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Solid-state nuclear magnetic resonance studies of the transformation of the zeolite Y catalyst in the course of hydrochlorination of 1-methylcyclohexene by thionyl chloride

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Abstract

1-Methylcyclohexene was hydrochlorinated with $SOCl_2$ to 1-chloro-1-methylcyclohexane at room temperature in CH_2Cl_2 as the solvent and in presence of the faujasitic zeolite ZF520 catalyst. 4-Coordinated framework aluminium in the parent sample coexisting with a small amount of immobile extra-framework aluminium at ca. −1 ppm is completely removed after just one reaction run and transformed into two distinct 6-coordinated species resonating at 0.2 and −3.1 ppm. The former line is assigned to $Al(H_2O)_6^{3+}$ cations, the latter is likely to come from a species with mixed solvation shells, probably $Al(Cl^-)(H_2O)_5^{2+}$ and $Al(OH^-)(H_2O)_5^{2+}$. Crystallinity of the catalyst is seriously affected by the reaction. The spectra confirm that before reaction the zeolite contains Si(3Si,1OH) and Si(2Si,2OH) groups. During the reaction most hydroxyl groups created by dealumination are removed, although some Si(3Si,1OH) remain. MAS NMR spectra are fully consistent with the proposed reaction mechanism.

Keywords: catalyst characterization (NMR, XRD); methylcyclohexene hydrochlorination; nuclear magnetic resonance; reaction mechanism; thionyl chloride; zeolite Y; zeolites

INTRODUCTION

The chemical state and transformations of zeolitic catalysts used in various chemical processes are of considerable interest and can be profitably studied

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by solid-state NMR. We have used X-ray diffraction (XRD) in combination with ^{27}Al, ^{29}Si and ^{1}H solid-state NMR to investigate the faujasitic catalyst ZF520 involved in the hydrochlorination of 1-methylcyclohexene by thionyl chloride.

EXPERIMENTAL

The hydrochlorination of 1-methylcyclohexene with $SOCl_2$ was performed at room temperature, in CH_2Cl_2 as the solvent and in presence of the faujasitic zeolite ZF520 (Zeocat, Montoir de Bretagne; Si/Al=20). The reaction time was 20 h for each run. The zeolite powder was regenerated by washing with CH_2Cl_2 prior to reuse. The percentages of conversion of 1-methylcyclohexene and the yield of 1-chloro-1-methylcyclohexane were obtained by gas chromatography (Table 1).

Solid-state magic-angle-spinning (MAS) NMR spectra were recorded using a double-bearing probehead. ^{1}H, ^{27}Al and ^{29}Si frequencies were 400.13, 104.22 and 79.5 MHz, respectively. ^{1}H–^{29}Si cross-polarization (CP) experiments were carried out to investigate the status of hydrogen in the samples. Zirconia rotors were spun in air at 5 kHz for ^{29}Si MAS and CP/MAS experiments and at 15 kHz for ^{1}H and ^{27}Al MAS experiments. The magic angle was set precisely by observing the ^{79}Br resonance of KBr [1]. The ^{1}H and ^{29}Si MAS spectra were acquired with $\pi/4$ pulses. The ^{29}Si CP/MAS experiments were carried out with single contacts and contact times of 4 ms. The Hartmann-Hahn condition was set using a sample of kaolinite [2]. ^{27}Al NMR Bloch decays were recorded at 104.26 MHz with very short, 0.7 μs (less than 10°), radiofrequency pulses and 0.5 s recycle delays. XRD patterns were collected on a Philips automatic diffractometer fitted with a vertical goniometer using Cu Kα radiation.

