

^1H - ^{31}P HETCOR NMR elucidates the nature of acid sites in zeolite HZSM-5 probed with trimethylphosphine oxide

Carlos Bornes,^a Mariana Sardo,^a Zhi Lin,^a Jeffrey Amelse,^a Auguste Fernandes,^b Maria Filipa Ribeiro,^b Carlos Geraldes,^{c,d} João Rocha^a and Luís Mafra^{*,a}

^a. CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

^b. Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

^c. Department of Life Sciences and Coimbra Chemistry Center, Faculty of Science and Technology, University of Coimbra, 3000-393 Coimbra, Portugal

^d. CIBIT- Coimbra Institute for Biomedical Imaging and Translational Research, Edifício do ICNAS, 3000-548 Coimbra, Portugal

Experimental procedure

Sample preparation

Two ZSM-5 materials with distinct acidic properties were prepared from the ammonium exchanged ZSM-5 (CBV3024E) obtained from Zeolyst International. HZSM-5 was prepared by calcining 2.5 g of the initial material under 5 L/h air flow, at 500 °C. In order to avoid the formation of large amounts of EFAL species, a two-step calcination procedure was used. The temperature was ramped from room temperature to 200 °C at 2 °C/min, kept at 200 °C for 1 hour, and then ramped to 500 °C at 2 °C/min, and held for 6h. Steam-HZSM-5 was prepared in similar conditions: the sample was exposed to a flow of water vapor (2.3 L/h) for 2 hours upon reaching 500 °C. Elemental analysis using ICP-OES resulted in a bulk Si/Al ratio around 13.5. Deconvolution of the ^{29}Si MAS NMR spectra resulted in a framework Si/Al ratio around 16.12 and 17.83 for the parent ($\text{NH}_4\text{ZSM-5}$) and calcined (HZSM-5) samples, respectively. Pure silica MFI material (silicalite-1) was prepared as follows: 1.50 g of tetrapropylammonium bromide (TPABr, 98 wt%, Aldrich) were dissolved in 14.70 mL of H_2O ; then 5.60 g of tetrapropylammonium hydroxide solution (1 M TPAOH in H_2O , Aldrich) was added to that solution. Finally, a mixture of 6.48 g of tetraethylorthosilicate (98 wt%, Aldrich) and 5.60 g of ethanol was added; the resulting precursor was agitated in an autoclave for 6 hours and then treated at 180 °C for 4 days without agitation. Finally, the solid product was collected by centrifugation, washed thoroughly with water, and dried at 80 °C. The removal of the organic template was carried out by calcining at 550 °C for 8 h following a ramp rate of 3 °C/min. Powder X-ray diffraction was used to ascertain the degree of crystallinity of the sample upon dealumination (97% referred to the calcinated sample). The medium pore AMS-1B borosilicate molecular sieve is disclosed in M.R. Klotz, U.S. Patent 4,269,813 (1981). The hydrogen form of AMS-1B, designated as HAMS-1B can be formed directly after calcination without the need for exchange, from gels substantially free of alkali metals following the disclosure of M.S. Haddad in U.S. Patent 5,053,211 (1991). The H-[B]-ZSM-5 sample used in this study was prepared by the method of Haddad.

TMPO was loaded using a solvent-free method, to avoid the solvent that usually remains when using the conventional method (solution of TMPO in chloroform). 50 mg of material were placed inside a 4 mm rotor that was then dehydrated overnight at 300 °C under high vacuum (10^{-5} mbar). To avoid the readsorption of water, the adsorption cell was filled with helium gas, the rotor closed inside the adsorption cell, and quickly transferred to a glove box ($\text{H}_2\text{O} < 1$ ppm). 3.2 mg of TMPO were added to the dehydrated zeolite. The rotor was closed and then transferred to the same cell, and placed in an oven at 150 °C to adsorb the TMPO in the zeolite by sublimation.

