

SUPPLEMENTARY INFORMATION

Investigating the role of framework topology and accessible active sites in silicoaluminophosphates for modulating acid-catalysis

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Silicon substitution mechanisms

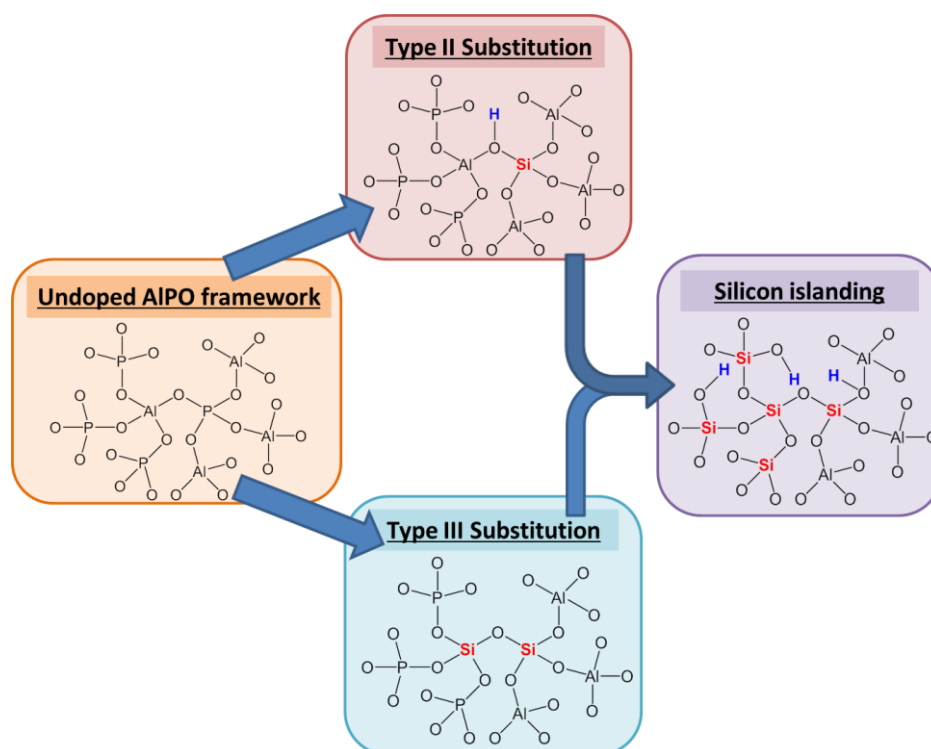


Figure S1: Possible silicon substitution mechanisms in AlPO frameworks.

Experimental details

Synthesis details

SAPO materials were synthesized according to previous reported literature protocols, the details of which are outlined below:

SAPO-5 and -41 were hydrothermally synthesized by the method reported by Meriaudeau et al.^[1] Aluminum source was added to the mixture of phosphoric acid and water that was then stirred for 4 h until homogeneous gel was achieved. After addition of the template triethylamine for SAPO-5 (dipropylamine for SAPO-41) to the silica sol, the mixture was stirred for 2 h and transferred to a Teflon-lined steel autoclave and heated in the oven at 200°C for 24 h (SAPO-5) and 96 h (SAPO-41). The autoclave contents were filtered, washed with deionized water, left drying at room temperature, followed by calcination at 600 °C for 10 h in air.

The standard synthesis procedure for large pore SAPO-37 (7.4 Å) is as per our previous work.^[2,3] Pseudo-boehmite was added to the mixture of phosphoric acid (85 % in water) and water, and the mixture was then stirred for 7 h. Fumed silica was slowly added to a stirred solution of TPAOH and TMAOH · 5H₂O, was stirred for 2 h and added to the first mixture. The gel was stirred for 68 h before it was transferred to a Teflon-lined tube, sealed inside a stainless-steel autoclave that was put in the oven at 200 °C for 24 h. The contents were then centrifuged, filtered and washed with deionized water.

The material was dried overnight at room temperature. Before catalysis the white solid was calcined at 550 °C for 8 h and stored under inert atmosphere.

SAPO-34 synthesis involved initially adding 31.10 g of tetraethyl ammonium hydroxide (35 % in H₂O, Aldrich) to 15.10 g aluminum isopropoxide (Aldrich) and allowing the mixture to stir for 1.5 h. 0.66 g of fumed silica (Aldrich) was added to the above solution, which was stirred for a further 30 minutes. A homogeneous solution of 8.52 g of phosphoric acid (85 % in H₂O, Aldrich) in 12.2 mL of water was added to the above solution which was stirred for a further 2 h to obtain a gel with the composition 1.0Al:1.0P:0.15:Si:1.0TEAOH:50H₂O. The contents of the gel were sealed in 2 Teflon-lined stainless-steel autoclaves, which were then transferred to a pre-heated, fan-assisted oven (WF-30 Lenton) that was set to the desired temperature of 200 °C, prior to the onset of the crystallization. The autoclave was heated at 200 °C under autogenous pressure for 60 h. The white solid product was collected by centrifuge, washed with approx. 100 mL deionized water, and dried in air (60 °C) overnight. The as-prepared sample was calcined in a tube furnace under a flow of air at 575 °C for 16 h yielding a white solid.

The exact gel ratios are given below:

Table S1: Molar gel compositions for synthesis of SAPO materials.

	H ₃ PO ₄	Al ₂ O ₃	SDA	SiO ₂	H ₂ O
SAPO-5	2.0	1.0	2.0	0.4	50.0
SAPO-34	2.0	1.0	1.0	0.15	50.0
SAPO-37	2.0	1.0	0.97 & 0.025	0.21	50.0
SAPO-41	2.0	1.2	3.0	0.6	50.0

Zeolite-Y and ZSM-5 samples were obtained from Zeolyst, for more information see reference 4.

Characterization protocols

Powder XRD

Powder X-Ray diffraction patterns were obtained using a Siemens D5000 diffractometer using Cu K_{α1} radiation, whereby $\lambda = 1.54056 \text{ \AA}$. Reitveld refinement was performed assuming a P1 symmetry.

N₂ physisorption measurements

N₂ physisorption was performed using a Micromeritics Gemini 2375 surface area analyzer and prepared using flow gas preparation. Total surface areas were quantified using the BET model, whereas external surface areas were quantified using the T-plot method.

