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Solid-State NMR Studies of the Shape-Selective Catalytic Conversion of Methanol into Gasoline on Zeolite ZSM-5

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Abstract: ^{13}C Magic angle spinning (MAS)–NMR of thermally treated samples of zeolite H-ZSM-5 with adsorbed methanol identifies the organic species present *in the adsorbed phase*, monitors their fate, and distinguishes between mobile and attached species. Only MeOH is present at room temperature; in samples treated at 150 °C dimethyl ether (DME) is also found. At 250 °C and above a new signal, due to CO intermediate, appears. A number of aliphatic and aromatic compounds form at 300 °C and above, and the role of CO in this process is discussed. Neither 1,2,3- or 1,3,5-trimethylbenzene is found in the products, but both are present in the adsorbed phase, which is the first direct experimental demonstration of product selectivity. Tetramethylbenzenes have not been found in the products of the reaction at 300 °C, but all three are present in the adsorbed phase in considerable concentrations. Their distribution (tetramethylbenzenes are *not* formed in the thermodynamic equilibrium distribution) reveals the presence of a new kind of shape selectivity. At 370 °C the shape-selective action is still present but is different because of the increased effective channel diameters. MAS-NMR has a considerable potential for monitoring and prediction of the course of catalytic reactions directly at the active centers in molecular sieves and will assist the design of shape-selective solids.

The important process[1] of catalytic conversion of methanol (MeOH) to hydrocarbons in the gasoline boiling range (30–200 °C) using zeolite ZSM-5 at ca. 370 °C has attracted a great deal of attention and is now used on an industrial scale. Mass spectrometry, gas chromatography,[2-5] infrared,[6,7] and NMR[8-14] studies established that MeOH is first dehydrated to dimethyl ether (DME) and that the equilibrium mixture of MeOH and DME is then converted to olefins, aliphatics, and aromatics up to C_{10}. However, the details and the mechanism of the reactions involved, particularly concerning the formation of the first carbon–carbon bond and the nature of the intermediates,[15] remain a matter of speculation. It is agreed that either ethylene or propylene is the first olefin formed, to be then converted to higher alkenes, alkanes, and aromatics via conventional carbenium ion routes. However, none of the proposed mechanisms for the formation of the first C–C bond have been confirmed experimentally. These involve carbenoid species,[2,16] carbenium ions,[17] or oxonium/oxonium ylide ions[3,18-21] as intermediates. Here we report that, with use of ^{13}C magic angle spinning (MAS)–NMR, we have been able to (i) study a reaction under conditions of temperature and pressure which closely resemble those typical of commercial catalytic processes; (ii) identify no fewer than 29 different organic species *in the adsorbed phase* with resolution similar to that afforded by gas chromatographic analysis of the products; (iii) demonstrate experimentally, for the first time, the reality of product shape selectivity in a zeolite; (iv) observe a new type of shape selectivity; (v) identify CO as an intermediate in the reaction; and (vi) distinguish unequivocally between mobile and attached species.

Derouane et al.[8] were the first to study the reaction in situ by using ^{13}C NMR of static samples. They observed three very broad signals and derived information on the relative numbers of CH_3–, CH_2–, CH_3–O, etc. groupings. To account for shoulders in ^{13}C NMR spectra, surface methoxy groups were postulated.[11,13] However, because of relatively poor spectral resolution, NMR did no more in those instances than corroborate more detailed results from gas chromatography. We demonstrate that the enormous enhancement in spectral resolution brought about by the use of MAS allows the detailed assignment of NMR spectral lines to individual molecular species.[22]

Experimental Section

Zeolite H-ZSM-5 with Si/Al = 30 was prepared by ammonium exchanging Na-ZSM-5 and calcination at 550 °C in flowing air. MeOH 99.9% enriched in ^{13}C (Aldrich) was diluted to 30% (w/w) with ordinary MeOH and purified by the freeze–pump–thaw method. NMR samples were contained in specially designed capsules[23] which could be spun at up to 4 kHz inside a zirconia rotor of a double-bearing MAS probehead. Sample preparation was as follows. A high-purity Pyrex tube was closed at one end and blown to form a capsule 7-mm o.d. connected to the rest of the tube by a narrow neck. The capsule was then lap-ground to fit precisely inside the MAS rotor. The powdered sample was transferred into the capsule to fill it completely and evenly. The tube was then connected to a gas-handling line. The sample was dehydrated by evacuation followed by heating at 400 °C for 6 h. The final gas pressure above the sample was less than 10^{-5} Torr. The sample was cooled to room temperature prior to adsorption of 50 Torr of ^{13}C-enriched MeOH and allowed to equilibrate for 1 h before being isolated from the bulk of the gaseous MeOH. It was then cooled with liquid nitrogen; since the volume of gas above the sample was kept to a minimum, this resulted in only a small additional uptake of MeOH. The neck of the capsule was finally sealed with a micro-torch flame, while the sample itself was

