Low-temperature oligomerization of small olefins on zeolite H-ZSM-5 : an investigation with high-resolution solid-state ^{13}C -NMR

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Low-Temperature Oligomerization of Small Olefins on Zeolite H-ZSM-5. An Investigation with High-Resolution Solid-State ^{13}C -NMR

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Oligomerization reactions of ethene, propene, isobutene, and 2-methyl-butene-1 on zeolite H-ZSM-5 at 300 and 373K were investigated using high-resolution solid-state ^{13}C -NMR spectroscopy. It is shown that at 300K only linear oligomers are formed, while at 373K some branching is observed. Thus at 300K on zeolite H-ZSM-5 initially formed branched oligomers are stretched in consecutive isomerization reactions. Differential scanning calorimetry experiments on the adsorption of *n*-hexane and isohexane show that the specific pore dimensions of zeolite ZSM-5 are responsible for an increased heat of adsorption of linear paraffins compared to branched paraffins. A reaction scheme is presented to explain the experimental data.

INTRODUCTION

In a recent paper we proposed a reaction mechanism for the conversion of methanol into olefins, paraffins, and aromatics on zeolite H-ZSM-5 (1). In this mechanism ethene and propene are expected to be the primary formed olefins. The reactivity of these small olefins on zeolite H-ZSM-5 has been extensively studied (2–5). It has been shown that these olefins are readily converted; even ethene can be oligomerized at 300K. Until recently it was difficult to investigate the type of products formed by these oligomerization reactions. Infrared experiments have provided some evidence that oligomerization of ethene leads to linear molecules. It was impossible to detect these species (2, 4) with conventional high-resolution ^{13}C -NMR because the strong adsorption of the oligomerization products causes line broadening beyond detection limits.

However, application of high-resolution solid-state (HRSS) ^{13}C -NMR spectroscopy has recently provided evidence for the lin-

ear oligomerization of ethene on zeolite H-ZSM-5 at room temperature (3). On the other hand, in experiments on partially dehydroxylated Na,H-Y zeolite (6, 7) showed that highly branched oligomers were formed:

$$\nu_{\text{CH}_3} (2955 \text{ cm}^{-1})/\nu_{\text{CH}_2} (2930 \text{ cm}^{-1}) \geq 1.1.$$

Infrared experiments on the ethene oligomerization on H-mordenite at 370K (8) have also indicated the formation of branched oligomers: $\nu_{\text{CH}_3}/\nu_{\text{CH}_2} \approx 1$. These data show that linear oligomerization of ethene is specific for zeolite H-ZSM-5, possibly due to its pore dimensions of $0.54 \times 0.56 \text{ nm}$. In this report these preliminary conclusions will be further discussed.

On the basis of TG data it was suggested in previous reports (2, 3) that reactions of propene and isobutene at room temperature lead to the formation of branched oligomers. New HRSS- ^{13}C -NMR experiments were carried out to check this proposal. These data will be compared with some analogous experiments on zeolite H-mor-

denite. A reaction scheme will be presented to explain the experimental data.

EXPERIMENTAL

Materials. The H-ZSM-5 samples were prepared according to previously described procedures (9) and were characterized by chemical analysis, X-ray diffraction, and *n*-C₄ adsorption. The H-mordenite was Norton Zeolon (lot No. BD 18). Prior to each experiment the zeolites were calcined in air at 823K for 1 hr. Results are given in Table 1.

The vector gas He was purified by passing it successively over BTS, Carbosorb, and molecular sieve columns. In the ¹³C-NMR experiments C₂H₄-1-¹³C, 90% enriched, from Stohler Isotope Chemicals, was used after dilution to 10% enrichment. Propene, isobutene, and 2-methyl-butene-1 were high-purity reagents (99+%) and were used without further purification. The same holds for *n*-hexane and 2-methyl-pentane used in the DSC experiments.

HRSS-¹³C-NMR experiments. The spectra were obtained at room temperature using a Bruker CXP-300 spectrometer (7.05 T magnetic field, ¹³C frequency 75.45 MHz). The probe has a modified magic angle adjustment (10). The hollow rotors used in this investigation are made from coated boron nitride, which yields no background signals in the spectrum. Rotation rates between 2.5 and 4.5 kHz were used. We em-

ployed single cross-polarization contacts with contact times of 2 ms. Recycle times between acquisitions were 5 s; the acquisition time was 100 ms using a sweep width of 20 kHz. The B₁ field strength was 10 G and 40 G for the proton and carbon channels, respectively.

