FULL PAPER

Formation of Carboxylic Acids from Small Alkanes in Zeolite H-ZSM-5

Mikhail V. Luzgin,[a] Alexander G. Stepanov,*[a] Alain Sassi,[b] and Jean Sommer*[b]

Abstract: The activation of propane and isobutane in acidic zeolite H-ZSM-5 in the presence of both CO and H_2O has been studied by in situ solid-state NMR and GC analysis. Evidence was provided for the conversion of propane to isobutyric acid at 373–473 K by cleavage of the C−C bond; methane and ethane are also produced. Isobutane is transformed into pivalic acid with simultaneous production of hydrogen. The low conversion (1–2%) at this temperature was rationalized by the existence of a small number of sites that are capable of generating carbenium ions which are trapped by CO at this temperature. A formate species was observed when CO and H_2O were present on H-ZSM-5. This species disappeared in the presence of the alkane. At 573 K, the generation of large amounts of CO_2 indicates a much higher conversion of the alkanes into carboxylic acids which, however, decompose under the reaction conditions.

Keywords: alkanes · carboxylic acids · carbon monoxide · NMR spectroscopy · zeolites

Introduction

Activation of saturated hydrocarbons is an important goal for industrial organic chemistry. However, the chemical inertness of alkanes towards most of the usual reagents greatly complicates their conversion into primary chemical building blocks, such as olefins, dienes, or aromatic compounds, for use in organic syntheses. To overcome the inertness of alkanes, refinery operations, such as catalytic reforming and vapor-cracking, which require noble-metal catalysts and high temperatures, are needed.[1]

Liquid superacids are suitable for the activation of alkanes at low temperatures and pressures.[2, 3] However, the main problem in the application of such reactions is the low selectivity owing to the very high reactivity of the cationic reaction intermediates, which results in cracking and rearrangement of the hydrocarbon skeleton. The use of carbon monoxide as a trapping agent for the highly reactive intermediate carbenium ions inhibits these competitive side reactions in superacidic media and gives rise to useful products—carboxylic acids.[4–6] These acids are generally prepared from alkenes in sulfuric acid (Koch reaction);[7, 8] however, we have recently shown that they can also be selectively synthesized from an olefin and CO on an acidic zeolite under mild temperature and pressure conditions.[9]

On the other hand, on the basis of regioselective H/D exchange between isoalkanes and zeolites, Sommer et al.[10, 11] and Hall and Engelhardt[12] have suggested that alkenes and carbenium ions occur as reaction intermediates on solid acids at 373–473 K. We also reported that carbon monoxide blocked this exchange by trapping the carbenium ion intermediates.[13] Taking these two results into account, we could expect that carbon monoxide and alkanes should interact on zeolite at temperatures greatly below the usual working temperatures at which cracking is observed.

While various suggestions concerning the route of the initial formation of the carbenium ions during the cracking reaction can be found in the literature, the chain mechanism of alkane cracking at 573–673 K over acidic zeolites via carbenium ion intermediates is that generally accepted nowadays.[14, 15] Once the carbenium ion is formed, it undergoes further transformations: isomerization, hydride transfer, deprotonation with formation of an olefin that leads to oligomerization, aromatization, or cracking by β-scission to generate a smaller carbenium ion and an olefin. The addition of carbon monoxide and water to the initial alkane would be expected to change the pattern of the cracking products. Indeed, by trapping the intermediate carbenium ions at the initial stages of the cracking reaction performed on acidic zeolite, carbon monoxide could terminate the carbenium chain mechanism and produce valuable carboxylic acids instead of olefins and aromatics.

Herein we report our results on the activation of small alkanes (propane and isobutane) on acidic zeolite H-ZSM-5

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in the presence of carbon monoxide and water at temperatures well below those of previously observed transformations of the alkanes by the cracking reaction.

Results and Discussion

Formation of carboxylic acids from alkanes, CO and water at moderate temperatures (373–473 K)

As both propane and isobutane undergo H/D exchange of methyl hydrogens at 373–473 K on solid acids, including H-ZSM-5 zeolite,[10–13] we chose these saturated hydrocarbons to check our hypotheses concerning the interaction of small alkanes with CO on acidic zeolites at moderate temperatures.

Propane: Figure 1a shows the ^{13}C CP/MAS NMR spectrum recorded after heating the zeolite sample with coadsorbed propane, ^{13}CO, and water for 2 h at 473 K. In addition to the signals from adsorbed propane at $\delta = 17.0$ and $\delta = 18.2$,[16] a broad signal of low intensity at $\delta = 191$ is observed. This signal is in the region typical for carbonyl groups;[17] however, its

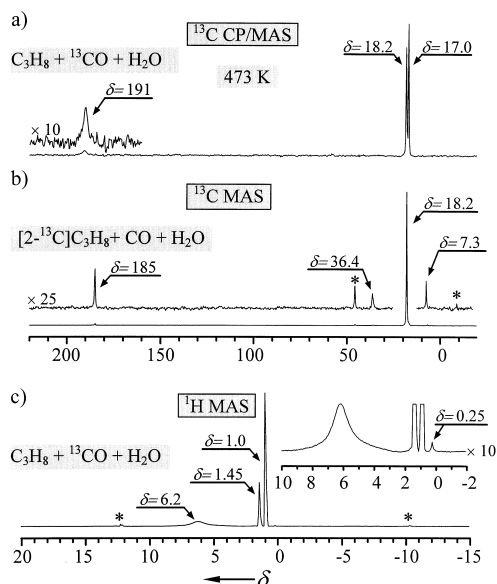**Abstract in Russian:**

С помощью спектроскопии ЯМР твердого тела in situ и ГХ анализа изучена активация пропана и изобутана на кислотном цеолите H-ZSM-5 в присутствии CO и H₂O. Показано, что пропан реагирует с CO и водой посредством разрыва C–C связи с образованием изобутановой кислоты и выделением метана и этана при 373-473 К. Изобутан превращается в пивалевую кислоту с одновременным образованием молекулярного водорода. Низкая степень превращения (1-2 %) при 373-473 К объясняется наличием в цеолите небольшого числа активных центров, способных образовывать карбениевые ионы, которые реагируют с окисью углерода. Взаимодействие CO с Бренстедовскими кислотными центрами цеолита в присутствии H₂O приводит к образованию формиатных структур, которые исчезают в присутствии алкана. При 573 К происходит образование значительных количеств CO₂, что указывает на большую степень превращения алканов в карбоновые кислоты, которые, однако, разлагаются в данных условиях реакции.