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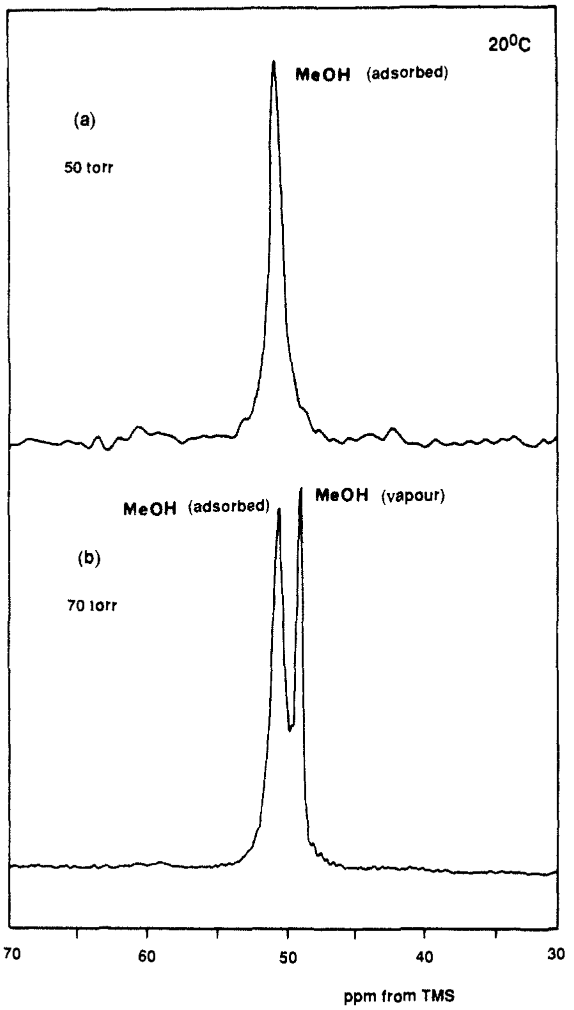

Figure 1. ^{13}C MAS-NMR spectra (proton decoupling only) of a sample with (a) 50 Torr and (b) 70 Torr of MeOH and no thermal treatment.

maintained at −196 °C. Sealed sample capsules were placed in a furnace and maintained at precisely controlled temperatures in the range of 20–370 °C for various lengths of time and then quenched in liquid nitrogen. ^{13}C NMR spectra were measured at room temperature under the following sets of conditions: 1. static (no MAS); 2. MAS but no proton decoupling; 3. MAS and high-power proton decoupling; and 4. MAS and ^{13}C–^{1}H cross-polarization.

We were able to discriminate between mobile and immobile species (by comparing spectra **1–3** with spectra **4**) and to establish whether protons are attached to a given carbon atom (by comparing spectra **2** and **3**). Experiments were performed at 100.613 MHz on a Bruker MSL-400 spectrometer equipped with a variable-temperature MAS probehead. High-power decoupling experiments were carried out with 40° ^{13}C pulses and a 10 s recycle time. We have found that ^{13}C spin–lattice relaxation times of all species observed are very similar and of the order of 2.5 s. Experiments without high-power decoupling used the same acquistion parameters. Cross-polarization[24] (CP) spectra were acquired with a 4.5 μs proton 90° pulse, a 2 ms contact time, and a 5 s repetition time. No sideband suppression techniques were used. Chemical shifts are referred to external tetramethylsilane (TMS).

Results

The NMR spectrum of zeolite H-ZSM-5 with 50 Torr of adsorbed MeOH and maintained at 20 °C [Figure 1a] contains a single resonance at 50.8 ppm, which represents a small downfield shift from liquid MeOH (49.3 ppm) and MeOH vapor (49.2 ppm). When excess MeOH is deliberately adsorbed, an additional signal is found, as shown in Figure 1b where 70 Torr of MeOH was initially adsorbed. This is due to highly mobile MeOH, which is either gaseous or adsorbed on the outer surface of the crystallites. The intensity of the signal from the adsorbed MeOH is considerably increased in comparison with that from the vapor when the spectrum is recorded with CP (not shown), which indicates that the motion of the adsorbed species is restricted. Figure 2 gives the spectra taken after heating the sample to 150 °C for (a) 5 and (b) 20 min. In both cases two signals are observed, at 50.5 and 60.5 ppm, corresponding to MeOH and DME, respectively. The ratio of intensities is 3.6 and remains constant when the sample is treated for longer periods at the same temperature. However, since the spectra were recorded with CP, the intensity ratio cannot be considered as quantitative.[24] The resonance from the adsorbed DME is shifted 1.2 ppm downfield from the liquid.

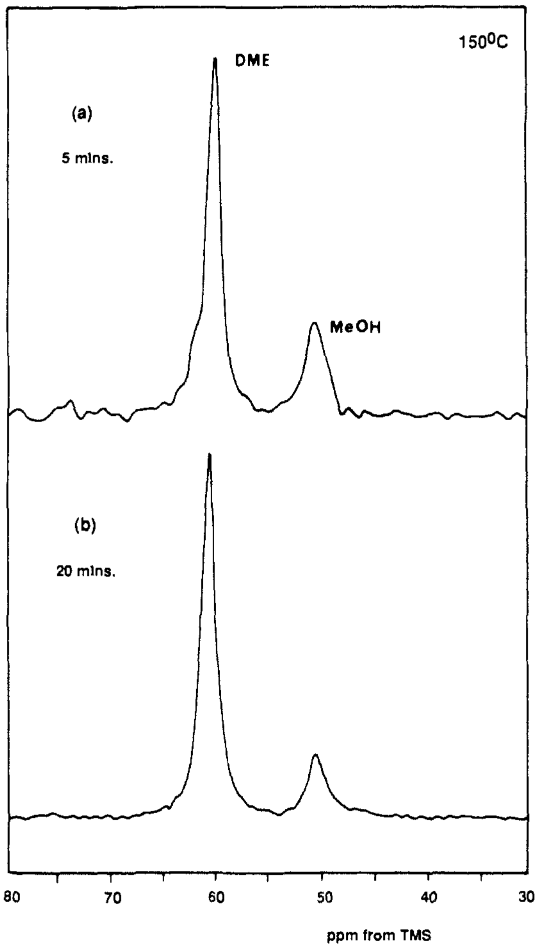

Figure 2. ^{13}C CP/MAS-NMR spectra of a sample heated to 150 °C for (a) 5 min and (b) 20 min.

