dissociative adsorption by interaction with zinc-sites.

The process of the dissociative adsorption seems to be common for the small alkanes, which are adsorbed on zinc-modified zeolites. The formation of 1-propylzinc species from propane on Zn/H-ZSM-5 was already shown by $^{13}$C MAS NMR and FTIR [12]. Strong adsorption complexes were registered by FTIR upon interaction of ethane and methane with Zn-ZSM-5 [32,33]. These complexes were ascribed to zinc-alkyl fragments formed due to dissociative adsorption of alkanes. The behavior of the signals from alkanes (ethane and methane) and corresponding zinc-alkyl species in dependence on the reaction time (Fig. 1) points to an equilibrium established between alkane and zinc-alkyl species: the signals from zinc-ethyl fragments decrease with decreasing the signal from ethane. The signals from methane and zinc-methyl increase in parallel. $^{13}$C MAS NMR provides the evidence that the alkane is a prevalent species over zinc-alkyl fragment in each equilibrium.

The products of ethane conversion on Zn/H-BEA zeolite were also analyzed by gas-chromatography mass-spectrometry (GC-MS) after being extracted from the catalyst with acetone, the reaction conditions were 12 h at 573 K, i.e., similar to Fig. 1b. The analysis confirmed the data by $^{13}$C MAS NMR about formation of methane and aromatics, while no ethylene oligomers were found among extracted hydrocarbons. The following composition of aromatic compounds was established by GC-MS: 15% benzene, 52% toluene, 30% xylenes, and 3% methylethylbenzenes (or trimethylbenzenes).

3.2. Analysis of the kinetics of ethane conversion with $^1$H MAS NMR

Fig. 2 shows the $^1$H MAS NMR spectra acquired at 573 K as a function of the reaction time. A decrease in the signal from ethane (0.9 ppm) and increase in the signal from methane (ca. 0.0 ppm) with increasing the reaction time is observed. Contributions from adsorbed and gaseous forms of methane (0.1 and −0.2 ppm) and ethane (0.9 and 0.6 ppm) can be observed. Also, the signals from zeolite SiOH groups (at 1.8 ppm) and from AlOHSi groups between 4.0 and 5.0 ppm are present in the $^1$H MAS NMR spectra. Small intensity signals around 7.5 ppm are attributed to the spinning sidebands from methane. Any notable intensity signals from aromatics and Zn-ethyl species have not been detected. However, the aromatic products can contribute to the weak signals at 7.5 ppm.

To characterize quantitatively the amount of aromatics and other products, which are not detected by $^1$H MAS NMR, the overall balance of atoms was used. The intensities of signals of both ethane and methane were normalized to the known initial amount of ethane in a sample. This gives the kinetic curves for ethane and methane in the terms of amount of hydrogen atoms in Fig. 3a. Fig. 3a shows that the amount of hydrogen atoms lost from ethane is larger than the quantity of hydrogen atoms received by methane. It means that a portion of the hydrogen atoms from ethane is transferred to the products other than methane. We denote these products as 'invisible' products, since they could not be observed in our kinetics measurements. The corresponding kinetic curve (denoted as ‘H-invisible’ in Fig. 3a) are calculated via subtracting the values of both methane and ethane kinetic curves from the intensity of the signal, corresponding to the initial amount of hydrogen atoms in ethane.
Similar, the amount of carbons, referred to unobservable products was calculated from $^1$H MAS NMR spectrum based on an overall balance of carbon atoms in initial ethane and the formed methane ("C-invisible" kinetic curve in Fig. 3b). At last, the ratio of H:C indicating the average composition of the unobservable products can be calculated from the H-invisible and C-invisible curves. Thus the kinetic curves “H-invisible” and “C-invisible” represent a time-dependent total amount of hydrogen and carbon atoms in the products on the catalyst surface (such as oligomeric and aromatic hydrocarbons) which are not observable under the conditions of kinetic measurements. Comparative analysis of the signal intensities from ethane and methane at the beginning and at the end of reaction indicates that 58% of carbon atoms of initial ethane are transformed to methane, the rest 42% of the ethane carbon atoms are converted to aromatics, ethylene oligomers and Zn-ethyl species. Fig. 3c shows the H:C ratio among unobservable products decreases from ca. 3.0 at the beginning to ca. 1.6 at the end of the kinetics. This corresponds to a change of a composition of the adsorbed unobservable products in the course of reaction.

