Catalysis Letters 11 (1991) 267–276

In-situ ^{13}C magic-angle-spinning NMR measurements of the conversion of ethene to aliphatic hydrocarbons over structurally different zeolites

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Received 27 September 1991; accepted 16 October 1991

Solid-state ^{13}C NMR analysis of the oligomerisation of ethene over H-ZSM-5, H-Y and H-mordenite, indicates that the degree of branching of the final products increases with increasing pore dimensions of the zeolite. In order to monitor the formation of intermediate reaction products, we investigated the oligomerisation of ethene in zeolite H-ZSM-5 at lower temperature. Ethene sorbed in ZSM-5 is stable below 0°C, but at higher temperatures it is oligomerised to higher, branched reaction products. The use of sealed capsules enabled us to identify several (apparently highly reactive) higher olefins as intermediates. Although the observation of intermediate olefinic oligomers is in line with the classical reaction mechanism of acid-catalysed oligomerisation via carbenium ions, no such charged species could be detected. Alkoxide species, on the other hand, were observed, and these may very well be involved in the reactions.

Keywords: Zeolite Y; ZSM-5; mordenite; acid-catalysed ethene oligomerisation; carbenium-ion chemistry; alkoxides; reaction intermediates; ^{13}C CP-MAS NMR

1. Introduction

On account of their acidic character and structural (shape-selective) properties, zeolites are extensively used in the petrochemical industry as heterogeneous catalysts for the conversion of hydrocarbon molecules. In general, the evidence for shape-selective effects comes from the gas-chromatographic and/or mass spectrometric analysis of the final products obtained during a particular reaction. Evidently, such analyses only give information on the nature of products with molecular dimensions sufficiently small to allow diffusion out of the micropores of the zeolite catalyst involved.

In order to improve our understanding of the origin of the shape-selective properties and to gain insight into the mechanism of the reactions proceeding within the intracrystalline zeolite pores, it would be desirable if we could identify the primary reaction products present in the *interior* of the zeolite. In principle such information can be provided by nuclear magnetic resonance (NMR) spectroscopy [1–8].

Various authors have applied high-resolution solid-state ^{13}C NMR to investigate the structure and the nature of the reaction products formed in the micropores of a particular zeolite. For instance, Anderson and Klinowski were able to monitor the intermediate products formed during the conversion of methanol over zeolite H-ZSM-5 [1,2]. They demonstrated the presence of trimethylbenzenes in the interior of the zeolite. These reaction products are too bulky to diffuse out of the H-ZSM-5 crystals, and that is why these products have never been detected by analysis techniques monitoring the composition of the gas phase.

Haw et al. investigated the conversion of propene in zeolite H-Y by *in-situ* variable-temperture ^{13}C solid-state NMR [3]. They suggested that oligomerisation of propene occurs via the addition of an isopropyl group to a propene molecule, yielding a six-carbon alkoxy species. Further reaction, finally, leads to the formation of longer carbon chains and branched olefins. They also carried out similar experiments in order to monitor the conversion of butadiene in zeolites H-Y and H-ZSM-5 [4], and to identify the hydrocarbons produced upon the oligomerisation of propene in zeolite H-Y [5].

In previous work at our Laboratory, the oligomerisation of ethene in zeolite H-ZSM-5 was studied by means of ^{13}C solid-state NMR [6,7]. We have now extended this work by including various structurally different zeolites in order to investigate whether the structure of the zeolite indeed influences the degree of branching of the oligomers formed in the zeolite pores. Furthermore, by application of *in-situ* ^{13}C solid-state NMR, the mechanism of the oligomerisation reaction has been studied in more detail. For this purpose, a procedure was devised in which sealed-capsule samples were prepared at low temperature (77 K) and rapidly transferred to a pre-cooled magic-angle-spinning (MAS) NMR probe. By stepwise heating of the sample thus prepared, we were able to monitor *in-situ* the various (olefinic) products formed in the micropores during the reaction of ethene over zeolite H-ZSM-5.