ICP Analysis

A Perkin-Elmer Optimum 3000 DV was used for ICP analyses with calcined samples prepared and fully digested in 10 mL of deionized water and 10 mL of ACS Plus Certified H₂SO₄ (Fisher Scientific). Solutions of standard concentrations were used for calibration.

Scanning electron microscopy

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.

MAS NMR

Typical spectra were acquired on samples dried at 120 °C under vacuum prior to the NMR experiments. All NMR measurements were performed on widebore 9.4 T Avance II magnet, using a Chemagnetics Infinity 400 spectrometer and a 4 mm MAS double-resonance APEX probe for some samples and a Bruker Neo console and a RevolutionNMR 4 mm triple resonance probe for SAPO-41 and SAPO-5, following an upgrade of the NMR equipment in our laboratory. Samples were packed in zirconium oxide rotor within our glovebox and then spun at 8 kHz using compressed nitrogen, in order to prevent sample degradation in air, for bearing, drive and purge. The nitrogen gas was generated in-house from evaporation of liquid nitrogen in high pressure 1300 L tanks suitably connected to the NMR facility. ²⁷Al NMR experiments were performed using direct acquisition (128 scans with and a pulse delay of 2 s between scans). ³¹P NMR data were acquired with direct acquisition (4 scans and 120 s delay between scans). ²⁹Si NMR data for all 1D experiments were performed using cross-polarization and SPINAL64 decoupling.^[5] Spectra were recorded with 8192 scans (thin wall rotors) or 40000 scans (normal wall rotors, for SAPO-41 and SAPO-5) and 2 s between scans, with 7 ms contact time. The chemical shift axes in the ²⁷Al, ³¹P and ²⁹Si spectra were referenced using 1M AlCl₃ aqueous solution (0 ppm), 85 % H₃PO₄ (0 ppm) and silicon rubber (-22.42 ppm) respectively, following the convention described in reference 6. The NMR data was processed using the commercial software Mestrenova.

Low-temperature CO adsorption FT-IR

All IR experiments were performed in a custom designed IR flow cell that allowed for sample heating and cryogenic cooling. As-synthesized samples were ground and pressed into 13 mm diameter self-supporting pellets (~8 mg/cm²) and heated at 10 °C/min to 550 °C in a mixture of 20 % O₂ in N₂ [Matheson UHP grade further purified using a P400 air purifier(VICI)] and held for 1 h. The flow was then switched to helium [Matheson UHP grade further purified using a P-100 helium purifier(VICI) and an indicating OMI-1 purifier(Supelco)] and held for an additional hour. The system was then cooled to ~-175°C and a spectrum recorded. Nine 0.02 cm³ injections of CO (Matheson research purity) were added to the system followed by a final injection of 0.20 cm³. After each injection, the system was equilibrated for 3 min and a spectrum recorded. All spectra were collected on a Nicolet Nexus 870 FT-IR spectrometer using a cooled MCT detector. Each spectrum was obtained by co-adding 128 scans at a resolution of 2 cm⁻¹. All spectral processing was done using the GRAMS/AI 9 software (Thermo Scientific). All spectra are normalized to a 10 mg pellet weight. Difference spectra were obtained by subtracting the spectrum of the sample before adsorption of the probe molecule.

Collidine adsorption FT-IR

As-synthesized samples were ground and pressed into 13 mm diameter self-supporting pellets (~8 mg/cm²) and heated at 10 °C/min to 550 °C in a mixture of 20 % O₂ in N₂[Matheson UHP grade further purified using a P400 air purifier(VICI)] and held for 2 h. The system was then cooled to 30 °C and a

spectrum recorded. The sample was equilibrated with collidine (helium saturated with collidine vapor at 7 °C) for 1 h at 150 °C. Stepwise desorption of collidine was done at 150, 300 and 450 °C. After 1 h hold at desorption temperature, the sample was cooled to room temperature and a spectrum recorded. All spectra were collected on a Nicolet Nexus 870 FT-IR spectrometer using a cooled MCT detector. Each spectrum was obtained by co-adding 128 scans at a resolution of 2 cm⁻¹. All spectral processing was performed using the GRAMS/AI 9 software (Thermo Scientific). All spectra were normalized to a 10 mg pellet weight. Difference spectra were obtained by subtracting the spectrum of the sample before adsorption of the probe molecule. Integrated values were converted from au/mg to mmol/g by multiplying by a factor of 0.0769 cm μmol.^[4]

Temperature-programmed desorption

All TPD measurements were performed on a custom built system using TCD detectors to monitor ammonia concentration. As-synthesized materials were pretreated 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 h. The samples were exposed to ammonia and allowed to equilibrate at 150 °C for 8 h. 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.

Catalytic procedure

Liquid-phase Beckmann rearrangement of cyclohexanone oxime

The liquid-phase Beckmann rearrangement of cyclohexanone oxime was performed thus: 100 mg of cyclohexanone oxime, 100 mg of catalyst and 20 mL of benzonitrile (Aldrich) were put into a glass reactor and stirred at 500 rpm at 130 °C under reflux. Samples were taken hourly.

Vapor-phase Beckmann rearrangement of cyclohexanone oxime

The vapor-phase 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 h. The temperature was reduced to 573 K and a liquid feed of 10 wt% of cyclohexanone oxime in ethanol was fed into the reactor, maintaining a WHSV of 0.4 hr⁻¹, with samples being analyzed on an hourly basis (under steady-state conditions). The temperature was then increased to the desired value (623 and 673) and samples were taken at each temperature after being allowed to equilibrate for 1 h.

GC sample analysis

All samples were analyzed on a Varian Star 3400CX gas chromatogram with flame ionization detector (FID). Samples were injected into a Perkin Elmer a HP1 cross linked methylsiloxane (30 m x 0.32 mm x 1 μm film thickness) column. The samples were mass balanced using chlorobenzene as an internal standard. The following GC method was used:

Start at 120 °C, Hold 2 min, Ramp at 15 °C/min up to 220 °C, Hold for 5 min at 220 °C. The method is 13 minutes and 40 seconds long in total. The benzonitrile solvent peak is a large peak at 3.5 min, the cyclohexanone oxime is at 4.0 min, ε-caprolactam peak is at 5.8 min, the by product is at 6.6 min.