Figure 3 gives the spectra of a sample treated at 250 °C. After 3 min [Figure 3a] only DME is produced with the [DME]/[MeOH] ratio similar to that found at 150 °C. However, after 24 min (not shown) and 54 min [Figure 3b] a new single signal at 184 ppm appears, due to carbon monoxide. We have confirmed this assignment by, first, noting that the species responsible is stable at ambient temperature and gives rise to a *single* resonance; second, by acquiring the spectrum without proton decoupling to find that the 184 ppm signal is unsplit, i.e., no *J*-coupling to protons is present; third, by measuring the spectrum with CP whereupon the signal disappeared; and fourth, by reference to literature results.[25] Ketone carbons have a chemical shift greater than 206 ppm and are therefore excluded, as are other carbonyl species such as esters and carboxylic acids which give rise to more than one NMR signal. After 54 min at 250 °C the same sample was heated to 300 °C. After 5 min at 300 °C no change in the spectrum was observed. However, after 10 min the spectrum shown in Figure 4 was measured, containing signals from various aliphatic carbons as well as MeOH, DME, and CO. The ratio of the intensity of the DME/MeOH signals is now 0.55.

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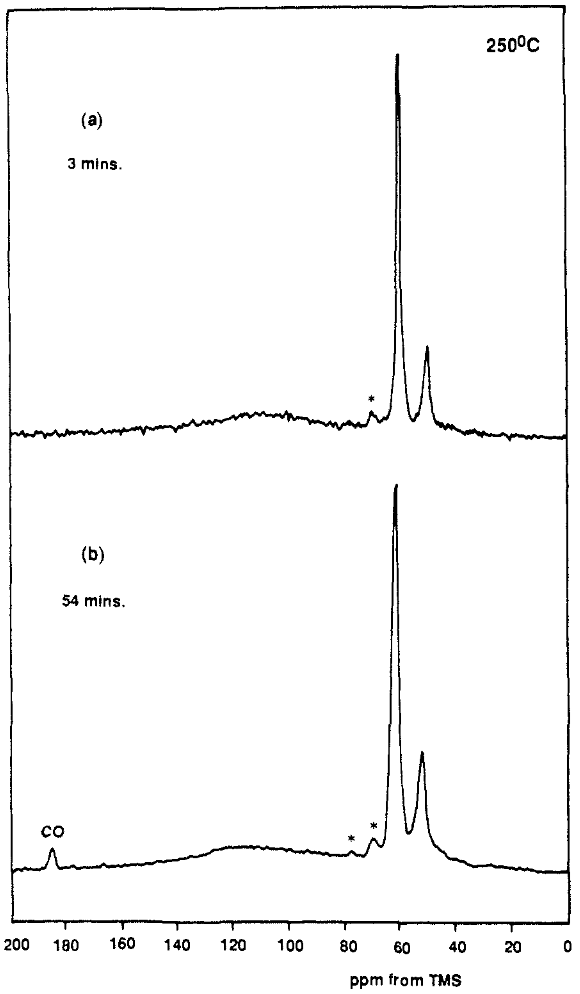

Figure 3. ^{13}C MAS-NMR spectra (proton decoupling only) of a sample heated to 250 °C for (a) 3 min and (b) 54 min. Asterisks denote spinning sidebands. The broad signal centered at ca. 110 ppm is due to the background and is also found without the sample present in the probehead.

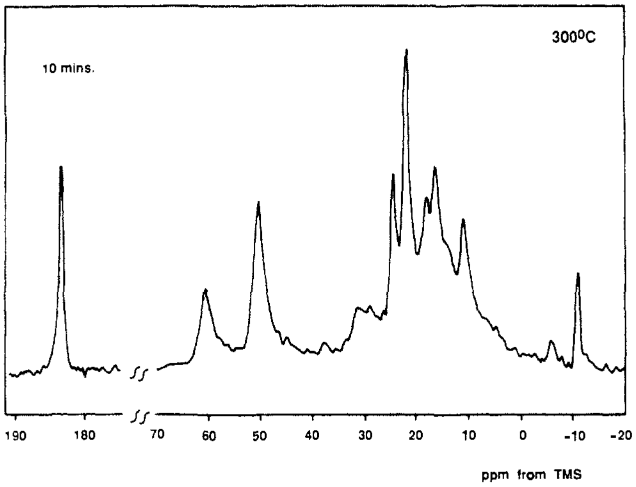

Figure 4. ^{13}C MAS-NMR spectrum (proton decoupling only) of a sample heated to 250 °C for 54 min and then to 300 °C for 10 min.