2. Experimental

SAMPLE CHARACTERISATION AND PREPARATION

The first series of experiments was carried out to investigate the effect of pore structure on the degree of branching of the final oligomers. The molar Si/Al ratios of the three zeolites H-Y, H-mordenite and H-ZSM-5 were 5, 17, and 20 mol/mol, respectively. Prior to use the materials were activated in vacuo at 320°C. After cooling down to 100°C the catalysts were exposed to 20 kPa ethene (containing 10 mol% $^{13}C{=}C$). Due to adsorption and reaction the pressure dropped to 6–15 kPa. In order to selectively remove the reaction products from the outside of the zeolite crystals (external surface), the samples (still at 100°C) were subsequently evacuated for about 10 minutes down to 200 Pa. After cooling to ambient temperature the samples were transferred directly to the magic-angle-spinning rotor.

The second series of experiments was carried out to monitor the primary products formed during ethene oligomerisation in zeolite H-ZSM-5. For this purpose sealed Pyrex capsules containing H-ZSM-5 (with a Si/Al molar ratio of 13) and ethene were prepared by the following procedure.

First, the sample was degassed in the Pyrex capsule at 400°C for at least 6 h *in vacuo*. Subsequently, the H-ZSM-5 crystals in the capsule were loaded with (99 mol%) ^{13}C-enriched ethene. In the loading procedure special care was taken to prevent the ethene from undergoing rapid oligomerisation by keeping the activated zeolite material (200 mg) at liquid-nitrogen temperature. At this temperature the zeolite material was allowed to sorb twenty equal volumes (0.4 ml total) of ethene (1 kPa; at room temperature), resulting in a maximum loading of about 4 mmol ethene/g zeolite. The sample capsules (still at liquid-nitrogen temperature) were quickly sealed according to the procedure previously described [9], with some modifications to prevent reactant conversion by local sample heating. Before measurement the sealed sample capsules were kept in liquid nitrogen. For measurement the capsules were placed inside a MAS rotor and transferred to a pre-cooled MAS NMR probe. The heat treatments were carried out with adjustment of the temperature inside the probe.

NMR SPECTROSCOPY

For the NMR measurements of the final products formed upon conversion of ethene in the various zeolites, ^{13}C cross-polarisation (CP) MAS NMR spectra were obtained at room temperature with a Bruker CXP 300 spectrometer (carbon frequency 75.46 MHz) and a double-bearing CP-MAS probe using cross-polarisation (2 ms contact time) and high-power proton-decoupling (with a B_1-field strength corresponding to a 90°-pulse of 4 μs). The temperature of the sample (see figure captions) was controlled by a Bruker B-VT 1000 variable-temperature unit. All spectra were referenced using adamantane as an external reference, with the upfield methine peak at 29.23 ppm [8]. The MAS NMR experiments were carried out at spinning rates in the range 3–6 kHz.

For the low-temperature *in-situ* NMR measurements of sealed capsules the ^{13}C NMR spectra were recorded on a Bruker MSL 300 instrument (carbon frequency 75.46 MHz). Highly symmetrical sealed capsules of Pyrex were packed in a 7-mm zirconia rotor. Here, the MAS NMR experiments were carried out at spinning rates in the range 1–3 kHz. In case of the ethene/H-ZSM-5 samples, with temperatures below room temperature, nitrogen gas was passed through a Dewar containing liquid nitrogen. Measurements were started at low temperature (223 K) and the temperature was increased stepwise. After each step the temperature was allowed to equilibrate typically for about 5 minutes. Other relevant experimental parameters are specified in the figure captions.