The injector port is set to 220 °C, the detector is set to 250 °C. The carrier pressure (Helium) is at 14 psig. The method is given 1 min to equilibrate before injection. Typically 5µl of centrifuged sample is injected.

The response factors were used to calculate the moles of cyclohexanone oxime, ε-caprolactam and by-products (response factor assumed to be 1.00). The conversion is calculated as:

Conversion = 100x(initial moles of oxime – moles of oxime detected)/initial moles of oxime

Selectivity = 100x(moles of caprolactam)/moles of products detected

Error is considered to be +/- 3 mol%, in line with standard errors from GC analysis.

Further characterization data

Unit-cell parameters

Table S2: Full optimized P1 unit cell parameters for SAPO materials.

Material	a / Å	b / Å	c / Å	α / °	β / °	γ / °	Space group
SAPO-5	13.56	13.60	8.39	90.43	89.21	119.32	P6cc
SAPO-34	13.72	13.77	15.01	88.13	90.42	119.77	R-3m
SAPO-37	24.31	24.32	24.32	89.70	90.10	89.98	Fd-3m
SAPO-41	9.57	25.68	8.38	89.61	89.92	89.78	Cmcm

Complete ICP analysis

Table S3: Full ICP analysis

Material	Al / wt%	P / wt%	Si / wt%
SAPO-5	21.9	24.1	1.4
SAPO-34	23.1	20.8	3.4
SAPO-37	23.5	20.8	3.0
SAPO-41	21.6	24.8	1.1

²⁷Al and ³¹P MAS NMR spectra

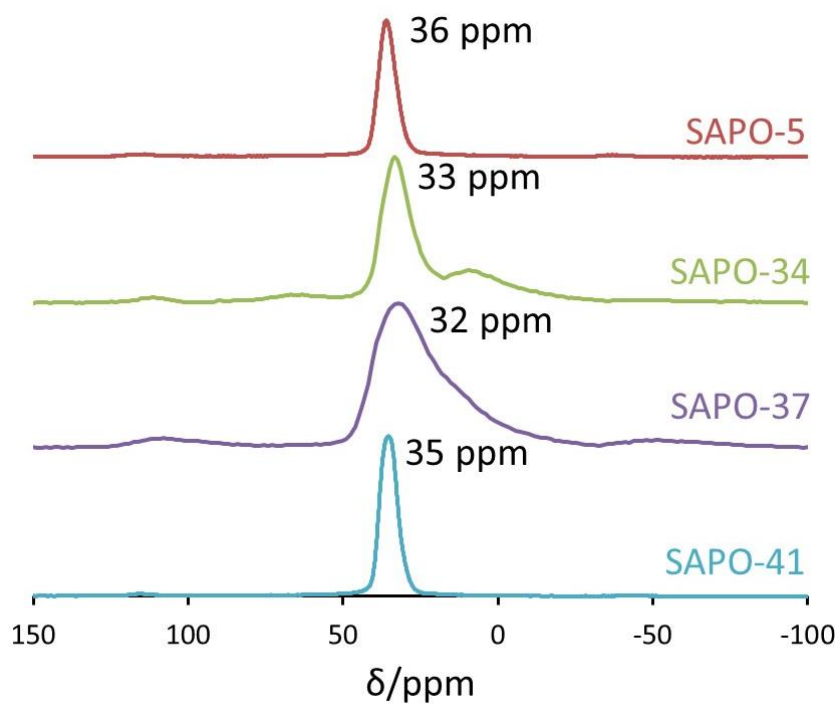


Figure S2: ²⁷Al MAS NMR to probe the local aluminum environments, peak maxima shown. Spinning side-bands can be seen at 105 and -50 ppm.

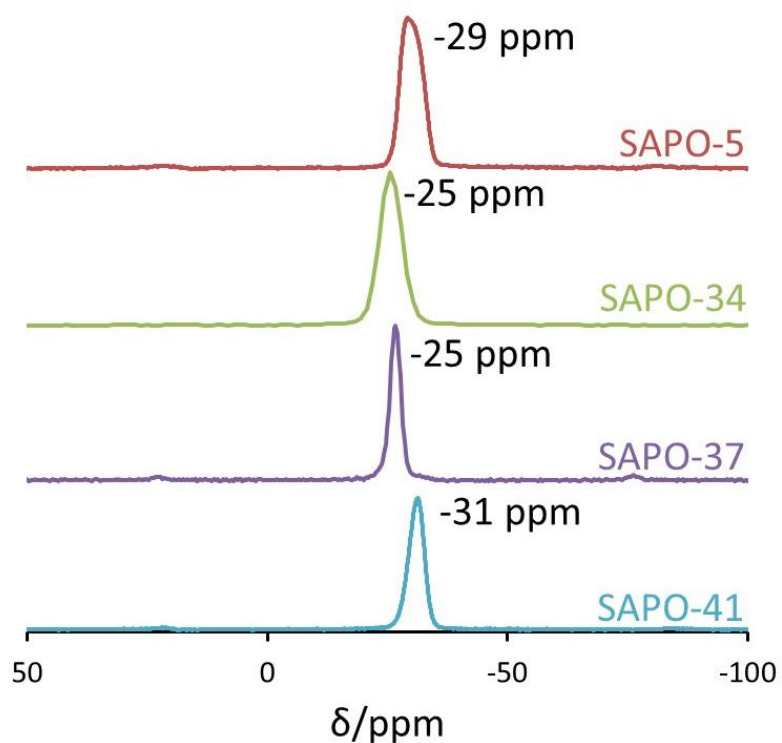


Figure S3: ³¹P MAS NMR to probe the local phosphorus environments, peak maxima shown.