TABLE 1

Conversion of 1-methylcyclohexene and the yield of 1-chloro-1-methylcyclohexane as determined by gas chromatography for the same batch of zeolite ZF520 as that used in the consecutive catalytic runs

No. of runs	Conversion (%)	Yield (%)
1	87	67
2	80	80
3	87	65
4	86	62
5	86	68

RESULTS AND DISCUSSION

The ^{27}Al spectra in Fig. 1 show that 4-coordinated framework aluminium in the parent sample coexisting with a small amount of immobile extra-framework Al at ca. −1 ppm is completely removed after just one reaction run and transformed into two distinct 6-coordinated species resonating at 0.2 and −3.1 ppm. The narrowness of these lines indicates a high mobility of the attendant species and correspondingly small quadrupolar interactions. On the basis of the chemical shift the line at 0.2 ppm is assigned to $Al(H_2O)_6^{3+}$ cations. The line at −3.1 ppm probably comes from a species with mixed solvation shells. The most likely candidates are those with one water molecule substituted by Cl^- or OH^-, that is $Al(Cl^-)(H_2O)_5^{2+}$ and $Al(OH^-)(H_2O)_5^{2+}$, respectively. The assignment is justified by the chemical shifts in $Al(SO_4^{2-})(H_2O)_5^+$ (−3.3 ppm) [3] and $Al[(MeO)_3PO](H_2O)_5^{3+}$ (−3.7 ppm) [4].

The XRD patterns given in Fig. 2 show that the crystallinity of the zeolite is seriously affected by the reaction. This is a consequence of extensive dealumination, monitored by ^{27}Al NMR (Figure 1), which substantially weakens the zeolitic framework. XRD peaks marked with asterisks in Fig. 2 come from $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ (tschermigite), a new crystalline phase made possible by the presence of residual NH_4^+. The formation of another $A^+Al(SO_4)_2$ alum-like species, $(H_3O)Al(SO_4)_2 \cdot 12H_2O$, is also a possibility. Detailed examination of the XRD patterns also reveals that another crystalline phase, probably $Al_2(SO_4)_3 \cdot 17H_2O$, is formed in minute amounts after nine or more catalytic runs.

The reaction under study converts 1-methylcyclohexene to 1-chloro-1-methylcyclohexane through electrophylic addition of HCl according to Markovnikov's rule (see for example ref. 5). Moreover, thionyl chloride reacts with water and organic compounds containing hydroxyl groups to produce the required HCl [5,6]. It is well known that dealumination of zeolites creates hydroxylic nests [7]. We can therefore assume that the following reactions occur:

$$SOCl_2 + H_2O \rightarrow 2HCl + SO_2 \quad (1)$$

$$2SOCl_2 + {=}Si(OH)_2 \rightarrow {=}SiCl_2 + 2HCl + 2SO_2 \quad (2)$$

$${=}SiCl_2 + 2H_2O \rightarrow {=}Si(OH)_2 + 2HCl. \quad (3)$$

Reaction (1) dehydrates the zeolite during the first catalytic run. Reaction (2) is the main source of HCl necessary for hydrochlorination. Reaction (3) regenerates the hydroxyl groups when the zeolite sample is exposed to air moisture between the runs and produces an extra amount of HCl. The zeolitic framework is saturated with HCl, so that the catalyst exhibits a prolonged activity (Table 1).