3. Results and discussion

EFFECT OF ZEOLITE STRUCTURE ON PRODUCT FORMATION

The ^{13}C CP MAS NMR spectra recorded with ethene-loaded zeolite H-Y, H-mordenite and H-ZSM-5 are shown in fig. 1. Whereas the spectra recorded with H-Y and H-MOR indicate that the final products are heavily branched, the spectrum obtained with the H-ZSM-5 sample indicates the presence of a significant amount of more linear saturated hydrocarbons (C_6–C_8). The peaks at 14, 23 and 32 ppm arise from the first three carbon atoms in a linear chain, and the peak at 30 ppm is ascribed to carbon atoms present in the central part of the chain [6,7,10]. The weak signal at 40 ppm points to some 2-methyl branching [6,7,10]. The spectra recorded with zeolite H-Y (fig. 1A) and H-mordenite (fig. 1B) show less well-defined peaks compared to H-ZSM-5, indicating an increased degree of branching. This is consistent with the absence of a clear peak at 14 ppm, the characteristic spectral position of a terminal methyl group in a linear chain [6,7]. Notice its presence in the spectrum obtained with H-ZSM-5 (fig. 1C). The peak at 23 ppm is assigned to the two methyl groups present in a two-methyl-branched chain [10]. Signals at 28 and 42 ppm (2-methylpentane) and 28 and 39 ppm (2-methylheptane) are also related to this structure. The peaks at 12 ppm (terminal CH_3) and at 19 ppm (pendant CH_3) point to 3-methyl branching.

The results of these experiments clearly demonstrate that the amount of branched hydrocarbons is significantly smaller in zeolite H-ZSM-5 than in H-mordenite and H-Y. Since the mean pore dimensions increase in the order H-ZSM-5 < H-MOR < H-Y, it can be concluded that the degree of branching of the *final* products increases with the pore dimensions of the various zeolites.

PRIMARY CONVERSION PRODUCTS IN ZEOLITE H-ZSM-5

In a second series of experiments we investigated the various steps during the oligomerisation of ethene in zeolite H-ZSM-5 in more detail. Since, to the best of our knowledge, there is currently no evidence in the literature for the existence of stable small olefinic molecules in aluminium-containing H-ZSM-5