Abstract in French: *L'activation du propane et de l'iso–butane par une zeolithe acide de type HZSM-5 en presence de CO et H₂O a ete etudiee par spectroscopie RMN du solide in-situ et analyse CPG. Il a ete montre que le propane reagissait a 373–473 K par protolyse de la liaison C-C avec formation d'acide isobutyrique, de methane et de propane. Dans les memes conditions l'isobutane produit l'acide pivalique et de l'hydrogene. La faible conversion (1–2 %) observee a cette temperature est expliquee par le faible nombre de sites capables, a cette temperature, de generer les carbocations qui sont pieges par CO. Lorsque seuls CO et H₂O etaient presents sur le catalyseur une espece formiate etait observee qui disparaissait en presence d'alcane. La formation de grandes quantites de CO₂ a 573 K est l'indication d'une conversion bien plus elevee en acides carboxyliques qui se decomposent cependant dans les conditions de la reaction.*

Figure 1. NMR spectra of propane, carbon monoxide, and water coadsorbed on H-ZSM-5 zeolite. The samples were heated at 473 K for 2 h. a) ^{13}C CP/MAS NMR, coadsorption of propane, ^{13}CO (90% ^{13}C enrichment) and water; b) ^{13}C MAS NMR, coadsorption of [2-^{13}C]propane (99% ^{13}C enrichment), unlabeled CO and water; c) ^1H MAS NMR spectrum of the sample (a). 16 000 scans were collected for (a) and (b), 120 scans for (c). Spinning rate was 4.5 kHz for (a) and (c), 2.7 kHz for (b). Asterisks (*) in the spectra denote spinning side bands.

position and lineshape differ from those reported previously for a signal at $\delta = 184 – 185$ from ^{13}CO adsorbed on H-ZSM-5.[9, 18–21] The position of this signal at $\delta = 191$ is characteristic of the carbonyl group of a carboxylic acid adsorbed onto H-ZSM-5.[9] Thus, the appearance of the signal at $\delta = 191$ is in agreement with a reaction between propane, carbon monoxide, and water during which ^{13}CO was transformed into a ^{13}C-labeled carbonyl group of a carboxylic acid.

To elucidate the reaction pathway further, we then used ^{13}C-labeled propane for the coadsorption. When the reaction was carried out with [2-^{13}C]propane, unlabeled CO and water, a weak signal at $\delta = 7.3$ from ethane[16] and a signal at $\delta = 36.4$ were observed in the ^{13}C MAS NMR spectrum, in addition to the intense signal at $\delta = 18.2$ from the ^{13}C-labeled carbon of the methylene group in propane (Figure 1b). The signal at $\delta = 36.4$ should be assigned to the carboxylic acid, which also exhibits the signal at $\delta = 191$ in Figure 1a. The ^1H MAS NMR spectrum (Figure 1c) of coabsorbed unlabeled propane, ^{13}C-labeled CO, and water, exhibits a signal at $\delta = 0.25$ from methane[22] along with signals from propane at $\delta = 1.0$ (CH₃) and $\delta = 1.45$ (CH₂)[22] as well as that from H₂O adsorbed on a zeolite Si-OH-Al group at $\delta = 6.2$.[23] To sum up, these NMR observations are in accordance with the formation of methane, [1-^{13}C]ethane and [2-^{13}C]isobutyric acid (IBA) during activation of [2-^{13}C]propane by H-ZSM-5 at 473 K in the presence of CO. Whereas the Haag Dessau mechanism[24] is generally accepted to rationalize the product distribution at higher temperatures ($\geq$ 573 K), no conversion of propane was reported at 473 K and below.[13] However, in analogy with the superacid-catalyzed protolytic activation of propane,[5, 6] the Haag and Dessau mechanism (Scheme 1) would rationalize the formation of the same products.
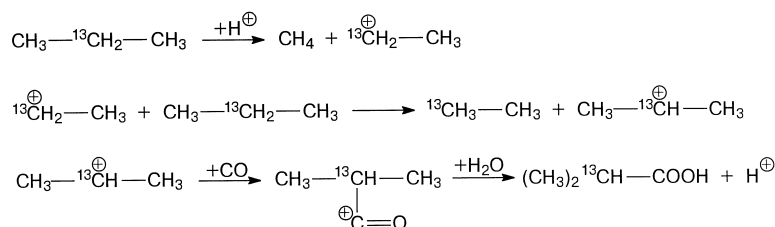
Scheme 1. Mechanism of [2-^{13}C]propane carbonylation into [2-^{13}C]isobutyric acid in H-ZSM-5 at 373 – 473 K.

intense signals from unreacted isobutane at $\delta = 1.0$ (CH$_3$) and $\delta = 1.8$ (CH)[22] and H$_2$O/Si-OH-Al protons at $\delta = 6.6$,[23] two signals for the reaction products: $\delta = 4.10$ from molecular hydrogen, H$_2$[22] and the signal at $\delta = 1.45$.

New signals at $\delta = 193$, 40.9 and 27.7 in the ^{13}C NMR spectra

Indeed, according to Scheme 1, during the course of the reaction, the selectively ^{13}C-labeled CH$_2$ group of [2-^{13}C]propane is transformed into the labeled CH group of IBA, giving rise to the signal at $\delta = 36.4$, close to that for liquid IBA at $\delta = 34.8$.[25] Unlabeled methane is generated by protolytic attack on the C–C bond of propane. The formation of [1-^{13}C]ethane occurs via hydride abstraction from the second propane molecule to give the isopropyl cation. The resultant isopropyl cation reacted with CO and water to produce isobutyric acid with the selective ^{13}C label at the CH group. The amount of propane converted into IBA, as estimated from ^{13}C MAS NMR spectra, was 1 % at 473 K.