The kinetic curves in Fig. 3 can be used for kinetic analysis of the possible reaction mechanisms. It is generally accepted that the aromatization of low alkane includes a dehydrogenation, in order to form the olefin and afford the further steps of oligomerization, dehydrogenation, and cyclization. The following different routes can be taken into account, in order to rationalize the formation of methane during the ethane aromatization: (i) protolytic cracking of C–C bond in ethane by Haag-Dessau mechanism on acid sites of the zeolite [34,35], (ii) direct hydrogenolysis of alkane molecule on Zn-sites [12], and (iii) hydrogenolysis of side chains in the formed bulk aromatic molecules [36]. A direct protolytic cracking of ethane by Haag-Dessau mechanism should not be accounted, because the reaction temperature used in this study is low ($\leq 573$ K) [34]. Therefore, we further discuss the analysis of the kinetics based on two mechanisms, which account methane evolution either by direct hydrogenolysis of ethane or by hydrogenolysis of side chains in bulk aromatics.

3.3. Mechanism of methane formation via direct hydrogenolysis of ethane

The route of hydrogenolysis of propane over Zn/H-ZSM-5 was supposed by Kolyagin et al. [12]. The hydrogen atoms required for the reaction of hydrogenolysis may be delivered from dehydrogenation of alkane or dehydro-oligomerization process. Based on this suggestion and assuming that the first step of ethane conversion includes a dissociative adsorption, Scheme 2 was proposed for kinetic modeling of the experimental curves.

The first stage of Scheme 2 accounts the dissociative adsorption of ethane on Zn-sites that leads to a formation of zinc-ethyl and ZnOH fragments. Both zinc-ethyl and ZnOH fragment are considered as a single kinetic component H–Zn–C$_2$H$_5$ in Scheme 2. Zinc-ethyl intermediate decomposes to ethylene and dihydrogen in the second stage. The third stage is hydrogenolysis of ethane to yield two molecules of methane from ethane and hydrogen. The last stage accounts ethylene oligomerization and aromatization to form aromatics and dihydrogen. Aromatic hydrocarbons in Scheme 2 are represented by a single product, toluene C$_7$H$_8$, which is the most abundant aromatic product according to GC-MS analysis. All the intermediate steps of ethylene oligomerization and further dehydrogenation and cyclization to aromatics are treated as one stage ($k_4$). The reversibility of the first two stages related to the alkane dehydrogenation with intermediate

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\begin{align*}
C_2H_8 & \xrightleftharpoons{\frac{k_1}{k_{-1}}} H-Zn-C_2H_5 \\
H-Zn-C_2H_5 & \xrightarrow{k_{2}} C_2H_4 + H_2 \\
C_2H_6 + H_2 & \xrightarrow{k_3} 2 \text{CH}_4 \\
C_2H_4 & \xrightarrow{k_4} \frac{2}{7} C_2H_8 + \frac{6}{7} H_2
\end{align*}
$$

Scheme 2. Kinetic scheme for ethane conversion to aromatics, which implies methane formation via hydrogenolysis of ethane.
formation of Zn-alkyl species is justified by earlier isotope tracing experiments [25] and kinetic modeling of alkane aromatization [36].

Simulation of kinetics based on Scheme 2 is shown in Fig. 4. A good accordance between calculated and experimental curves for CH₄, C₂H₆ as well as for both H-invisible and C-invisible curves is achieved provided that conversion of the intermediate zinc-ethyl (H–Zn–C₂H₅) is very fast. The calculated curves for invisible products (C₂H₄, H–Zn–C₂H₅, C₇H₈, H₂) are shown in Fig. 5a. Added together these curves give the kinetics of H-invisible and C-invisible in Fig. 4b. The concentration of zinc-ethyl species is the lowest among invisible products (≈10 μmol g⁻¹). It constitutes ca. 3% of the concentration of ethane during the whole kinetics. It could be seen from Fig. 5 that decrease in H:C ratio among unobservable products in the course of reaction is obliged to a decrease in ethylene concentration, the final H:C ratio being determined by the formed aromatics and dihydrogen.

The simulation of kinetics based on Scheme 2 offers an accuracy of 20–30% for the values of rate constants k₁, k₃, k₄. The other three rate constants (k₁, k₂, k₂) are obtained with larger uncertainty of 50–100%. However, the simulated curves for ethane and methane still fit the experimental curves well, provided that the quantity of the intermediate zinc-ethyl species corresponds to its quasi-stationary concentration of ca. 10 μmol g⁻¹.

The unobservable products C₆H₆, H₂, C₇H₈ are formed in a quantity comparable to that of ethane at the end of the kinetics. A possible explanation for the absence of the corresponding signals in ¹H MAS NMR spectrum during kinetic measurements is a spread of the signals in the spectrum of the reaction products, exhibiting different chemical shifts and large line widths. An absence of the signal from gaseous dihydrogen (the expected signal at 4.1 ppm [37]) may indicate that the hydrogen atoms, which are formed in dehydrogenation of ethane or further aromatization of ethylene, do not undergo a complete recombinative desorption. They seem to remain dissociatively adsorbed on ZnO species of the zeolite [38].

