



Surface species formed during propane aromatization over Zn/MFI catalyst as determined by in situ spectroscopic techniques

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ABSTRACT

The propane conversion was studied by in situ ¹H, ¹³C MAS NMR and IR spectroscopic techniques over Zn/H-MFI catalyst. Propane 2-¹³C, propane 1-¹³C, propene 1-¹³C, propene 2-¹³C and benzene ¹³C were used as labelled reactants. The results pointed to the propane activation via dissociative adsorption over zinc oxide sites, as evidenced by zinc propyl surface species observation at the onset of propane conversion. Zinc propyl species convert further into propene, which forms asymmetric π -complex with zinc cations. At the later reaction steps, propene oligomerizes to give charge delocalized carbanionic species stabilized on zinc cations. The role of carbanionic species in consecutive reaction steps is discussed.

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1. Introduction

The development of in situ spectroscopic techniques [1–4] allowed monitoring of the catalytic transformations directly on a catalyst surface during the course of the reaction. These techniques were shown to be very powerful in the mechanistic catalytic studies over heterogeneous catalysts, in particular, zeolite catalysts. Among the in situ techniques used for the investigation of hydrocarbon transformations over zeolites, MAS NMR [1] and IR [2] spectroscopic techniques turned out to be very informative for the elucidation of the surface species formed on the catalyst.

Application of in situ ¹³C MAS NMR spectroscopy allowed Derouane and co-workers to propose the detailed bifunctional mechanism of propane activation over Ga-modified acidic MFI zeolite [1a–c,5–7]. This mechanism implies synergetic action of acidic and (Ga³⁺–O²⁻)-ion pair sites in the formation of the protonated pseudocyclopropane (PPCP) intermediate, which further decomposes into propene and dihydrogen, methane and ethene or recombines back to propane [1a–c,5–7].

In contrast to Ga-containing zeolites, different reaction pathway was observed for propane activation over zinc modified

catalyst. In situ ¹³C MAS NMR and IR spectroscopy pointed to propane activation via dissociative adsorption over zinc sites [8–10].

While the initial stages of propane activation are now studied in detail, the information on the further reaction steps and, in particular, on the surface species formed during these steps is still very limited. This paper is aimed to clarify this point. The surface species formed during propane aromatization over Zn/H-MFI catalyst are monitored by in situ ¹H, ¹³C MAS NMR and IR spectroscopic techniques.

2. Experimental

Starting zeolite MFI with Si/Al ratio of 40 was provided by Zeolyst in NH₄-form. H-form was prepared by calcination at 823 K for 6 h in flow of dry air. Preparation of Zn-containing MFI catalyst (Zn/H-MFI) was carried out by the impregnation with aqueous solution of Zn(NO₃)₂, subsequent drying at 393 K for 15 h and calcination at 823 K for 12 h. The content of zinc was of 8.0 wt%.

The materials were characterized by elemental analysis, XRD, SEM, UV–vis diffuse reflectance spectroscopy, solid state ¹H, ²⁷Al and ²⁹Si MAS NMR spectroscopy, nitrogen adsorption and FTIR of adsorbed pyridine and CO. The elemental analysis of zeolites was performed by atomic absorption spectroscopy. The XRD pat-

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terns were recorded with a DRON-3M diffractometer, using Cu K α radiation. SEM images were obtained on CAMSCAN electron microscope. UV–vis diffuse reflectance spectra were measured on Specord M-40, equipped by reflectance accessory. ^1H , ^{27}Al and ^{29}Si MAS NMR experiments were performed on a AVANCE-II 400 Bruker spectrometer. Sorption–desorption isotherms of nitrogen were measured at 77 K using an automated porosimeter (Micromeritics ASAP 2000). IR spectra were recorded on Nicolet Protégé-FT-IR spectrometer with 4 cm^{-1} optical resolution.

Controlled-atmosphere studies of propane and propene transformations over Zn/H-MFI were performed after their adsorption onto the catalyst activated at 723 K overnight under vacuum in NMR or IR cells. NMR cells with catalysts and adsorbates were sealed out before the experiment, while IR cell was tightly closed. Before the adsorption, adsorbates were purified by three pump–freeze cycles. The amount of adsorbates was dosed volumetrically using Varian gauge.