NMR measurements

^{31}P and ^1H NMR spectra were acquired on a Bruker Avance III 400 spectrometer operating at a B_0 field of 9.4 T with ^{31}P and ^1H Larmor frequencies of 161.9 and 400.1 MHz, respectively, using a 4 mm Bruker MAS probe. The samples were packed into 4 mm ZrO₂ rotors with Macor (with o-ring) caps. ^{27}Al spectra were acquired on a Bruker Avance III 700 spectrometer operating at a B_0 field of 16.4 T with ^{27}Al Larmor frequency of 182.4 MHz, using a 1.9 mm Bruker MAS probe. The samples were packed into 1.9 mm ZrO₂ rotors with Vespel caps. Chemical shifts are quoted in ppm using the following secondary references: solid adamantane (1.85 ppm), an aqueous solution of $\text{Al}(\text{NO}_3)_3$ (0 ppm) and solid $\text{Na}_4\text{P}_2\text{O}_7$ (-2.09 ppm for the furthest upfield resonance) for ^1H , ^{27}Al and ^{31}P , respectively. ^{31}P single-pulse excitation MAS NMR spectra were acquired at a spinning rate of 15 kHz using a 3.2 μs pulse (90° flip angle) that corresponds to a radio-frequency (rf) field strength of 78 kHz. A recycle delay (RD) of 20 s was used. ^{27}Al single-pulse MAS NMR spectra were acquired at a spinning rate of 40 kHz using a quantification pulse of 0.36 μs (10° flip angle) corresponding to a rf field strength of 250 kHz. ^1H - ^{31}P HETCOR NMR spectra were acquired using a ^1H 2.8 μs pulse width (90° flip angle) corresponding to a rf of 90 kHz, the cross-polarization

step was performed using a contact time of 2000 μs with a 70–100% RAMP shape on the ^1H channel and a square shaped pulse of 51 kHz on the ^{31}P channel, a RD of 2.25 s and a spinning rate of 15 kHz. A SPINAL-64 decoupling scheme was used with pulse length of 6 μs at a rf field strength of 80 kHz. 145 t1 points with 2048 scans each were recorded along the indirect dimension.

Computational methods

The 8T cluster models used to investigate the adsorption of TMPO onto Brønsted acid sites with distinct acid strength were constructed from the ZSM-5 crystalline structure. The Al atom was introduced in position T12 to mimic a Brønsted acid sites at the crossing of the straight and the sinusoidal channels of ZSM-5. The terminal Si-H moieties were fixed at the crystallographic positions to maintain the zeolites integrity while the central part ($\text{O}_3\text{-Si-O(H)-Al-O}_3$) was allowed to relax. Si-H bond lengths changed from 1.30 to 2.75 Å to model a stronger Brønsted acid sites. NMR and geometry optimization calculations were performed using PBE1PBE/6-311g(2d,2p)//PBE1PBE/6-31+(g) (NMR//Geometry Optimization), that has been suggested as a good combination to accurately predict ^{31}P chemical shifts at a reasonable cost.¹ All DFT calculation were preformed using Gaussian 09 Rev. E.01.² The calculated chemical shifts were referenced to TMPO (41 ppm) and TMS (0 ppm) for ^{31}P and ^1H , respectively.

Table S1. FTIR results of *in-situ* pyridine adsorption showing the conversion of Brønsted to Lewis acid sites as the samples are steamed at different temperatures.

Sample	% Brønsted	% Lewis
HZSM-5	90.44	9.56
Steam HZSM-5 (500 °C)	63.77	36.23
Steam HZSM-5 (600 °C)	62.59	37.41