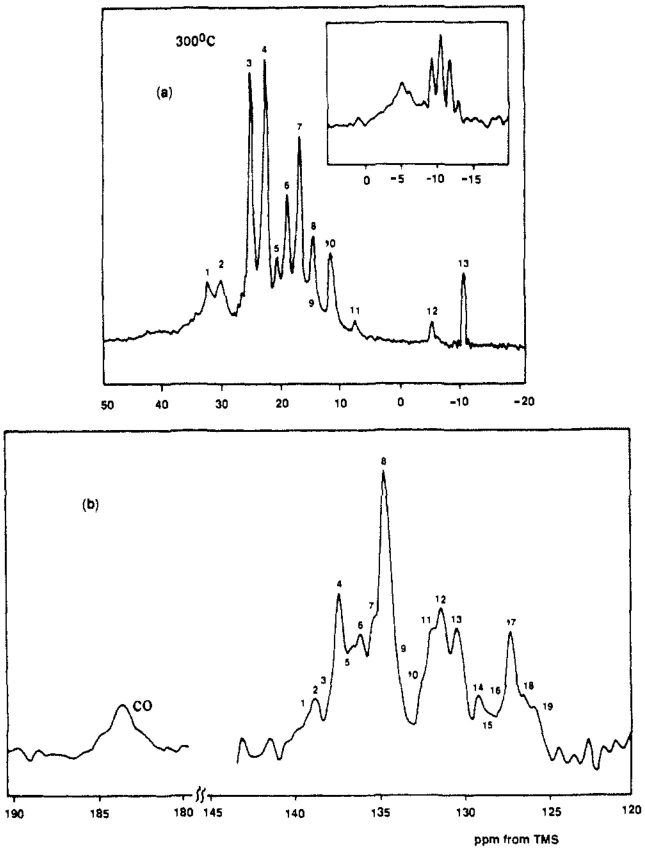

Figure 5. ^{13}C MAS-NMR spectra of a sample heated to 300 °C for 35 min and recorded with proton decoupling only (a) aliphatic region and (b) aromatic and CO region. Intensities in (a) and (b) are not on the same scale. The insert shows J-coupling of methane and cyclopropane carbons (recorded without decoupling). Spectral assignments are given in Table I.

Table I. Assignment of ^{13}C MAS-NMR Signals for the Sample Treated at 300 °C for 35 min

compound	aliphatic		aromatic peak no.
	peak no.[a]	intensity[b]	
isobutane	3	s	
propane	7	s	
carbon monoxide		s	
n-butane	3, 9	m	
n-hexane	1, 4, 8	m	
isopentane	1, 2, 4, 10	m	
n-heptane	1, 2, 4, 8	m	
methane	13	m	
ethane	11	w	
cyclopropane	12	w	
o-xylene	5	s	4, 12, 17
1,2,4,5-tetramethylbenzene	6	s	8, 11
p-xylene	6	s	7, 13
1,2,4-trimethylbenzene	5, 6	m	4, 6, 8, 11, 13, 16
1,2,3,5-tetramethylbenzene	5, 8	m	5, 7, 10, 13
toluene	5	w	2, 13, 14, 18
m-xylene	5	w	2, 12, 15, 17
1,3,5-trimethylbenzene	5	w	3, 16
1,2,3-trimethylbenzene	5, 8	w	5, 7, 16, 19
1,2,3,4-tetramethylbenzene	5, 8	w	7, 9, 16

[a] Refers to Figure 5. [b] s = strong; m = medium; w = weak. Owing to the nuclear Overhauser effect these intensities give only a rough guide to the concentration of each species.

Another sample was treated at 300 °C for 5, 25, and 35 min and examined after each step. The first step gave very similar NMR spectra as those for 150 °C (see Figure 2). The other two treatments resulted in spectra identical with each other. Figure 5a gives the spectrum of the 35-min sample recorded with high-power proton decoupling only. There is a series of sharp peaks in the aliphatic region and a number of signals in the aromatic region; the CO peak is also found. When the spectrum is recorded with CP (not shown), the signals in the aromatic region, the CO signal, and the two aliphatic signals at -6.1 and -10.7 ppm all disappear. The assignment of all the signals is given in Table I. Although some signals overlap, especially those from methyl

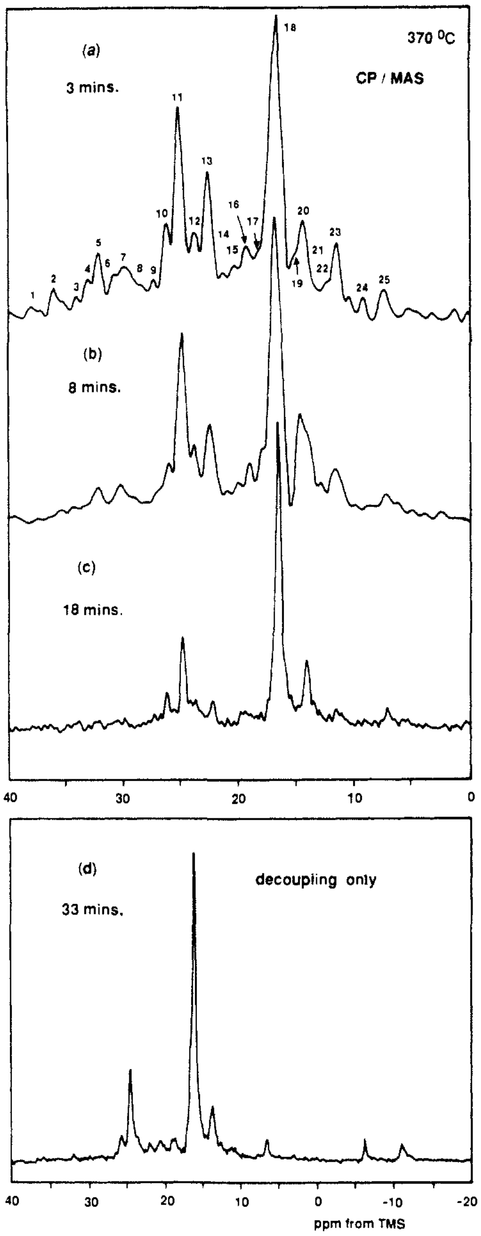

Figure 6. ^{13}C MAS-NMR spectra of the aliphatic region of a sample heated to 370 °C. (a)-(c) are recorded with CP after heat treatment for (a) 3 min; (b) 8 min; and (c) 18 min. (d) shows the spectrum, acquired with proton decoupling only, of a sample heated for 33 min.