For the NMR experiments propane $1\text{-}^{13}\text{C}$, propane $2\text{-}^{13}\text{C}$, propene $1\text{-}^{13}\text{C}$, propene $2\text{-}^{13}\text{C}$ and benzene ^{13}C (99.9% enriched) purchased from ICON Services Inc. were used as labelled reactants. The amount of adsorbed labelled compound was calculated on the basis of one molecule of adsorbate per unit cell of the zeolite. To achieve quantitative adsorption the part of the NMR cell with zeolite was cooled down to the temperature of liquid nitrogen during the adsorption and sealing off procedures.

^1H and ^{13}C MAS NMR measurements were carried out on AVANCE-II 400 Bruker spectrometer operating at 400.1 MHz for ^1H and 100.4 MHz for ^{13}C , respectively. The samples spinning rate for MAS experiments was $\sim 6\text{ kHz}$. Quantitative conditions for ^1H and ^{13}C were achieved by direct polarization NMR experiment with using DEPTH-2 composite pulse for suppression of background signal (5 s recycle delay for ^1H and ^{13}C spectra) [11]. The residual background signal in ^1H spectra was corrected manually by third-order spline curves. To eliminate multiplicity in ^{13}C spectrum SW-TPPM high-power proton decoupling was used ($\tau = 8\ \mu\text{s}$, $\varphi = 15^\circ$) [12]. The experiments involving cross-polarization from protons to carbon ($^1\text{H}\text{-}^{13}\text{C}$ CP/MAS) were performed using RAMP/CP method [13], with ramping of ^1H -channel power from 100 to 70%, 2 ms contact time and a 2.0 s recycle delay; the Hartmann–Hahn conditions were adjusted for 85%. ^{13}C chemical shifts were referenced relatively to the CH_2 group of solid adamantane [14]. ^1H chemical shifts were referenced relatively to TMS. Controlled-atmosphere experiments were performed in sealed pyrex NMR cells containing catalyst and adsorbed compounds labelled with ^{13}C and fitting precisely into 7-mm Bruker zirconia rotors.

In situ IR experiments were performed on a Nicolet Protégé-FT-IR spectrometer at 4 cm^{-1} optical resolution with one level of zero-filling for the Fourier transform. Prior to the measurements, the catalysts were pressed in self-supporting discs (diameter: 1.6 cm, 7 mg cm^{-2}) and activated in the IR cell attached to a vacuum line. The adsorption of propane or propylene was carried out at ambient temperature. The spectra were recorded after adsorption, heating to selected temperature and subsequent evacuation at ambient temperature to monitor the most strongly adsorbed species. The sample temperature during the treatment was controlled by a chromel–alumel thermocouple inserted into the heater of the cell.

The analysis of the products and intermediates accumulated on the surface of the catalyst during the in situ experiments was performed by GC–MS on GC/MS HP 5972 and Agilent Technologies 7683B complex. The products were removed from the catalysts surface either by evacuation in a specially constructed unit attached

to the vacuum line or by extraction with CH_2Cl_2 . Both procedures gave similar results.

3. Results and discussion

3.1. Catalysts characterization

The zeolite used for the preparation of Zn-containing catalysts was characterized by XRD, SEM, ^{27}Al and ^1H MAS NMR, nitrogen adsorption and FTIR spectroscopy of adsorbed pyridine. The XRD data confirmed the MFI type structure of the starting material. SEM images revealed that the average crystal size is $\sim 0.5\ \mu\text{m}$. ^{27}Al MAS NMR indicated the absence of extraframework aluminum. FTIR spectra in the OH stretching region indicated that H-MFI contains Brønsted acid groups (3610 cm^{-1}) associated with framework aluminum, isolated external silanol groups (3740 cm^{-1}), as well as free internal silanol groups (3726 cm^{-1}) and delocalized hydrogen-bonded groups (3500 cm^{-1}) of lattice defects. ^1H and ^{29}Si MAS NMR data confirmed these assignments. Chemisorption of pyridine on H-MFI led to a conversion of Brønsted acid sites into pyridinium ions characterized by the band at 1546 cm^{-1} , and indicated the formation of small amount of Lewis sites (1455 cm^{-1}) upon zeolite dehydroxylation.