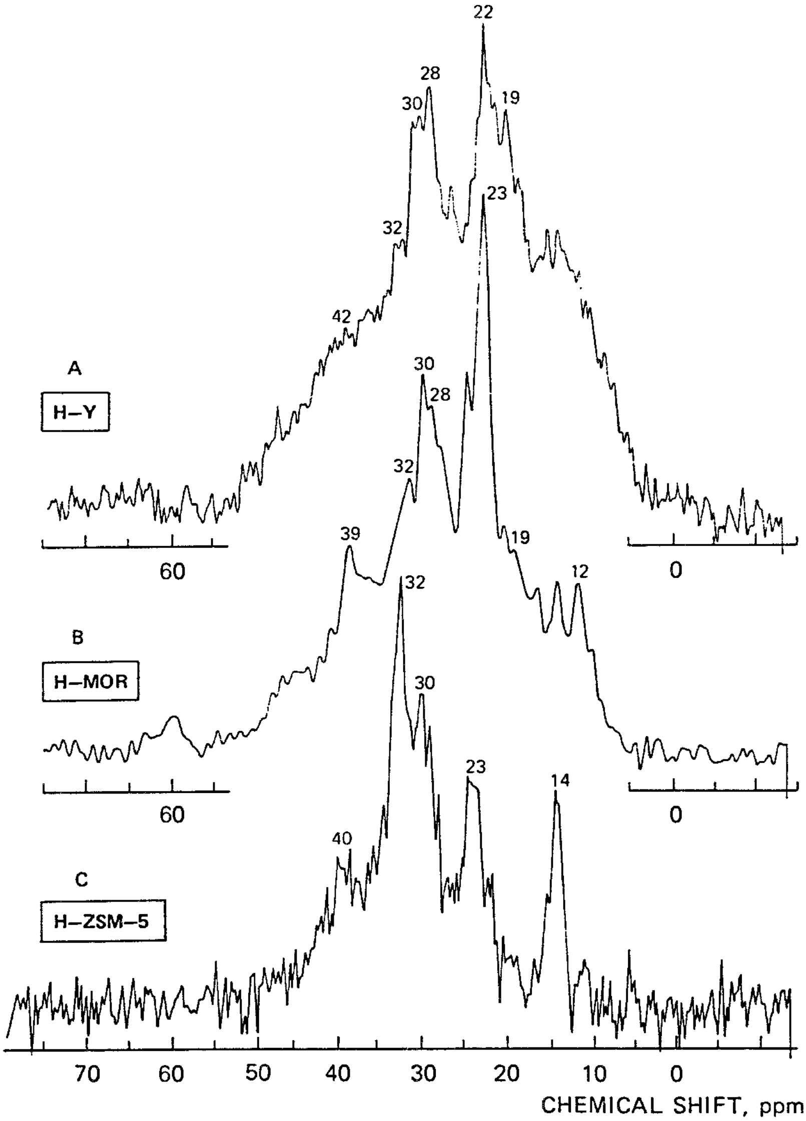


Fig. 1. 75.48 MHz ^{13}C CP MAS NMR spectra of various zeolites after loading at 100°C with 20 kPa ethene (10 vol% ^{13}C=C): the influence of pore dimensions on final product formation. Zeolite H-Y (A), H-mordenite (B) and H-ZSM-5 (C). The numbers denote ppm values. The relaxation delay was 6 s; the contact time was 2 ms; the proton 90°-pulse was 4 μs.

zeolites, we first examined the stability of ethene sorbed in the pores of zeolite H-ZSM-5 at low temperature (-50°C).

Fig. 2 shows the CP MAS NMR spectra of 99 mol% ^{13}C-enriched ethene in zeolite H-ZSM-5 at -50°C (A), during the first 8 hours after increasing the temperature to 0°C (B), and after 20 h at 0°C (C).