groups attached to aromatic rings, all could be reliably assigned because most compounds give rise to several NMR peaks. The two peaks with negative chemical shifts (−6.1 and −10.7 ppm) are assigned to cyclopropane and methane, respectively, after Denney et al.[26] who found that when adsorbed on zeolite Y these compounds give rise to ^{13}C resonances close to those in the gas phase rather than in the liquid (the chemical shifts of gaseous cyclopropane and methane are −7.64 and −11.53 ppm, respectively). The large upfield shifts in comparison with the liquid are due to the substantial contribution of the van der Waals term to the chemical shift. Further support for these assignments comes from the spectrum recorded without decoupling and given in the insert in Figure 5a. The signal at −10.7 ppm is split into a quintet with the individual components in the intensity ratio close to 1:4:6:4:1 with J_{CH} = 124 Hz, characteristic of methane. Similarly, the signal at −6.1 ppm is split into a (less well-defined) triplet, with $J_{CH} \approx 100$ Hz. The fact that a spectrum can be obtained at all without decoupling indicates the relatively fast motion of all species. However, it is still important to spin the sample in order to average chemical shift anisotropy. MAS at 1 kHz reduces NMR line widths to ca. 50 Hz. Higher spinning rates (up to 4 kHz) did not bring about any further improvement in spectral resolution.

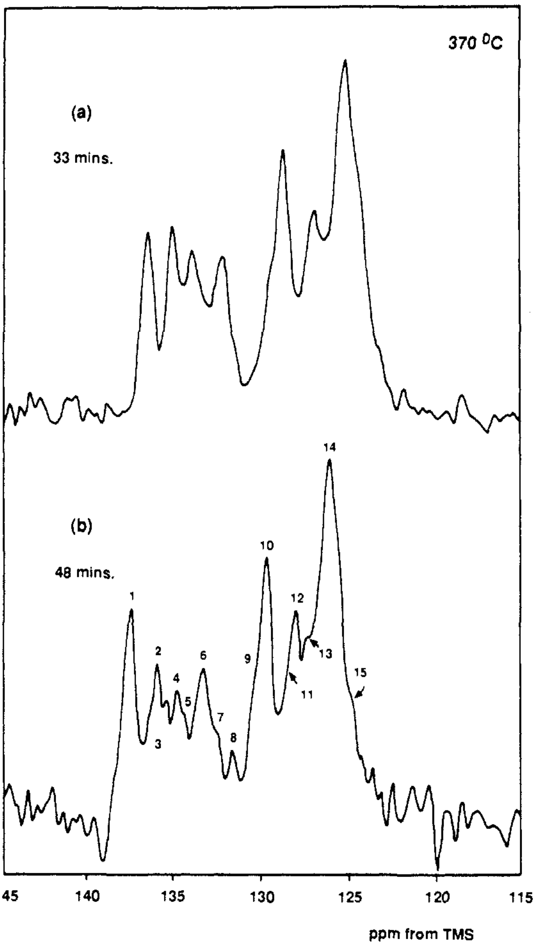

Figure 7. The aromatic region of ^{13}C MAS-NMR spectra (proton decoupling only) of a sample heated to 370 °C for (a) 33 min and (b) 48 min. Spectral assignments are given in Table II.

Figure 5b shows that the predominant aromatic species formed at 300 °C are *o*-xylene, *p*-xylene, and 1,2,4,5-tetramethylbenzene; 1,2,4-trimethylbenzene and 1,2,3,5-tetramethylbenzene are also present. The amounts of other trimethyl- and tetramethylbenzenes as well as of toluene and *m*-xylene are small; there is no evidence of any alkenes. The dominant signals in the aliphatic region come from isobutane and propane with fairly strong signals from *n*-butane, *n*-hexane, *n*-heptane, isopentane, and methane; weaker signals come from ethane and cyclopropane.

Figure 6 shows the aliphatic region of the CP spectrum of a sample of H-ZSM-5 treated at 370 °C for 3, 8, and 18 min. After 18 min the spectrum *in this region* does not change further. Also given is the spectrum after 33 min, recorded with proton decoupling but without cross-polarization, in order to show signals from cyclopropane and methane which are suppressed under CP. The *aromatic* region changes little during the initial heating period, but after 33 min some subtle changes do take place. Figure 7 shows this region, recorded without CP, after 33 and 48 min treatment, and the signals are assigned in Table II. The strongest signals in the aromatic region come from *o*- and *m*-xylenes and slightly weaker ones from toluene, *p*-xylene, and 1,2,3- and 1,2,4-trimethylbenzene. By comparison with the 300 °C sample, the 370 °C sample contains considerably more *m*-xylene and toluene and much less 1,2,4,5-tetramethylbenzene. It also contains some penta- and hexamethylbenzene.

The aliphatic region of the spectrum in Figure 6 exhibits many of the signals already seen in the sample treated at 300 °C. However, after 3 min at 370 °C a number of branched alkanes, notably 3-methylpentane and 2,3-dimethylbutane appear. The

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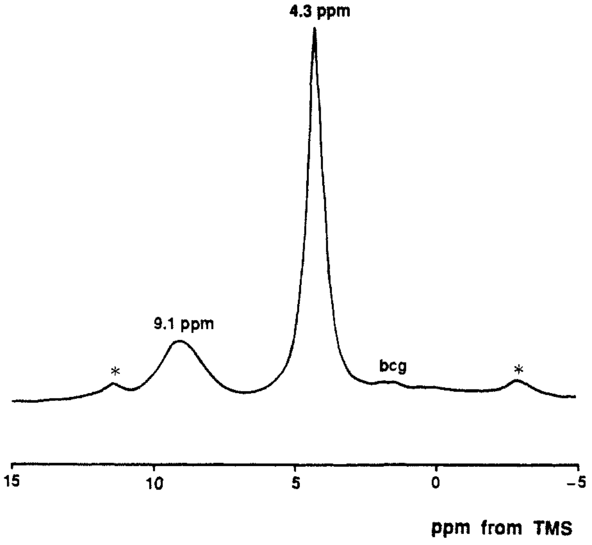

Figure 8. ^{1}H MAS-NMR spectrum of H-ZSM-5 with 50 Torr of adsorbed MeOH and no thermal treatment. Asterisks denote spinning sidebands; "bcg" denotes the proton background of the probehead.

