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MULTINUCLEAR MAS NMR STUDIES ON COKED ZEOLITES H-ZSM-5

H.Ernst, D.Freude, M.Hunger and H.Pfeifer

Sektion Physik der Karl-Marx-Universität Leipzig, Linnéstraße 5, DDR-7010 Leipzig, GDR

SUMMARY

During the cracking process carbonaceous materials are deposited on the outer or inner surface of the catalyst. These deposits are in many cases the main cause of catalyst deactivation. Magic angle spinning (MAS) NMR investigations and catalytic n-hexane cracking were carried out on H-ZSM-5 zeolites after a mild hydrothermal dealumination. By ^{13}C CP MAS NMR it could be shown that the enhanced catalytic activity does not enhance the coke formation and that the chemical nature of these deposits is essentially aromatic. From ^{1}H MAS NMR studies performed on shallow-bed activated sealed samples and ^{27}Al and ^{29}Si MAS NMR on rehydrated samples it follows that for high coke concentrations the catalyst deactivation is caused mainly by blocking of Brönsted acid sites.

INTRODUCTION

The activity, selectivity and deactivation by coking have an important influence on the industrial applicability of zeolites (refs.1-7). In agreement with other authors (refs.9-11) in a previous study (ref.12) using ^{1}H, ^{27}Al and ^{29}Si MAS NMR as well as the catalytic cracking reaction of n-hexane we have found, that a mild hydrothermal dealumination of zeolite H-ZSM-5 results in an enhanced catalytic activity. Here we report ^{1}H, ^{13}C, ^{27}AL and ^{29}Si MAS NMR studies on such hydrothermal treated uncoked and coked samples to elucidate where the carbonaceous products are deposited. Whereas in some previous papers H-ZSM-5 was assumed to produce coke preferentially on the external surface of the crystallites (refs.13,14), recent studies give clear evidence of coke formation in the interior pore system of the crystallites (refs.15-19).

METHODS

Hydrothermal treatment

The zeolite with a framework Si/Al ratio of 15 synthesized without template was the same as used in ref.12. The hydrothermal treatment of the binder free samples was carried out in a tube of

50mm inner diameter with a maximum bed-depth of the zeolite material of 8mm. The temperature was increased at a rate of 10K per min. The steaming was carried out at 540°C for 150min under a water vapour pressure, which was adjusted by the temperature of the water bath, through which the nitrogen was flowing.

Catalytic reaction

Catalytic activity was determined for the n-hexane cracking reaction in an integral flow reactor. The reactor contained o.25g zeolite in the form of binder free pellets with diameters of 0.3-0.4mm. The catalyst was heated at a rate of 6K per min to 450°C and then maintained at this temperature for 1h in a hydrogen flow. Since it is known, that the deactivation of H-ZSM-5 zeolites in the n-hexane cracking (refs.6,20,21) and methanol conversion (ref.22) proceeds only slowly with hydrogen as a strem gas, we have used nitrogen ($T=450°C, p_{N2}=6kPa$, $p_{n\text{-}hexane}=92kPa$). During the rection time of 15h a gaschromatographic analysis of the reaction products was carried out. If U denotes the relative molar conversion, the reaction rate constant k is determined by the equation

$k=-\ln(1-U)$.

The conditions of the hydrothermal treatment as well as values for the relative rate constant k/k_o after coking are given in Table 1. k_o denotes the rate constant extrapolated to zero time.

Table 1

Conditions of hydrothermal treatment and values for relative rate constant k/k_0 after n-hexane cracking for the samples under study.

Sample	Conditions of hydrothermal treatment			rel. rate constants k/k_0 ±15%
	t(h)	T(°C)	p_{water}(kPa)	
H-ZSM-5/0	2.5	540	0	0.76
H-ZSM-5/10	2.5	540	10.7	0.58
H-ZSM-5/40	2.5	540	40	0.65

NMR measurements

^{13}C, ^{27}Al and ^{29}Si MAS NMR measurements were generally carried

out on rehydrated samples. For the ^{1}H MAS NMR measurements the samples were pretreated under shallow-bed conditions in a glass tube of 5.5mm inner diameter and with a bed-depth of 10mm for zeolite material. The temperature was increased at a rate of 10K per h. The samples were kept at the final activation temperature of 400°C under a pressure below 10mPa for 24h, and than cooled and sealed. Measurements were made on a homemade spectrometer HFS 270 and on a Bruker MSL 300 spectrometer. The homemade MAS equipment for the rotation of the fused glass ampoules (ref.23) was carefully cleaned to avoid spurious proton signals. As a reference for the ^{27}Al intensity measurements, a well-characterized sample of H-ZSM-5 with a framework Si/Al ratio of 15 was used. The total concentration of OH groups in the activated samples was determined by comparison of the initial value of the free-induction decay of the sample with the corresponding value for a standard (water). As a reference for the ^{13}C CP NMR intensity measurements a coked sample of H-ZSM-5 characterized by chemical analysis with respect to the carbon content and the H/C ratio was used.