Modification of the zeolite with zinc led to the appearance of two bands in UV–vis diffuse reflectance spectra of H-MFI at about 265 and 375 nm, corresponding to sub-nanometric ZnO clusters inside zeolitic pores and large ZnO crystals on the external surface of the zeolite, respectively [15]. The content of large ZnO crystals was determined from XRD [16] to be not higher than 0.4 wt%. The nitrogen adsorption data confirmed the decrease of pore volume by $\sim 10\%$ due to deposition of ZnO particles inside the pores of H-MFI.

The FTIR spectra of adsorbed CO on Zn/H-MFI revealed that besides ZnO particles the sample contains zinc ions, evidenced by the appearance of the band at 2230 cm^{-1} due to CO adsorption on zinc cations [17]. The FTIR spectra in the OH stretching region, ^1H MAS NMR data and FTIR spectra of adsorbed pyridine confirmed the consumption of Brønsted acid groups ($\text{Si}(\text{OH})\text{Al}$) in the ion-exchange process and pointed to the formation of Lewis acid sites induced by the presence of zinc ions. Besides that, the appearance of the weak band at ca. 3670 cm^{-1} due to ZnOH groups was observed.

The comparison of relative intensities of the bands at 1546 cm^{-1} on H-MFI and Zn/H-MFI suggests that $\sim 80\%$ of protons are involved in ion-exchange for zinc cations. Assuming that each Al atom generates a Brønsted site in H-MFI (a hypothesis sustained by the absence of extraframework aluminum) and supposing that the protons are replaced by monopositive ZnOH^+ cations, it was estimated that the maximum content of Zn in cationic positions may amount to 2.6 wt% in Zn/H-MFI zeolite.

It was thus concluded that the sample studied contains three types of Zn species: small and large ZnO clusters and zinc cations. The simple estimations derived from XRD data, FTIR data and chemical analysis suggest that the most part of Zn species exists in the form of sub-nanometric ZnO clusters inside the zeolitic pores.

With respect to cationic species, it is difficult to conclude, what type of cations are present in Zn/H-MFI. The literature data suggest that most probable cationic species formed upon ion-exchange with zinc nitrate solutions is ZnOH^+ , but this species is not stable and undergoes dehydration upon calcination [18]. At low Zn loadings, ZnOH^+ couples with nearby proton, forms Zn^{2+} and water, which desorbs. At high Zn loadings ($>1.3\text{ wt}\%$), ZnOH^+ may interact with another ZnOH^+ or a SiOH group leading to the formation of $(\text{OZ})^- (\text{Zn-O-Zn})^{2+} (\text{OZ})^-$ [18] or $(\text{ZO})^- \text{Zn}^+-\text{O}-\text{Si}$ [19], respec-

These results confirm our previous conclusion that the first step of propane activation over Zn/H-MFI is dissociative adsorption over zinc sites leading to formation of *n*-propyl zinc species. Besides that, the longer accumulation of ^1H - ^{13}C CP/MAS NMR spectra undertaken in this study allowed to detect the conversion of zinc propyl species into propene, which gives asymmetric π -complex with zinc cations. It is interesting to note that no ^{13}C scrambling occurs in propene molecule during the initial step of the reaction: propane 1 - ^{13}C gives propene 1 - ^{13}C , while propane 2 - ^{13}C yields propene 2 - ^{13}C . This observation evidences that the protonic sites of the zeolite do not participate in the initial step and only zinc sites are responsible for propane activation and propene formation.

Heating of the samples for longer reaction times leads to the following changes in the spectra (Fig. 2):

- the lines of ethane ($\delta=6.5$ ppm) and methane ($\delta=-7.3$ ppm) appear due to propane hydrogenolysis;
- partial ^{13}C label scrambling in propane and propene is observed as confirmed by the appearance of the small resonance lines at ca. 16.2 and 115 ppm, respectively, in the experiment with propane 2 - ^{13}C starting reactant;
- ^1H - ^{13}C CP/MAS NMR spectra reveal the appearance of the new lines at ca. 12.9, 26, 92 and 140 ppm. The two former lines can be attributed to methyl and methylene groups of *n*-butane [5–7], while the latter were not observed previously. It is important to note that the same lines were detected in the experiments with propane 1 - ^{13}C as starting reactant. This observation suggests that the species corresponding to these lines underwent complete label scrambling. The origin of these lines is discussed later in the paper.