CO FT-IR – Hydroxyl region (4000 – 3000 cm^{-1})

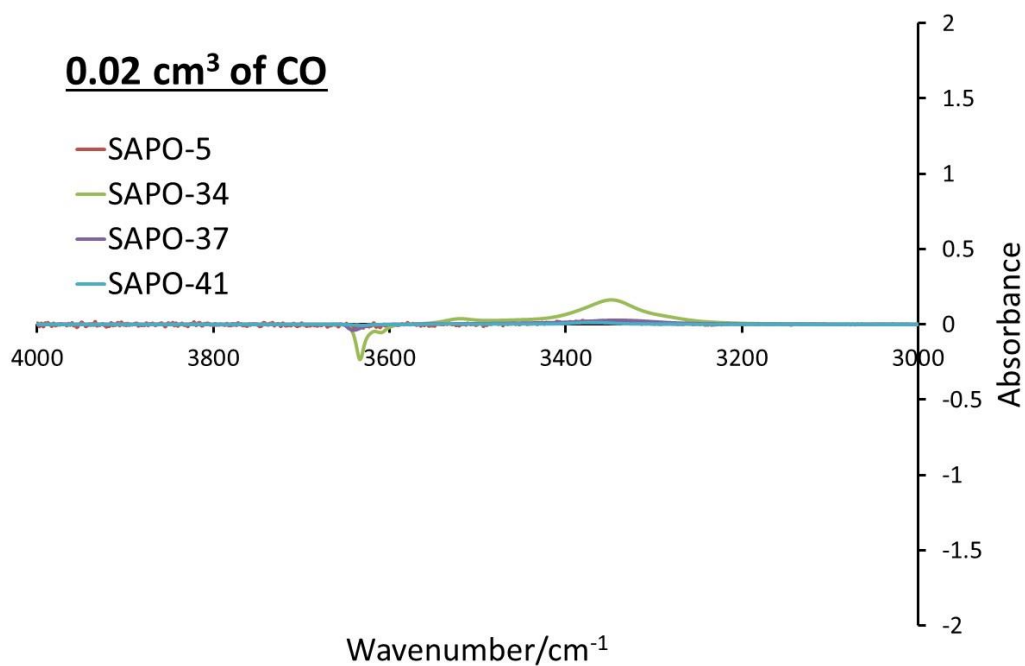


Figure S4: CO FT-IR of hydroxyl region after 0.02 cm^3 of CO at 100 K.

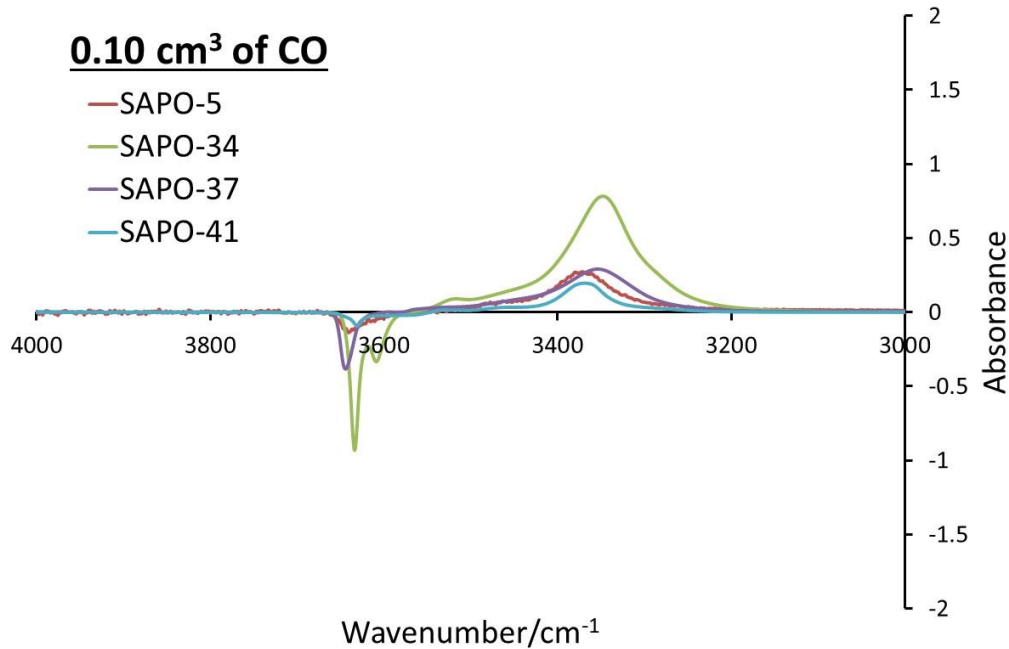


Figure S5: CO FT-IR of hydroxyl region after 0.10 cm^3 of CO at 100 K.

CO FT-IR – CO region (2250 – 2100 cm^{-1})

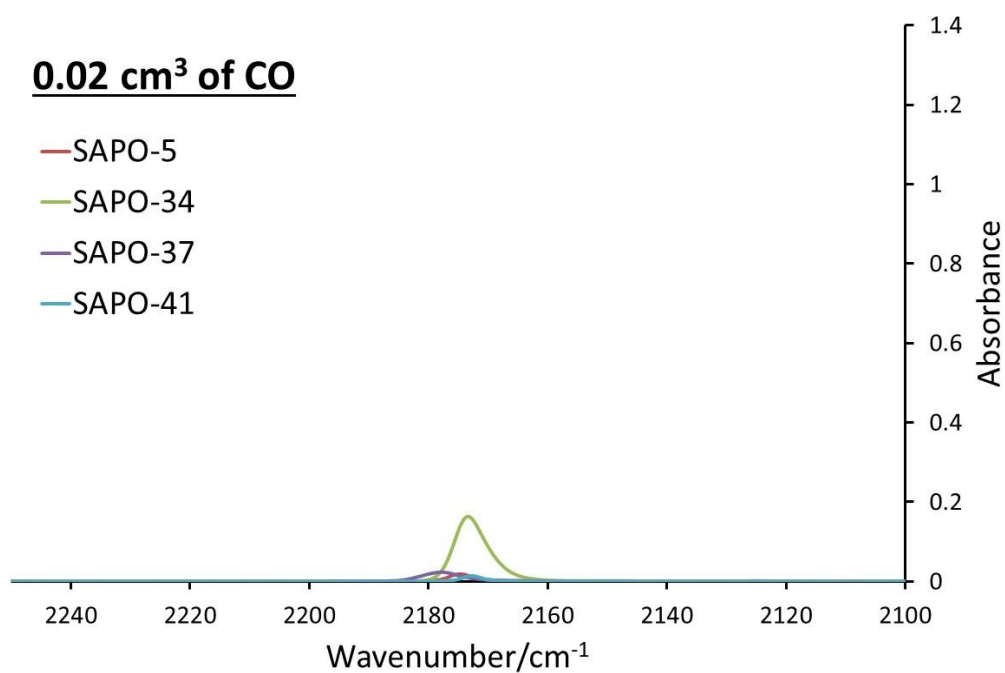


Figure S6: CO FT-IR of CO region after 0.02 cm^3 of CO at 100 K.