^{29}Si MAS NMR spectra were found to be insensitive to dealumination. In

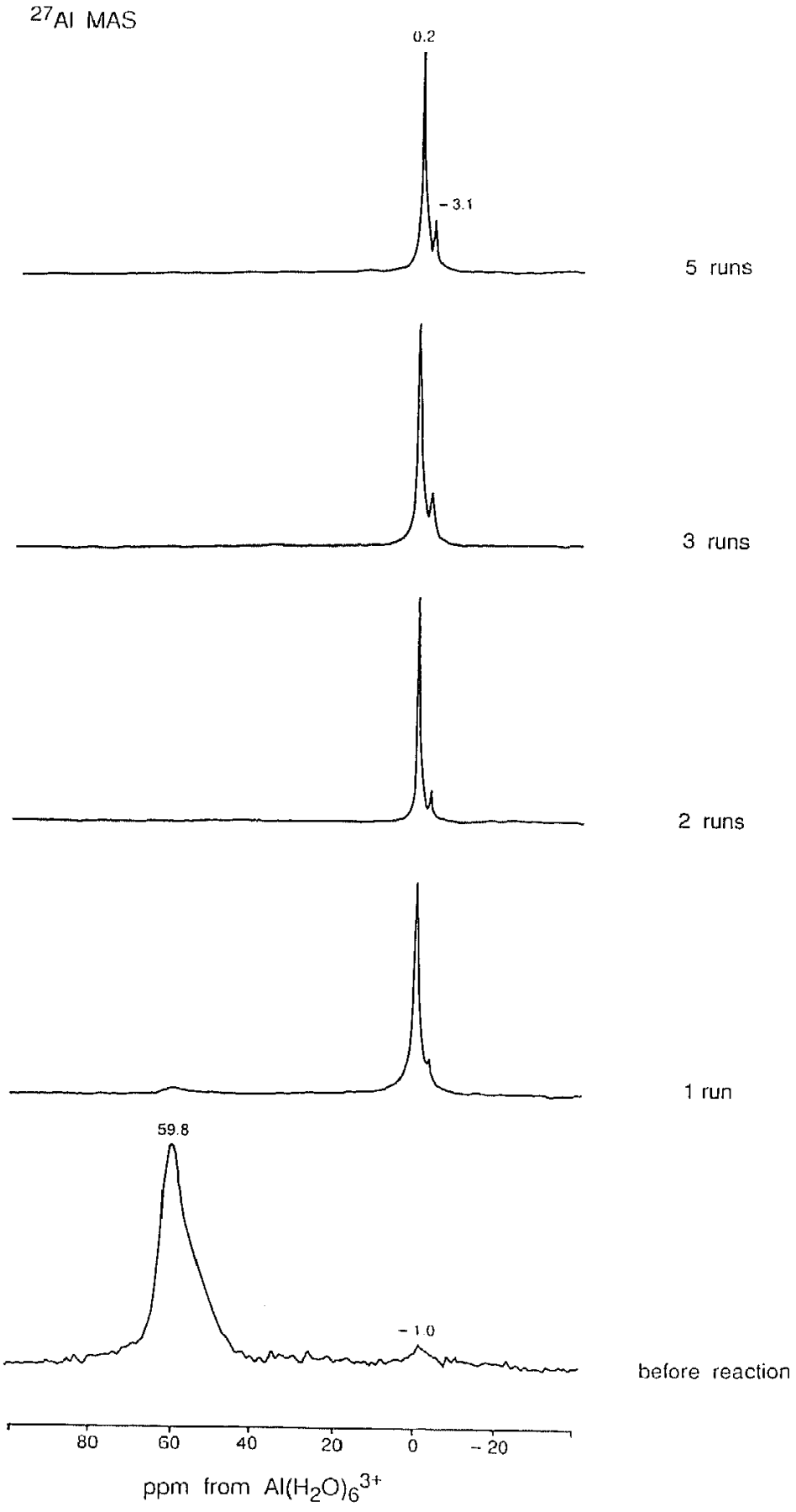

Fig. 1. ^{27}Al MAS NMR spectra of the catalyst before the reaction and after the consecutive catalytic runs.