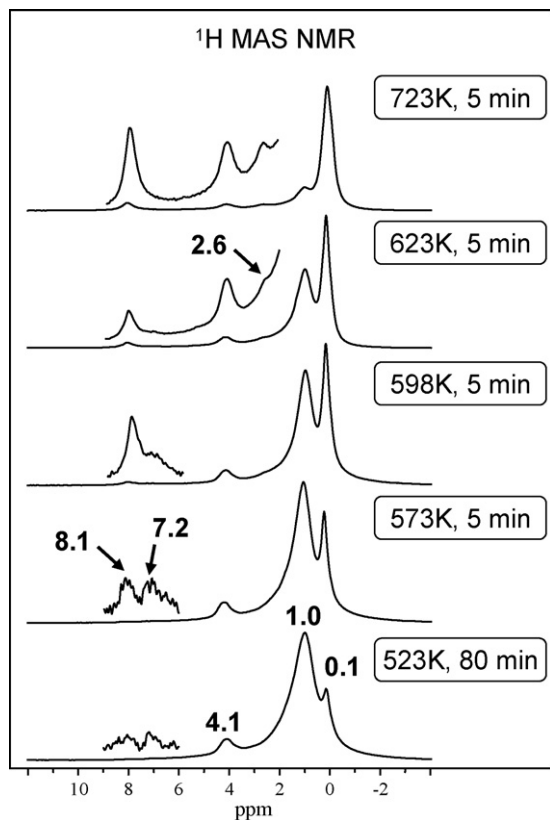


Fig. 3. ^1H MAS NMR spectra observed in the course of propane reaction over Zn/H-MFI catalyst at elevated temperatures.

^1H MAS NMR spectrum (Fig. 3) obtained after reaction of propane over Zn/H-MFI at 523 K corresponds to those of ^{13}C MAS NMR (Fig. 2). Along with the lines due to zeolite Brønsted acid groups ($\delta=4.1$ ppm), the lines which can be assigned to the protons of propane, ethane (broad resonance centered at ca. 1 ppm) and methane ($\delta=0.1$ ppm) are observed. Besides that, weak resonances at ca. 8.1 and 7.2 ppm can be distinguished in the region of olefinic or aromatic protons. These two lines could hardly be attributed to propene, which is usually characterized by the line at ca. 5.3 ppm. The latter should overlap with the broad resonance of acidic protons of the zeolite. They also cannot be due to aromatics, since no aromatics formation is observed at this temperature (Fig. 2). They most probably have the same origin as the lines at ca. 92 and 140 ppm observed in ^{13}C MAS NMR.

Further heating of the sample at elevated temperatures results in the decrease of propane resonances and the increase of the contribution of ethane and methane lines (Fig. 2). Meanwhile a new resonance line appears at ca. 133 ppm at 573 K and starts to grow with temperature. The appearance of the line at 133 ppm is accompanied by the line at 19.8 ppm, which shows the same behaviour with increasing temperature. The line at 19.8 ppm can be attributed to methyl group in methylsubstituted aromatics [1b,7,20], however, the aromatic carbons in these compounds are usually characterized by the line at 128–129 ppm [1b,7,20]. The resonance observed in our case is shifted downfield with respect to these values. To verify the assignment of this line, labelled benzene ^{13}C was adsorbed on Zn/MFI zeolite. Two lines emerged at ca. 129 and 132 ppm. The lines were attributed to gaseous and adsorbed benzene, respectively. As in the case of propene, π -electrons of benzene can interact with zinc cations. This accounts for downfield shift of the resonances of aromatic carbons in methylsubstituted aromatics. It was thus confirmed that the lines at 133 and 19.8 ppm belong to methylsubstituted aromatics.