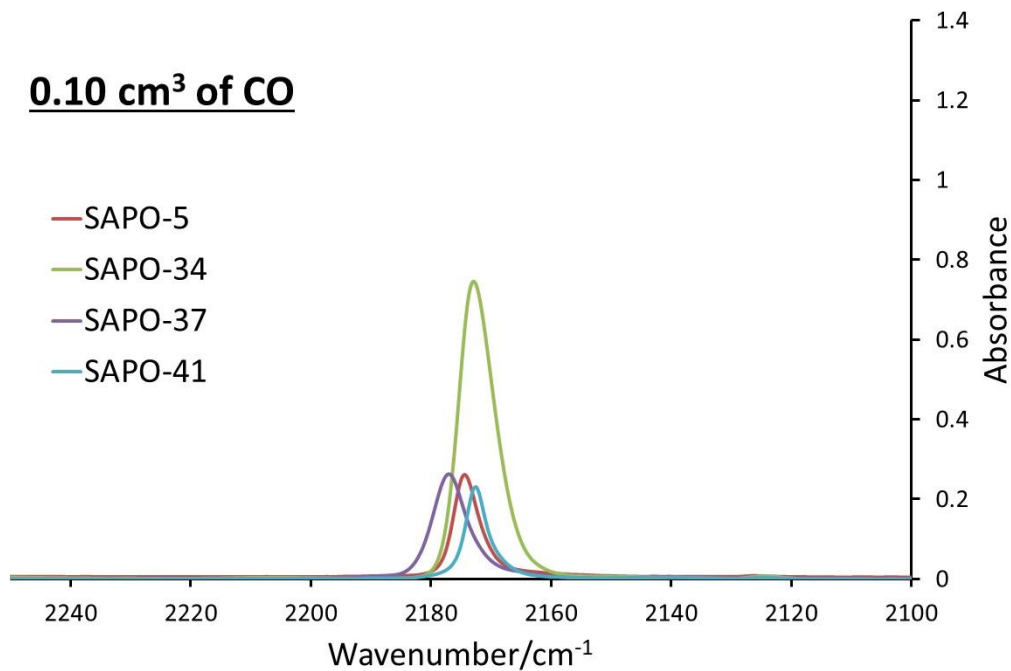


Figure S7: CO FT-IR of CO region after 0.10 cm^3 of CO at 100 K.

Table S4: Quantified CO FT-IR data.

Material	Shift 1	Shift 2	CO area on 0.20 cm ³ of CO added (au)
SAPO-5	270	N/A	0.229
SAPO-34	286	329	1.084
SAPO-37	305	N/A	0.854
SAPO-41	190	260	0.182

NH₃-TPD

Table S5: Full NH₃-TPD data.

Material	Peak area (mmol/g)					Total	Peak maximum
	150 – 200	200 – 300	300 – 400	400 – 500	500 – 600		
SAPO-5	0.001	0.088	0.071	0.009	0.003	0.17	294
SAPO-34	0.0008	0.0602	0.2533	0.4268	0.0811	0.82	450
SAPO-37	0.0000	0.2370	0.5630	0.0940	0.0330	0.93	338
SAPO-41	0.0007	0.0721	0.1205	0.0223	0.0134	0.23	311

Collidine FT-IR data

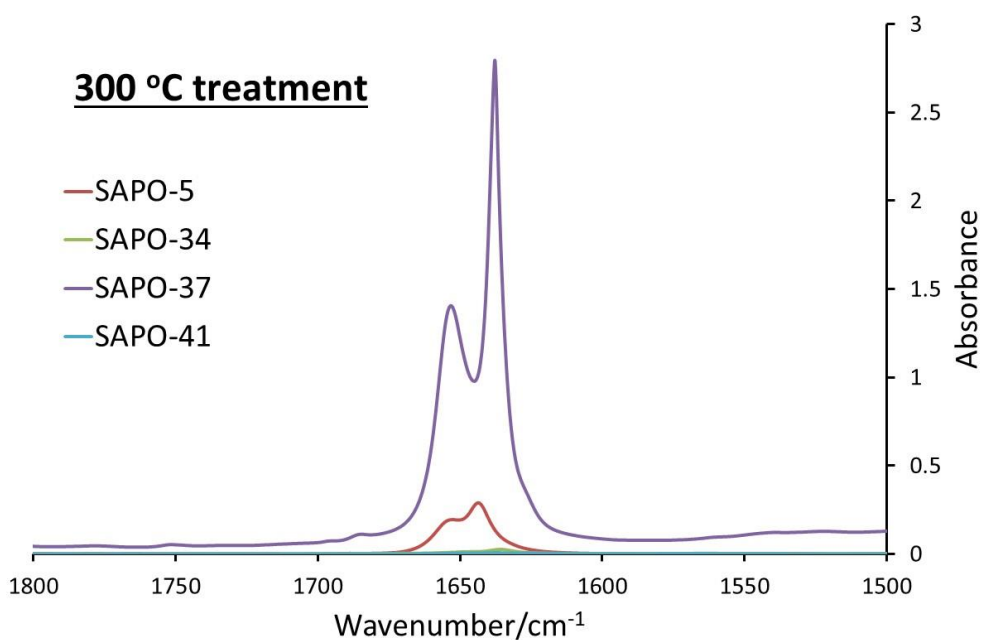


Figure S8: Collidine probed FT-IR spectra after being treated at 300 °C.

