

Supplementary information

Investigating the site-specific interactions and probing their role in modifying the acid-strength in framework architectures

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Experimental

Catalysis synthesis

The protocol for the synthesis of ZnSiAlPO-5 is described (below); analogous methods was employed for the preparation of similar Zn-containing AlPO-5 analogues, details of which are provided in Table SX and in earlier publications (29 US Pat., US20100249476A1, 2010.). 4.3 g of aluminium hydroxide hydrate (Aldrich) was added to a stirred solution of 5.4 g of phosphoric acid (85% in H₂O, Aldrich) in 20 ml of water. A solution of 0.4 g of zinc acetate (Aldrich) in 10 ml of water and 0.7 g of fumed silica (Aldrich) were separately added to the above solution, which was further stirred to obtain a homogeneous gel. 8.6 g of N,N-methyldicyclohexylamine (structure-directing agent (SDA) Aldrich) was then added followed by 20 ml of water with vigorous stirring for 60 minutes to obtain a white gel with the composition 1.0Al: 0.85P: 0.80MDCHA: 50H₂O: 0.03Zn: 0.20Si. The contents of the gel were sealed in a Teflon-lined stainless-steel autoclave, and crystallised in a pre-heated, fan-assisted oven (WF-30 Lenton) at 190 °C under autogeneous pressure for 2 hr. The white solid product was collected by filtration, washed with *ca.* 1 litre deionised water, and dried in air (60 °C) overnight. The as-prepared sample was calcined in a tube furnace under a flow of air at 550 °C for 12 h (to remove the SDA) yielding a white solid. The synthesis procedures of the other catalysts involved in this study varied only by crystallization temperature and gel composition, as shown in Table SX.

Table S1 Specific synthesis conditions for metal-substituted AlPOs.

Sample	Molar gel composition	Crystallization temp/°C
ZnAlPO-5	1.05P:1.00Al:0.04Zn:0.80MDCHA:65H ₂ O	190
MgZnAlPO-5	1.50P:1.00Al:0.03Mg:0.03Zn:0.80MDCHA:50H ₂ O	180
ZnSiAlPO-5	0.85P:1.00Al:0.03Zn:0.20Si:0.80MDCHA:50H ₂ O	190

Characterisation methods

X-Ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer using Cu K_{α1} radiation, where $\lambda = 1.54056 \text{ \AA}$. Scanning electron microscopy images were obtained using a JEOL-JSM5910 microscope with accelerating voltage of 0.3-30 kV. In this case, 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 10 ml of deionised water and 10 ml 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 823 K in oxygen to clean the surface from pre-adsorbed species before the FTIR experiments. CO was adsorbed at 80 K and 2,6-dimethylpyridine (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 <10⁻⁵Torr) to perform *in situ* adsorption-desorption

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.

Catalysis protocol

The Beckmann rearrangement of cyclohexanone oxime was performed in a fixed-bed, quartz reactor (4 mm in diameter) with a glass frit, in which a layer of pelletized catalyst (0.25 g) was packed between two layers of glass beads. This was pre-heated by a jacket in the flow-reactor to 673 K under a 20 ml/min flow of helium gas for 1 hour. The temperature was reduced to 573 K and a liquid feed of 300 g/l of cyclohexanone oxime in methanol was fed into the reactor, maintaining a WHSV of 3.3 hr⁻¹, with samples being analysed on an hourly basis (under steady-state conditions). The temperature was then increased to the desired value (598, 623, 648 and 673 K) and samples were taken at each temperature after being allowed to equilibrate for an hour. Samples were analysed using a Clarus 400 gas chromatogram with FID and using an Elite 5 column, the peak areas were calibrated using known response factors.

An analogous reactor set up and pre-treatment protocol was employed for the isopropylation of benzene. After pre-treatment at 673 K, the temperature was reduced to 523 K and a liquid feed with 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 gas. Samples were analysed and quantified as described above.

