Probing acid sites in MAPO-36 by solid state NMR

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An ordering of magnesium is observed in the as-synthesized MAPO-36 molecular sieve. Upon calcination, part of the magnesium is removed from the sample and part occupies extraframework positions thus rendering a random distribution of magnesium in the lattice. The shoulder observed in the ^{31}P spectrum of the calcined sample is assigned to P(3Al, 1Mg) sites in conflict with the earlier assignment to P–OH groups. The bridging hydroxyl groups located at these sites are detected in the ^{1}H MAS spectrum at 3.6 ppm. Further, MAPO-36 catalyzed acetone conversion to mesityloxide that cracked at elevated temperature to yield acetic acid and aliphatics.

Keywords: metal–AlPO$_4$; NMR spectroscopy; acid site; acetone conversion

1. Introduction

Divalent metal–aluminophosphate molecular sieves (MeAPO) are acidic in nature due to the substitution of metal for the aluminum in the neutral AlPO$_4$ framework [1]. The extent of metal incorporation controls the acid strength, and this in turn depends on the framework structure type. For MeAPO to be active in catalytic transformations, it is desirable that it has a larger channel dimension and higher extent of incorporated metal. Magnesium substituted type 36 (MAPO-36) has an elliptical 12-member ring channel (7.4 Å × 6.5 Å) containing annular side-pockets [2,3]. The channel dimension is smaller than the 7.3 Å circular pore opening of AlPO$_4$-5, but the sorption capacity for water, oxygen and hydrocarbons has been found to be higher due to the presence of these side-pockets [4]. Nakashiro and Ono [5] estimated the strength of the acid sites to be similar to, though less in number than, H-ZSM-5. Further, the catalytic activity in hydrocarbon transformations was found to be comparable to that of HY and H-ZSM-5. Later, Akolekar compared MAPO-36 with MAPO-5, SAPO-5 and AlPO$_4$-5 in a variety of catalytic transformations [6]. The higher activity was attributed to the presence of stronger acid sites. In ethylbenzene conversion, deactivation of MAPO-36 was the lowest among the catalysts studied. Thus, MAPO-36 seems to be a reasonable candidate for an in situ NMR study to probe catalyst acidity [7].

2. Experimental

MAPO-36 was synthesized by treating a gel having composition of 0.92Al$_2$O$_3$–0.17MgO–1.0P$_2$O$_5$–1.8TPA –40H$_2$O at 378 K for 48 h and further at 423 K for 24 h, where TPA stands for tripropylamine, following the procedure of Akolekar [8]. The molecular sieve was calcined at 813 K for 18 h to remove the occluded TPA.

All MAS NMR spectra were acquired using a Chemagnetics 360 spectrometer operating at 93.73, 145.62 and 359.73 MHz for ^{27}Al, ^{31}P and ^{1}H, respectively. Al(NO$_3$)$_3$ solution (0 ppm), the upfield signal of (−)(2S, 3S)-bis(diphenylphosphino)butane-(S, S)-chiraphos (−13.3 ppm with reference to 85% phosphoric acid), and acetone (2.11 ppm with reference to TMS) were used as chemical shift references for ^{27}Al, ^{31}P and ^{1}H, respectively. The following MAS NMR experiments were performed: ^{27}Al, single pulse excitation, pulse delay = 2 s, pulse length = 1 μs (< 10°), 400 transients; ^{31}P, single pulse excitation with proton decoupling, pulse delay = 30 s, pulse length = 5.2 μs (90°), 64 transients; CP, contact time = 0.1–10 ms, pulse delay = 5 s, pulse length = 4.3 μs (90°), 128 transients; ^{1}H, single pulse excitation, pulse delay = 10 s, pulse length = 5 μs (90°), 64 transients. A spinning frequency of 4 kHz was used in all the experiments unless otherwise stated. X-ray diffraction pattern was obtained using a Seitert-Scintag powder diffractometer PAD 5 fitted with Cu Kα radiation. Chemical analysis was carried out by Galbraith laboratories.