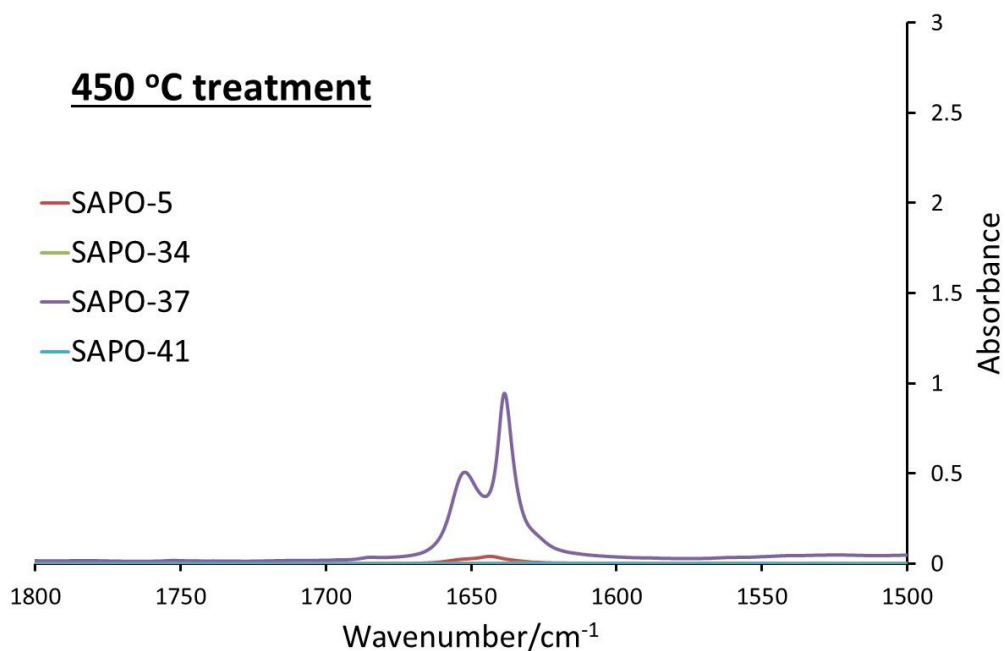


Figure S9: Collidine probed FT-IR after being treated at 450 °C.

Table S6: Fully quantified Collidine FT-IR data.

Material	Acid sites/(mmol/g)			Total
	150 – 300 °C	300 – 450 °C	> 450 °C	
SAPO-5	0.001	0.040	0.007	0.048
SAPO-34	0.012	0.004	0.001	0.017
SAPO-37	0.070	0.219	0.124	0.413
SAPO-41	0.005	0.001	0.000	0.006
Zeolite-Y ^a	0.048	0.062	0.097	0.207
ZSM-5 ^a	0.008	0.006	0.003	0.017

a) Adapted from reference 4 in the ESI.

Table S7: Proportion of acid sites, which are accessible in each SAPO-material.

Material	Acid sites from NH ₃ -TPD/(mmol/g)	Acid sites from collidine FT-IR/(mmol/g)	Proportion of accessible active sites/%
SAPO-5	0.172	0.048	30
SAPO-34	0.822	0.017	2
SAPO-37	0.927	0.413	44
SAPO-41	0.203	0.006	3

Catalysis Data

Liquid-phase Beckmann rearrangement of cyclohexanone oxime

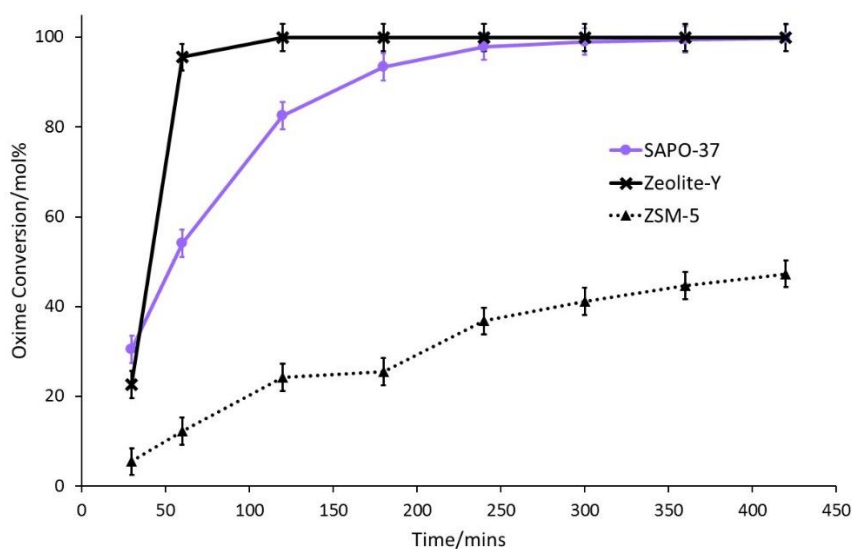


Figure S10: Kinetic conversion data for liquid phase Beckmann rearrangement. Conditions: 130 °C, 7 h, 20 mL Benzonitrile, 100 mg of Cyclohexanone oxime, 100 mg of Catalyst.

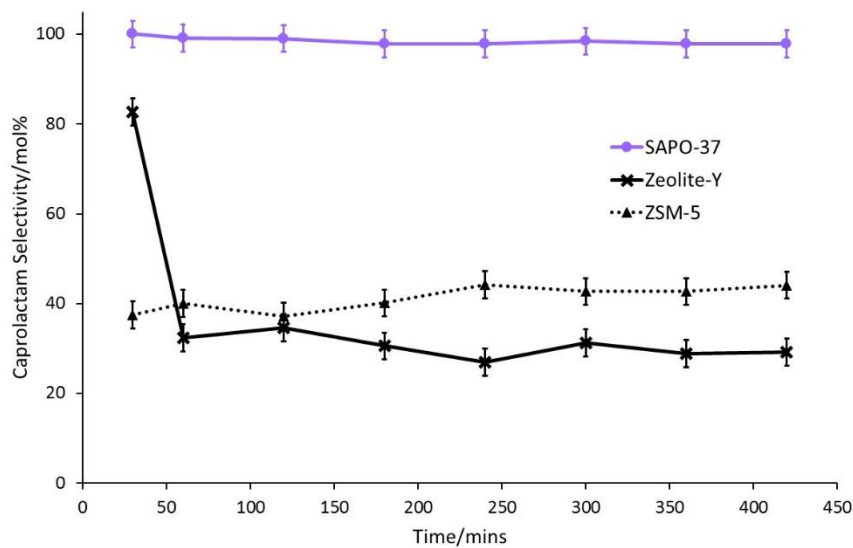


Figure S11: Kinetic selectivity data for liquid phase Beckmann rearrangement. Conditions: 130 °C, 7 h, 20 mL Benzonitrile, 100 mg of Cyclohexanone oxime, 100 mg of Catalyst.