Structural characterisation data

Table S2: Full ICP data

System	Al/wt%	P/wt%	Zn/wt%	Mg/wt%	Si/wt%
AlPO-5	18.1	16.7	-	-	-
ZnAlPO-5	16.4	21.2	2.11	-	-
MgAlPO-5	15.9	20.6	-	0.85	-
MgZnAlPO-5	17.0	22.9	1.86	0.72	-
SiAlPO-5	19.8	14.7	-	-	1.69
ZnSiAlPO-5	18.7	15.9	1.33	-	1.66

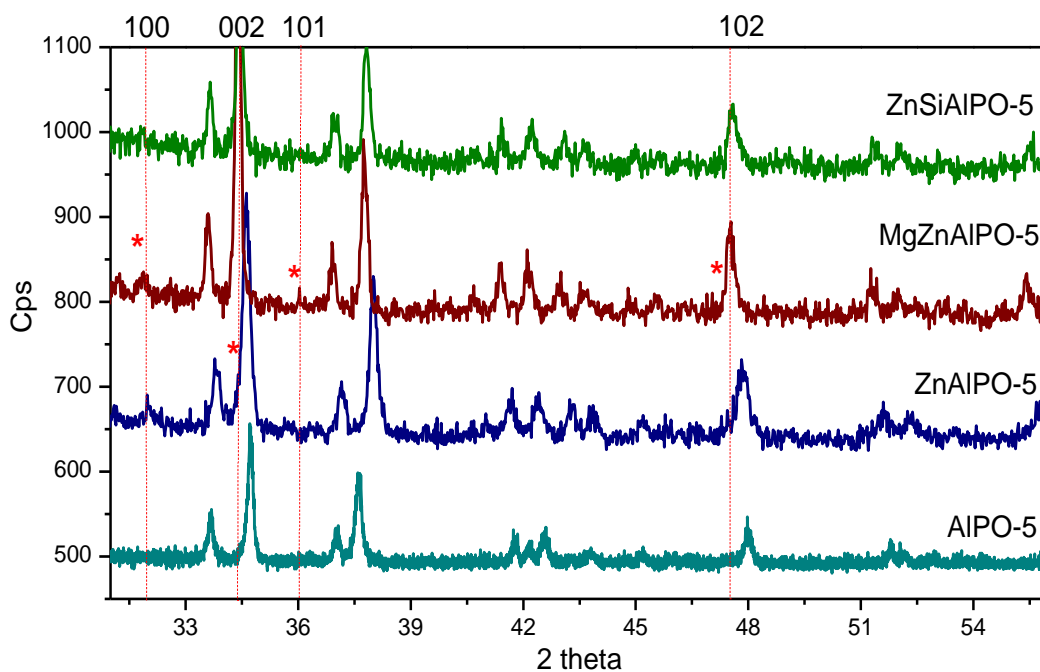


Figure S1: Zoomed XRD pattern of Zn-containing species revealing trace quantities of ZnO hexagonal phase (red asterisks, JCPDS file number 00-003-0888).

FT-IR spectra

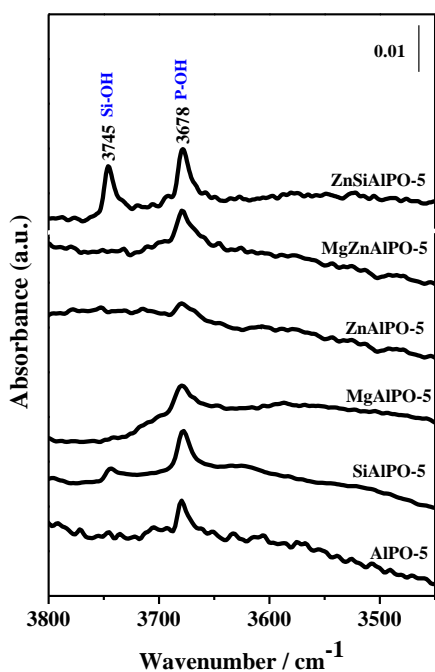


Figure S2: FTIR spectra of the OH stretching region for metal-substituted AlPO-5 systems