Chemical shifts are given with respect to an external sample of liquid TMS. The sample-to-sample shifts are possibly only accurate to within ±1.0 ppm, as it is impossible to avoid problems of bulk susceptibility shifts in the study of solids. This is due to the fact that an external chemical shift reference is the only means of calibration. However, the internal shifts within a spectrum are expected to be accurate to better than ±0.1 ppm.

Prior to measurement the samples were evacuated (0.13 Pa) at 573K for 2 hr. After this the adsorptions were performed at the temperatures and pressures as given in Table 2 and subsequently stored overnight at room temperature. The amount of hydrocarbon finally chemisorbed at room temperature (RT) for each sample corresponds with the TG data reported before (3, 18). The number of scans for each spectrum is given in the captions to the figures.

DCS experiments. A DuPont 910 Differential Scanning Calorimeter System with a DuPont 990 Thermal Analyzer was used. Before adsorption the H-ZSM-5 sample (BII) was evacuated (~100 Pa) at 573K for

TABLE I
Chemical Composition and Pore Volume of the Zeolite Samples

Samples	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	SiO ₂ /Al ₂ O ₃ mole ratio	No. H ⁺ sites ^a (mmol/g)	Pore volume ^b (ml/g)
H-ZSM-5:							
BII	94.2	3.17	0.07	0.11	50.5	0.59	0.151
DII	93.8	3.34	0.26	0.55	47.7	0.38	0.160
GII	88.3	4.48	0.37	0.37	33.5	0.70	0.126
DXII	92.1	2.50	0.56	0.45	62.6	0.22	0.116
H-mord.	81.0	10.35	0.36	0.45	13.3	1.93	0.099

^a No. of H⁺ sites = mmol Al/g—[mmol Na⁺/g + mmol K⁺/g].

^b Determined at RT by *n*-C₄ adsorption (*P*/*P*₀ = 0.2).

TABLE 2
Adsorption Conditions for the HRSS-¹³C-NMR Experiments

Adsorbates	H-ZSM-5 sample	Adsorption temperature (K)	P_{eq} (kPa)
C ₂ H ₄ -1- ¹³ C (10%)	GII	200 → 300 ^a	13.3
C ₃ H ₆	DII	300	13.3
<i>i</i> -C ₄ H ₈	DII	300	8.9
2-Me-C ₄ H ₇ -1	DXII	300	25.3
C ₂ H ₄ -1- ¹³ C (10%)	DXII	373	15.5
C ₂ H ₄ -1- ¹³ C (10%)	H-mordenite	373	30.4

^a First adsorption of ethene at 200K. Afterwards the sample was slowly warmed to room temperature.

1.5 hr. The adsorption was performed isothermally at 323K by saturation of a N₂

flow (40 ml/min) with *n*-hexane and 2-methyl-pentane, respectively, at room temperature.

RESULTS

The HRSS-¹³C-NMR spectrum of the oligomerization product of ethene strongly adsorbed on zeolite H-ZSM-5 (3) has clearly shown that under these conditions linear paraffins are formed. In that experiment we used C₂H₄-1,2-¹³C, 90% enriched without any dilution. This resulted in very broad signals, almost certainly because of the fact that ¹³C-¹³C (homonuclear) dipolar coupling is a homogeneous interaction and to average it out requires rotation rates far in excess of those employed (11).

We then performed the same experiment

TABLE 3
Chemical Shifts (ppm to Liquid TMS) of Oligomers of Small Olefins Adsorbed on Zeolite H-ZSM 5

Adsorbed on H-ZSM-5:									
C ₂ H ₄ (RT)	40		32			24		14	
C ₃ H ₆ (RT)			32			24		14	
<i>i</i> -C ₄ H ₈ (RT)	39		32			24		14	
2-Me-C ₄ H ₇ -1 (RT)			31			24		14	
C ₂ H ₄ (373K)	38		32	29		23	21	14	11
Adsorbed on H-mordenite:									
C ₂ H ₄ (373K)	47	39		30		23	19	14	11
	y	e	b	a		x	c	z	d

