

SUPPORTING INFORMATION

Rationalising the role of solid-acid sites in the design of versatile single-site heterogeneous catalysts for targeted acid-catalysed transformations.

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Experimental

Synthesis

The synthetic protocol for the isomorphous substitution of Mg and Si into the AFI framework (MgSiAlPO-5) is described (below); an analogous method was employed for the preparation of the mono-substituted counterparts, details of which are provided in Table 1 (below). The synthesis method to form MgSiAlPO-5 involved initially adding 4.0 g of aluminium hydroxide hydrate (Aldrich) to a homogeneous solution of 5.0 g of phosphoric acid (85% in H₂O, Aldrich) in 20 ml of water and allowing the mixture to stir for 10 minutes. Aqueous homogeneous solutions of 0.33 g of magnesium(II) acetate tetrahydrate (Aldrich) in 10 ml of water and 0.62 g of fumed silica (Aldrich) were added simultaneously to the above solution, which resulted in the formation of a viscous gel, which was stirred for a further 30 minutes in order to obtain a homogeneous mixture. N,N-methyldicyclohexylamine (SDA) (Aldrich) (8.0 g) was then added slowly followed by 20 ml of water with vigorous stirring for 60 minutes in order to obtain a white gel with the composition 1.0Al: 0.85P: 0.80MDCHA: 50H₂O: 0.03Mg: 0.20Si.

The contents of the gel were sealed in a Teflon-lined stainless-steel autoclave, which was then transferred to a pre-heated, fan-assisted oven (WF-30 Lenton) that was set to the desired temperature of 190 °C, prior to the onset of the crystallisation. The autoclave was heated at 190 °C under autogeneous pressure for 2 hr. The white solid product was collected by filtration, washed with approx. 500 ml deionised water, and dried in air (60 °C) for 12 hours. The as-prepared sample was calcined in a tube furnace under a flow of air at 550 °C for 12 hours yielding a white solid. The synthesis procedure for other samples in this study, were analogous to the above, but with appropriate variations in the crystallisation temperature and gel composition that are shown in Table S1.

Table S1. Specific synthesis conditions for metal-substituted AlPOs.

Sample	Molar gel composition	Crystallization temp/ °C
AlPO-5	1.00P:1.00Al:0.75TEA:25H ₂ O	200
MgAlPO-5	1.50P:1.00Al:0.04Mg:0.80MDCHA:60H ₂ O	200
SiAlPO-5	0.75P:1.00Al:0.25Si:0.65MDCHA:40H ₂ O	200
MgSiAlPO-5	0.85P:1.00Al:0.03Mg:0.20Si:0.80MDCHA:50H ₂ O	190

Characterisation

X-Ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer using Cu K α 1 radiation, where $\lambda = 1.54056 \text{ \AA}$. Scanning electron microscopy images were obtained using a JOEL-JSM5910 microscope with accelerating voltage of 0.3-30 kV. The samples were prepared by carbon coating. BET surface area measurements were performed using a Micromeritics Gemini 2375 surface area analyser and prepared using flow gas preparation. A Perkin-Elmer Optimum 3000 DV was used for ICP analyses with calcined samples prepared and fully digested in 10ml of deionised water and 10ml of ACS Plus Certified H₂SO₄ (Fisher Scientific). Solutions of standard concentrations were used for calibration. FTIR spectra of self-supporting wafers of the samples (ca. 5 mg cm⁻²) were recorded with a Bruker IFS88 spectrometer at a resolution of 4 cm⁻¹. All samples were re-calcined at 823K in oxygen to remove the adsorbed species before the FTIR experiments. CO was adsorbed at 80K and 2,6-DMP was adsorbed at room temperature on the calcined samples, using specially designed cells which were permanently connected to a vacuum line (ultimate pressure <10⁻⁵ Torr) to perform adsorption-desorption in situ measurements. FTIR spectra were reported in difference mode by subtracting the spectrum of the sample in vacuo to the spectrum of the adsorbed probe molecules. Multi-peak fitting was performed by employing ORIGIN 6.1 Scientific Graphics and Analysis Software. Lorentzian functions were used and a R² =0.99714 was obtained. All TPD measurements were performed on a custom-built system using TCD detectors to monitor ammonia concentration. As-synthesised materials were pre-treated by heating at 10°C/min to 550°C in a 20% O₂/ helium mixture [Matheson UHP grade passed through a Drierite/molecular sieve gas purifier (Alltech Associates)] and held for 2 hours. The samples were exposed to ammonia and allowed to equilibrate at 150°C for 8 hours. Desorption was performed in flowing helium [Matheson UHP grade further purified with an Oxy-Trap (Alltech Associates) and an indicating OMI-1 purifier (Supelco)] at 10°C/min to 600°C and held for 40 minutes at 600°C.