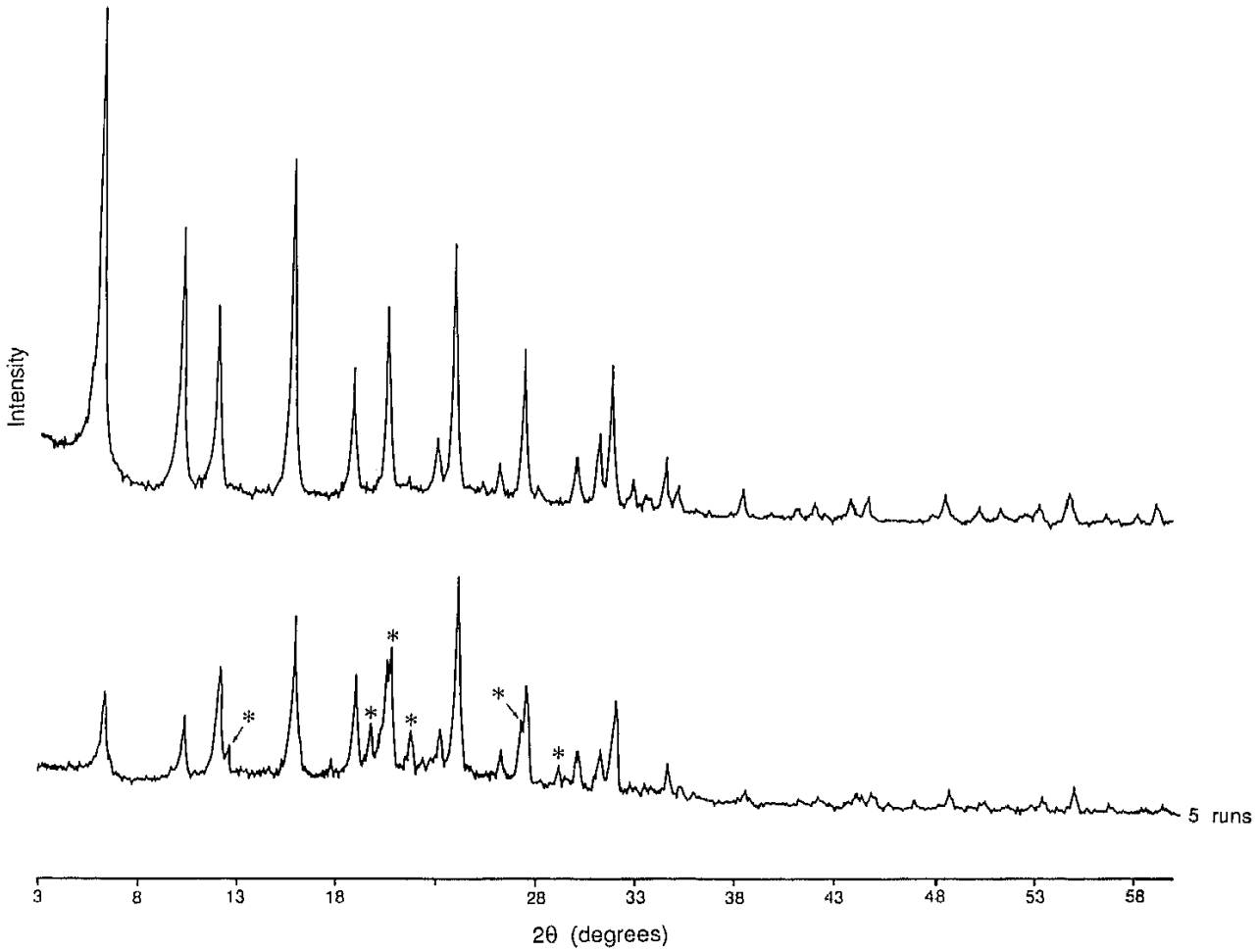

Fig. 2. The XRD patterns of the catalyst before the reaction and after five catalytic runs. Peaks marked with asterisks come from $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ and possibly from $(H_3O)Al(SO_4)_2 \cdot 12H_2O$.

theory, the framework aluminium content of highly siliceous samples such as ours should obey the equation

$$(Si/Al)_{NMR} = \frac{I_{Si(0Al)} + I_{Si(1Al)}}{\frac{1}{4} I_{Si(1Al)}} \quad : \quad (4)$$

where $I(n=0$ and $1)$ denotes the intensity of Si(4Si,0Al) and Si(3Si,1Al) lines which appear in our spectra (Fig. 3) at -107.4 and -102 ppm, respectively. In practice, the calculation is inaccurate because the intensity of the Si(3Si,1Al) line is too low and because it coincides with the Si(3Si,1OH) line [8]. The lines of the ≡Si-Cl and $=SiCl_2$ groups are either obscured by the overall ^{29}Si MAS pattern or too broad to be observed as a result of dipolar coupling to the abundant quadrupolar ^{35}Cl nucleus.