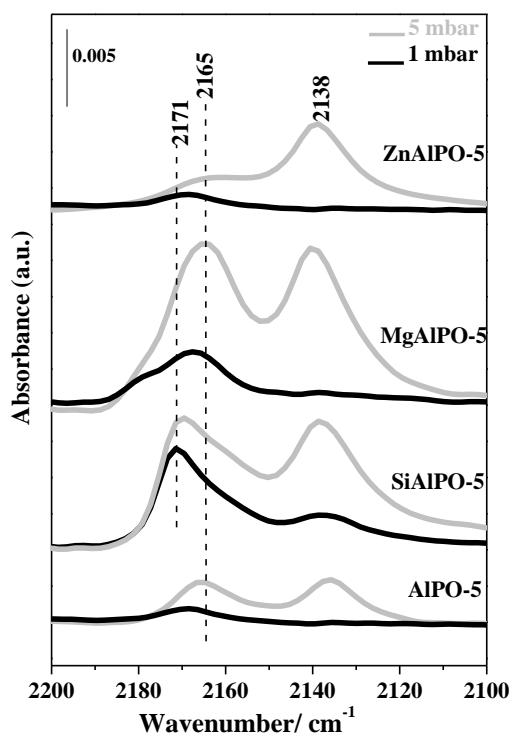


Figure S3: FTIR spectra of CO adsorbed at 80K on calcined AlPO-5, SiAlPO-5, MgAlPO-5 and ZnAlPO-5; black curve: 1 mbar, grey curve: 5 mbar of CO.

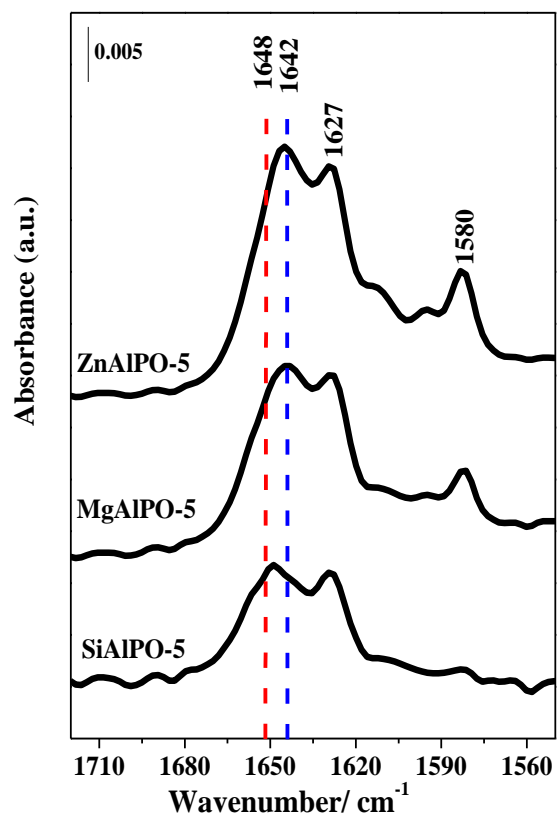


Figure S4: FTIR spectra of outgassed 2,6-DMP at 298K on calcined SiAlPO-5, MgAlPO-5 and ZnAlPO-5.