The products observed by NMR are in agreement with primary products expected for propane cracking at higher temperatures. According to reference [26], the rates of formation of methane and ethene considerably exceeded the rate of dehydrogenation to produce propene and hydrogen at 623 K. Our GC analysis of the head-space gas-phase has shown the absence of hydrogen and propene and confirmed the formation of methane and ethane.

It should be emphasized that we did not observe the formation of a carboxylic acid from alkane and CO if water was not coadsorbed on zeolite. Therefore, we conclude that the specific role of water in this reaction is to trap the isopropyloxocarbenium ion, formed from the isopropyl cation, to produce the acid and to regenerate the acidic proton of the Al-OH-Si group in accordance with Scheme 1.

Interestingly, the primary ethyl cation is not trapped by CO; a situation which is quite similar to that observed for the carbonylation of ethene on H-ZSM-5 at low temperature,[9] where the rate of oligomerization of the initially formed and very unstable primary ethyl carbenium ion greatly exceeded the rate of its carbonylation.

Isobutane: When a sample of ^{13}CO, unlabeled isobutane, and water was heated at 373 or 423 K, three signals appeared in the ^{13}C CP/MAS NMR spectrum that differed from those of the initial isobutane and ^{13}CO (Figure 2 a): at $\delta = 193$ and $\delta = 172$ from ^{13}C-labeled carbonyl groups, and at $\delta = 27.7$, a small signal near the intense signal from CH$_3$ and CH groups of unreacted isobutane at $\delta = 25.5$.[16] For the reaction of coadsorbed isobutane, ^{13}C-labeled at the quaternary carbon atom ([2-^{13}C]i-C$_4$H$_8$), unlabeled CO and water, two signals are detected in the spectrum: at $\delta = 25.5$ from unreacted isobutane and the signal at $\delta = 40.9$ from the reaction product (Figure 2 b). The ^{1}H MAS NMR spectrum (Figure 2 c) of ^{13}CO, unlabeled isobutane, and water exhibited, besides the
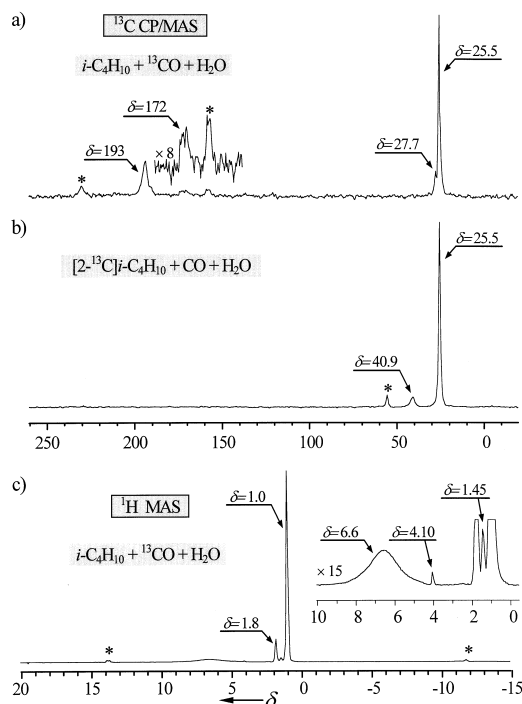

Figure 2. NMR spectra for isobutane, CO, and water coadsorbed on H-ZSM-5 zeolite. The sample was heated at 423 K for 2 h. a) ^{13}C CP/MAS NMR, coadsorption of unlabeled isobutane, ^{13}CO (90 % ^{13}C enrichment) and water; b) ^{13}C CP/MAS NMR, coadsorption of [2-^{13}C]isobutane (82 % ^{13}C enrichment), unlabeled CO and water; c) ^{1}H MAS NMR spectrum of the sample (a). 16 000 scans were collected for (a) and (b), 240 scans for (c). Spinning rate was 4.7 kHz for (a), 3.0 kHz for (b), 5.1 kHz for (c). Asterisks (*) in the spectra denote spinning side bands.

provide evidence for the formation of trimethylacetic (pivalic) acid (TMAA). The signal at $\delta = 193$ can be assigned to the carboxylic group of TMAA, the signals at $\delta = 40.9$ and $\delta = 27.7$ to the quaternary carbon and methyl groups of this acid, respectively. The position of these three signals is similar to those for both liquid TMAA[27] and that adsorbed on H-ZSM-5.[9] The signal at $\delta = 1.45$ in the ^{1}H NMR spectrum (Figure 2 c), a position analogous to that for methyl protons of liquid TMAA,[22] further supports its formation inside the zeolite. The observed NMR intensities correspond to $\approx 2 \%$ conversion of isobutane into TMAA at 423 K.

When taken together, the ^{13}C and ^{1}H NMR data are in good agreement with the reaction of isobutane given in Scheme 2.
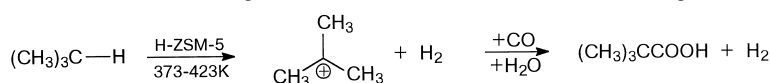
Scheme 2. Mechanism of isobutane carbonylation into trimethylacetic acid in H-ZSM-5 at 373 – 423 K.