Catalysis

Beckmann rearrangement of cyclohexanone oxime

A cylindrical quartz fixed-bed reactor (4 mm in diameter) with a quartz frit was packed with a 5 mm layer of glass beads, a 40 mm layer of pelletized catalyst (0.25 g) and a further 60 mm layer of glass beads, was placed inside the heater unit of the reactor assembly. The sample was then pretreated at 673 K under a 20 ml/min flow of helium gas for 1 hour. The temperature was then decreased to 573 K and a liquid-feed of 300 g/litre of cyclohexanone oxime in methanol was fed into the reactor, maintaining a WHSV of 3.3 hr⁻¹ that was controlled by an electronic mass-flow controller, with a sample being taken after an hour, when steady-state was achieved. The temperature was then systematically increased to 598, 623, 648 and 673 K and samples were taken at each temperature after being allowed to equilibrate for an hour. The temperature was then held at 673 K while the flow-rate was systematically changed employing the mass-flow controller to give a WHSV of 2.0, 1.0 and

0.5 hr⁻¹. Samples were taken at each flow rate after being allowed to equilibrate for one hour. Samples were analysed using a Clarus 400 gas chromatogram with FID and using an Elite 5 column, the peak areas were calibrated using pre-determined response factors.

Isopropylation of Benzene

The quartz reactor and catalyst were pre-treated as described above. The temperature was decreased to 523 K and a liquid feed of 6:1 molar ratio of benzene:isopropanol was employed with a WHSV of 3.5 hr⁻¹ under a flow of 10 ml/min of helium carrier gas. Samples were taken after 1 hour of equilibration and were analysed by GC as described above.

Substitution mechanisms

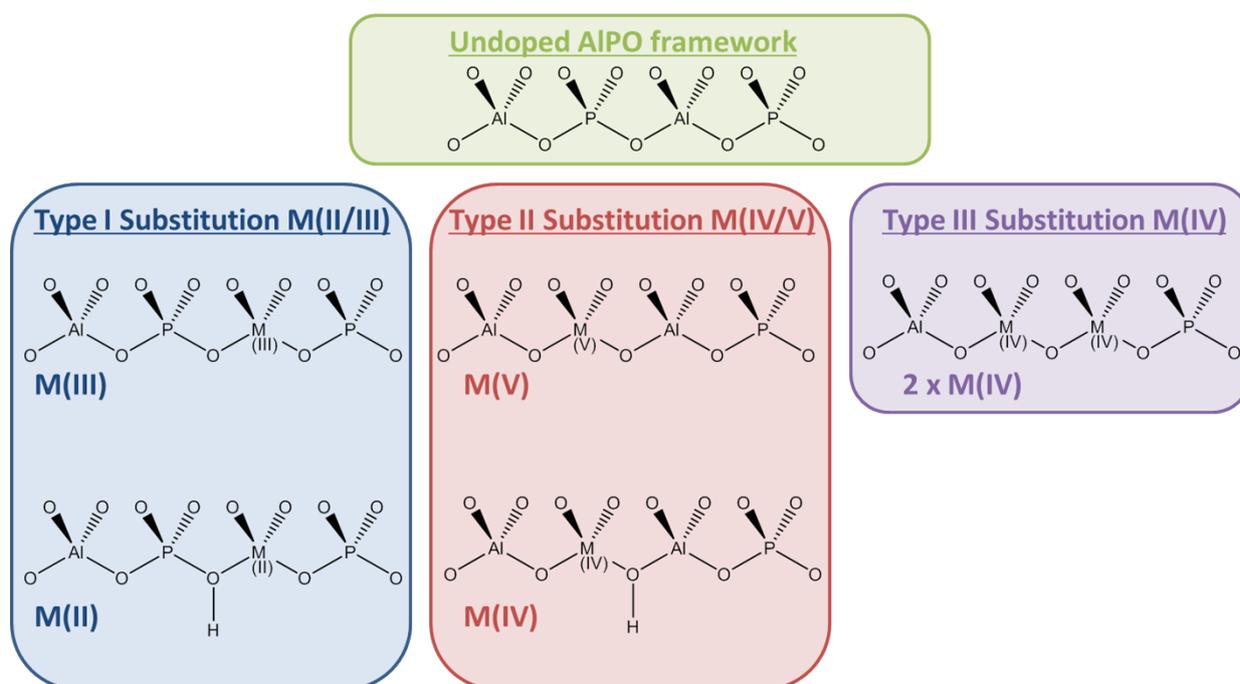


Figure S1: Scheme outlining the metal substitution mechanisms in AIPO frameworks.