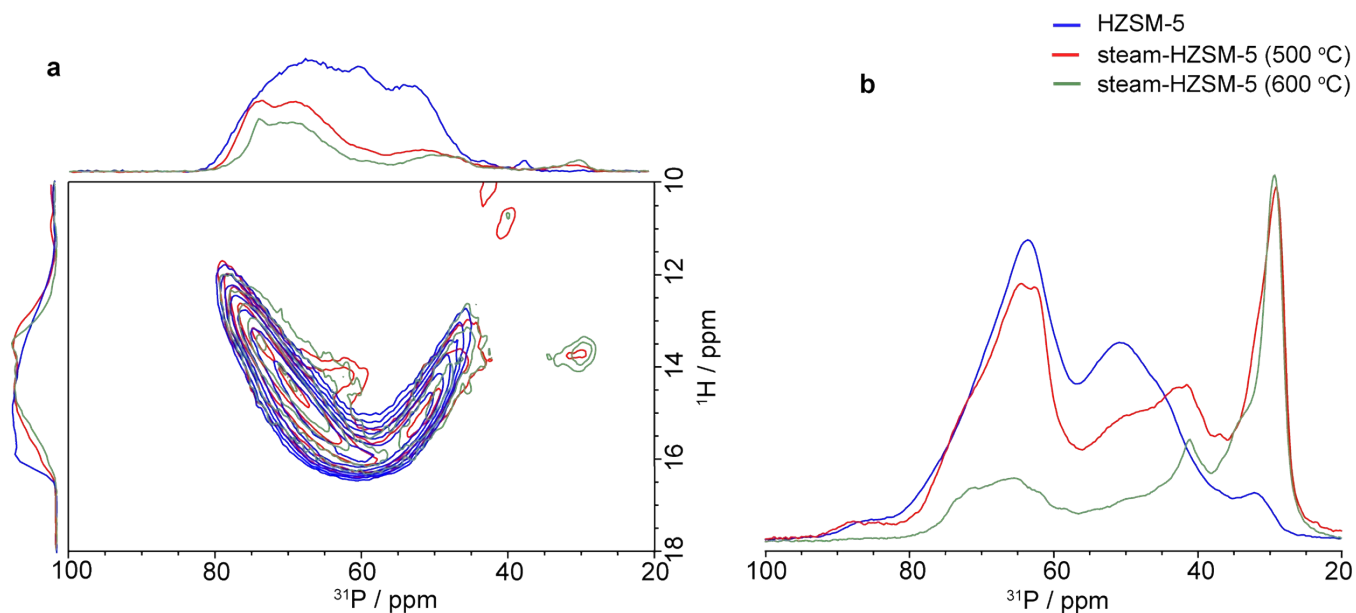


Figure S1. (a) ^1H - ^{31}P HETCOR and (b) ^{31}P MAS NMR spectra of HZSM-5, steam-HZSM-5 (500 °C) and steam-HZSM-5 (600 °C). The top projections of the ^1H - ^{31}P HETCOR depict the ^{31}P CPMAS spectra. The ^{31}P absolute intensity spectra were acquired with the same experimental parameters. ^{31}P MAS and ^{31}P CPMAS spectra were recorded with 1536 and 2000 scans, respectively. After steaming (dealumination), the intensity of the ^{31}P resonances assigned to TMPO molecules interacting with Brønsted acid sites decreases, especially for $\delta_p < 60$ ppm. The strong resonance at $\delta_p \sim 41$ ppm is given by excess crystalline TMPO.

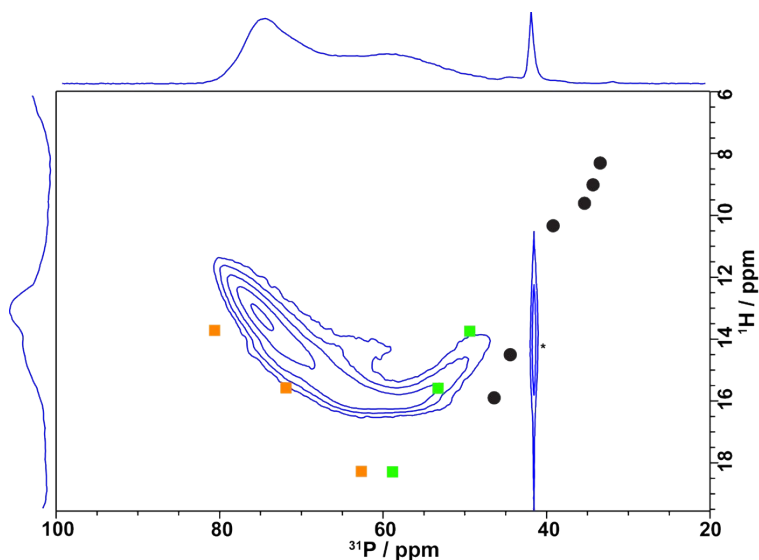


Figure S2. ^1H - ^{31}P HETCOR NMR spectra of TMPO-loaded H[B]ZSM-5. ● (black) and orange and green ■ depict the calculated (δ_{H} , δ_{P}) pairs extracted from the ZH...TMPO, Z...TMPOH⁺ and (d) (TMPO)₂H⁺...Z⁻ models, respectively. Further details on the models and calculated (δ_{H} , δ_{P}) pairs are depicted in Table S2. * denotes crystalline TMPO.