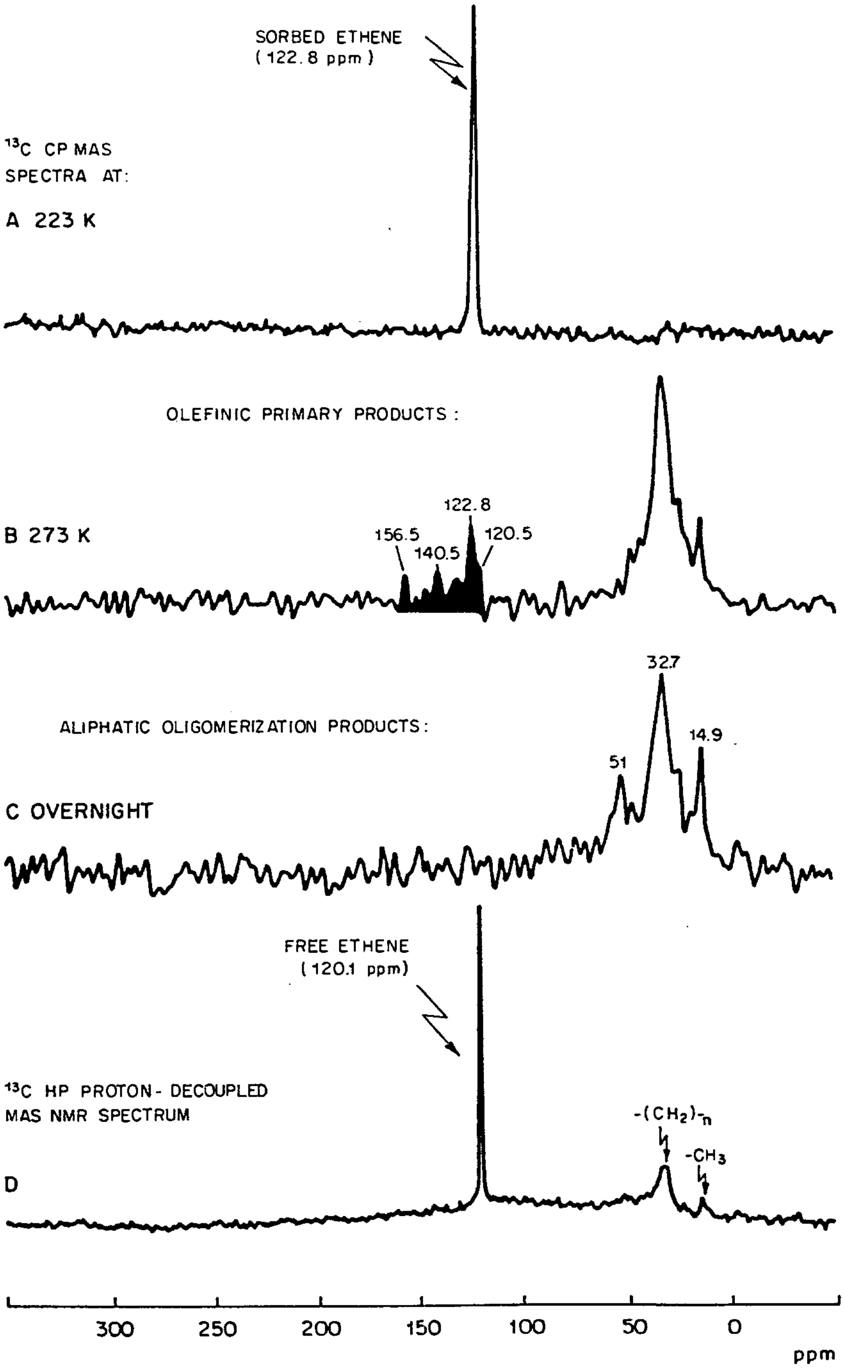


Fig. 2. 75.48 MHz ^{13}C CP MAS NMR spectra of ^{13}C-enriched ethene in zeolite H-ZSM-5 at −50°C (A), recorded during the first 8 h at 0° (B) and after 20 h at 0°C (C). The relaxation delay was 6 s; the contact time 5 ms; the number of scans was 1674 (A), 4800 (B) and 695 (C). Fig. 2D: 75.48 MHz ^{13}C direct excitation high-power proton-decoupled MAS NMR spectrum of the final products after conversion of ^{13}C-enriched ethene by zeolite H-ZSM-5 at 30°C. The relaxation delay was 6 s; the proton 90°-pulse was 5 μs, and the number of scans was 695.

Before the heat treatment (i.e. at −50°C), a single peak is observed at 122.8 ppm, which can be attributed to ethene species physisorbed in the micropores of H-ZSM-5 crystals as the peak position is close to the gas-state value of 120.1 ppm. This value was observed using a capsule containing only ^{13}C-enriched ethene, i.e. without H-ZSM-5 (data not shown). The downfield shift of 2.7 ppm is due to ethene physisorption in the zeolite and/or to the different magnetic susceptibility inside the zeolite lattice. Similar spectra to the one shown in fig. 2A have been recorded at various temperatures in the range from −50 to about 0°C (data not shown), thus demonstrating that ethene can be kept stable inside the micropores of H-ZSM-5 at temperatures below 0°C.

However, after a more prolonged period of time (20 h) at 0°C, the oligomerisation reaction has already proceeded to a significant extent, as is evidenced by the spectrum (fig. 2C). Several linear oligomerisation products that have been reported before [11,12] are indicated by aliphatic peaks at 14.9 and 32.7 ppm. With regard to the aliphatic region of the spectrum, virtually the same peaks are present as in the spectrum obtained from the final conversion products (fig. 1C). Hence, in order to detect primary olefinic products, measurements have to start at low temperatures (−50°C) followed by a stepwise increase in temperature (to, e.g., 0°C).

The spectrum recorded after keeping the sample for a limited period of time (8 h) at 0°C (fig. 2B) indicates the formation of saturated hydrocarbons with peaks at 14.9 and 32.7 ppm arising from the first carbon atoms in a linear chain [6,7,11,12]. However, this spectrum also features peaks in the olefinic region, viz. at 165.5., 140.5 and 120.5 ppm. These peaks indicate the presence of primary (intermediate) olefinic products. The peaks at 140.5 and 120.5 ppm are ascribed to olefins, most likely to olefins such as butene-2 (*a*), 3-methylpentene-2 (*b*) and/or 3,4-dimethylhexene-3 (*c*). In the liquid state these compounds have olefinic peaks at 125 and 123 ppm, at 138 and 118 ppm, and at 140 and 118 ppm, respectively [13]. The signal observed at 120.5 ppm accounts for the second olefinic species. As mentioned above, the slight differences in the observed peak positions as compared to those in the liquid state may be due to sorption of the olefin in the micropores of the zeolite and/or to the different magnetic susceptibility inside the zeolite framework. The peak at 156.5 ppm is also due to an olefin, most likely 2-methyl, 3-ethylpentene-2 (*d*). In the liquid state the resonances of the two olefinic carbon atoms in this compound occur at 148 and 116 ppm [13].