Table II. Assignment of ^{13}C MAS NMR Signals for the Sample Treated at 370 °C

	aliphatic				aromatic	
		int[c]				int[c]
compound	peak no.[a]	3 min	8 min	18 min	peak no.[b]	33 min
isobutane	11	s	s	m		
propane	18	s	s	s		
isopentane	5, 7, 13, 23	m	w			
n-butane	10, 20	m	w	w		
n-hexane	4, 12, 19	w	w			
n-heptane	4, 6, 12, 19	w	w			
3-methylpentane	1, 7, 16, 18	w	w			
2,3-dimethylbutane	3, 15	w	w			
n-pentane	1, 8, 19	w	w			
methane		w	w	w		
cyclopropane		w	w	w		
ethane	25	w	w	w		
neopentane	5, 8	w	w			
toluene	13				1, 10, 11, 15	m
o-xylene	13				2, 10, 14	s
m-xylene	13				1, 10, 13, 14	s
p-xylene	15				5, 10	m
1,2,3-trimethylbenzene	14, 18				3, 5, 12, 15	m
1,2,4-trimethylbenzene	14, 15				2, 4, 6, 9, 10, 13	m
1,3,5-trimethylbenzene	13				1, 13	w
1,2,4,5-tetramethylbenzene	15				6, 8	w
1,2,3,5-tetramethylbenzene	13, 14, 19					
1,2,3,4-tetramethylbenzene	14, 18					
pentamethylbenzene	14, 18				5, 7, 8	w
hexamethylbenzene	17				10	w
benzene					11	w

[a] Refers to Figure 6a. [b] Refers to Figure 7b. [c] Intensity.

concentration of straight-chain alkanes decreases with treatment time until after 18 min only propane and *n*-butane remain. The strongest signals are due to propane and isobutane but with the ratio [propane]/[*n*-butane] increasing with reaction time. Once again no alkenes are found. The low intensity CO signal at 184 ppm is found for all treatments at this temperature.

Discussion

At 150 °C only DME is produced (Figure 2). We did not find spectral line broadening claimed[8] to be caused by the presence of "a variety of aliphatic ethers" or any evidence for the existence of surface methoxy groups. There appears to be a fundamental difference between the adsorbed species formed on zeolites H-Y[27] and H-ZSM-5. This may be due to the different temperature of activation, 380 °C for zeolite H-Y and below 250 °C in the present work. However, the assignment of the species reported at 59.2 ppm in H-Y to surface methoxy groups seems questionable. If such groups do exist in H-Y or H-ZSM-5, either their lifetime is too short for them to be observed by NMR or the resonance is obscured by the DME signal. On the other hand, there is good IR evidence[7,28] that surface methoxy groups do exist.

The resonances from adsorbed MeOH and DME are slightly shifted downfield, but we believe this is a consequence of changes in magnetic susceptibility of the sample rather than of the appearance of a new chemical species. At 150 °C the equilibrium between MeOH and DME is established after 5 min, and their relative concentrations remain nearly constant thereafter (Figure 2). If we disregard the effect of possible difference in the efficiency of cross-polarization for MeOH and DME (although we are dealing with methyl groups only in both cases), at equilibrium [DME]/[MeOH] = 1.8. Chang and Silvestri[2] and van den Berg et al.[3] found that when used as the feed gas DME is partly converted to MeOH, even in the absence of water. The reaction is therefore likely to involve the zeolitic Brønsted acid sites. However, below 200 °C the conversion of DME to MeOH via this route is insignificant and so the equilibrium can be written simply as

$$2CH_3OH \overset{k}{\leftrightarrow} CH_3OCH_3 + H_2O \qquad (1)$$

$$\text{with } k = \frac{[CH_3OCH_3][H_2O]}{[CH_3OH]^2} = \frac{[CH_3OCH_3]^2}{[CH_3OH]^2}$$

It follows that at 150 °C in a static reactor $k = (1.8)^2 = 3.24$. The reaction has generally been thought to be acid catalyzed: a molecule of MeOH would be protonated by a zeolitic acid site before reacting with another MeOH molecule. In order to test this hypothesis we have measured ^{1}H MAS-NMR spectra of our sealed samples. The experiments were carried out at 400.13 MHz with MAS at 3.5 kHz, with use of a probehead acquired from Sektion Physik, Karl-Marx-Universität, Leipzig.[29] Figure 8 shows the proton spectrum of H-ZSM-5 with MeOH adsorbed at room temperature. The two resonances at 4.3 and 9.1 ppm correspond to methyl protons and the hydroxyl group, respectively. Pure methanol gives a hydroxyl resonance at 1.2 ppm, and the enormous (7.9 ppm) downfield shift of this signal in the adsorbed phase is due to very strong hydrogen bonding of the hydroxyl group or even protonation of the methanol[30]

$$CH_3OH + HZ \leftrightarrow (CH_3OH_2)^+ + Z^- \qquad (2)$$

where Z denotes the zeolitic framework. The reaction can then continue:

$$(CH_3OH_2)^+ + CH_3OH \leftrightarrow CH_3OCH_3 + H_3O^+ \qquad (3)$$

A corresponding downfield shift of the proton NMR signal of water generated during this dehydration provides the evidence that H_3O^+ is also present.[30]