In situ NMR experiments on acetone-2-^{13}C were performed by adsorbing the vapors on a CAVERN device [9]. Prior to the adsorption, the catalyst was dehydrated by a multiple step temperature protocol [10] up to a maximum of 673 K and cooled to room temperature. ^{13}C (Bloch decay and cross polarization) spectra were acquired at various temperatures. The ^{13}C Bloch decay, cross polarization and CP with interrupted decoupling [11] (50 μs dephasing time) experiments were also done

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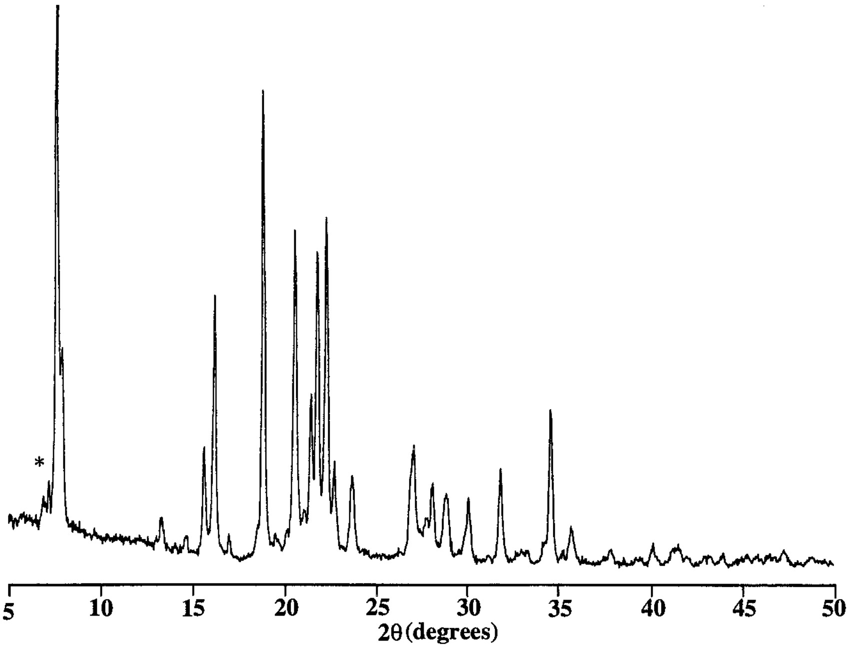


Fig. 1. X-ray diffraction pattern of as-synthesized MAPO-36 molecular sieve. The minor impurity peak is marked.

on the as-synthesized material. The methyl signal of hexamethylbenzene (17.4 ppm with respect to TMS) was used as a secondary chemical shift reference.

3. Results and discussion

The MAPO-36 had an X-ray pattern similar to that reported in the literature (fig. 1) [3,4]. The ^{13}C MAS NMR spectrum of the as-synthesized MAPO-36 containing trapped tripropylamine (fig. 2a) shows three signals attributed to the Cα (56 ppm), Cβ (18.3 ppm) and Cγ (11.8 ppm) carbons of the amine molecule. The signal of the Cα carbon next to the amino group is broadened due to the carbon–nitrogen dipolar coupling [12]. In the CP spectrum (fig. 2b), a shoulder can be seen at 50 ppm. In addition, a small peak at 25 ppm can be seen that precludes any assignment. In the interrupted decoupling experiment (fig. 2c), the peaks at 55 and 18 ppm are strongly attenuated indicating that the $-CH_2$ species are incapable of motion under the 50 μs time scale. The ^{27}Al NMR spectrum shows a broad single resonance at 38.5 ppm (fig. 3a). The ^{31}P spectrum has a peak at 28 ppm (attributed to P(4Al) sites [13]) and a broad shoulder at 23 ppm (fig. 3c). The shoulder is indicative of phosphorus having a neighbor other than aluminum, i.e. P(3Al, 1Mg) site [14]. Further downfield at -16.4 ppm, a very broad signal contributing 5.8% in the spectrum is assigned to non-framework precursor species present in the gel [15]. Decomposition of the ^{31}P spectrum gives the framework composition given in table 1. The Mg/Al ratio of the product (determined by chemical analysis and NMR) is slightly higher than that of the gel. The distribution of P(nAl, mMg) sites was calculated from the binomial theorem [16]. For the as-synthesized material, the calculated distribution varies significantly over the observed distribution by NMR (table 2); hence the Mg is ordered in MAPO-36. Earlier reports indicated an ordering of magnesium in MAPO-20 [14] and a random distribution in MAPO-5 and MAPO-34 [17].