The silicon atoms bearing the hydroxyl groups can be conveniently studied by ^{29}Si CP/MAS NMR. The spectrum shown in Fig. 4 shows that before the reaction the zeolite clearly contains Si(3Si,1OH) and Si(2Si,2OH) groups which are responsible for the well cross-polarizing lines at -101.2 and -95.0

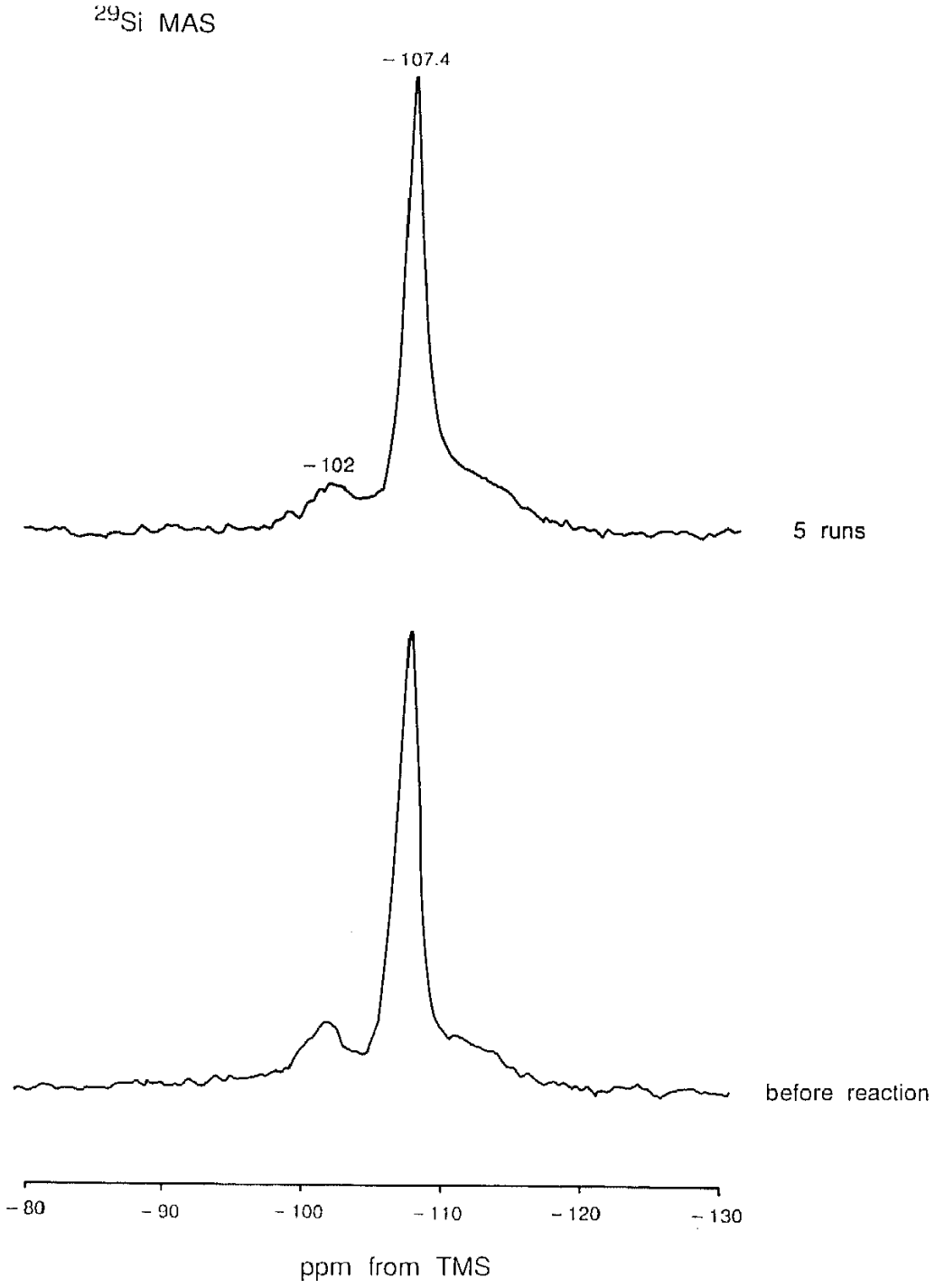

Fig. 3. ^{29}Si/MAS NMR spectra of the catalyst before the reaction and after five catalytic runs.

ppm, respectively. A shoulder at −112 ppm probably comes from amorphous silica [9–12]. During the reaction most hydroxyl groups created by dealumination are removed by chlorination, although some Si(3Si,1OH) remain, because the line at −101.2 ppm is still present after 5 runs.

^{1}H MAS NMR spectra are given in Fig. 5. The line at 7.17 ppm in the parent sample comes from the residual NH_4^+ cations which were not decomposed during the activation of the zeolite. The line at 4.63 ppm is a combined line of