It is noteworthy that none of the recorded spectra gave an indication of peaks of the positively charged carbon atoms in alkyl carbocation compounds (to be expected at 310–330 ppm; [10,12]). Interestingly, it appears that the peaks at 49 and 51 ppm can be ascribed to alkoxide species, i.e. reactant molecules (covalently) bonded to the oxygen atoms adjacent to the aluminum sites in the zeolite framework, for the following reasons.

(i) Alkoxides are considered to be reaction intermediates in the conversion of ethene over H-ZSM-5 [6,7].

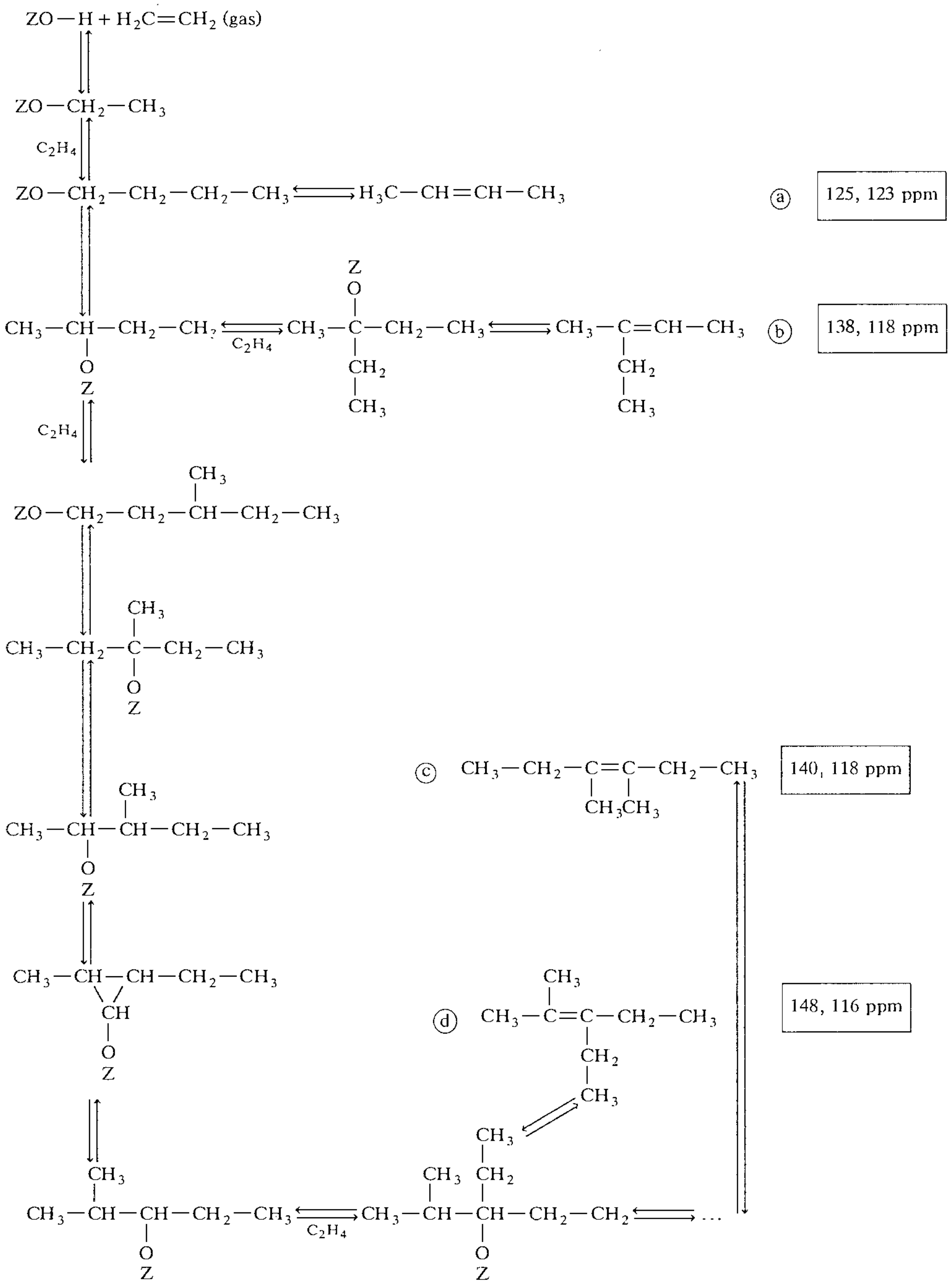
(ii) The resonance positions in the ^{13}C NMR spectra of carbon atoms of branched hydrocarbons in H-ZSM-5 were reported to be in the range from 39 to 48 ppm [6,7,12], i.e. in a significantly *lower* ppm range.