Full catalysis data

Vapour-phase Beckmann rearrangement - Monometallics

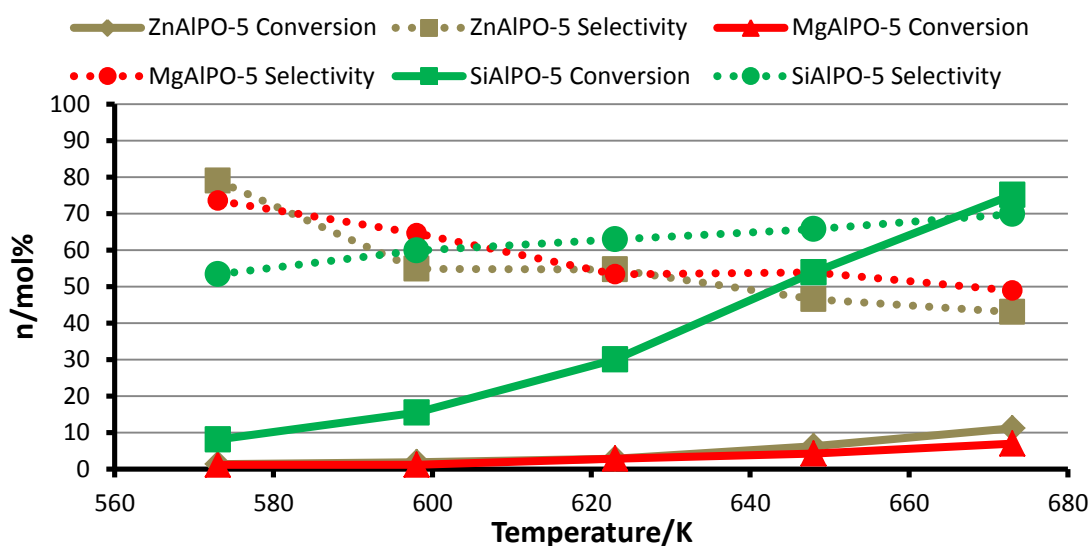


Figure S5: Catalytic data for the vapour-phase Beckmann rearrangement of cyclohexanone oxime using monometallic AlPO-5 systems. Reaction conditions: WHSV 3.3 hr⁻¹, Helium carrier gas flow 20 ml/min, 0.3 g of catalyst, liquid feed 300g/l of cyclohexanone oxime in methanol, temperature as shown.