At 250 °C DME is again the first adsorbed species formed. CO appears after 10 min at that temperature and persists at fairly low but significant concentrations for up to 54 min. At 250 °C no higher molecular weight hydrocarbons are formed. CO has been observed before in the reaction products of MeOH conversion,[20,31-35] although usually at much higher temperatures,

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typically 500 °C, and always accompanied by a host of other hydrocarbons. What is significantly different in our work is that CO is observed as an *intermediate* subsequent to the formation of DME but prior to the onset of hydrocarbon formation; it is the only such intermediate found so far. Note also that at higher temperatures, when hydrocarbons are being formed, the concentration of CO begins to decrease, suggesting that CO is required for their formation. CO could be formed either from DME or MeOH. However, the mechanism suggested by Olah et al.[20] which involves a three-step conversion of DME via formaldehyde and formic acid is unlikely, as methane is not observed at this stage:

$$CH_3OCH_3 \rightarrow CH_4 + CH_2O \tag{4}$$

$$2CH_2O \rightarrow CH_3OH + HCOOH \tag{5}$$

$$HCOOH \rightarrow H_2O + CO \tag{6}$$

Chu and Chang[35] suggest a radical pathway from DME, but this also involves the production of methane. In the conversion of MeOH over aluminum-free ZSM-5[31] the main products were formaldehyde and CO; the conclusion was that the latter species is produced via the former

$$CH_3OH \rightarrow CH_2O + H_2 \tag{7}$$

$$CH_2O \rightarrow CO + H_2 \tag{8}$$

and that the active sites were the residual sodium cations present. If this stepwise dehydrogenation does take place in our samples, then all formaldehyde is completely converted to CO. The conversion of formaldehyde could also proceed via reactions 5 and 6, as formic acid is known to decompose readily over H-ZSM-5.[36] The role of CO in the subsequent synthesis of hydrocarbons is unclear, but the fact that at higher conversions the concentration of CO decreases rather than increases strongly suggests that it is involved. If transition-metal impurities are present in the zeolite the hydrocarbonylation of MeOH to ethanol is very likely:[37]

$$CH_3OH \xrightarrow[\text{transition metal}]{CO/H_2} CH_3CH_2OH \tag{9}$$

Subsequent dehydration of ethanol yields ethylene:

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O \tag{10}$$

Indeed, when we partially ion exchange H-ZSM-5 with Fe^{3+} ethylene is the major olefin present in the sample treated at 300 °C (not shown). Evidence from other workers which supports the hypothesis that iron might be important in the initial stages of the reaction is as follows: (1) the incorporation of transition metals into zeolite X[38] and chabazite/erionite[39] promotes the formation of hydrocarbons; (2) such transition metals bring about selectivity for ethylene and propylene; (3) when iron-impregnated H-ZSM-5, a polyfunctional catalyst, is used to convert syn-gas to hydrocarbons, the overall conversion is increased;[41] and (4) CO is incorporated into the products when MeOH is converted in its presence.[10]

As the $MeOH/DME/H_2O/CO/H_2$ soup begins to be converted to hydrocarbons, only aliphatics are initially produced (Figure 4), and the [DME]/[MeOH] ratio decreases considerably. This suggests that either the higher molecular weight hydrocarbons are forming from DME rather than from MeOH with a rate constant greater than that for the DME/MeOH equilibrium or that, because of the production of water by subsequent dehydration reactions, the equilibrium 1 is shifted in favor of MeOH.

After treatment at 300 °C for 5 min only water and DME are produced, although many hydrocarbons appear after longer reaction times. This indicates that there is an induction time, which in turn suggests that some species other than MeOH, DME, or water must be formed for hydrocarbon chain growth to begin. The formation of this species is the rate-determining step. Autocatalysis such as this has been reported.[17,41]

The external surface of a typical zeolite crystallite amounts to ca. 1% of the total BET surface area, and therefore the vast majority of catalytic sites are confined inside the crystallite. Since the zeolitic apertures are restricted in size, the probabilities of forming various products are determined to a great extent by molecular dimension and configuration. Three kinds of shape selectivity have been envisaged as early as 1960 in the classic paper reporting the discovery of catalytic activity of zeolites.[42] *Reactant selectivity* occurs when, for reasons of size, only certain reactant molecules can access the intracrystalline space and react there, other molecules being too large to enter the pores. *Product selectivity* occurs when, from various species formed within the channels and cavities, only some can diffuse out of the crystallite and appear as reaction products; larger product species must first be converted to smaller molecules. The familiar example of this is *p*-xylene, which can diffuse out of zeolite ZSM-5 while *o*- and *m*-xylenes can do so less readily.[44,45] Finally, *restricted transition-state selectivity* occurs when certain reactions cannot proceed at all because they would involve transition states requiring more room than is available in the intracrystalline space. However, the evidence for shape selectivity in zeolites is indirect insofar as it relies on the absence of certain species in the products (as observed by gas chromatography) rather than on the presence of others on intracrystalline active sites, something which could not, until now, be directly monitored. For example, prior to this work (see below), there was no *direct* proof that all three trimethylbenzenes are indeed produced inside a ZSM-5 particle at 300 °C.