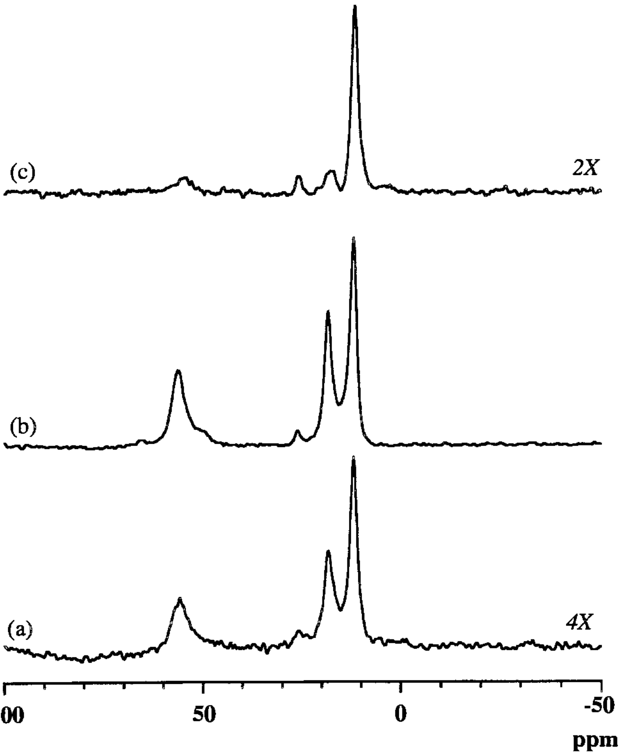


Fig. 2. ^{13}C MAS NMR spectra of as-synthesized (template occluded) MAPO-36. (a) Bloch decay, (b) cross polarization, (c) cross polarization with interrupted decoupling.

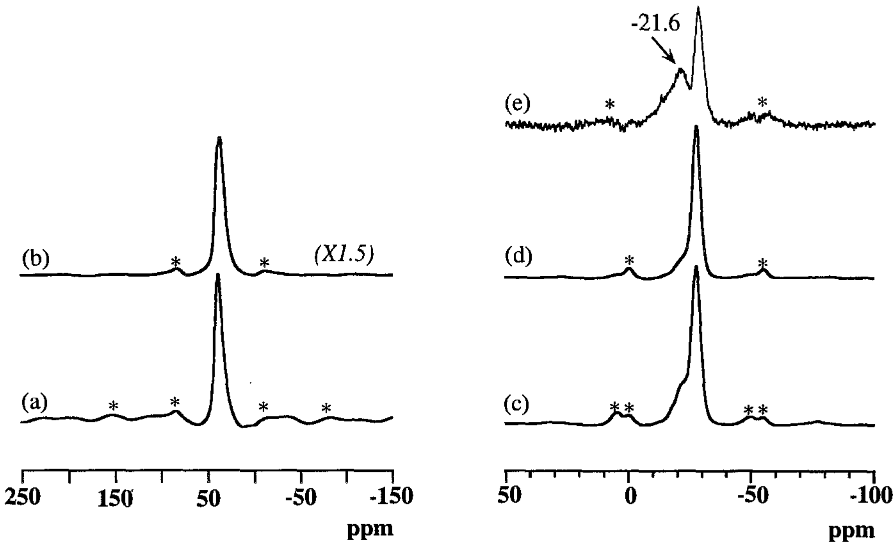


Fig. 3. (a) ^{27}Al MAS and (c) ^{31}P MAS spectra of as-synthesized MAPO-36. (b) ^{27}Al MAS, (d) ^{31}P MAS and (e) ^{31}P CP/MAS spectra of calcined dehydrated MAPO-36 (contact time 2 ms).