Powder XRD analysis post-reaction

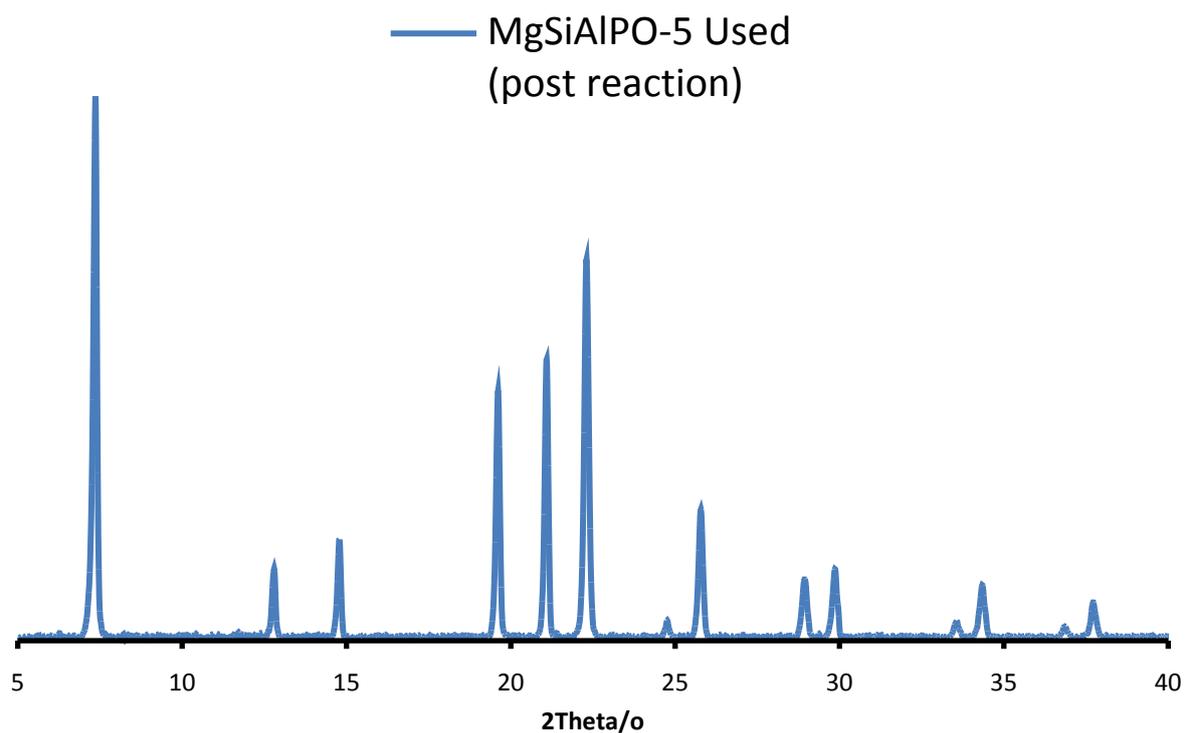


Figure S2: Powder XRD pattern of the used MgSiAlPO-5 catalyst after the Beckmann rearrangement reaction (8 hours, time-on-stream).

Full ICP results

Table S2: Full ICP results of AlPO-5 systems

Sample	Al/wt%	P/wt%	Mg/wt%	Si/wt%
AlPO-5	18.1	16.7	N/A	N/A
MgAlPO-5	15.9	20.6	0.85	N/A
SiAlPO-5	19.8	14.7	N/A	1.69
MgSiAlPO-5	18.0	14.6	0.89	1.70