Table S2. Results of the DFT calculation of one TMPO molecule adsorbed at ZSM-5 Brønsted acid site cluster models. Distances are quoted in Å where Si-H is the distance of the terminal Si-H bonds used to tune the model acid strength by changing the O_Z-H distances (between the zeolite oxygen atom, O_Z, and the acidic proton) and O_P-H distances (between the acidic proton and the TMPO oxygen). Calculated δ_{H} and δ_{P} values are quoted in ppm and were obtained using the PBE1PBE/6-311g(2d,2p)//PBE1PBE/6-31+(g) combination.

Si-H (Å)	1 TMPO per acid site				2 TMPO per acid site					
	O _Z -H (Å)	O _P -H (Å)	δ_{P} (ppm)	δ_{H} (ppm)	O _Z -H (Å)	O _{P1} -H (Å)	O _{P2} -H (Å)	δ_{P1} (ppm)	δ_{P2} (ppm)	δ_{H} (ppm)
1.30	1.06	1.42	49.6	14.8	1.04	3.10	1.51	27.6	44.4	13.3
1.40	1.08	1.37	50.3	16.0	1.05	2.91	1.47	28.7	45.8	14.2
1.50	1.09	1.35	51.8	16.5	1.05	2.90	1.46	29.0	46.0	14.4
1.60	1.41	1.07	75.6	15.5	4.32	1.39	1.06	51.3	73.8	15.2
1.75	1.50	1.03	76.8	13.3	4.28	1.39	1.06	51.8	74.7	15.2
2.00	1.57	1.02	80.4	12.0	4.45	1.39	1.06	51.9	74.8	15.0
2.25	1.61	1.01	83.7	10.9	3.92	1.44	1.05	47.3	78.5	14.3
2.30	1.63	1.01	85.1	10.6	3.94	1.43	1.05	47.4	78.9	14.4
2.35	1.65	1.00	86.4	10.3	3.77	1.43	1.05	47.6	79.0	14.5

Table S3. Results of the DFT calculation of one TMPO molecule adsorbed at H-[B]-ZSM-5 Brønsted acid site cluster models. Distances are quoted in Å, where Si-H is the distance of the terminal Si-H bonds used to tune the model acid strength by changing the O_Z-H distances (between the zeolite oxygen atom, O_Z and the acidic proton) and O_P-H distances (between the acidic proton and the TMPO oxygen). Calculated δ_H and δ_P values are quoted in ppm and were obtained using the PBE1PBE/6-311g(2d,2p)//PBE1PBE/6-31+(g) combination.

1 TMPO per acid site					2 TMPO per acid site					
Si-H (Å)	O _Z -H (Å)	O _P -H (Å)	δ _P (ppm)	δ _H (ppm)	O _Z -H (Å)	O _{P1} -H (Å)	O _{P2} -H (Å)	δ _{P1} (ppm)	δ _{P2} (ppm)	δ _H (ppm)
1.30	0.99	1.72	33.01	8.38	1.00	6.03	1.67	29.29	41.83	9.19
1.40	0.99	1.71	33.78	8.61	1.00	5.97	1.64	31.49	42.17	9.56
1.50	1.00	1.67	34.19	8.99	1.01	5.58	1.65	31.47	42.85	9.86
1.60	1.00	1.65	35.19	9.55	1.01	5.06	1.62	31.98	43.40	10.23
1.75	1.01	1.61	36.49	10.36	1.02	5.06	1.59	31.73	44.81	11.01
2.00	1.02	1.55	39.57	11.95	1.03	4.86	1.52	31.54	46.55	12.70
2.25	1.05	1.45	44.71	14.64	4.29	1.20	1.28	59.82	62.47	18.20
2.30	1.06	1.43	46.46	15.58	4.46	1.36	1.07	53.33	72.10	16.10
2.35	1.66	1.01	82.94	10.71	4.62	1.45	1.04	49.20	80.11	13.67

Table S4. Textural properties of HZSM-5 samples.

Sample code	S _{BET} (m ² ·g ⁻¹)	S _{EXT} (m ² ·g ⁻¹)	V _{micro} (cm ³ ·g ⁻¹)	V _{meso} (m ² ·g ⁻¹)
HZSM-5	439	101	0.138	0.104
Steam HZSM-5 (500 °C)	377	112	0.111	0.106
Steam HZSM-5 (600 °C)	349	144	0.087	0.125