Again, the product distribution observed for this reaction by NMR is in agreement with that expected for isobutane cracking on acidic zeolites at $T \leq 623$ K.[28] At $T \geq 773$ K, the initial cleavage occurs most readily at the C−C bond.[29] Indeed, the initiation of isobutane cracking by the cleavage of the C−C is a more activated process compared to that by dehydrogenation.[30] Thus, at the moderate temperatures used in this study, the rate of primary activation of isobutane by C−H cleavage essentially exceeds that of C−C bond cleavage.[28] In order to check these results that were obtained by in situ NMR spectroscopy, we used GC analysis to investigate the product distribution after conversion of isobutane on the zeolite in the presence of CO and H_2O in a static glass reactor. When about 1 mmol of isobutane was heated at 423 K in the presence of CO and water on H-ZSM-5 (3.6 g, i.e. ca. 1 mmol of acid sites) and the composition of the head space was checked at various time intervals, we noticed that the conversion ($\approx 3\%$ of isobutane) was essentially achieved in the first 2 h and increased only very slowly thereafter. The detected product was mainly hydrogen. This seems to indicate that in H-ZSM-5, isobutane is essentially activated by protolysis of the tertiary C−H bond following the Haag–Dessau scheme.[6, 24, 31]

We suggest that the trapping of carbenium ions with CO results in the formation of carboxylic acids, which become detectable by NMR spectroscopy. However, only 1–2% of alkane is converted into acid. The low conversion observed, which does not increase substantially with reaction time, cannot be rationalized unambiguously. Low conversion of isobutane may be related to the thermodynamic limitations. Indeed, estimation of the Gibbs free energy for the reaction with isobutane under standard conditions gave a positive value of $\Delta G^{\circ}_{r,298} = +28$ kJ mol^{-1},[32a] this makes the reaction thermodynamically unfavorable. However, it should be kept in mind that all the processes that define the thermodynamics of the reaction inside a zeolite can hardly be taken into account. Indeed, the conversion of alkanes into acids is essentially higher in superacidic media,[4–6] than that observed in zeolite. In the case of propane, the carbonylation reaction has no thermodynamic limitation. The calculation gave negative values of $\Delta G^{\circ}_{r,298} = -53$ kJ mol^{-1}.[32b] This should result in a higher conversion into the acid than that observed in our experiments. Therefore, we believe that if the reactions observed on the zeolite are not thermodynamically limited, the low conversion may be related to a noncatalytic reaction pathway. In this respect we may suggest that only 1–2% of the zeolite acid sites are capable of protolytic activation of propane and isobutane at 373–423 K and that these sites are consumed in the protolysis but not regenerated later with the same strength, because the reaction products, namely the carboxylic acids, remain adsorbed on the zeolite acid sites.

The participation of only a limited number of acid sites in the reaction is in contrast with our previous findings on the H/D exchange reaction observed between deuterated zeolite and isobutane[10, 11, 13] for which all the acid sites of the zeolite are involved in the hydrogen exchange with isobutane. In that case, the carbenium ion intermediates are involved in a catalytic cycle (ion deprotonation–alkene reprotonation) for which very strong acid sites are not necessary. In the present

study we assume that the strongest acid sites are not regenerated.

Considering the very low conversion, the question may also be raised as to whether trace amounts of iron could be at the origin of the alkane conversion. To check this possibility we repeated the experiment with isobutane and a sample of H-ZSM-5 that contained 0.015% instead of 0.0036% Fe_2O_3: the same conversion was observed.

On the role of the formate species in alkane activation

We noticed that for $^{13}CO + H_2O$ reacting with isobutane (Figure 2a) and, in some cases with propane, an additional signal was observed from the carbonyl moiety at $\delta = 172$. Moreover, the ^{13}C CP/MAS NMR spectrum of the sample that contained only ^{13}CO and H_2O without coadsorbed alkane on H-ZSM-5 and heated under the same conditions reveals a similar weak and broad signal at $\delta = 172$ (Figure 3a). We assume that this signal, which is outside the region of the
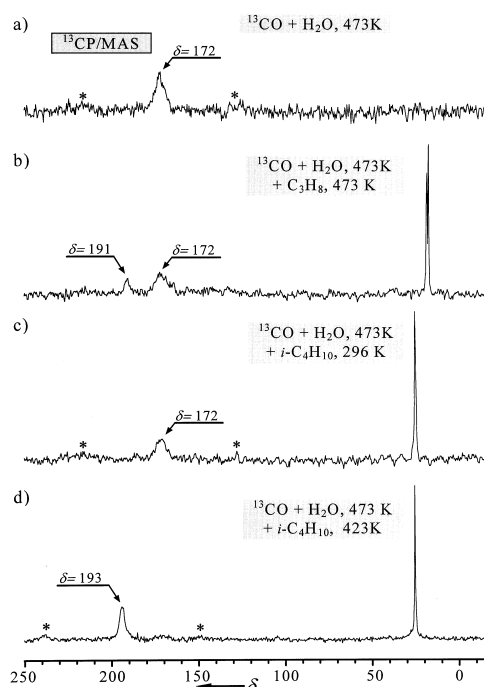
Figure 3. ^{13}C CP/MAS NMR spectra for: a) ^{13}CO (90% ^{13}C enrichment) and H_2O coadsorbed on H-ZSM-5 zeolite. The sample was heated at 473 K for 2 h; b) after adsorption of unlabeled propane on the sample a) and heating at 473 K for 2 h; c) after adsorption of unlabeled isobutane on the sample prepared similarly to (a); d) after heating of the sample (c) at 423 K for 2 h. 24 000 scans were collected for (a), 20 000 scans for (b), 21 000 scans for (c), 18 000 scans for (d). Spinning rate was 4.4 kHz for (a) and (b), 4.5 kHz for (c) and (d). Asterisks (*) in the spectra denote spinning side bands.

signals from carboxylic acids,[9] belongs to a formate species that has already been reported on acidic zeolites[33] and on other oxide catalysts.[34] It should be emphasized that the formation of small quantities of formate could not be explained by the presence of a small concentration of reducible oxides. On the one hand, the concentration of iron in our sample did not exceed 27 ppm; it is 0.13% of the

concentration of bridged Si-OH-Al groups. The intensity of observed signal from the surface formate corresponds to at least 1% of the total concentration of acidic OH groups. Evidently, the interaction of CO with iron oxide impurities could not give rise to the observed intensity of formate. On the other hand, a formate species bound to paramagnetic Fe^{3+} would not be detectable by ^{13}C NMR spectroscopy. Thus, the major part of the formate species observed is, in fact, the formate bound to the Si-O-Al groups.