BET isotherms

MgSiAlPO-5

Nitrogen Isotherm

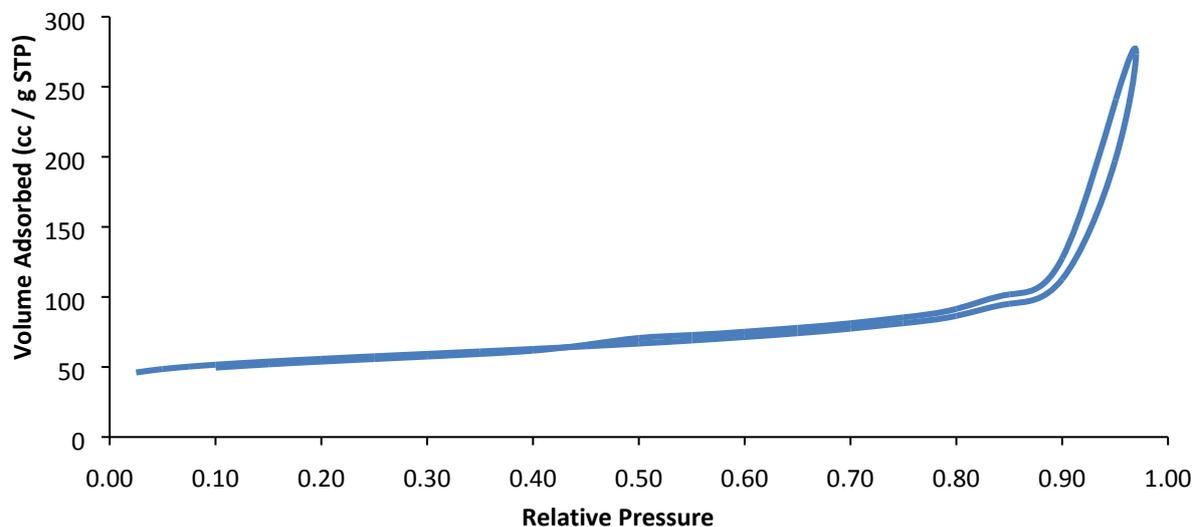


Figure S3: Nitrogen adsorption isotherm for MgSiAlPO-5

BJH Adsorption Model

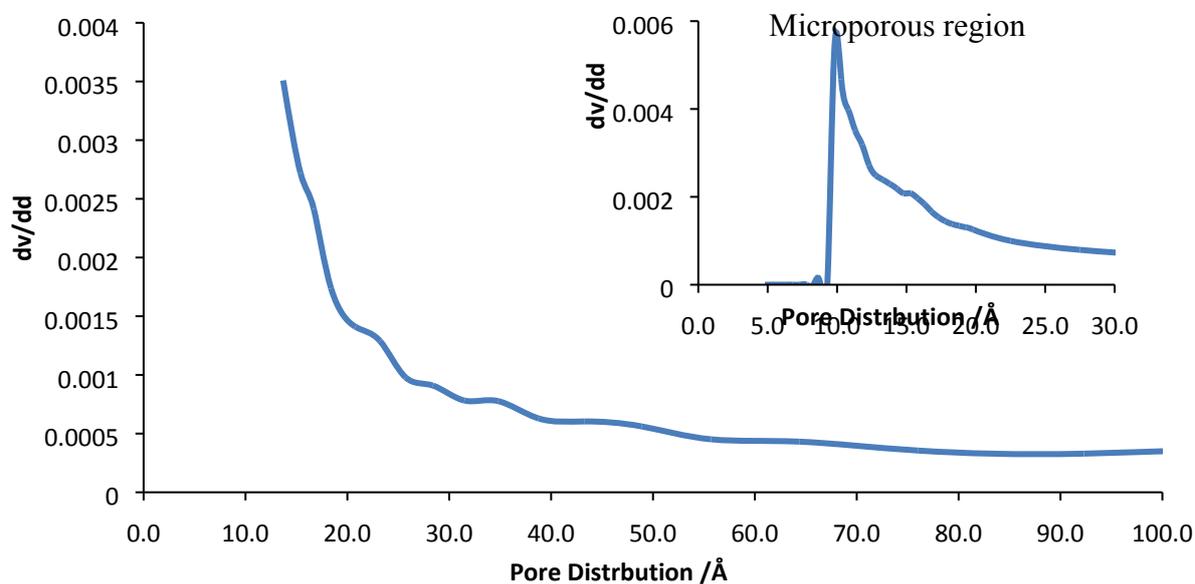


Figure S4: BJH Adsorption model plot for MgSiAlPO-5

SiAlPO-5

Nitrogen Isotherm

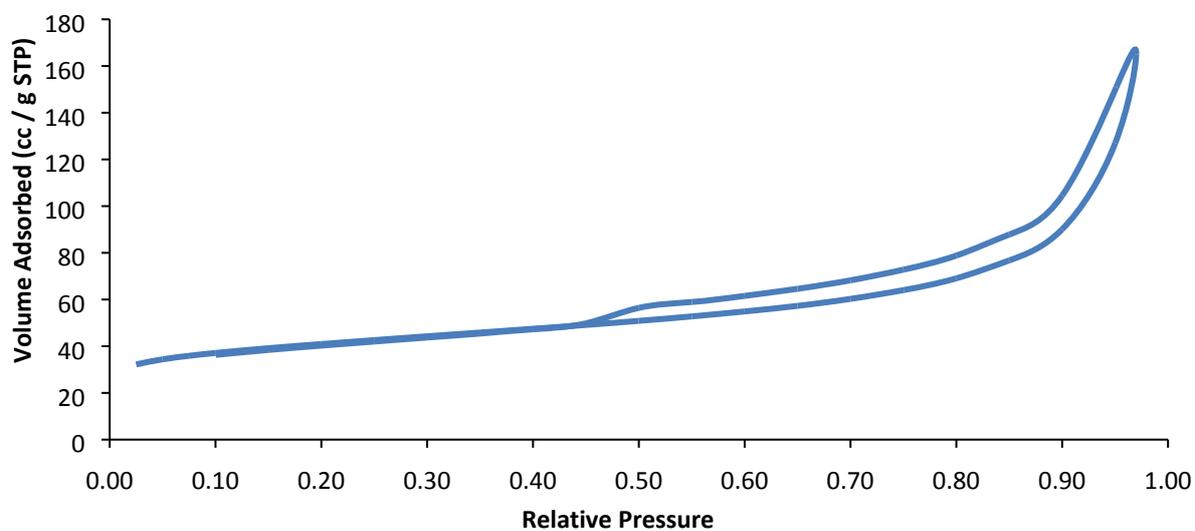


Figure S5: Nitrogen adsorption isotherm for SiAlPO-5