In ^1H MAS NMR experiments (Fig. 3) similar observations are made. The decrease of the intensity of propane and ethane line ($\delta=1.0$ ppm) is accompanied by the increase of the intensity of methane line ($\delta=0.1$ ppm) and the lines corresponding to aliphatic ($\delta=2.6$ ppm) and aromatic ($\delta=7.9$ ppm) protons in methylsubstituted aromatics.

Both ^1H and ^{13}C MAS NMR experiments (Figs. 2 and 3) indicate the formation of olefinic surface species at the onset of aromatics formation. The NMR lines corresponding to these species were never observed before in course of in situ NMR studies of propane transformations, neither on H- [22] nor Ga-forms [5,6] of zeolites and are typical for Zn/MFI catalysts. It was thus of great importance to understand the origin of these lines.

For this purpose, in situ FTIR study of propane conversion was performed over the same sample (Fig. 4). The initial reaction product observed at the temperatures starting from 448 K is propene, as evidenced by five weak but well-resolved bands in the 1350 – 1600 cm^{-1} region. Four bands at 1376, 1451 and 1411, 1428 cm^{-1} correspond to the CH_3 bending modes and in-plane deformation of the vinylic group, respectively, while the band at ca. 1585 cm^{-1} can be attributed to $\text{C}=\text{C}$ stretching vibration. The frequency of $\text{C}=\text{C}$ stretching mode of propene is sensitive to the type of adsorption site and has been observed in the wide spectral range of 1580 – 1650 cm^{-1} [3,9,23]: 1645 cm^{-1} on silanol groups, ~ 1630 cm^{-1} on acidic protons, 1585 cm^{-1} on zinc cations. The observed downscale shift in the case of adsorption on Zn/MFI is due to strong interaction of π -electrons of propene with zinc cations and formation of π -complex, which is in line with ^{13}C NMR data discussed above. The preservation of propene bands upon evacuation confirmed its strong chemisorption over Zn/MFI catalyst.

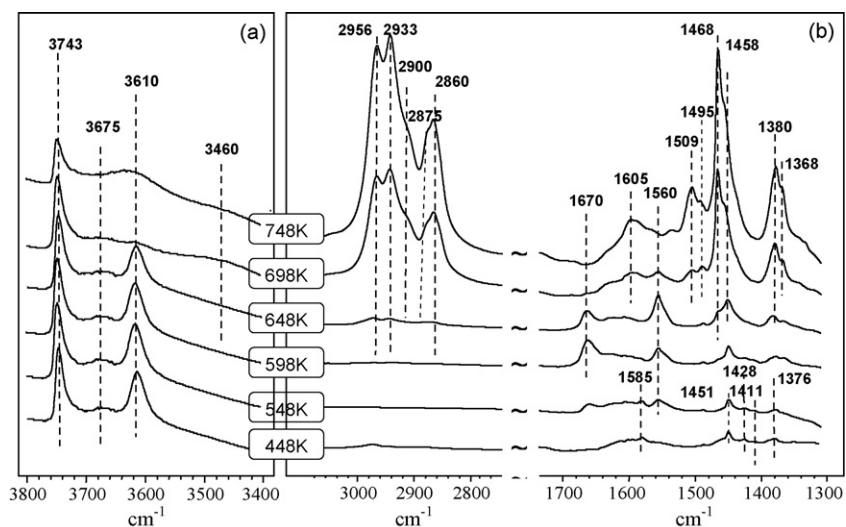


Fig. 4. FTIR spectra observed in the course of propane reaction over Zn/H-MFI catalyst in the region of OH groups vibrations (a) and in the regions of hydrocarbon bonds vibrations (difference spectra) (b). The spectra are recorded after propane adsorption, heating to selected temperature and evacuation at ambient temperature to monitor the most strongly adsorbed species.

Besides the bands corresponding to propene, very weak bands at 1384, 1392, 1434, 1463 and 1469 cm^{-1} were detected at the initial stage of the reaction, when the spectrum was enlarged in intensity. As it was discussed in our previous communication [9], these bands are due to zinc propyl species.

It should be noted that the bands observed in the region of OH groups vibrations remained intact during the initial steps of the reaction (Fig. 4a). This observation confirms that neither silanol groups, nor Brønsted acid sites participate in the step of propane dissociation and supports the conclusion that propane activation occurs on zinc sites.