Thus Scheme 2 represents a reasonable model for describing the experimental kinetics of ethane conversion to aromatics and methane formation as well as a variation of composition of the products on zeolite surface in the course of reaction. A good correspondence of simulated kinetics to experimental values within the frame of Scheme 2 demonstrates that the formation of a large amount of methane in this reaction occurs by direct hydrogenolysis of ethane. This leads to the conclusion that direct hydrogenolysis of ethane can be the reason for the formation of a notable amount of methane in the process of ethane aromatization on Zn-modified zeolites [24,25].

3.4. Mechanism of methane formation via hydrogenolysis of side chains in aromatic

Another possible route for the methane production includes the hydrogenolysis of side-chains of bulk aromatics, which were formed by ethane dehydro-oligomerization. Final products of such reaction network may be simple aromatics (benzene, toluene) and methane (Scheme 3). The first two stages of Scheme 3 offer ethylene and dihydrogen via intermediate zinc-ethyl species. The third stage is the formation of alkyl-substituted (bulk) aromatics of the total composition C₇×ₐH₈×₂a from ethylene.
Further cracking of side chains consumes dihydrogen $H_2$ and yields toluene and methane $CH_4$.

The simulation of the experimental kinetics based on Scheme 3 has shown that the parameter $a$ should be equal or greater than 9. Otherwise, the simulated methane curve never reaches the experimentally observed values. Bulk aromatics in Scheme 3 should have a composition not less than $C_{16}H_{26}$, it means a formation of benzene rings with at least 10 carbons in a side alkyl chain, e.g., dipropyl-diethylbenzenes.

A simulation of the experimental kinetics based on Scheme 3 with parameter $a = 9$ is shown in Figs. 6 and 7. A close coincidence of simulated and experimental kinetics is achieved for methane and ethane (Fig. 6a), provided that the rate constant $k_3$ is one-two order of magnitude higher than other rate constants.

Scheme 3. Kinetic scheme for ethane conversion to aromatics implying methane formation via hydrogenolysis of side chain in bulk aromatics.

Otherwise, we have an induction period for the methane formation. However, we note that the simulation is not as perfect as that based on Scheme 2. Reaction mechanism of Scheme 3 implies more hydrogen unsaturated set of unobservable products on the catalyst surface in the initial part of kinetics, compared to experimentally observed set of products, based on C:H ratio. The simulated values of the H-invisible curve at 100–200 min are lower than the experimental values (Fig. 6b). Therefore, the values for H:C ratio are also lower (Fig. 7b). The variation of expected composition of unobservable products in the course of reaction, which is expected from Scheme 3, does not correspond to the experimental values. The calculations imply a rather high concentration of dihydrogen $H_2$ (see Fig. 7a). As a result we obtain the higher values for simulated curve of H-invisible products at the end of kinetics compared to the experimental one (see Fig. 6b). Also, it can hardly be assumed that such essential amount of hydrogen $H_2$ is not observed by $^1H$ MAS NMR.

Thus Scheme 3, where methane production occurs exclusively from hydrogenolysis of side chains of aromatics, fails to rationalize all features of the experimental kinetics. This mechanism requires formation of the intermediate bulk aromatics $C_{16}H_{26}$ and implies a formation of less hydrogen saturated intermediates (unobservable products) on the surface of the catalyst at the initial part of the kinetics. The expected more significant production of dihydrogen, which is predicted by Scheme 3, is not observed in the $^1H$ MAS NMR spectra. This leads us to conclude that Scheme 3 does not rationalize the routes for hydrogen expenditure. The kinetics modeling based on Scheme 3 confirms a
necessity to take into account the involvement of dihydrogen in a direct hydrogenolysis of alkane molecules as was considered in Scheme 2. Nevertheless, a possible formation of methane via hydrogenolysis of side chains in aromatics cannot be entirely ruled out, especially at long reaction times.

4. Conclusions

The conversion of ethane on Zn-modified zeolite BEA to simple aromatic products has been monitored by MAS NMR in situ at 573 K. Zn-ethyl species as an intermediate of this reaction was detected. The kinetics of this reaction was followed by $^1$H MAS NMR, which offered information on the methane formation and the evolution of the composition of the products on the catalyst surface in the course of the reaction. The simulation of the kinetics of ethane conversion, methane formation and evolution of composition of the reaction intermediates and products was carried out by means of two possible kinetic schemes of the reaction. This allowed us to conclude that a large quantity of evolved methane is produced mainly by the direct hydrogenolysis of ethane. Thus, the notable quantity of methane, which was detected among the reaction products of small alkane aromatization on Zn-modified zeolites [24,25], may be formed by the direct alkane hydrogenolysis.

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