BJH Adsorption Model

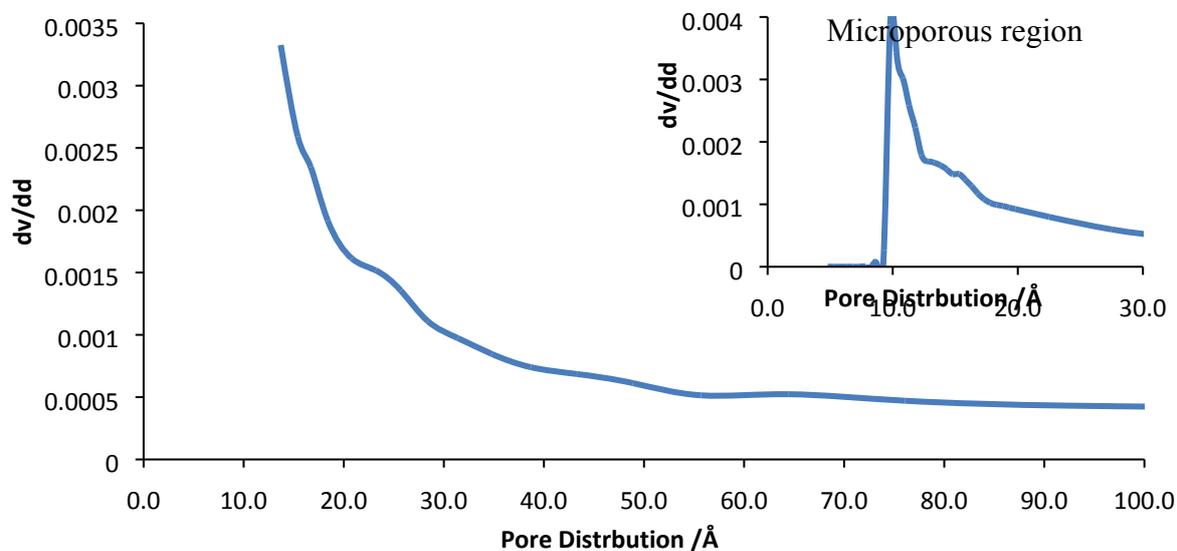


Figure S6: BJH Adsorption model plot for SiAlPO-5

MgAlPO-5

Nitrogen Isotherm

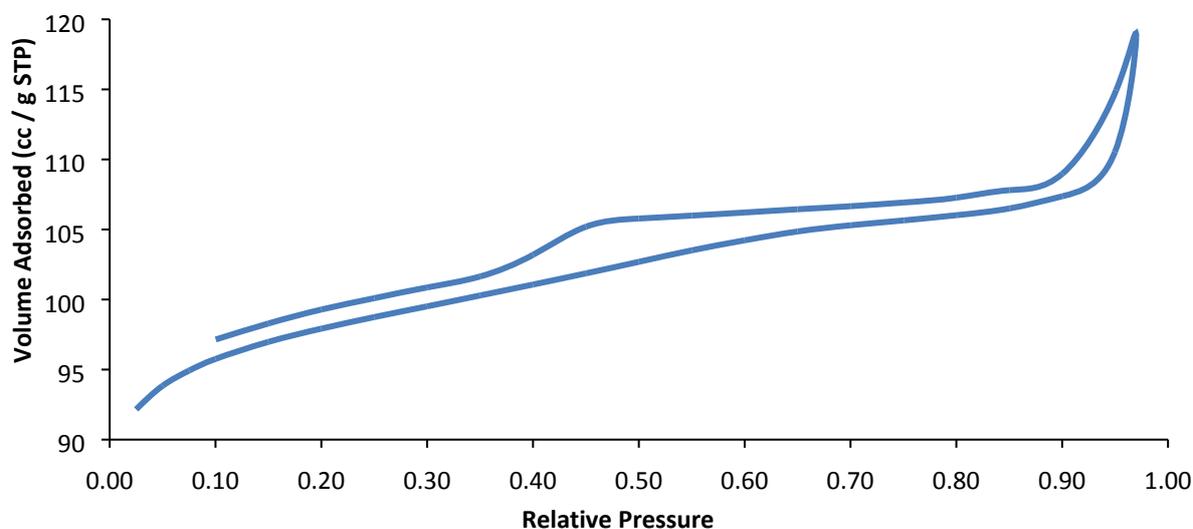


Figure S7: Nitrogen adsorption isotherm for MgAlPO-5

BJH Adsorption Model

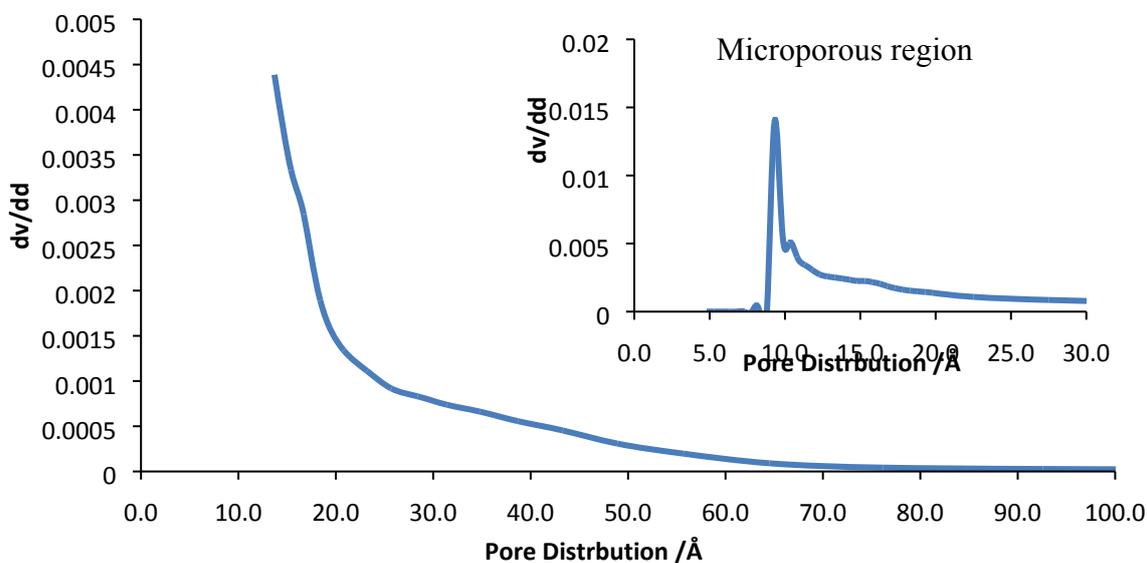


Figure S8: BJH Adsorption model plot for MgAlPO-5.