Heating the sample to 548 K, results in the appearance of the new bands at 1560 and 1670 cm^{-1} (Fig. 4b). At 598 K the intensity of these bands increases, whereas the band due to C=C vibration in propene vanishes completely. Meanwhile the bands, which are due to propene oligomers start to develop in 2800–3000 cm^{-1} and 1350–1470 cm^{-1} spectral regions. The bands at 2860, 2933 and 2875, 2956 cm^{-1} correspond to symmetric and asymmetric stretching modes of CH_2 and CH_3 groups, respectively; the band at 2900 cm^{-1} is due to CH groups; the bands at 1368, 1468 and 1380, 1458 cm^{-1} correspond to symmetric and asymmetric bending modes of CH_2 and CH_3 groups [24]. Comparison of the intensities of the bands corresponding to CH_2 and CH_3 groups suggests that branched oligomers are formed.

Further increase of the reaction temperature to 648 K results in the increase of the intensity of the bands due to oligomers and the appearance of the new broad bands in the 1590–1630 cm^{-1} and 1480–1540 cm^{-1} spectral regions due to formation of aromatic compounds [25]. Finally, raising the reaction temperature to 698–748 K leads to further development of the bands of oligomers and aromatics and complete disappearance of the bands at 1560 and 1670 cm^{-1} .

The accumulation of oligomers and aromatics causes the disappearance of the band 3610 cm^{-1} (Fig. 4a) corresponding to Brønsted acid groups (Si(OH)Al). Instead, the broad band at ca. 3460 cm^{-1} corresponding to hydrogen-bonded complexes develops, suggesting that at this step of the reaction acidic protons are involved in the reaction pathway. At the later stages of the reaction (748 K), the bands corresponding to Si(OH) groups (3726 cm^{-1}) decrease in intensity and the broad band of corresponding complex starts to develop at 3600 cm^{-1} , most probably due to interaction

with condensed aromatics at the external surface of the sample.

Consequently, FTIR studies also pointed to the observation of the intermediate species at the onset of aromatics formation. These species are characterized by the intensive bands at 1670 and 1560 cm^{-1} . According to the literature data the former are most likely due to olefins with internal double bond or polyenic species [3,24,26], while the bands in the region of 1570–1505 have a number of assignments according to different authors [3,23b,25b,26b,27–30]. One group of authors attributes this band to π -complex formed between the double bond and acidic proton or zeolite cation [3,23b]. Another group assigns it to aromatics or precursors of aromatic compounds [3,25b,27]. Finally, the third assignment is C–C stretching mode in charge delocalized alkenyl carbenium ions [26b,28] or carboanions [29,30]. The first assignment is not applicable in our case because π -complex of propene was identified to appear at another wavenumber (1585 cm^{-1}). For the second assignment the temperature is too low. Thus, it can be supposed that the line at ca. 1560 cm^{-1} is due to C–C stretching vibrations in charge delocalized carbocation or carbanion. The formation of alkenyl carbocations is generally due to protonation on acidic sites of a zeolite [26b,28], while carbanions were shown to be formed on cations [29,30]. Our observation that the band of acidic OH groups remains intact at the reaction temperatures when the band at 1560 cm^{-1} is observed makes less likely the former assignment.

The analysis of the NMR data for alkenyl cations on zeolites and charge delocalized carbanions on metal cations allows for more reliable discrimination between these two types of species. In conjugated alkenyl carbenium ions and carbanions the ^{13}C NMR chemical shifts of the even-numbered carbon atoms are close to those of neutral olefins ($\delta = 120\text{--}150$ ppm). In contrast, the NMR lines of odd-numbered carbons are shifted significantly: downfield in carbocations [20,31] and upfield in carbanions [20,30,32]. Thus, the odd-numbered carbons in alkenyl cations are usually characterized by the NMR signals in the spectral region of 190–260 ppm [20,31]. On the contrary, for charge delocalized carbanionic species the chemical shifts in the region of 65–100 ppm are typical [20,30,32]. The resonances observed in our NMR experiments at ca. 92 and 140 ppm are consistent with chemical shifts of odd- and even-numbered carbon atoms in delocalized carbanions.