We have found that the surface formate species was only generated from CO on H-ZSM-5 in the presence of water. Moreover, the formate species was only stable under a CO atmosphere (similar to formyl cation in superacids);[35] the evacuation of the sample containing coadsorbed CO and water led to the disappearance of the signal at $\delta = 172$ from the formate. Thus, an equilibrium between carbon monoxide and the surface formate exists inside H-ZSM-5, and water is unambiguously involved in the process of the formate formation (Scheme 3).
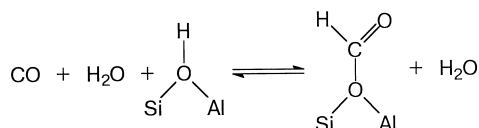
Scheme 3. Formation of formate species from CO in H-ZSM-5 in the presence of water.

In the presence of CO and water, the signal withstands prolonged heating within the temperature range 373–473 K (Figure 3a). However, when propane (or isobutane) was adsorbed on the sample corresponding to the spectrum in Figure 3a, namely containing pregenerated formate from the interaction of CO and H_2O, and the sample was heated further at 473 K, the signal at $\delta = 172$ decreased and the peak assigned to the carbonyl group of IBA at $\delta = 191$ appeared (Figure 3b). In the case of isobutane, the signal from the formate species disappeared almost completely if the sample was heated at 423 K, and the signal at $\delta = 193$ from TMMA appeared (see Figures 3c and 3d).

At the present stage we have no additional experimental data which could help us elucidate whether the formyl species is involved in the activation step of the alkane or if it only regenerates CO, which is then trapped by the carbenium ions.

Conversion of alkane in the presence of CO and H_2O at 473–573 K

Propane at 523 K: Considering the very low conversions observed at ≤ 473 K, we repeated our experiments at higher temperatures. Figure 4a shows the ^{13}C MAS NMR spectrum of the sample with adsorbed [2-^{13}C]propane and heated at 523 K. Besides the signal from the initially labeled CH_2 group of [2-^{13}C]propane at $\delta = 18.2$, the second intense signal at $\delta = 17.0$ from the CH_3 groups[16] of propane is observed. The signal at $\delta = 17.0$ arises from the scrambling of the selective ^{13}C-label from CH_2 into the CH_3 group of the propane molecule.[36] The signals of lower intensity in Figure 4a are assigned to n-butane [$\delta(CH_3) = 14.6$, $\delta(CH_2) = 27.1$],[16] isobutane [$\delta(CH_3$ and

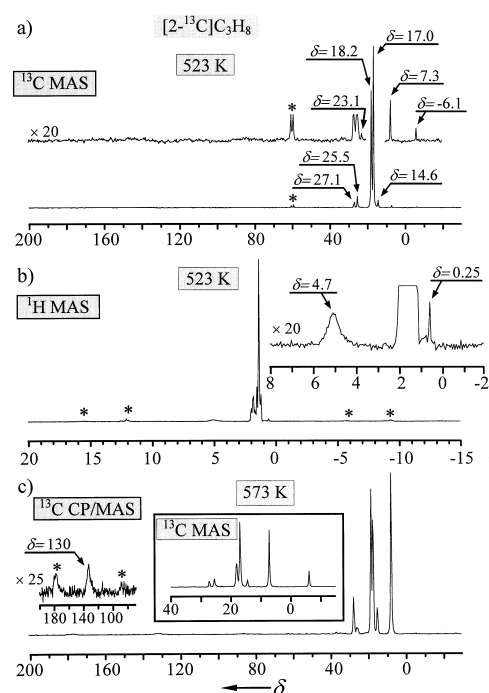Figure 4. NMR spectra for [2-^{13}C]propane (99% ^{13}C enrichment) adsorbed on H-ZSM-5 zeolite in the absence of CO and water: a) ^{13}C MAS NMR and b) ^{1}H MAS NMR for the sample heated at 523 K for 2 h; c) ^{13}C CP/MAS NMR for the sample heated at 573 K for 10 h. Insert: ^{13}C MAS NMR spectrum of sample (c) for the region of $\delta = -15$ to $+40$ is given. 5000 scans were collected for (a), 128 scans for (b), 18000 scans for (c). Spinning rate was 4.3 kHz for (a) and (b), 4.5 kHz for (c). Asterisks (*) in the spectra denote spinning side bands.

$CH) = 25.5$],[16] isopentane [$\delta(iso\text{-}CH_3) = 23.1$],[16] ethane [$\delta(CH_3) = 7.3$],[16] methane [$\delta(CH_4) = -6.1$].[18, 37] ^{1}H MAS NMR spectra of this sample also revealed the signal at $\delta = 0.25$ from methane (Figure 4b). No hydrogen generation was observed in the ^{1}H MAS NMR spectrum at this temperature, which indicates that the main pathway of propane activation involves C–C bond cleavage, that leads to propane cracking.

The observed product distribution is in good agreement with the accepted mechanism of the alkane cracking reaction[14, 15] to produce C_4–C_6 carbenium ions which can then alkylate an olefin molecule to give rise to more bulky carbenium ions. Confirmation of these processes lead to more stable cyclopentenyl cations[16, 37] or aromatic compounds.[16] The final product mixture at $T \geq 573$ K[16] consisted of small (C_1–C_5) alkanes and secondary products of olefin oligomerization, that is aromatic compounds (the signal at $\delta = 130$ in Figure 4c). We assume that the cyclopentenyl cations were not observed in our ^{13}C MAS NMR spectra at 523 K on account of the low conversion of propane itself as well as the large linewidth of the signals from the cyclopentenyl cations[16, 37] compared to those from alkanes.