The hysteresis plots are consistent with those reported in the literature (G. C. Bond, et al., *J. Chem. Soc. Commun.*, 1988, **15**, 1056-1057; L. Zhou et al., *Micropor. Mesopor. Mater.*, 2012, **161**, 76-83) for analogous AlPO-5 catalysts and the BJH model shows no significant bands in the mesoporous region, thereby confirming the microporous nature of our catalysts.

Table S3: Micropore volume from BET T-plot

Sample	T-plot micropore volume/(cm ³ /g)
MgSiAlPO-5	0.057760
SiAlPO-5	0.03257
MgAlPO-5	0.115138

SEM images

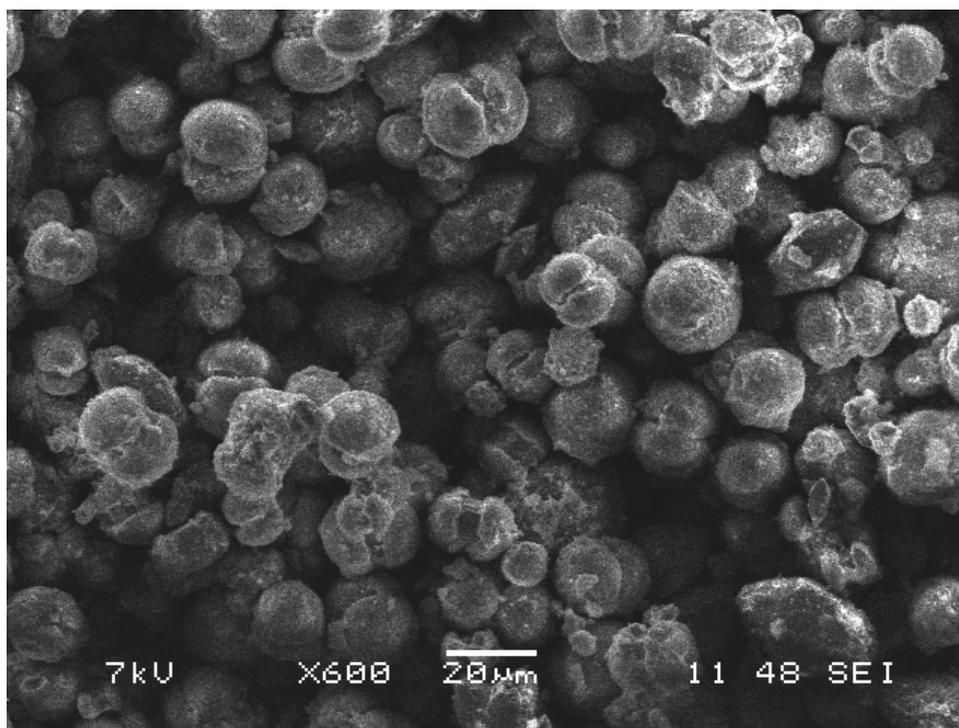


Figure S9: SEM image of MgAlPO-5

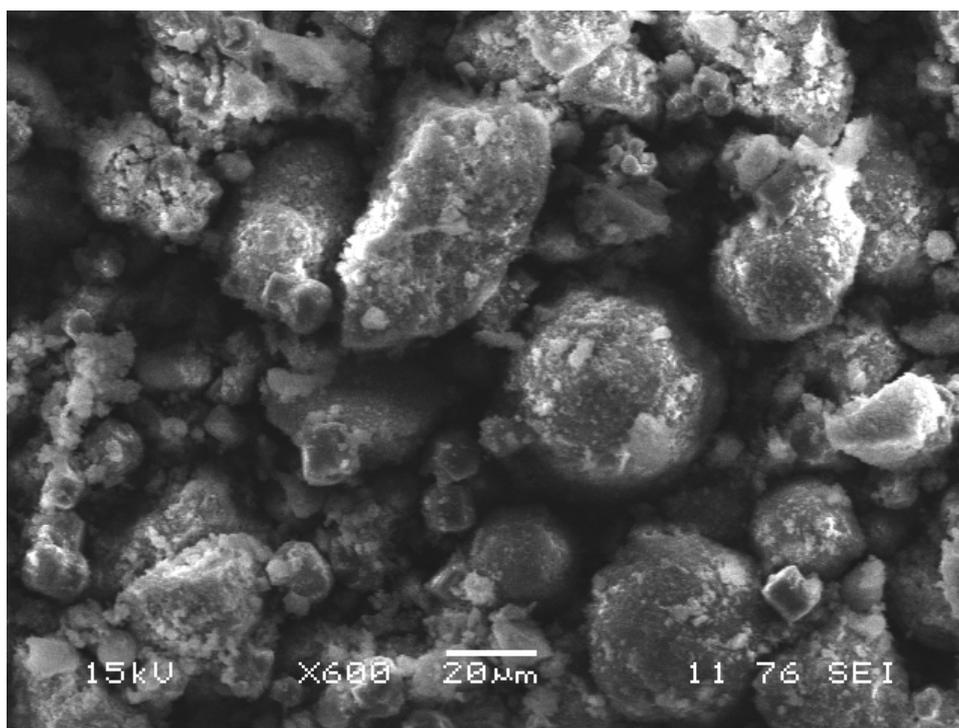


Figure S10: SEM image of SiAlPO-5

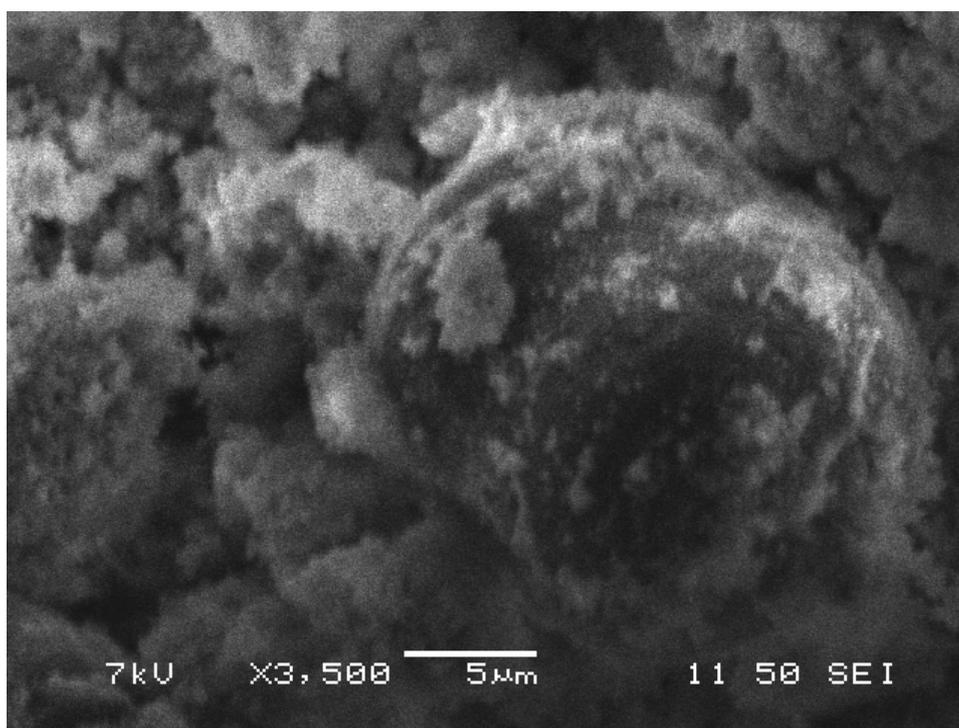


Figure S11: SEM image of MgSiAlPO-5

TPD Results

Table S4: Summary of TPD data

Sample	150-200 °C	200-300 °C	300-400 °C	400-500 °C	500-600 °C	Total
SiAlPO-5	0.002	0.047	0.044	0.030	0.015	0.138
MgSiAlPO-5	0.001	0.041	0.044	0.018	0.017	0.121
MgAlPO-5	0.001	0.054	0.093	0.052	0.030	0.229