The bulk chemical composition of the calcined material (table 1) indicates a loss of Mg (~ 40%) from the sample. We cannot rule out the possibility of removal of magnesium during the 18 h calcination period. There is a possibility of the reaction of magnesium during the oxidative decomposition of tripropylamine resulting in the formation of magnesium nitride that is removed from the sample. Magnesium nitride sublimes at 973 K [18]. Though a demetallization is observed, the Al and P are retained in the framework as shown in the respective spectra of the dehydrated sample (figs. 3b and 3d). We can see in table 2 that the calculated distribution of the P(*n*Al, *m*Mg) sites agrees closely with that derived from NMR data indicating a random distribution of Mg in the lattice. The framework composition as derived from the ^{31}P spectrum further verifies the fact that only 66% of the Mg is retained in the framework, the rest being present as non-framework species.

The substitution of magnesium in place of aluminum creates a negative charge in the framework that is balanced by a bridging proton (Mg–O–(H)–P) site imparting Brønsted acidity in our sample. The P(3Al, 1Mg) site at 21.6 ppm is retained as a shoulder in the ^{31}P spectrum of the calcined material (fig. 3d). This signal is enhanced in the ^{1}H–^{31}P cross polarization experiment (fig. 3e). Our assignment is substantiated by the assign-

Table 1
Product composition of MAPO-36 molecular sieve

Sample	Bulk chemical composition [a]	Framework composition [b]	$(Mg/Al)_{gel}$	(Mg/Al) [a]	(Mg/Al) [b]
as-syn	$(Mg_{0.046}Al_{0.445}P_{0.509})O_2$	$(Mg_{0.054}Al_{0.45}P_{0.5})O_2$	0.092	0.103	0.121
calcined	$(Mg_{0.027}Al_{0.452}P_{0.520})O_2$	$(Mg_{0.018}Al_{0.48}P_{0.5})O_2$	–	0.060	0.037

[a] By chemical analysis.
[b] By NMR (assuming $P = 0.5$).

Table 2
^{31}P MAS NMR data for as-synthesized and calcined dehydrated MAPO-36

	Material type	Peak 1	Peak 2	Peak 3	Peak 4
chemical shift (ppm)	as-syn	−27.4	−22.5	absent	−16.4
	calcined	−27.9	−21.6	absent	absent
linewidth (Hz)	as-syn	357.8	744.7	–	766.1
	calcined	335.9	599.5	–	–
relative population (NMR)	as-syn	53.4	40.8	–	5.8
	calcined	85.6	14.3	–	–
relative population (binomial distribution)	as-syn	63.6	30.6	5.6	–
	calcined	86.5	12.8	–	–
structural unit		P(4Al)	P(3Al, 1Mg)	P(2Al, 2Mg)	non-framework

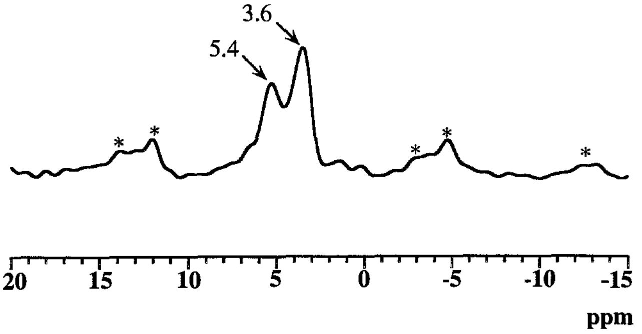
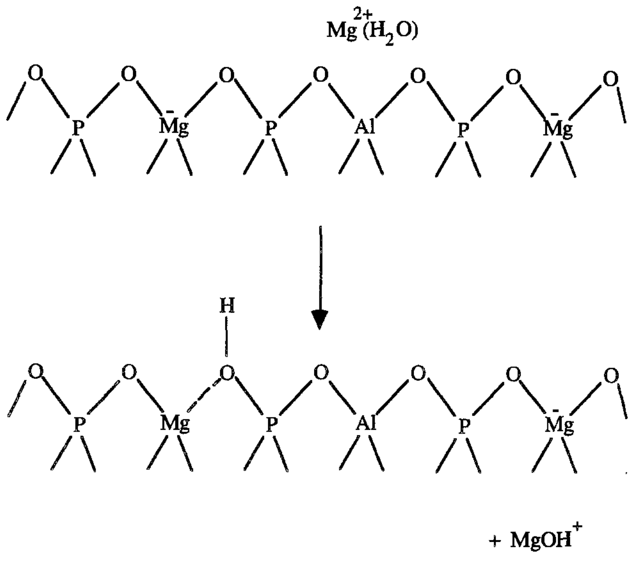