RESULTS

^{1}H MAS NMR

The ^{1}H MAS NMR spectra of the uncoked as well as of the coked sample H-ZSM-5/0 are shown in Fig.1. Four different signals can

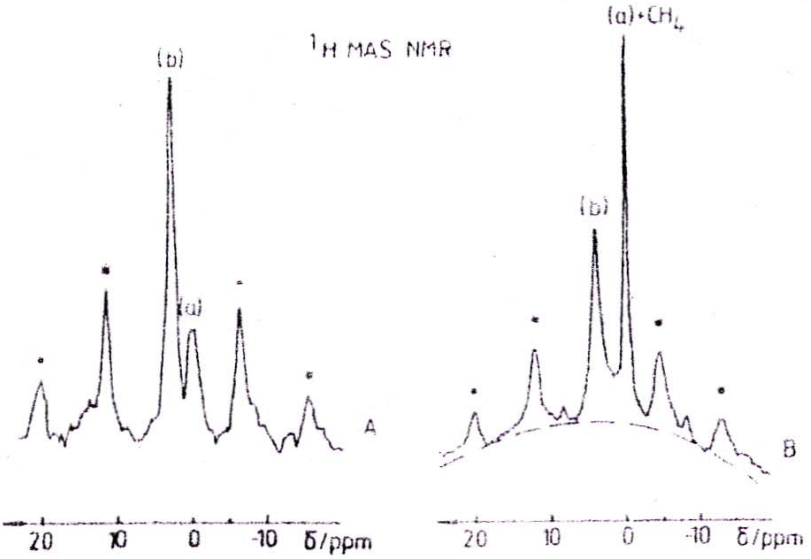


Fig.1 ^{1}H MAS NMR spectra of the sample H-ZSM-5/0 before (A) and after (B) coking.

be seen. (i) The line (a) at 2ppm is due to non-acidic hydroxyl groups at the outer surface of zeolite crystallites, at framework

defects and in the amorphous part of the sample (ref.16). (ii) For the coked samples this first line is superimposed by a signal of highly mobile molecules of methane, enclosed in the channels of the zeolite. (iii) The line (b) at 4.3ppm is caused by bridging (acidic) OH groups (ref.24). (iv) The very broad line in the spectrum of coked samples is not affected by MAS. Therefore, the line width is determined by proton-proton dipolar interaction. Table 2 summarizes for the six samples under study values for the total concentration (columns (1) and (2)) as well as for the concentration of OH groups contributing to line (b) (columns (3) and (4)). All concentrations are given in protons per u.c. of the zeolite.

Table 2
Concentration of protons and of framework aluminium atoms

Sample	$c_{Htot.}$ ±20%		$c_{H(b)}$ ±20%		$c_{Alfr.}$ ±15%		$c_{H(b)} * k/k_0$ ±35%	$c_{Hinv.}$
	unc.	c.	unc.	c.	unc.	c.#)	c.	c.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
H-ZSM-5/0	7.0	14.0	6.0	4.8	6.0	5.0	4.6	5.8
H-ZSM-5/10	5.0	10.5	3.4	2.5	3.5	2.7	2.0	6.1
H-ZSM-5/40	4.0	6.5	1.6	1.6	1.6	1.6	1.0	-

$c_{Htot.}$:Total concentration of protons; $c_{H(b)}$:Concentration of protons contributing to the line (b); $c_{Alfr.}$:Concentration of framework aluminium atoms; $c_{Hinv.}$:Concentration of protons per "NMR-invisible" site; unc.:Uncoked; c.:Coked; #):Apparent value. Concentrations in the columns (1)-(7) are given in protons per u.c. of the zeolite.