After treatment at 300 °C for 20 min equilibrium is established with MeOH and DME being completely converted to a mixture of aliphatics and aromatics. This is in agreement with earlier work[2,8] assuming that a sealed capsule is equivalent to a reactor working at very low space velocities. However, the distribution of adsorbed species is very different from that observed in the reaction products using conventional chromatographic techniques. The principal aromatics expected to be present[8] are *m*- and *p*-xylene, 1,2,4-trimethylbenzene, and toluene. However, the main species actually found in the adsorbed phase are *o*- and *p*-xylene and 1,2,4,5-tetramethylbenzene, with smaller amounts of 1,2,4-trimethylbenzene and 1,2,3,5-tetramethylbenzene; *m*-xylene and tri- and tetramethylbenzenes are also found but in smaller amounts. The distribution of the three trimethylbenzenes in the adsorbed phase reflects the thermodynamic equilibrium distribution (see Table III). The fact that 1,2,3- or 1,3,5-trimethylbenzenes (with kinetic diameters of 6.4 and 6.7 Å, respectively) are not found among the products but are present in the adsorbed phase, while the smaller 1,2,4-trimethylbenzene (6.1 Å) is found in both, clearly demonstrates the reality of the concept of product selectivity.[42-45] The channel dimensions of ZSM-5 are[46] 5.6 Å × 5.3 Å, but more space is available at the intersection of the straight and zigzag channels. The thermal vibrations of the framework, which increases the maximum effective size of the

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Table III. Distribution of Aromatics in the Reaction Products (from Gas Chromatography) and in the Adsorbed Phase (from ^{13}C NMR)

compound	distribution		reaction products by gas chromatography[b]		adsorbed phase by ^{13}C NMR[c]	
	statistical[a]	thermodynamic[48]	300 °C[8]	370 °C[2]	300 °C	370 °C
toluene			m	s	w	m
xylene						
o-	2	2	2.0 (w)	2.0 (m)	s	s
m-	2	4.9	(m) } 7.5	5.1 (s)	w	s
p-	1	2.2	(m)	2.2 (m)	s	m
trimethylbenzene						
1,2,4-	12	12	12.0 (m)	12.0 (m)	m	m
1,2,3-	5	1.3		1.0 (w)	w	m
1,3,5-	2	4.3		2.3 (w)	w	w
tetramethylbenzene						
1,2,4,5-	1	1		1.0 (w)	s	w
1,2,3,4-	2	0.44		0.5 (w)	w	vw
1,2,3,5-	2	1.5		0.9 (w)	m	vw
pentamethylbenzene				vw		w
hexamethylbenzene						w

[a] Expected for random methyl substitution on the benzene ring. [b] Normalized to the thermodynamic equilibrium distribution for *o*-xylene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene: s = strong, m = medium, w = weak, vw = very weak. [c] This work.

channels, allow the smaller isomer to diffuse out of the crystal. The two larger isomers, however, although formed, are unable to diffuse out at 300 °C and must isomerize to 1,2,4-trimethylbenzene.

The distribution of the tetramethylbenzenes in the intracrystalline space is most unexpected. None of them have ever been reported in the products of the reaction at 300 °C, and yet all three are clearly present in the adsorbed phase. Because of the restricted intracrystalline space they can only form at channel intersections but (unlike the trimethylbenzenes) are not generated in the thermodynamic equilibrium distribution. 1,2,3,5-Tetramethylbenzene (6.7 Å)[4,47] should be the dominant species on thermodynamic grounds (Table III); in fact it is 1,2,4,5-tetramethylbenzene (6.1 Å) which dominates. The thermodynamically least favored isomer, 1,2,3,4-tetramethylbenzene (6.4 Å), is found in small quantities. The fact that tetramethylbenzenes are not found in the products again demonstrates product shape selectivity. Their *relative abundance* in the adsorbed phase, on the other hand, shows that an additional kind of shape selectivity occurs within the intracrystalline space. It does not rely on the ability of species to enter or to leave the crystal, nor on the size of the transition state, nor is a combination of these: isomerization is sterically restricted within the crystallite at the active site itself. Selectivity of this kind is similar to the action of enzymes. We shall refer to it as *active site shape selectivity*.

Low molecular weight compounds dominate in a sample treated at 370 °C in both the adsorbed and gas phases (Table III). There is more *m*-xylene and toluene and much less 1,2,4,5-tetramethylbenzene than in the 300 °C sample. Small amounts of penta- and hexamethylbenzene are also found. At 370 °C all possible methyl-substituted benzenes up to C_{11} have been observed[2] in the products. The larger species are now able to leave the crystallite because of the increased effective channel diameter. Since gas chromatography shows that the distribution of trimethylbenzenes in the products is very close to that expected on thermodynamic grounds, it may appear, without the insight provided by NMR, that shape selectivity is absent. However, the spectra clearly show that a two-step shape selection is at work. First, steric effects restrict the formation of the largest 1,3,5-isomer in the intracrystalline space. Second, diffusion effects only allow the smallest 1,2,4-isomer to diffuse out of the particle to any great extent, although the 1,2,3-isomer is present in the adsorbed phase in comparable amounts.

At both 300 °C and 370 °C the aliphatic distribution in the adsorbed phase correlates closely with that found in the products.[2,8] The main species present are always isobutane and propane with lesser amounts of isopentane and *n*-butane. Cyclopropane is the only aliphatic species observed in the adsorbed phase which has never been reported in the products. This is interesting, since it has been suggested[20] that cyclopropane is an intermediate in the conversion ethylene to propylene. The apparent absence of olefins agrees with an earlier report[2] that their concentration diminishes drastically at low space velocities.

It is clear that MAS-NMR can probe directly the role of active sites in catalytic reactions on zeolites. The kind and quantity of chemical species present inside the particle can, for the first time, be directly monitored for a variety of reactions. This information, not forthcoming from other techniques, can be usefully compared with the composition of the gaseous products to give new insights into reaction mechanisms on molecular sieves.

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Registry No. DME, 115-10-6; MeOH, 67-56-1; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1,2,4-trimethylbenzene, 95-63-6; 1,2,3-trimethylbenzene, 526-73-8; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4,5-tetramethylbenzene, 95-93-2; 1,2,3,4-tetramethylbenzene, 488-23-3; 1,2,3,5-tetramethylbenzene, 527-53-7.

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