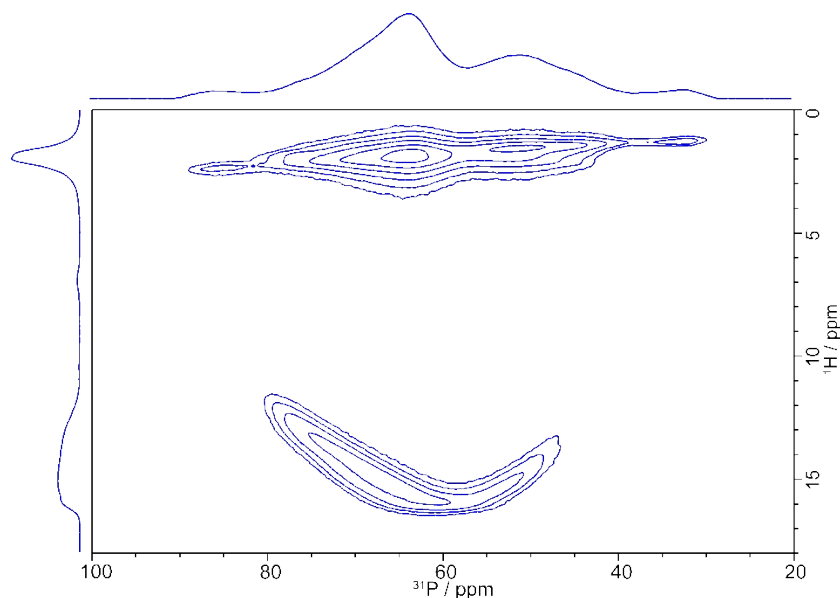


Figure S3. ¹H-³¹P HETCOR NMR spectrum of TMPO-loaded HZSM-5 zeolite with Si/Al ~ 27 (lower amount of Brønsted acid sites compared with the samples reported in the manuscript).

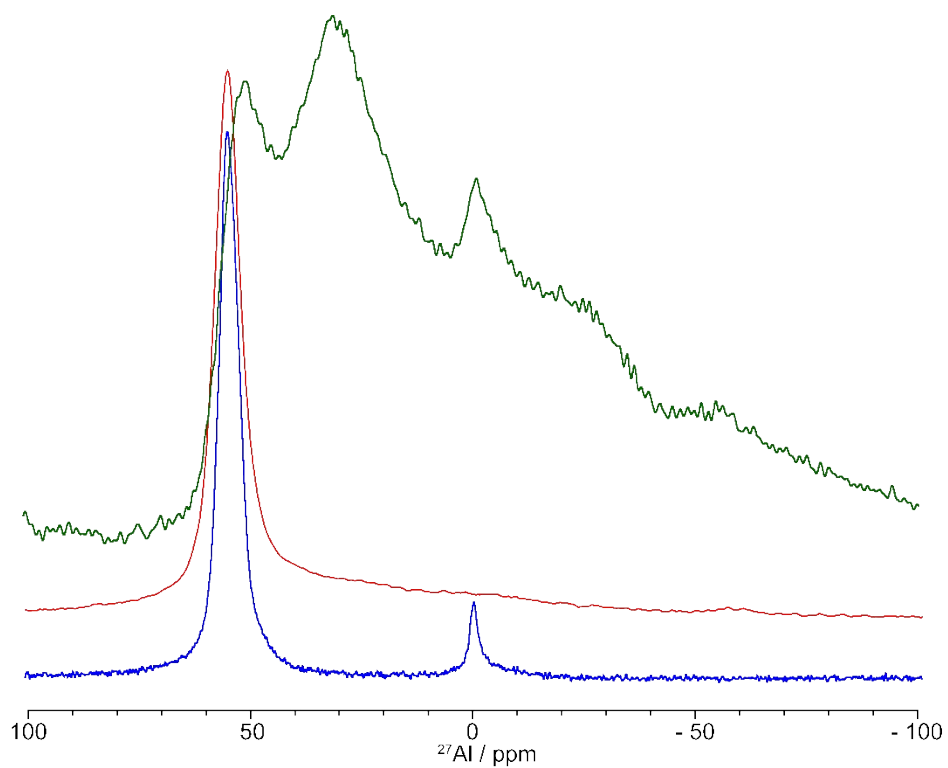


Figure S4. ^{27}Al MAS NMR spectra of fully hydrated (blue), TMPO-loaded (red) and dehydrated (green) HZSM-5 sample.

REFERENCES

- 1 S. K. Latypov, F. M. Polyancev, D. G. Yakhvarov and O. G. Sinyashin, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6976–6987.
- 2 D. J. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenb, 2009.