Fig. 4. ^{1}H MAS spectrum of calcined dehydrated MAPO-36 (spinning speed = 3 kHz).

ment of the two different bridging hydroxyl groups located at the P(3Al, 1Mg) and P(2Al, 2Mg) sites in the ^{31}P CP spectrum of calcined MAPO-20 [19]. However, Nakashiro et al. [20] attributed the enhanced signal in the CP spectrum to P–OH groups. The ^{1}H NMR of the sample shows this bridging proton at 3.6 ppm (fig. 4), a region where Brønsted protons resonate in substituted aluminophosphates [21]. Work done in our laboratory on ^{1}H NMR spectra of zeolites and borosilicates (in their as-synthesized forms) containing substantial amounts of alkali cations showed a signal at 5.0 ppm, while borosilicate prepared in a fluoride medium did not show such a signal. Thus the peak probably arises from water molecules associated with alkali cations. Recently Koller et al. [22] have drawn a similar conclusion in the interpretation of the ^{1}H NMR signal observed at 4.5–5.5 ppm in their zeolites. Hence, the broad peak at 5.4 ppm in the present sample arises from water molecules associated with extraframework Mg that are very difficult to remove even after dehydration at 673 K for more than 12 h. Minor resonances appeared at 1.4 ppm (P–OH) and 0.2 ppm ($MgOH^+$) [21], the latter species formed by the cation hydrolysis of the framework (scheme 1), a pattern similar to that proposed in zeolites [23].



Scheme 1.

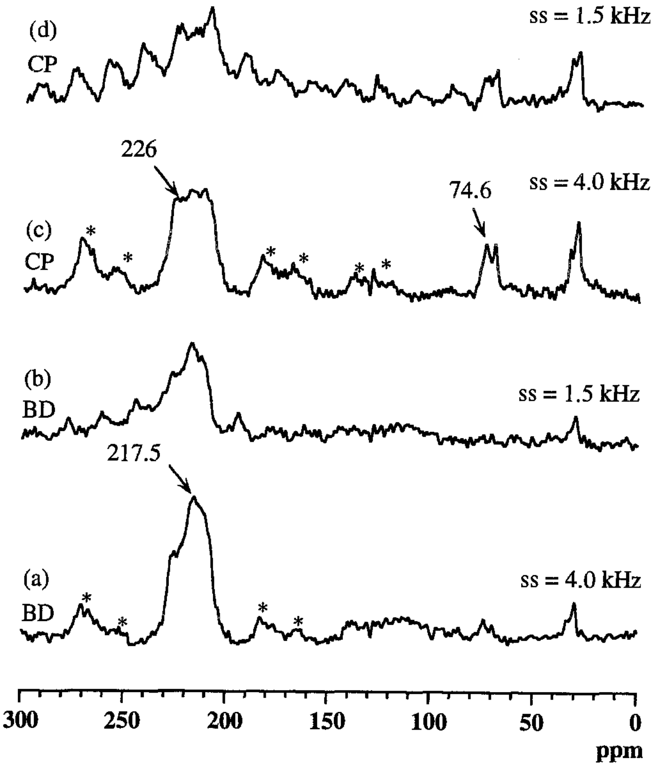


Fig. 5. Room temperature (298 K) ^{13}C spectra of acetone loaded MAPO-36. (a) Bloch decay and (c) CP spectra, spinning speed = 4 kHz. (b) Bloch decay and (d) CP spectra, spinning speed = 1.5 kHz.