In the presence of CO and water, paraffinic C_2–C_4 products of propane cracking together with the signals from carboxylic acids were observed in ^{13}C NMR spectrum (Figure 5). ^{13}C CP/MAS spectra of the sample with coadsorbed ^{13}CO, unlabeled propane and water exhibited the signals from ethane and butanes and the signal at $\delta = 191$ from the $^{13}COOH$ group of carboxylic acids. When the reaction was carried out with
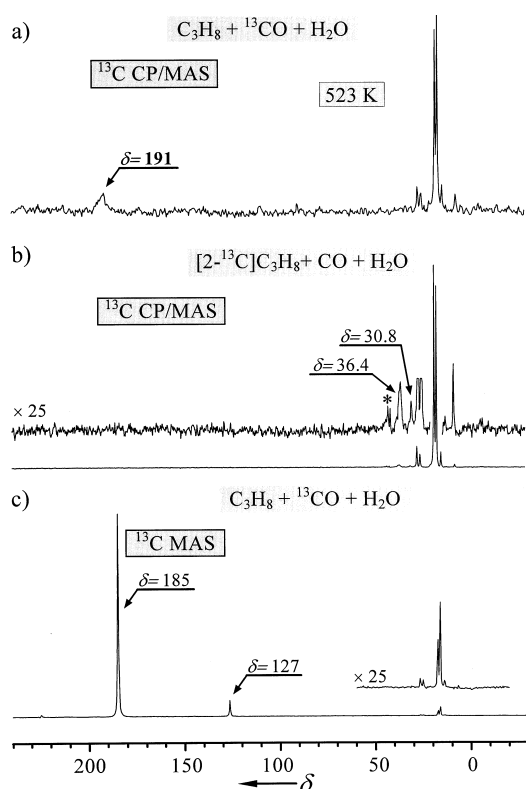
Figure 5. NMR spectra for propane, carbon monoxide, and water coadsorbed on H-ZSM-5 zeolite. The samples were heated at 523 K for 2 h: a) ^{13}C CP/MAS NMR, coadsorption of propane, ^{13}CO (90 % ^{13}C enrichment) and water; b) ^{13}C CP/MAS NMR, coadsorption of [2-^{13}C]propane (99 % ^{13}C enrichment), CO and water; c) ^{13}C MAS NMR spectrum of the sample (a). 16000 scans were collected for (a), 12000 scans for (b), 11200 scans for (c). Spinning rate was 4.0 kHz for (a) and (c), 2.5 kHz for (b).

[2-^{13}C]propane, unlabeled CO, and water (Figure 5b), we found a product distribution among the alkanes which was similar to that observed for the reaction of propane alone (Figure 4a). Simultaneously, two new signals were observed at $\delta = 36.4$ and $\delta = 30.8$. These signals appeared in the spectrum in parallel with the signal at $\delta = 191$ in Figure 5a and therefore they belong to carboxylic acids. The signal at $\delta = 36.4$, identified earlier in Figure 1b, indicates that isobutyric acid (IBA) is formed. The other signal at $\delta = 30.8$ can be attributed to the labeled CH_2 group of propionic acid, which usually exhibits a signal at $\delta = 27.6$ in solution.[17] However, we can not attribute this signal unambiguously to the propionic acid because all the intermediate carbenium ions generated during the propane cracking could react with CO to produce the corresponding carboxylic acids which would be responsible for this signal.

Importantly, in addition to these reactions, the decarboxylation of carboxylic acids[38, 39] was also observed at 523 K, as indicated by the appearance of the signal at $\delta = 127$ from gaseous $^{13}CO_2$[19, 40] in the ^{13}C MAS NMR spectrum (Figure 5c); the corresponding alkane being formed as the other reaction product (Scheme 4).
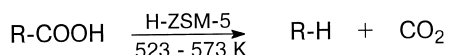
Scheme 4. Decomposition of a carboxylic acid in H-ZSM-5 at 523–573 K.

Thus, in the course of the reaction of propane in the presence of CO at 523 K, the following processes occur: the scrambling of the ^{13}C label in the propane molecule, cracking of propane, carbonylation of the intermediate olefins and decarboxylation of the carboxylic acids formed.

At first glance, the cracking and scrambling reactions strongly dominate over carbonylation. However, we did not observe the total amount of carbonylation products formed, since carboxylic acids are decomposed on H-ZSM-5 at this temperature. If the amount of carbon dioxide produced is used as an indicator of the carbonylation level, then the amount of CO transformed into carboxylic acids was estimated to be $\approx 10 \%$; however, the observed quantity of the acids did not exceed 1 % on account of their subsequent decomposition.

Importantly, the main route of propane transformation at 523 K, both in the absence and the presence of CO, is a scrambling of the ^{13}C label in a propane molecule.[36] This scrambling seems to proceed with carbenium ion intermediacy via protonated cyclopropane intermediates, as generally accepted for the scrambling of a ^{13}C label in hydrocarbons both in liquid and on solid acid catalysts.[31, 41–43]

Propane at 573 K: When the sample with [2-^{13}C]propane was heated further at 573 K, more cracking of the propane occurred according to the ^{13}C CP/MAS NMR spectrum (Figure 4c). Now ethane and methane are the prevailing reaction products (see Figure 4c, insert), in addition to butanes and aromatics (the signal at $\delta = 130$ in Figure 4c).

In the presence of CO and water, the heating of the samples at 573 K also produced methane, ethane, butanes and aromatics (Figure 6). The signals from the adsorbed aromatic species were observed at $\delta = 130$ (carbons atoms of aromatic ring) and at $\delta = 21$ (the signal from CH_3 group bound to the aromatic ring).[16] However, the distribution of paraffinic products differed from that observed for propane alone: approximately equal amounts of methane, ethane, and butanes were formed (see Figure 6c). Thus, the presence of CO and water influences the distribution of the cracking products: from the preferential formation of ethane and methane in the absence of CO to the formation of approximately equal amounts of $C_1 - C_4$ alkanes in the presence CO.