^{29}Si MAS NMR

In Fig.2 ^{29}Si MAS NMR spectra are shown of the sample H-ZSM-5/0 and of the hydrothermally treated sample H-ZSM-5/40 before and after coking. A fitting procedure using the programm "Linesim" yields three lines. It is well-known that the unresolved signal of Si(0Al) groupings in zeolites ZSM-5 consists of a peak at ca. -111ppm with a shoulder at ca. -115ppm. The line at ca. -106ppm arises from Si(1Al) groupings (ref.25). The framework Si/Al ratio determined from the relation (ref.25)

$$Si/Al = 4 * \sum_{n=0}^{4} Si(nAl) / \sum_{n=0}^{4} nSi(nAl)$$

where Si(nAl) denotes the intensity of the NMR signal attributable to Si(nAl) groupings is the same for both uncoked and coked sample and agrees very well in the case of uncoked samples with the result of the ^{27}Al MAS NMR measurements.

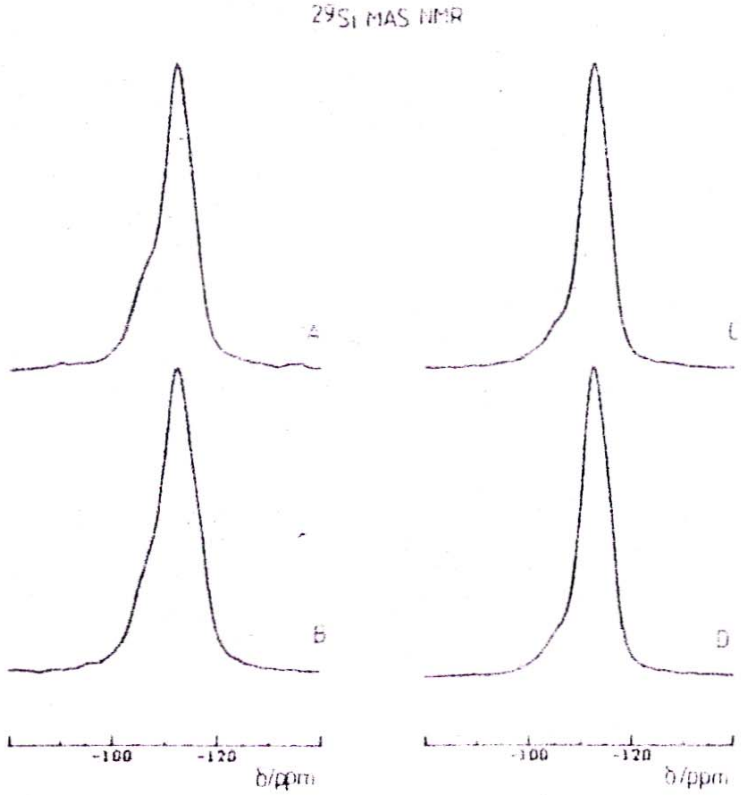


Fig.2 ^{29}Si MAS NMR spectra of the sample H-ZSM-5/0 and the hydrothermally treated sample H-ZSM-5/40 before (A,C) and after (B,D) coking.

^{27}Al MAS NMR

In Table 2 values are given for the number $c_{Alfr.}$ of framework aluminium atoms per u.c. (columns (5) and (6)). Because acid leaching was not performed, it is seen, that the coked samples contain "NMR invisible" aluminium.

^{13}C CP MAS NMR

The ^{13}C CP MAS NMR spectrum of the coked sample H-ZSM-5/0 shown in Fig.3A is dominated by three narrow lines due to residual n-hexane. This signal disappears by heating the sample up to 400°C and after a sufficiently long accumulation time (40.000 repetitions) the signals of the coke deposits can be

observed. Figs.3B,C,D show the ^{13}C CP MAS NMR spectra of the coked sample H-ZSM-5/0 and of the coked samples hydrothermally treated at 10.7 and 40kPa, respectively. The spectrum corresponding to Fig.3B but with total sideband supression (TOSS) is shown in Fig.3E.