(iii) A peak at 50 ppm was also observed in the ^{13}C NMR spectra of the primary products of *ethene* in zeolite H-Y, and it was assigned to the α-carbon atoms of alkoxides. They are particularly weakly deshielded by the oxygen atoms, because of their negative charge in the zeolite lattice [12]. Furthermore, the chemical shift of 50 ppm indicates the absence of a substantial charge on the carbon atom of the alkoxides.

(iv) Also in the conversion of propene over zeolite H-Y alkoxide peaks were observed in agreement with the proposed reaction mechanism [3,5]. For the α-carbon atom of the alkoxides that result from the oligomerisation of *propene*, the chemical shift is more downfield, i.e. at 87 ppm, presumably due to a somewhat bigger, but still relatively small, partial positive charge on the carbon of the proposed intermediate [3].

Finally, in order to discriminate between free and sorbed hydrocarbons, we have recorded direct-excitation [14] as well as cross-polarisation MAS NMR spectra. From the analysis of the oligomerisation products by high-power proton-decoupled MAS NMR, it follows unambiguously that a substantial amount of free, gaseous reactant is still present in the sealed capsule, even after reaction overnight (fig. 2D). This has been observed before for other hydrocarbon conversion reactions carried out in sealed sample capsules [3]. Furthermore, ethane and butane gas product molecules also contribute, viz. to the peaks at 14.9 and 32.7 ppm. Since the spectrum was recorded by direct excitation of the ^{13}C nuclei, the observed ethane and butane molecules are most likely very mobile in the zeolite pores.

In contrast to previous investigations in which ^{13}C solid-state NMR was used to monitor the products formed upon olefin oligomerisation in acid zeolites, this work shows that the application of *in-situ* ^{13}C solid-state NMR at lower reaction temperatures gives direct evidence of the presence of olefinic intermediates in the micropores of the zeolite during oligomerisation of ethene. In fact, although the different olefinic oligomers that were identified are fully in line with the classical carbenium ion reaction mechanism (see Scheme I) [6], the occurrence of alkoxide species, i.e. reactant molecules bonded to the oxygen atoms adjacent to the aluminium sites in the zeolite framework, in a manner as has been proposed by Kazansky [15] and also by Haw et al. [3], is a more realistic description of the actual situation.



Scheme 1. The first steps of the low-temperature oligomerisation of ethene over zeolite H-ZSM-5 [6], according to the classical carbenium ion reaction mechanism compared to the currently observed olefinic primary products inside the pores of the zeolite crystals.

The fact that we have observed these olefinic species only at low temperature and for a limited period of time after the exposure of the ethene to the acidic zeolite indicates that these olefins are highly reactive. It is well known that especially zeolite H-ZSM-5 is a very active catalyst for oligomerisation of olefins [16,17]. Provided the olefins are given sufficient time to react, ultimately all the intermediate, olefinic products are readily converted to paraffins (figs. 2C and 1C).

4. Conclusions

The ^{13}C solid-state NMR spectra in this study have indicated that the degree of branching of the hydrocarbon products formed upon adsorption of ethene in the zeolites increases with the dimensions of the pores. Upon oligomerisation of ethene, the medium-pore zeolite H-ZSM-5 produces more linear products than the large-pore zeolites H-MOR and H-Y. We have also shown that ethene, physisorbed in the micropores of zeolite H-ZSM-5, actually remains stable at temperatures below 0°C. Measurements at higher temperatures have indicated the onset of the reaction, and allowed us to identify several (apparently) highly reactive higher olefins as intermediate products. Our observation of intermediate olefinic oligomers inside the zeolite pores, although in line with the traditional model of acid-catalysed oligomerisations in which the reaction proceeds via carbenium ions, are probably better described in terms of a mechanism involving alkoxides species.

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