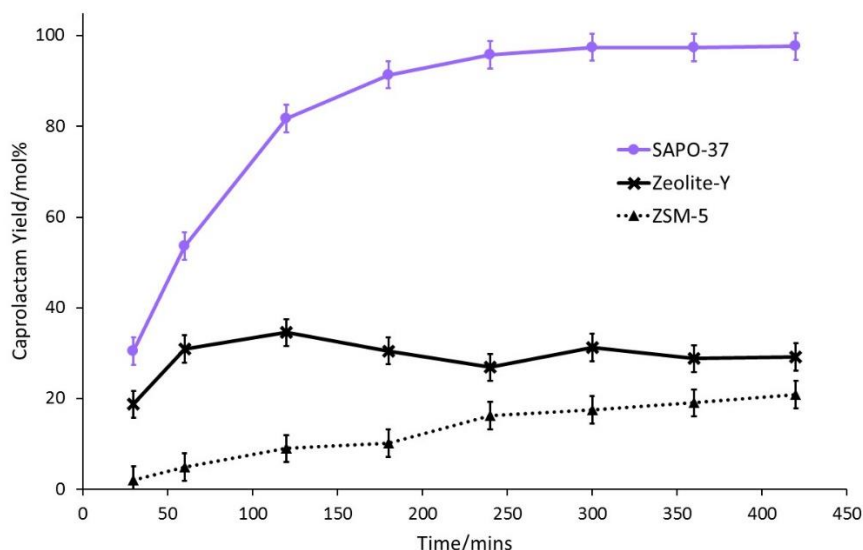


Figure S12: Kinetic yield data for liquid phase Beckmann rearrangement. Conditions: 130 °C, 7 h, 20 mL Benzonitrile, 100 mg of Cyclohexanone oxime, 100 mg of Catalyst.

Table S8: Full Liquid-phase data

Material	Oxime conversion / mol%	ϵ -Caprolactam selectivity / mol%	ϵ -Caprolactam yield / mol%	TON ^a	Lactam production efficiency ^b / mol _{Lactam} /mol _{Si}
SAPO-5	99.8	6.8	6.8	17.7	1.2
SAPO-34	18.6	87.3	16.2	1.4	0.2
SAPO-37	98.9	93.5	92.5	8.2	7.6
SAPO-41	71.6	40.6	29.1	16.2	4.7
Zeolite-Y ^c	99.9	27.3	27.3	N/A	N/A
ZSM-5 ^c	47.3	44.1	20.9	N/A	N/A

Conditions: 130 °C, 7 h, 20 mL Benzonitrile, 100 mg of Cyclohexanone oxime, 100 mg of Catalyst. a) TON based on the total quantity of Si in the framework. b) Lactam production per mole of silicon dopant. c) Adapted from reference 4 in the ESI.

Table S9: Recyclability data for SAPO-37

Reaction Cycle	Oxime conversion/mol%	Caprolactam selectivity/mol%	Caprolactam yield/mol%
Fresh	98.9	93.5	92.5
Recycle 1	99.2	94.0	93.2
Recycle 2	99.3	94.4	93.7

Conditions: 130 °C, 7 h, 20 mL Benzonitrile, 100 mg of Cyclohexanone oxime, 100 mg of Catalyst. Catalyst dried and recalcined between runs.

Vapor-phase Beckmann rearrangement of cyclohexanone oxime

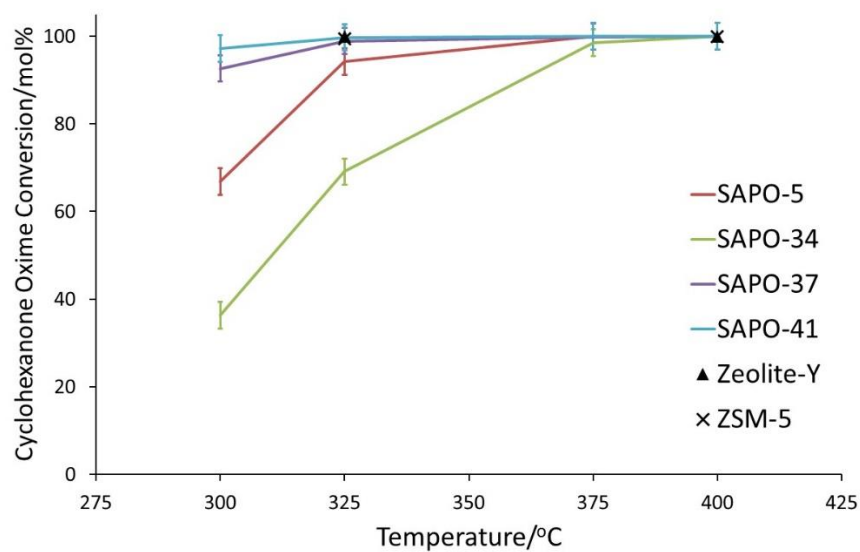


Figure S13: Oxime conversion for the vapor-phase Beckmann rearrangement. Conditions: Liquid feed of 10 wt% cyclohexanone oxime in ethanol, WHSV of 0.4 hr⁻¹, 33.3 mL of He carrier gas, 1 h on stream.

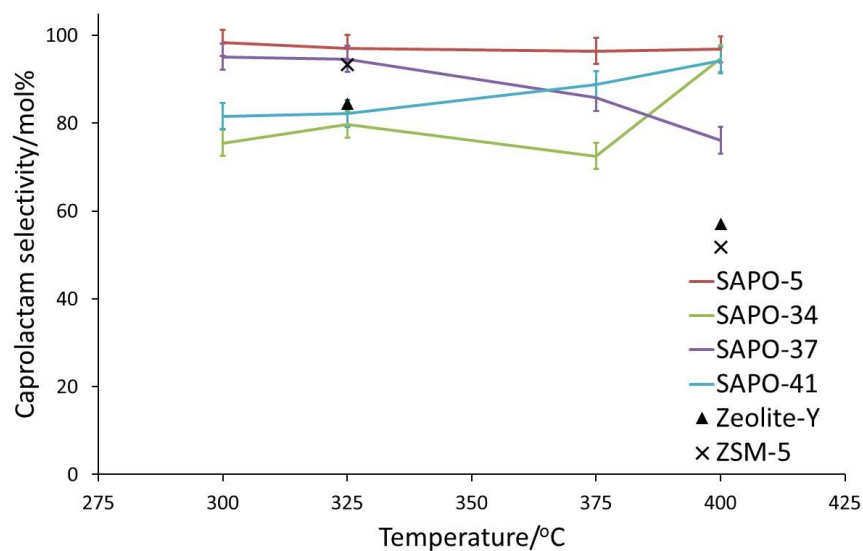


Figure S14: ϵ -Caprolactam selectivity for vapor-phase Beckmann rearrangement. Conditions: Liquid feed of 10 wt% cyclohexanone oxime in ethanol, WHSV of 0.4 hr⁻¹, 33.3 mL of He carrier gas, 1 h on stream.