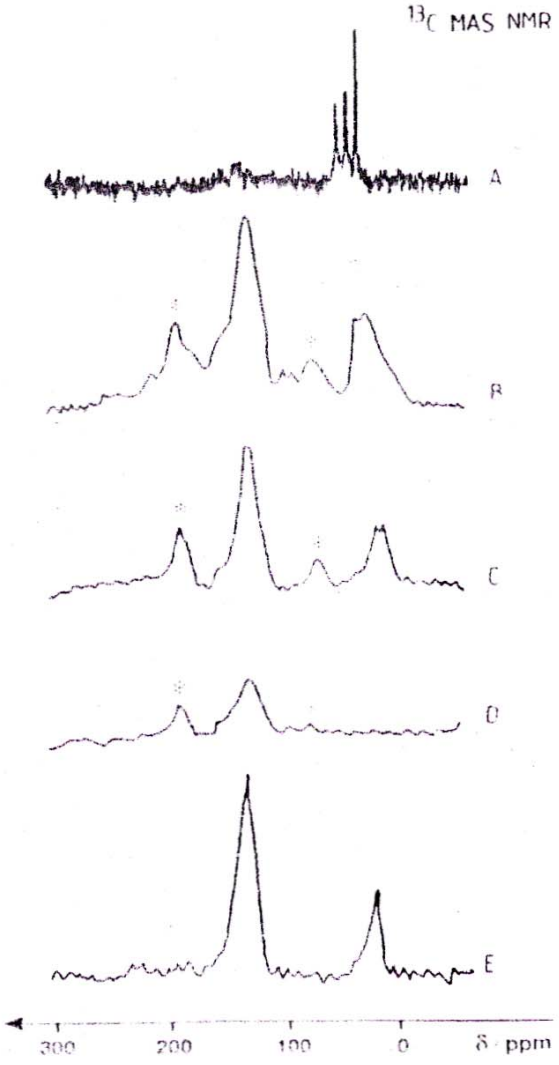


Fig.3 ^{13}C CP MAS NMR spectra of the coked samples : (A) H-ZSM-5/0 before heating at 400°C; (B,C,D,) H-ZSM-5/0, H-ZSM-5/10 and H-ZSM-5/40, respectively after heating the samples up to 400°C; (E) the same as Fig.3(B) but after total suppression of the spinning sidebands (TOSS) which are denoted by asterisks in Figs.3(B,C,D).

DISCUSSION

Figs.1 and 3 as well as Table 2 (columns (1)-(6)) show considerable changes in the ^{1}H, ^{13}C and ^{27}Al spectra caused by the coke formation in the channels of the H-ZSM-5 zeolites. The decrease of the intensity of line (b) at 4.3ppm in the ^{1}H MAS NMR spectra and that of the line at -106ppm in the ^{29}Si MAS NMR spectra with increasing water vapor pressure for the uncoked samples is caused by the dealumination of the zeolite (ref.12). On the other hand, coking leaves the ^{29}Si MAS NMR spectra unchanged. That means, that in the n-hexane cracking process no

further dealumination occurs. Therefore, the differences between the ^{27}Al MAS NMR spectra of uncoked and coked samples (cf. columns (5) and (6) in Table 2) must be explained by the existence of "NMR-invisible" framework aluminium. Such "NMR-invisible" framework aluminium is formed through the coverage of Brönsted sites by carbonaceous deposits which disturb the tetrahedral symmetry of the aluminium atoms (refs.17,26). The same reason is responsible for the decreased intensity of the line (b) and the appearance of the very broad line in the ^{1}H MAS NMR spectra after coking. Both the Brönsted OH groups which are poisoned by these deposits and the protons of the deposited molecules are characterized by a strong homonuclear dipolar interaction. The large difference in the ^{1}H and ^{27}Al MAS NMR spectra between uncoked and coked samples is a direct proof for the existence of carbonaceous deposits poisoning the Brönsted acid sites inside of the crystallites of the zeolite crystallites.

Assuming on the other hand that

$c_{H(b)\,coked} \approx (k/k_0) * c_{Alfr.uncoked}$

(ref.27) as well as

$c_{Alfr.coked} \approx (k/k_0) * c_{Alfr.uncoked}$

because $c_{Alfr.} \approx c_{H(b)}$ (ref.24) we can compare the experimental values given in Table 2, columns (4) and (6), with the computed values given in column (7). Their agreement is satisfying. Since the ratio k/k_0 is also effected by pore blockage (ref.5) the last values have to be generally smaller.

Furthermore, for the first two samples follows from the values given in Table 2, columns (1)-(4), that about 6 protons are connected with one Brönsted OH group poisoned by carbonaceous deposits (cf. column (8)). Considering that the aromatic to aliphatic ratio derived from the ^{13}C CP MAS NMR spectra shown in Figs.3B and C is ca. 3 we can conclude that (i) the H/C ratio of the carbonaceous deposits is smaller than one and (ii) that the coke content is 3±1wt.-% for the first two samples and 0.5±0.3wt.-% for the sample 3, respectively.

CONCLUSION

It has been shown in the present paper that besides the pulsed field gradient technique (ref.16), the ^{27}Al MAS NMR and the ^{29}Si MAS NMR (ref.17) the ^{1}H MAS NMR spectroscopy with sealed samples

is a suitable method to elucidate the location of carbonaceous deposites in zeolitic catalysts.

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