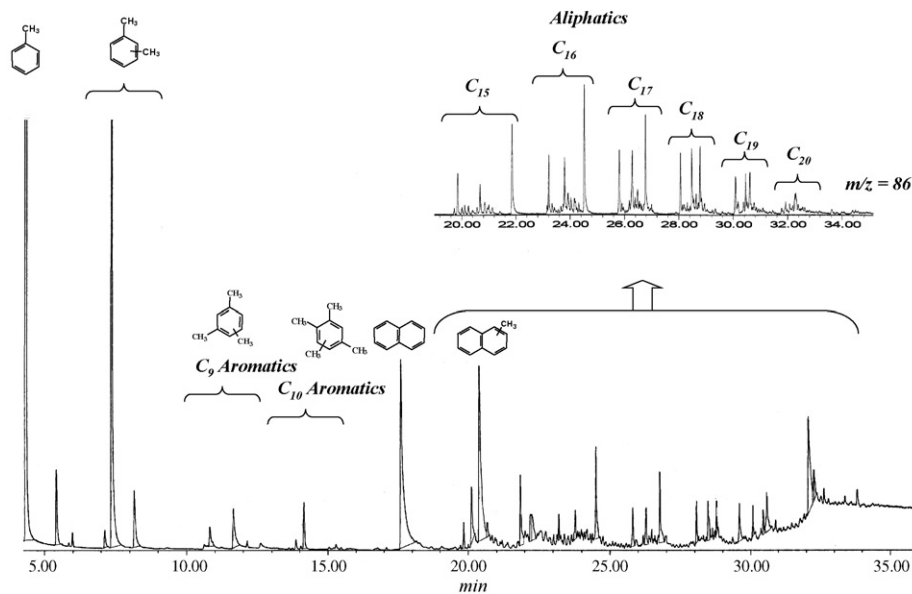


Fig. 5. The GC-MS spectrograph of the products extracted from the Zn/H-MFI catalyst after in situ MAS NMR experiment depicted in Fig. 2.

Thus, both techniques point to carbanionic nature of the species formed at the onset of aromatics formation. To get more detailed information on the nature of these species, the products extracted from the catalyst surface after NMR experiments were analysed by GC-MS. The results are presented in Fig. 5. The spectrograph shows the peaks corresponding to methylsubstituted benzenes (toluene, xylenes, trimethylbenzenes, and tetramethylbenzenes), naphthalenes and methylsubstituted naphthalenes. These compounds were indeed identified in our NMR experiments. Besides that, the peaks corresponding to C₁₅–C₂₀ aliphatic hydrocarbons were identified. Consequently carbanionic species observed could be due to aliphatic charge delocalized carbanions with the hydrocarbon chain length of 15–20 atoms.

To confirm the above assignment unambiguously, one would need to adsorb olefin or diene with the hydrocarbon chain length of 15–20 atoms on the same zeolite and to carry out an NMR experiment in the similar conditions. However, ¹³C labelled compounds of this type are hardly available. On the other hand, such or similar compounds can be easily obtained in situ by oligomerization of olefins over zeolite catalysts [31b,33]. We therefore performed in situ studies of propene reaction over Zn/H-MFI catalyst.

¹H-¹³C CP/MAS NMR experiments carried out with propene 2-¹³C revealed that upon adsorption, propene forms π -complex with zinc cations, characterized by NMR line at ca. 165 ppm. At longer reaction times at ambient temperature, propene is converted into oligomer, evidenced by the NMR lines at ca. 12.7, 17.7, 23.3 and 32.7 ppm, the latter resonance being the most intensive. Heating the sample to 423 K leads to the appearance of the lines due to carbanionic species at ca. 92 and 140 ppm. Further heating at elevated temperatures results in formation of aromatics and cracking of the oligomer accompanied by the disappearance of carbanionic species. Similar results were obtained with propene 1-¹³C starting reactant. The only difference was the observation in the initial NMR spectrum the line at ca. 110 ppm instead of the resonance at ca. 165 ppm, due to C-1 carbon atom in propene π -complex with zinc cations. Finally, the intermediate formation of carbanionic species from propene over Zn/MFI was confirmed by FTIR data. The band at ca. 1560 appeared at 373 K and vanished at 673 K at the onset of aromatics formation.