Isopropylation of benzene - Monometallics

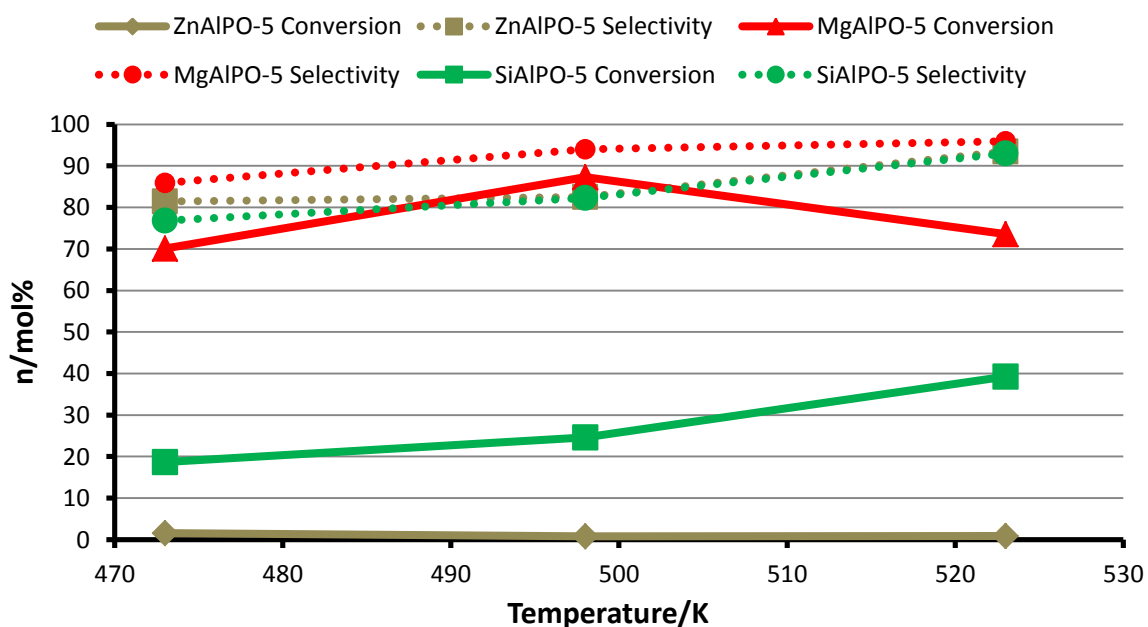


Figure S6: Catalytic data for the isopropylation of benzene using monometallic AlPO-5 systems. Reaction conditions: WHSV of 3.5 hr⁻¹, Helium carrier gas of 10 ml/min, feed 6:1 mole ratio of benzene:isopropanol, temperature as shown.

Vapour-phase Beckmann rearrangement - Mg systems

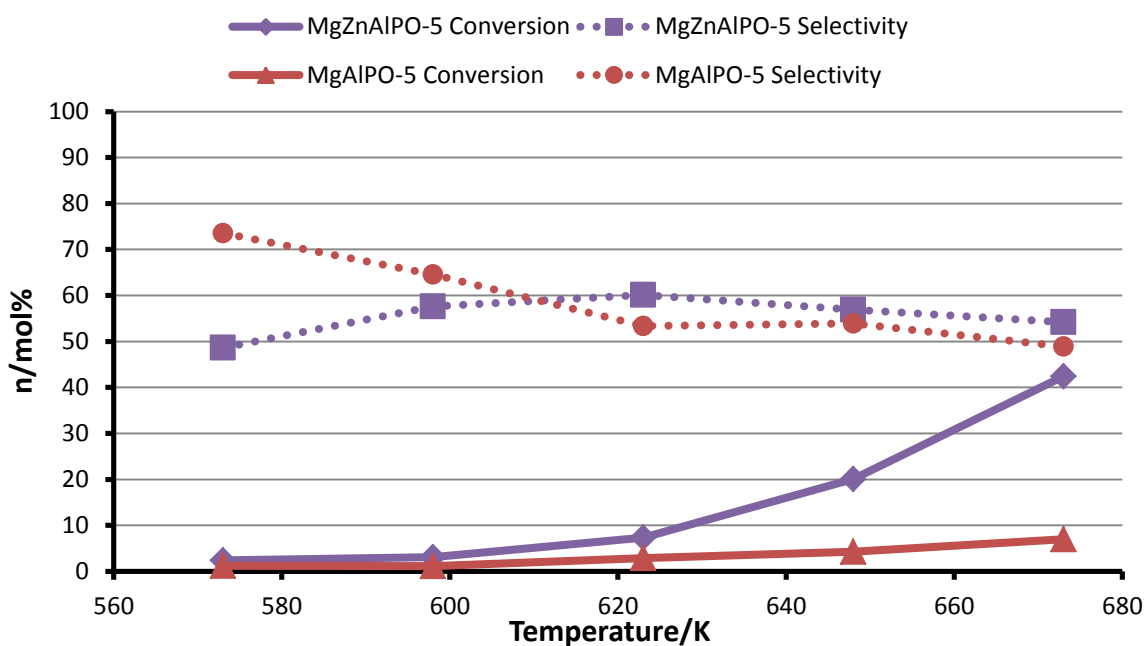


Figure S7: Vapour-phase Beckmann rearrangement of cyclohexanone oxime using Mg-containing AlPO-5 systems. Reaction conditions: WHSV 3.3 hr⁻¹, Helium carrier gas flow 20 ml/min, 0.3 g of catalyst, liquid feed 300g/l of cyclohexanone oxime in methanol, temperature as shown.