Figs. 5a and 5c show the room temperature ^{13}C Bloch decay and CP spectra of acetone-2-^{13}C adsorbed in MAPO-36. The loading was about 1 acetone per Mg in the calcined sample. The very broad peak in the region of 216–226 ppm indicates the presence of a variety of adsorbed species. The small resonance at 30 ppm is due to the natural abundant methyl group. The ^{27}Al and ^{31}P spectra of the acetone loaded sample (not shown) is similar to that of the calcined material. Thus the possibility of acetone adsorbed to these sites can be ruled out. The chemically shifted unreacted acetone resonates at 217.5 ppm, which is lower than the observed value of 222–224 ppm for H-ZSM-5, but comparable to that of HX (217 ppm) and chemically dealuminated Y zeolite (219 ppm) [7,24]. Adsorption of acetone produces a complex (**1**) with restricted mobility in the 12-ring tubular channel as evident in the spectra with low spinning speeds (figs. 5b and 5d).

The condensation product diacetyl alcohol (226 and 74.6 ppm) formed at room temperature (fig. 5a and 5c). The ^{13}C CP spectra of the in situ conversion of acetone is shown in fig. 6. Mesityloxide (211.9 and 175 ppm) formed at 378 K. The signal due to Cβ carbon at 175 ppm overlaps with spinning sidebands. At higher temperature (418–458 K), this product cracks in the presence of water giving acetic acid (182.2 ppm), isobutylene and its oligo

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4. Conclusions

The substitution of magnesium in the neutral AlPO$_4$-36 framework generates Brønsted acid sites in the structure, which could be detected by ^1H–^{31}P CP and ^1H MAS NMR experiments. The residual water molecules adhering to the extraframework magnesium sites (generated by calcination of the as-synthesized sample) are difficult to remove, and gives a signal at 5.4 ppm the ^1H MAS NMR spectrum. The ^{13}C chemical shift of adsorbed acetone at 298 K revealed the strength of acid sites in MAPO-36 to be less than ZSM-5.

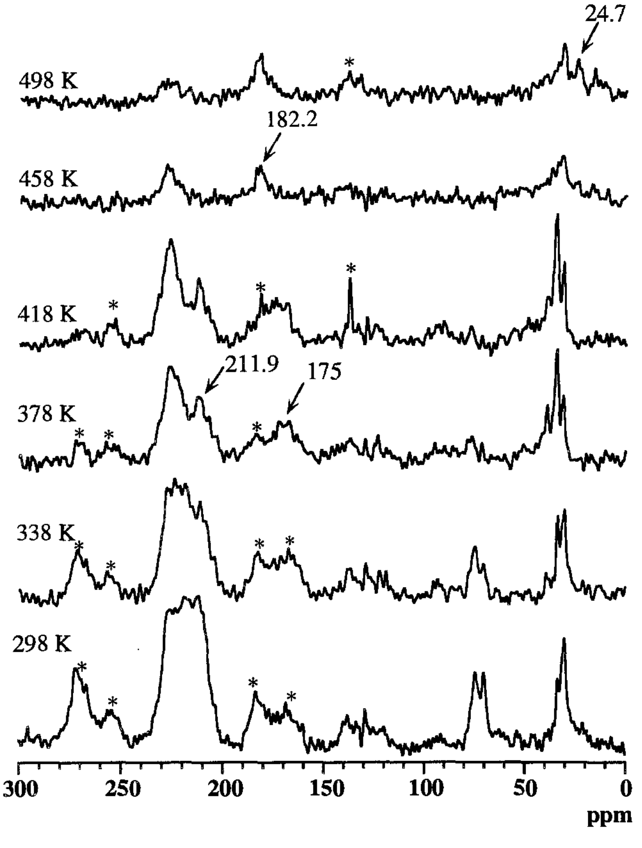

Fig. 6. Variable temperature ^{13}C CP/MAS spectra of acetone loaded MAPO-36.

Note

After the submission of our manuscript, a paper by Wright et al. [25] came to our attention. The properties of another magnesium substituted AlPO$_4$, Mg-DAF-1, were compared with MAPO-5 and MAPO-36. It was noted that a significant reduction in the intensity of the ^{31}P peak corresponding to the P(3Al, 1Mg) sites occurred on calcination. Though the fate of Mg in the calcined samples was not addressed, they reported a high intensity of P–OH groups (and low abundance of bridging hydroxyls) in the diffuse reflectance IR spectra, and concluded that an atomic rearrangement occurs and the nature of Mg after calcination is uncertain.

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