In summary, the results of ¹³C MAS NMR and IR spectroscopic in situ studies pointed to the formation of the following organozinc surface species in the course of propane transformation over Zn/H-MFI catalyst:

- at the onset of propane reaction, formation of zinc propyl species was evidenced by the NMR lines at ca. 12.2, 19.5 and 20.3 ppm and IR bands at 1384, 1392, 1434, 1463 and 1469 cm⁻¹;
- zinc propyl species were shown to convert into propene, which gives asymmetric π -complex with zinc cations (δ = 110, 165, 19 ppm and $\nu_{C=C}$ = 1585 cm⁻¹);
- at the onset of aromatics formation, carbanionic species were detected as confirmed by NMR lines at ca. 92 and 140 ppm and the IR band at 1560 cm⁻¹.

As it was discussed previously [9], observation of propyl zinc species points to propane activation via dissociative adsorption over zinc oxide sites, followed by dehydrogenation of propyl group and formation of propylene and dihydrogen. While propane dissociation was observed previously, the formation of carbonionic species in the course of propane conversion over Zn/MFI catalysts was detected for the first time. The role of these species in propane conversion into aromatics is not clear as yet. They may participate in propene oligomerization via anionic pathway or be involved in the latter stages of oligomer dehydrogenation, preceding its further cyclization into aromatic compounds. Stabilization of these species on Zn cations may prevent cracking of the oligomers towards short chain alkanes on acidic sites and favour aromatization into BTX fraction, which accounts for higher aromatization selectivity of Zn-containing zeolites with respect to pure acidic zeolite. On the other hand, it can be responsible for rapid Zn/MFI catalyst deactivation due to poisoning of the active sites by stable surface species or formation of condensed aromatics. Further work is needed to clarify all this points.

The mechanism proposed for propane activation over Zn/H-MFI catalysts is quite different from those proposed previously by Derouane and co-workers for Ga/H-MFI catalysts [1a–c,7]. On Ga/H-MFI, the acidic and Ga-sites were claimed to work in synergy at the very early stages of propane activation leading to the cyclic PPCP intermediate, which accounted for ¹³C scrambling in

propane as the main initial reaction pathway. In contrast, on Zn/H-MFI catalysts only Zn sites are found to be responsible for the initial propane activation leading to propane dissociative adsorption and dehydrogenation, while acidic sites are participating in further reaction steps. Besides that the results suggest that Zn sites may participate in propene oligomerization via anionic pathway and stabilization carbonionic species formed. Finally, Zn sites are shown to be very active in propane hydrogenolysis accounting for ethane and methane formation at the very early stages of the reaction. All these findings explain higher activity of Zn/H-MFI catalysts in propane conversion, but lower selectivity towards aromatics with respect to Ga/H-MFI catalysts, which is due to the enhanced ethane and methane formation [34].

4. Conclusions

The in situ ^1H , ^{13}C MAS NMR and IR spectroscopic studies of propane aromatization over Zn/H-MFI catalyst pointed to formation of three types of surface species strongly attached to zinc: (i) zinc propyl species, evidenced by the ^{13}C NMR lines at ca. 12.2, 19.5 and 20.3 ppm and IR bands at 1384, 1392, 1434, 1463 and 1469 cm^{-1} ; (ii) propene asymmetric π -complex with zinc cations, observed at $\delta = 110, 165, 19\text{ ppm}$ and $\nu_{\text{C}=\text{C}} = 1585\text{ cm}^{-1}$; (iii) carbanionic species, confirmed by NMR lines at ca. 92 and 140 ppm and the IR band at 1560 cm^{-1} .

Zinc propyl species were shown to be involved in the initial step of propane activation via dissociative adsorption over zinc oxide, resulting in propene and dihydrogen. Carbonionic species may participate in further reaction steps such as propene oligomerization via anionic pathway, oligomer dehydrogenation and aromatization. They can be also responsible for rapid Zn/MFI catalyst deactivation due to poisoning of the active sites by stable surface species or formation of condensed aromatics. Further work is underway to clarify these points.

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