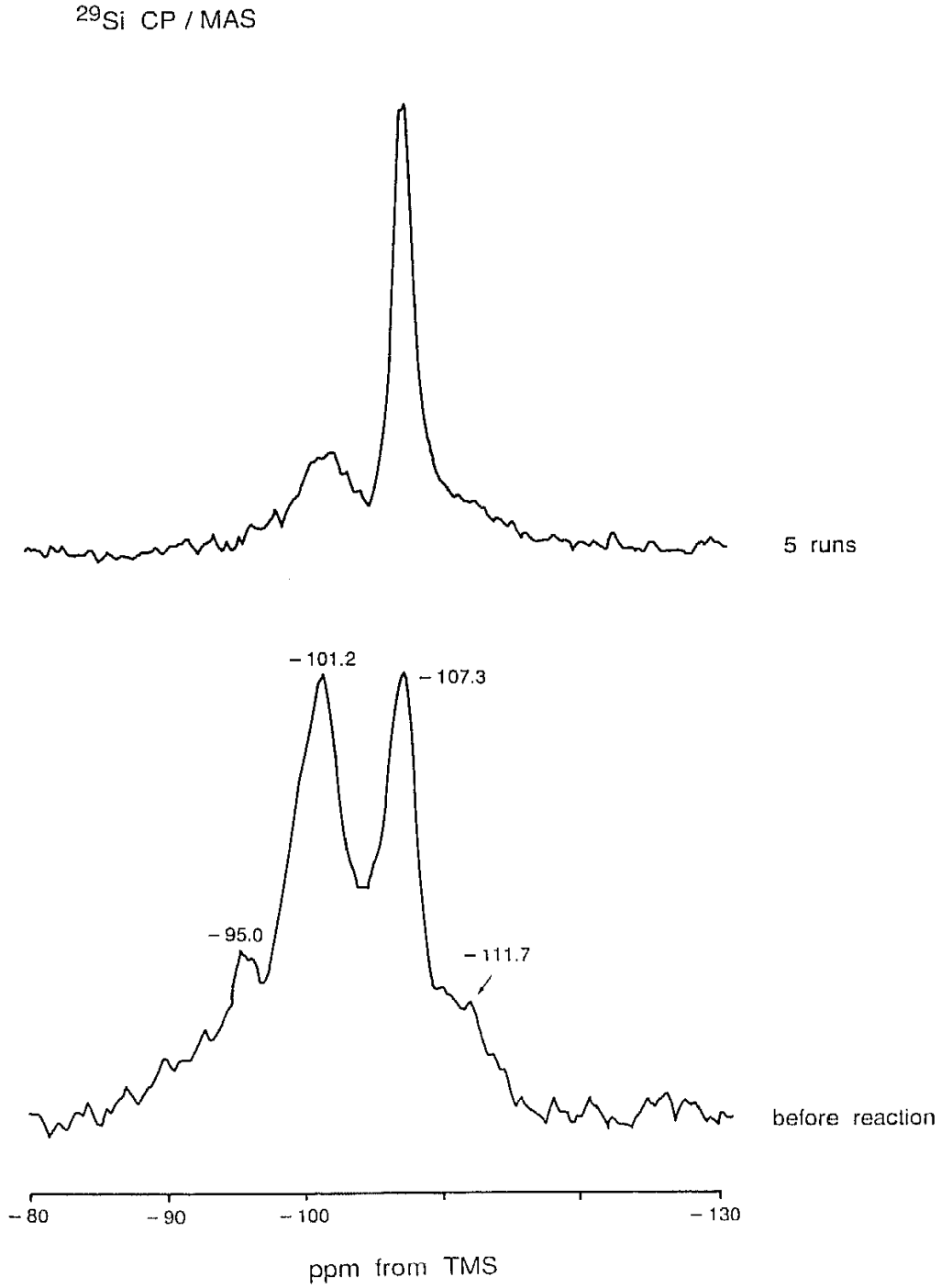

Fig. 4. ^{29}Si CP/MAS NMR spectra of the catalyst before the reaction and after five catalytic runs.

water and bridging Si–OH–Al hydroxyls. The small line at 1.2 ppm is due to terminal Si–OH groups. In the course of the reaction the water content is decreased and the main line shifts to 7 ppm, indicating its acidic origin associated with the formation of HCl. At this stage of the study it is difficult to say how HCl interacts with the zeolitic framework under the reaction conditions. The NH_4^+ cations are also gradually removed and their line appears as a shoulder of the intensive acidic peak. It is possible that the low intensity line at 3.84