No signal from the ^{13}C-labeled COOH group of the carboxylic acid was detected in the ^{13}C CP/MAS NMR spectra if we used the labeled ^{13}CO and unlabeled propane for coadsorption (Figure 6a). However, the ^{13}C MAS NMR spectrum of the same sample (Figure 6c) showed the formation of carbon dioxide[40] in considerable amounts, $\approx 50 \%$ of CO was converted into CO_2. We suggest that this CO_2 originates from the decarboxylation of the acids formed as unstable reaction intermediates.

Isobutane at 473–573 K: When the zeolite sample was heated with isobutane at 473 K in the presence of $CO + H_2O$, the cracking products appeared simultaneously with the signal from carboxylic acids, the intensity of which is now larger in Figure 7a (with respect to isobutane at $\delta = 25.5$) compared to that in Figure 2a. In addition to the intense signals from isobutane at $\delta = 25.5$ and carboxylic acids at $\delta = 193$, small
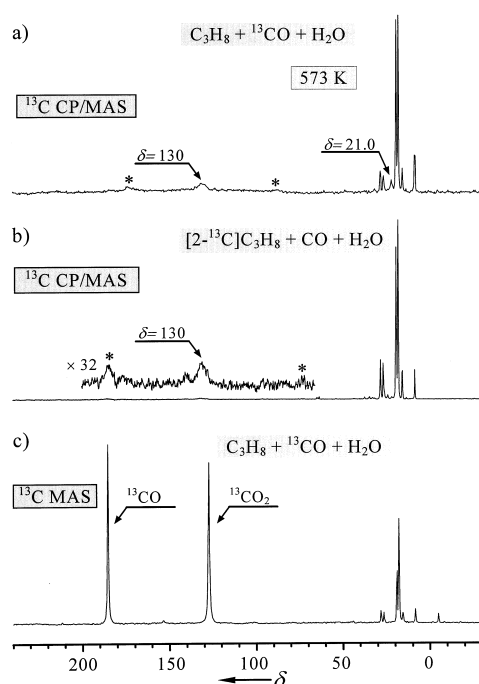
Figure 6. NMR spectra for propane, carbon monoxide, and water coadsorbed on H-ZSM-5 zeolite. The samples were heated at 573 K for 10 h: a) ^{13}C CP/MAS NMR, coadsorption of propane, ^{13}CO (90% ^{13}C enrichment), and water; b) ^{13}C CP/MAS NMR, coadsorption of [2-^{13}C]propane (99% ^{13}C enrichment), CO, and water; c) ^{13}C MAS NMR spectrum of the sample (a). 17400 scans were collected for (a), 17400 scans for (b), 3600 scans for c). Spinning rate was 4.2 kHz for (a), 4.6 kHz for (b), 2.5 kHz for (c). Asterisks (*) in the spectra denote spinning side bands.

Figure 7. ^{13}C CP/MAS NMR spectra for isobutane, ^{13}CO (90% ^{13}C enrichment), and water coadsorbed on H-ZSM-5 zeolite. The samples were heated for 2 h at: a) 473 K; b) 523 K; c) 573 K. 22700 scans were collected for (a), 18000 scans for (b), 13600 scans for (c). Spinning rate was 4.5 kHz for (a), 4.3 kHz for (b), 4.5 kHz for (c). Asterisks (*) in the spectra denote spinning side bands.
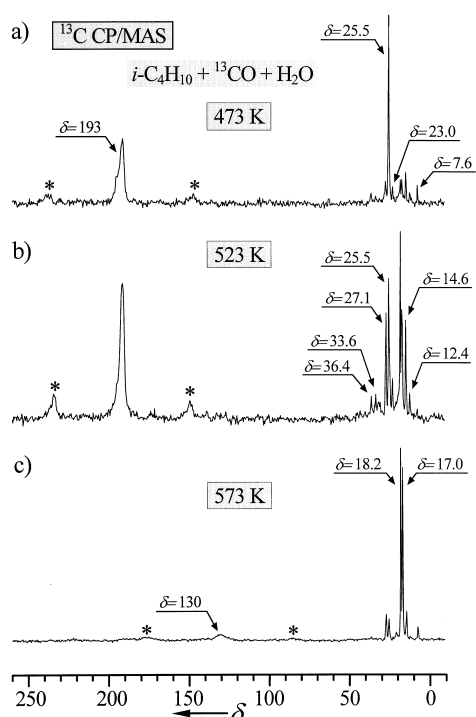
signals from the cracking products: propane ($\delta = 17.0$ and $\delta = 18.2$), ethane ($\delta = 7.6$), n-butane ($\delta = 14.6$ and $\delta = 27.1$) and isopentane [$\delta = 12.4$ (CH$_3$), $\delta = 23.0$ (i-CH$_3$), $\delta = 33.6$ (CH$_2$)] were observed. The CH group of isobutyric acid (IBA) exhibited a small signal at $\delta = 36.4$, while methyl groups of IBA and methyl groups of trimethylacetic acid contributed to the signals at $\delta = 23.0$ and $\delta = 27.1$, respectively (Figure 7a, b).

Further increase of the temperature to 523 K led to stronger cracking and conversion of isobutane with the formation of propane and n-butane. The intensity of the signal from the acids increased (Figure 7b). At 573 K, however, the acids were completely decomposed (Figure 7c); the signal from aromatics at $\delta = 130$ appeared and propane represented the prevailing product among the paraffins. Similar to the case with propane, as follows from ^{13}C MAS NMR, nearly 50% of the CO was converted into CO$_2$.

Thus, similar processes were observed for both propane and isobutane as the temperature increased, namely when both alkanes become involved in the cracking process. On the basis of NMR data we conclude that the total amount of the carboxylic acids formed increases as the temperature increases from 373 to 523 K. However, at 573 K the acids are completely decomposed to CO$_2$ and alkanes.