Isopropylation of benzene - Mg systems

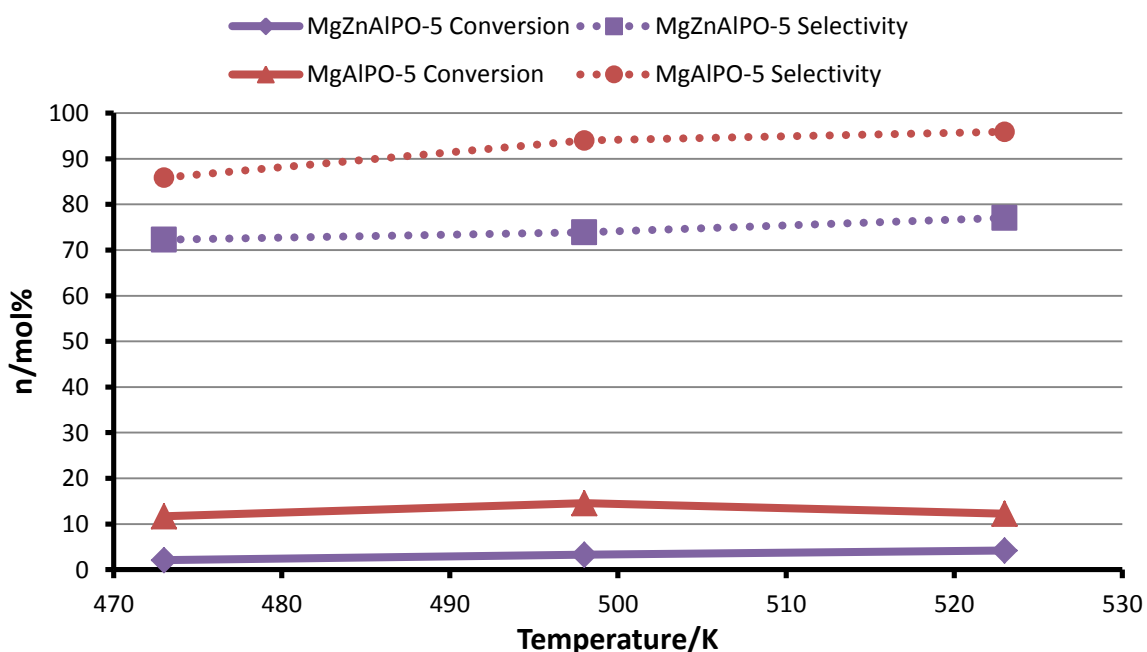


Figure S8: Isopropylation of benzene using Mg-containing AlPO-5 systems. Reaction conditions: WHSV of 3.5 hr⁻¹, Helium carrier gas of 10 ml/min, feed 6:1 mole ratio of benzene:isopropanol, temperature as shown.