The MgSiAlPO-5 and SiAlPO-5 catalysts have a comparable fraction of acid sites, whilst the MgAlPO-5 possesses a much higher density of strong acid sites. However, we believe that the type of substrates used in this study (cyclohexanone oxime and benzene) bear little resemblance to the NH₃ probe that has been used in the TPD measurements and, as such, it is difficult to ascertain subtle differences between the MgSiAlPO-5 and SiAlPO-5 catalysts on the basis of purely the NH₃-TPD data. In light of this, we have resolved and quantified the signals observed using the 2,6-DMP probe (Table 2 on page 5 in the main paper, and Figure S12 below). This shows the subtle differences in acid site strength that exists between the two catalysts and more importantly highlights the differences in the quantity of accessible active (acid) sites.

Fitting of FTIR spectra

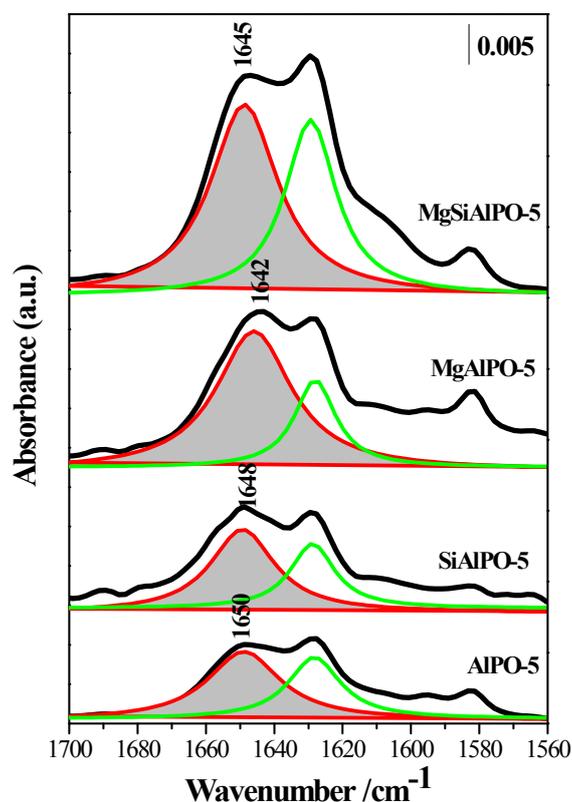


Figure S12: FTIR spectra of outgassed 2,6-DMP at 298K on mono- and bi-substituted AlPO-5 catalysts. Red and green lines: simulated spectra obtained by a curve fitting procedure.