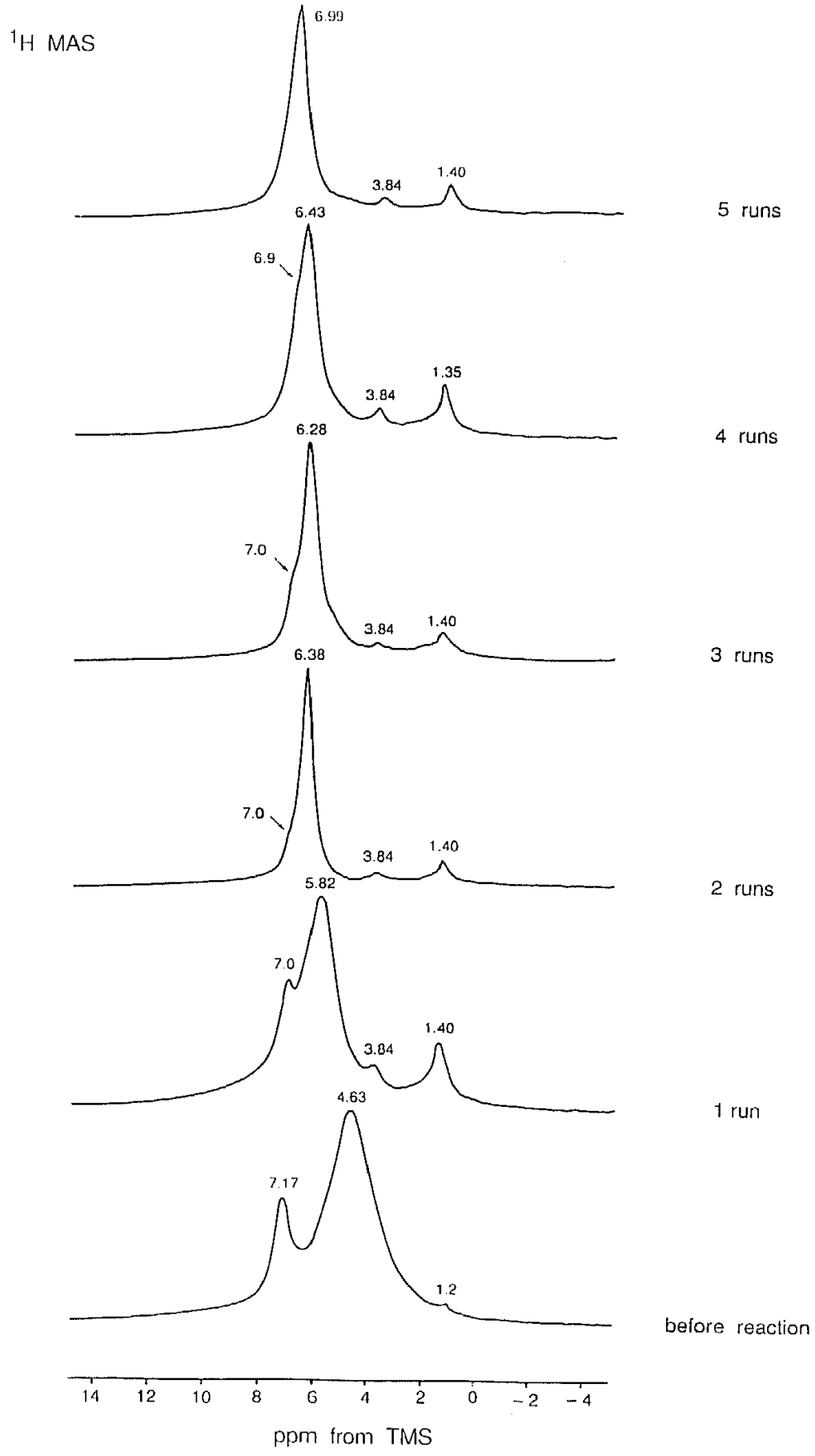

Fig. 5. ^{1}H MAS NMR spectra of the catalyst before the reaction and after the consecutive catalytic runs.

ppm (Fig. 5) is completely hidden by the 4.63 ppm line in the sample before reaction, and can be seen only when the latter line is shifted to low field. The line at 3.84 ppm may come from impurities in the sample. Other low intensity lines must be associated with the organics present. We thus assign the line at 1.4 ppm to the methyl groups in the substrate and the product. Their methylene groups give a broad resonance at ca. 2 ppm. We conclude that the ^{1}H MAS NMR spectra of the catalyst are fully consistent with the proposed reaction mechanism.

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REFERENCES

1 J.S. Frye and G.E. Maciel, J. Magn. Reson., 48 (1982) 125.
2 J. Rocha and J. Klinowski, J. Magn. Reson., 90 (1990) 567.
3 J.W. Akitt, N.N. Greenwood and B.L. Khandelwal, J. Chem. Soc. Dalton Trans., 12 (1972) 1226.
4 D. Canet, J.J. Delpuelch, M.R. Khaddar and P. Rubini, J. Magn. Reson., 9 (1973) 329.
5 R.T. Morrison and R.N. Boyd, Organic Chemistry, Allyn and Bacon, Boston, 1973.
6 J.W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. X, Longmans, Green and Co., London, 1947.
7 R.M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, London, 1978.
8 G. Engelhardt and D. Michel, High-Resolution Solid-State NMR of Silicates and Zeolites, Wiley, New York, 1987.
9 M.W. Anderson and J. Klinowski, J. Chem. Soc., Faraday Trans. 1, 82 (1986) 1449.
10 C.A. Fyfe, G.C. Gobbi and G.J. Kennedy, J. Phys. Chem., 89 (1985) 277.
11 J. Klinowski, J.M. Thomas, C.A. Fyfe, G.C. Gobbi and J.S. Hartman, Inorg. Chem., 22 (1983) 63.
12 G.J. Ray, A.G. Nerheim and J.A. Donohue, Zeolites, 8 (1988) 458.