Conclusions

From the results of investigations with ^{13}C MAS and ^1H MAS solid-state NMR spectroscopy and GC analysis on the conversion of small alkanes on zeolite H-ZSM-5 in the presence of CO and water, the following conclusions have been drawn on the chemical processes proceeding on H-ZSM-5:

At $T = 373 - 473$ K, 1% of propane was transformed selectively into isobutyric acid, while methane and ethane were formed as the other reaction products. At $T = 373 - 423$ K, isobutane produced trimethylacetic acid and hydrogen with 2% conversion. Therefore, the first evidence has been obtained for the conversion of small alkanes into carboxylic acids on purely acidic zeolite catalysts at moderate temperatures that are $100 - 150\,^\circ$C lower than those used in the previously observed transformation of the alkanes by a cracking reaction.

An increase of the temperature up to 573 K resulted in a complete decomposition of the carboxylic acids formed; the main reaction products observed in the NMR spectra, C$_1$–C$_4$ alkanes and aromatics, arose from the cracking of the alkane. However, the analysis of the intensities of the signals from CO and carbon dioxide formed by the decomposition of the carboxylic acids indicated that $\approx 50\%$ of CO has been converted into carboxylic acids. This means that, at 573 K, the conversion of alkanes into the acids is important; however, the carboxylic acids do not survive prolonged heating at 573 K under the conditions in a static reactor and exist inside the zeolite as unstable intermediate species at this temperature.

Experimental Section

Sample preparation for NMR experiments: Zeolite H-ZSM-5 (Si/Al = 49) was synthesized according to reference [44] and characterized by X-ray powder diffraction and chemical analysis. According to chemical analysis, the content of iron in the sample was 27 ppm (0.0036 wt % Fe_2O_3). The zeolite (≈ 0.1–0.15 g) was loaded into a glass tube and the sample was heated at 723 K for 2 h in air to remove atmospheric moisture, and for 4 h under vacuum at 10^{-3} Pa. After cooling the sample to ambient temperature (296 K), equal amounts of alkane, CO and water (≈ 1 equiv of each coadsorbate per Al atom, 300 µmol g^{-1}) were frozen out onto H-ZSM-5 under vacuum at the temperature of liquid nitrogen, and the glass tube with the zeolite was then sealed off from the vacuum system. The sample was then heated at 373–573 K for 1–10 h for the reaction to proceed under static conditions in the sealed tube. After quenching the tube with the sample to room temperature, it was tightly packed into a 7 mm zirconia NMR rotor for NMR analysis. The reaction products were analyzed in situ directly inside the zeolite pores by both ^{13}C and ^{1}H NMR. To facilitate NMR analysis, the alkanes and CO with selective ^{13}C labels (80–99 % of ^{13}C isotope enrichment) were employed.

NMR analysis of the reaction products: ^{13}C NMR spectra with high-power proton decoupling and magic angle spinning (MAS) and with or without cross-polarization (CP) (denoted below as ^{13}C CP/MAS NMR and ^{13}C MAS NMR), and ^{1}H MAS NMR spectra were recorded at 100.613 MHz (^{13}C) and at 400.13 MHz (^{1}H) (magnetic field of 9 Tesla), respectively, on a Bruker MSL-400 spectrometer at 296 K. The following conditions were used for recording spectra with CP: proton high-power decoupling field 11.7 G (5.0 µs length of 90° ^{1}H pulse); contact time 5 ms at Hartmann–Hahn matching condition of 50 kHz; delay time between scans 3 s. One-pulse excitation ^{13}C MAS spectra were recorded with 45° flip angle; ^{13}C pulses of 2.5 µs duration, and 10–15 s recycle delay, which satisfied a 10 T_1 condition. High-power proton-decoupling in these experiments was used only during the acquisition time. This eliminated Nuclear Overhauser Enhancement of the signal areas and allowed quantitative assessment of the signal areas.[45] One-pulse excitation ^{1}H MAS NMR spectra were recorded with 45° flip angle pulses of 5 µs duration and 5 s recycle delay. ^{13}C and ^{1}H chemical shifts (δ) for carbon nuclei of adsorbed organic species were measured with respect to TMS as the external reference with accuracy $\Delta\delta = \pm 0.5$. Precision in the determination of the relative line position was $\Delta\delta = 0.1$–0.15 for ^{13}C NMR and $\Delta\delta = 0.05$ for ^{1}H NMR. The temperature of the samples during acquisition of NMR spectra was controlled with a BVT-1000 variable-temperature unit.

Sample preparation for GC analysis: The reaction was carried out in a glass reactor equipped with a septum (static conditions). H-ZSM-5 (≈ 3.6 g, 1 mmol H$^+$) was pretreated at 723 K under vacuum for 1 h. Isobutane or propane (0.89 mmol), CO (1.34 mmol), and H$_2$O (0.9 mmol) were introduced at 273 K with a syringe. For the reaction with isobutane, ethane was added to the system and used as an internal standard (i.e. 1.2 % of ethane in isobutane was used as starting material, considering the low reactivity of ethane). The reactor was heated (≤ 13 h) at 423 K for the reaction with isobutane and at 473 K (≤ 20 h) with propane. The head-space gas phase was analyzed by GC.

Hydrocarbons: [2-^{13}C]Propane (99 % ^{13}C enrichment) was purchased from IC Chemikalien GmbH, Germany. [2-^{13}C]Isobutane was prepared by a five-step synthesis, starting from [1-^{13}C]acetic acid (82 % ^{13}C enrichment). Propane purchased from Alphagaz (purity: N35) was used after a purity check by GC. Isobutane purchased from Alphagaz (purity: N35) was liberated from isobutene impurities (< 1000 ppm) by hydrogenation at 353 K on Pt (Adams) under H$_2$ and then filtered at room temperature on fresh H-ZSM-5 (used after activation at 773 K).

GC analysis of the reaction products: Hydrocarbons were analyzed by GC with a Girdel 300 chromatograph equipped with a column (2 m, 1/8") filled with a Hayesep A 80/100 porous polymer. The helium pressure in the column was 2 bar and the analysis temperature was constant at 363 K. Hydrogen was analyzed with an Intersmat IGC112M chromatograph equipped with a 2 m column filled with a 5 Å molecular sieve and a catharometric detector. The Ar flow rate was 14 mL min^{-1} and the temperature was constant at 323 K.

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