$n = 4$ (12)

$n = 14$ (12, 13)

Isotactic

Syndiotactic

FIG. 1. High-resolution solid-state ^{13}C -NMR spectra of small olefins adsorbed on zeolite H-ZSM-5 at 300K. (a) C_2H_4 -1- ^{13}C (10% enriched) adsorbed on sample GII (200 scans). (b) C_3H_6 adsorbed on sample DII (519 scans). (c) $i\text{-C}_4\text{H}_8$ adsorbed on sample DII (817 scans). (d) 2-Me- C_4H_7 -1 adsorbed on sample CXII (825 scans).

with C_2H_4 -1- ^{13}C diluted to 10% enrichment (Fig. 1a). This spectrum clearly shows more narrow signals. In addition, there are differences in intensity ratios and chemical shifts. Experiments in which we used different ZSM-5 samples with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios resulted in nearly identical HRSS- ^{13}C -NMR spectra. We believe that the discrepancies between the experiments in which C_2H_4 -1.2- ^{13}C (90%) and C_2H_4 -1- ^{13}C (10%) were used can be mainly ascribed to differences in ^{13}C enrichment, i.e., ^{13}C - ^{13}C dipolar coupling effects.

Figures 1b, c, and d show the HRSS- ^{13}C -NMR spectra of the strongly adsorbed

products formed upon oligomerization of propene, isobutene, and 2-methyl-butene-1 at room temperature.

The chemical shifts of the distinct resonances are presented in Table 3 and compared to some literature data obtained from HRSS- ^{13}C -NMR spectra of silanized silica surfaces (12, 13) and crystalline polypropene (14). To compare the values of the spectra shown in Figs. 1a, b, c, and d the chemical shifts within one spectrum are normalized with respect to the $-\text{CH}_3$ resonance being + 14 ppm. Furthermore, the large signal at 31–32 ppm, because of the intensity ratios to be expected, has always

been attributed to the $-(CH_2)_n$ resonance. Comparison of the HRSS- ^{13}C NMR spectra of long linear aliphatic chains (C_{18}) (12, 13) with our spectra (Figs. 1a–d) clearly shows that in all these experiments linear oligomers have been formed (Table 3). The differences in the relative intensities of the peaks, a, b, c, and d (Table 3) indicate a decreasing average chain length in the series $C_2H_4 \gg C_3H_6 > i-C_4H_8 > 2-Me-C_4H_7-1$. The spectra of polypropylene (14) and other branched hydrocarbons show that resonances at 48, 45, 39, 27, 23, 21, and 9 ppm (Table 3) indicate the presence of branched hydrocarbons in the products. Comparison of these data with the spectra depicted in Figs. 1a–d shows that, because of the small signals at 39 and 40 ppm (Figs. 1a and c, respectively), minor amounts of branched hydrocarbons must be present. Although the signal-to-noise ratio is rather low in Figs. 1b and d, in line with the previous observation and the line broadening in the range of 38–40 ppm it seems justified to state that in these spectra some branched hydrocarbons may also be present.

Oligomerization of ethene at 373K (Fig. 2) results in a product with an average linear chain length comparable to that of the oligomerization product of 2-methyl-butene-1 formed at RT. Furthermore, a significant amount of branched hydrocarbons is

FIG. 2. High-resolution solid-state ^{13}C -NMR spectrum of $C_2H_4-1-^{13}C$ (10% enriched) adsorbed at 373K on zeolite H-ZSM-5 (sample CXII). No. scans: 12,977.

FIG. 3. High-resolution solid-state ^{13}C -NMR spectrum of $C_2H_4-1-^{13}C$ (10% enriched) adsorbed at 373K on zeolite H-Mordenite. No. scans: 50,850.

formed, based on the appearance of signals at 11, 21, and 38 ppm (Table 3). To check the influence of the zeolite structure in this type of reaction we also performed oligomerization of ethene on zeolite H-mordenite at 373K (Fig. 3). As shown in Table 3, this experiment resulted in the formation of highly branched oligomers.