Caprolactam yield comparisons

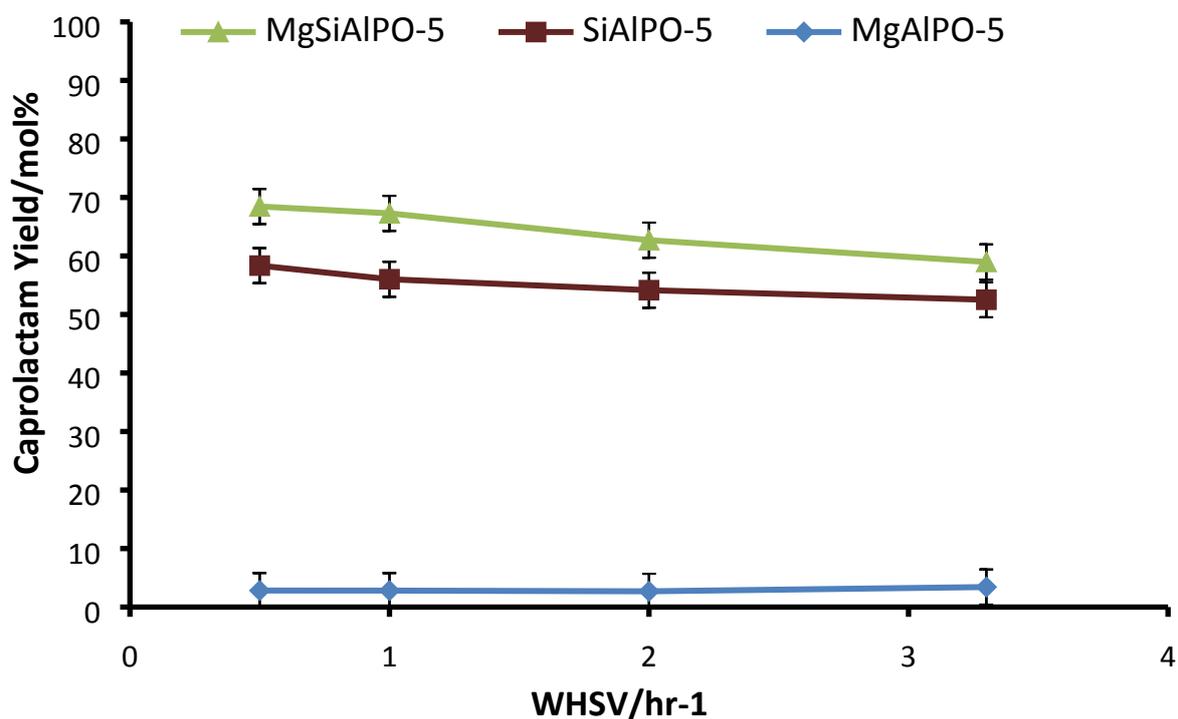


Figure S13: Caprolactam yield versus WHSV.

Carbon balance

The feed solution for assessing the carbon balance using chlorobenzene as the internal standard was composed of:

Chlorobenzene: 2.9929 g (0.026589 mol)

Cyclohexanone oxime: 15.0088 g (0.132633 mol)

Made up to 50 ml with methanol (solvent).

Response factor for Cyclohexanone oxime relative to Chlorobenzene = 1.2972 (Calibrated)

Response factor for Caprolactam relative to Chlorobenzene = 1.4516 (Calibrated)

Response factor of Others relative to Chlorobenzene = 1

Performing an identical procedure to the one described above the following GC data was obtained at 673 K, WHSV of 3.3 hr⁻¹:

Time/mins	Molecule	Area
2.7	Chlorobenzene	233780.63
4.1	Cyclohexanone oxime	216732.37
5.9	Caprolactam	489031.09
N/A	Others detected by GC	119505.20

Rearranging: Moles of A/Moles of B = RF x (Area of A/Area of B)

Gives: Moles of A = Moles of B x RF x (Area of A/Area of B)

Using the equations and response factors above the moles of the remaining molecules can be calculated by normalisation to the internal standard (0.026589 moles)..

Time/mins	Molecule	Area	Moles
2.7	Chlorobenzene	233780.63	0.026589
4.1	Cyclohexanone oxime	216732.37	0.031976
5.9	Caprolactam	489031.09	0.080739
N/A	Others detected by GC	119505.20	0.013592

Conversion = 100 x (Initial moles of oxime – Moles of oxime)/Initial moles of oxime

Conversion = 75.9 mol%

Selectivity = 100 x (Moles of Lactam)/Moles of converted oxime

Selectivity = 80.2 mol%

Yield = 100 x (Moles of Lactam)/Initial moles of oxime

Yield = 60.9 mol%

Mass balance = 100 x (Moles of [Oxime + Lactam + Others])/Initial moles of oxime

Mass balance = 95.2 mol%

Both the reproducibility and carbon balance (>95 mol%) are within accepted limits.