Vapour-phase Beckmann rearrangement - Si systems

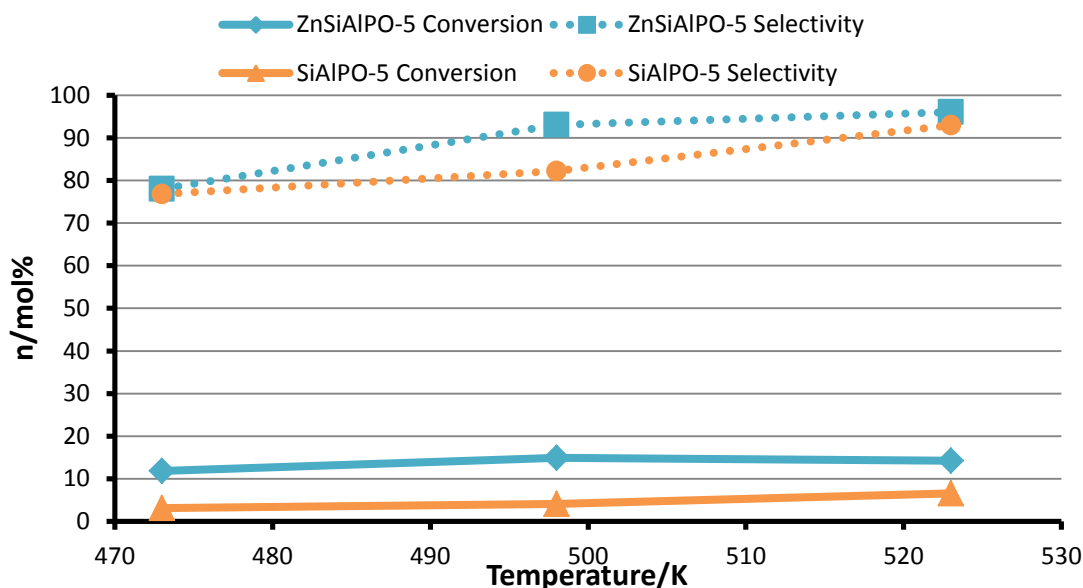


Figure S9: Full catalytic data for the vapour-phase Beckmann rearrangement of cyclohexanone oxime using Si-containing AlPO-5 systems. Reaction conditions: WHSV 3.3 hr⁻¹, Helium carrier gas flow 20 ml/min, 0.3 g of catalyst, liquid feed 300g/l of cyclohexanone oxime in methanol, temperature as shown.

Isopropylation of benzene - Si systems

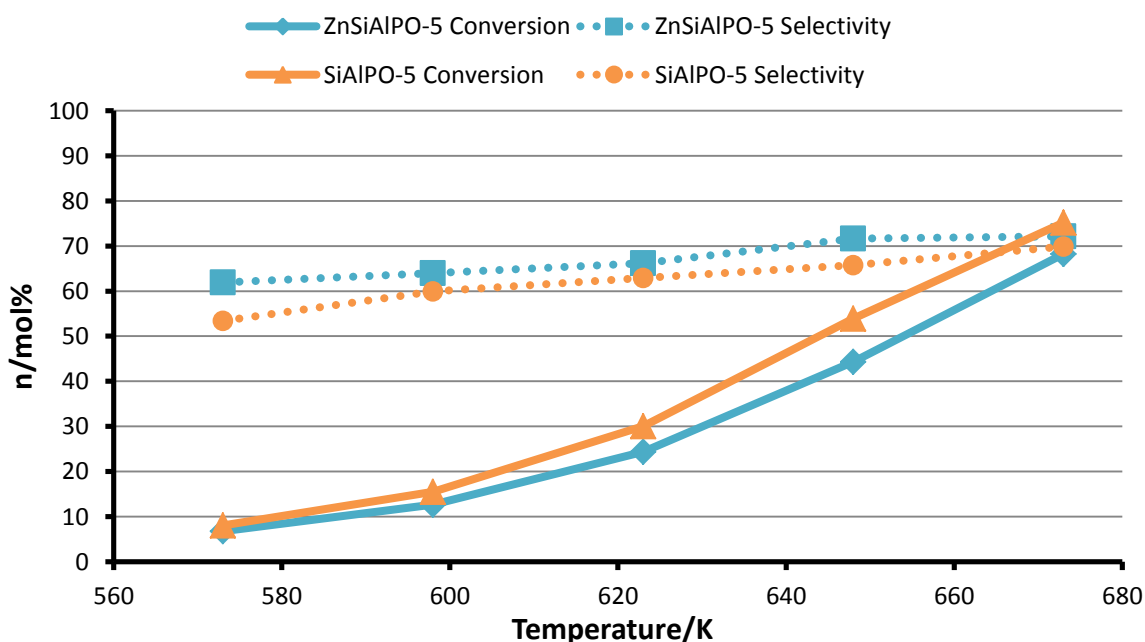


Figure S10: Full catalytic data for the isopropylation of benzene using Si-containing AlPO-5 systems. Reaction conditions: WHSV of 3.5 hr⁻¹, Helium carrier gas of 10 ml/min, feed 6:1 mole ratio of benzene:isopropanol, temperature as shown.