It is important to note that in all these ^{13}C -NMR spectra only saturated carbon resonances appear. We recorded all our spectra from 0 to 200 ppm; comparison with HRSS- ^{13}C -NMR spectra of silica surfaces covered with olefinic (~ 140 ppm) and aromatic (125–130 ppm) groups (12) proves that no unsaturated carbon signals are observed in our spectra. In the case of the ethene oligomer we expanded our sweepwidth up to 400 ppm but did not observe any signal. HRSS- ^{13}C -NMR spectra of carbenium ions show that R_3C^+ carbon atoms give resonances in the region of 160 to 250 ppm with respect to liquid TMS (15, 16). It can be concluded that in our oligomers this type of species is not present in any significant concentration. In addition, Eberly (17) reported that upon adsorption of hexene-1 on zeolite H-Y at 366K only paraffinic ir-absorption bands were detected. Until now we were not able to give a good explanation for this phenomenon.

DISCUSSION

The HRSS- ^{13}C -NMR experiments clearly show that ethene, propene, isobutene, and 2-methyl-butene-1 are linearly oligomerized in reactions at room temperature on zeolite H-ZSM-5. Based on TG experiments we have previously suggested (3) that propene and isobutene would result in branched oligomers at room temperature, because larger amounts of propene and isobutene are adsorbed than in the case of ethene.

In the ^{13}C -NMR spectra differences can be observed between the ethene oligomer on the one hand and the oligomers of propene, isobutene, and 2-methyl-butene-1 on the other. Considering the ratios of intensities of the main signals (i.e., a, b, c, and d, Table 3, Fig. 1) a rough estimation can be made of the average chain length. In doing so we estimate for ethene oligomer an average chain length of about C_{23} – C_{27} , while for the other isomerization products this number equals about C_8 – C_{12} . These numbers may well explain the TG experiments because shorter oligomers will fill the pore volume more effectively. Furthermore, it was observed in TG experiments that the rate of oligomerization of ethene was much slower than that of propene and isobutene. This can be easily understood because it is easier to protonate the latter olefins, forming secondary or tertiary cations, than to form the primary cations necessary in the oligomerization of ethene. The same fact may well be the reason for the difference in average chain length of the oligomers formed: obviously only the strongest Brønsted-acid sites participate in the oligomerization of ethene so fewer chains can be

formed and the average chain length will be greater. The oligomerization of ethene on zeolite H-ZSM-5 at 373K was performed in order to check this suggestion: TG experiments, to be discussed elsewhere (18), clearly show that under these conditions the oligomerization of ethene becomes very fast so that now all the Brønsted-acid sites may participate in the oligomerization.

Figure 2 indeed shows that the average linear chain length is comparable to the oligomerization product of 2-methyl-butene-1 formed at RT. This strongly supports the suggestions mentioned above. The branched hydrocarbons observed in this spectrum may well be due to fast reactions on the outer surface of the crystallites and will be further discussed in the context of TG experiments at intermediate temperatures (18).

Two intriguing aspects arise from these experiments.

(i) Even ethene is readily oligomerized at room temperature on zeolite H-ZSM-5, which indicates a very high activity of the Brønsted acid sites in this type of zeolite, as compared to the Na,H-Y zeolite (6, 7) and H-mordenite (8).

(ii) In all experiments at room temperature only linear oligomers were observed. Obviously the specific dimensions of the intracrystalline pores in zeolite ZSM-5, $0.54 \times 0.56 \text{ nm}$ (19), are responsible for this behaviour. An ethene oligomerization on zeolite H-mordenite at 373K, pore dimensions

TABLE 4	
Heat of Adsorption of Paraffins on Zeolite H-ZSM-5	
	ΔH (kJ/mol)
<i>n</i> -Hexane	67.2
	67–75 (20)
2-Me-pentane	44.5

FIG. 4. Energy diagram for the chemisorption of ethene on the zeolite surface (derived from (21)).

0.67 × 0.70 nm (19), resulted in highly branched oligomers (Fig. 3).

DSC experiments on the adsorption of *n*-hexane and 2-methyl-pentane on zeolite H-ZSM-5 clearly indicate that the adsorption of the linear chain is preferred over the

branched chain, the differences being about 23 kJ/mol (Table 4).

Cant and Hall (21) have described the adsorption of ethene on zeolite H-Y and reported an apparent activation energy for the formation of the ethyl cation (I),

of 67–80 kJ/mol. The precursor for this intermediate, however, is the hydrogen-bonded complex (B) visualized in Fig. 4, with a heat of adsorption of about 38 kJ/mol. The true activation energy for the formation of the ethyl cation must therefore be in the order of 120 kJ/mol. Once this ethyl cation is formed, the consecutive reactions with gas-phase ethene, forming the primary

n-butyl cation (II), will be relatively easy and will result in a linear oligomer. The equilibrium II ⇌ III, however, will be far to the right, Δ*H* being 45–55 kJ/mol (22).

A consecutive reaction of III with a gas-phase ethene molecule now results in the branched oligomer IV, as shown in the reaction

which will readily isomerize to the tertiary carbenium ion V, Δ*H* ≈ 90–110 kJ/mol (22). Note that although III is much more abundant than II the energy of activation for the consecutive reaction with a gas-phase ethene molecule is much higher when starting with III as compared to starting with II, because every oligomerization step in ethene oligomerization proceeds via a primary carbenium ion.

Based on these thermodynamic data, in the case of ethene oligomerization initially linear as well as branched oligomers may be formed; the direct formation of linear oligo-

mers may even be kinetically favoured. Furthermore, the ratio of linear to branched oligomers will be determined by the steric constraints at the site: at the channel intersections there is more space so the energetically more stable branched oligomer will be mainly formed while in the straight parts the formation of linear oligomers may be favoured. In ¹³C-NMR spectra mainly linear oligomers are observed, which indicates that the branched oligomers which are initially formed are stretched by isomerization reactions involving a protonated cyclopropane ring:

It is important to note that in this type of reaction no primary cations are involved, resulting in an energy of activation of only 70–80 kJ/mol (23), so it may be expected that the rearrangements depicted are rela-

tively fast compared to the oligomerization reaction.

The initial steps in the oligomerization of propene are shown in the reaction

By analogy with Fig. 4 the true activation energy for the formation of the propyl cation (X) must be on the order of 70–80 kJ/mol (21, 22). This reaction clearly shows that oligomerization of propene always results in branched oligomers. Stretching reactions, as shown in the third reaction, must explain that also in the oligomerization of propene (isobutene and 2-methyl-butene-1) at room temperature on zeolite H-ZSM-5 only linear oligomers are formed.

Two points to be considered are:

(i) The difference in the rate of oligomerization between ethene on the one hand and of propene, isobutene, and 2-methyl-butene-1 on the other can be well explained by considering that in ethene oligomerization a primary cation is involved in every consecutive oligomerization step, while in pro-

pene, isobutene, and 2-methyl-butene-1 oligomerization, linear paraffins can be formed by consecutive oligomerization and stretching reactions involving only secondary and tertiary carbenium ions, which are at least 45–55 or 90–110 kJ/mol lower in heat of formation than are the primary cations mentioned above.

(ii) In going from a branched to a linear carbocation the energy of activation is about 70–80 kJ/mol. The difference in heat of adsorption between *n*-hexane and isohexane of 23 kJ/mol (Table 4) indicates that the adsorption of linear molecules on zeolite H-ZSM-5 is favoured over adsorption of branched molecules. This may provide the driving force for the stretching reaction to occur as it may cause a shift of the equilibria towards the linear carbocation IX. In

this context it is important to note that the values for the energy of activation reported in the literature are mostly measured in solution. It may well be that in the zeolite pores the energy of activation of the rearrangement reactions (as well as the oligomerization reactions) is decreased due to a strong interaction of polar and/or ionic intermediate species with the strong electrostatic field, thus facilitating the described rearrangements. Indeed, Cant and Hall (21) reported that the energy of activation for the formation of the ethyl cation on zeolite H-Y was low compared to that of literature data obtained in solution.

CONCLUSIONS

High-resolution solid-state ^{13}C -NMR experiments clearly show that low-temperature oligomerizations of small olefins on zeolite H-ZSM-5 result in the formation of linear paraffins. At higher temperatures some branching is observed. The narrow pores in this zeolite are responsible for an increased heat of adsorption of linear paraffins compared to branched ones and obviously cause a decrease of the energy of activation of the stretching reaction of branched hydrocarbons.

High-resolution solid-state NMR spectroscopy has been demonstrated to be an excellent technique for obtaining information of strongly adsorbed reaction products.

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