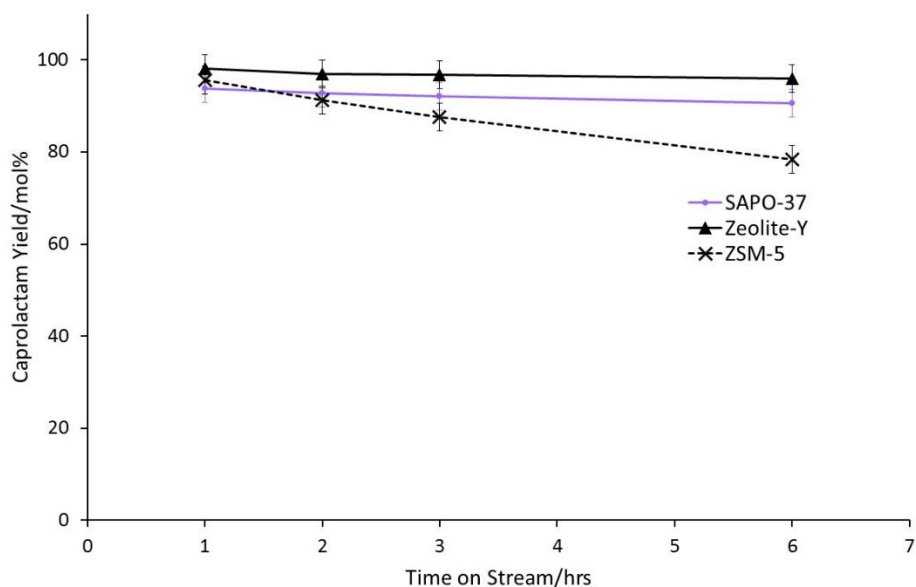


Figure S15: Time on stream data for SAPO-37, Zeolite-Y and ZSM-5 for the vapour-phase Beckmann rearrangement. Conditions: 325 °C, Liquid feed of 10 wt% cyclohexanone oxime in ethanol, WHSV of 0.4 hr⁻¹, 33.3 mL of He carrier gas.

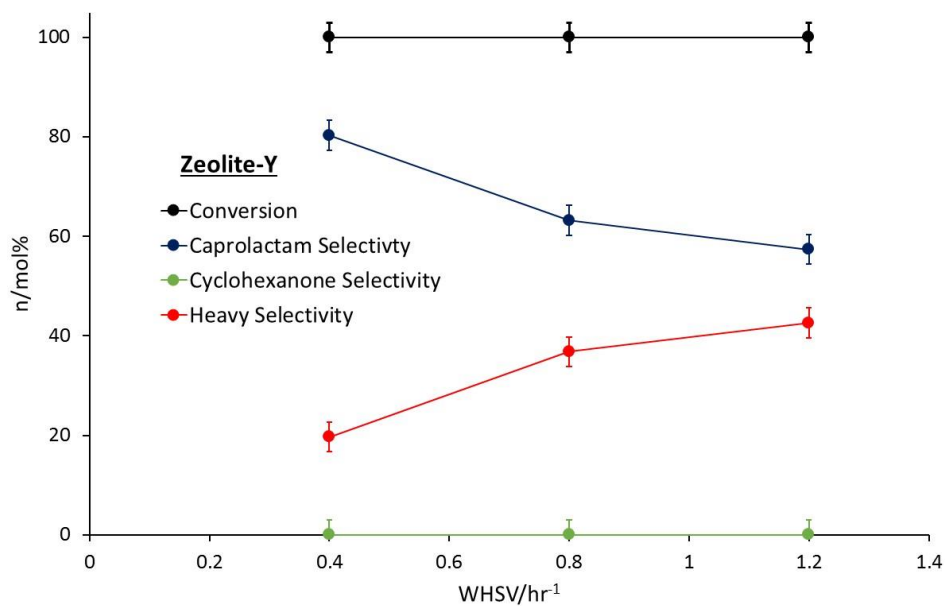


Figure S16: Showing the variation in WHSV for Zeolite-Y for the vapor-phase Beckmann rearrangement of cyclohexanone oxime. Conditions: 325 °C, Liquid feed of 10 wt% cyclohexanone oxime in ethanol, 33.3 mL of He carrier gas.

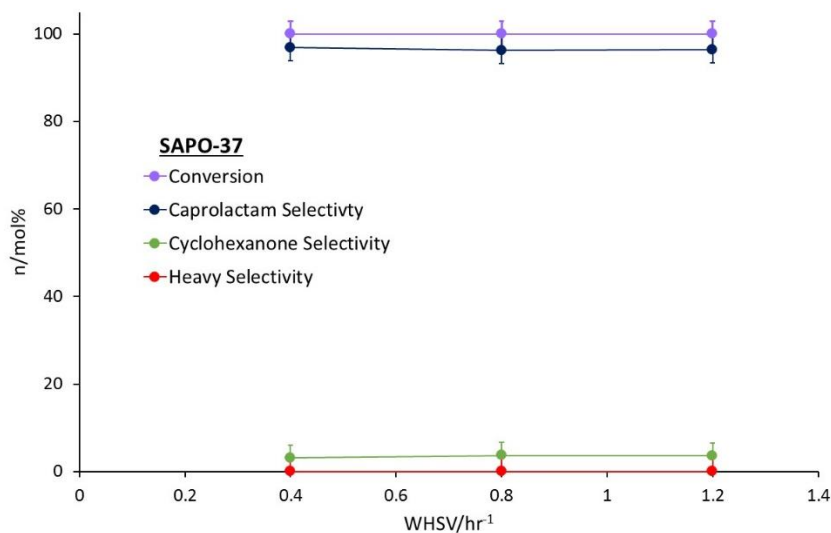


Figure S17: Showing the variation in WHSV for SAPO-37 for the vapor-phase Beckmann rearrangement of cyclohexanone oxime. Conditions: 325 °C, Liquid feed of 10 wt% cyclohexanone oxime in ethanol, 33.3 mL of He carrier gas.

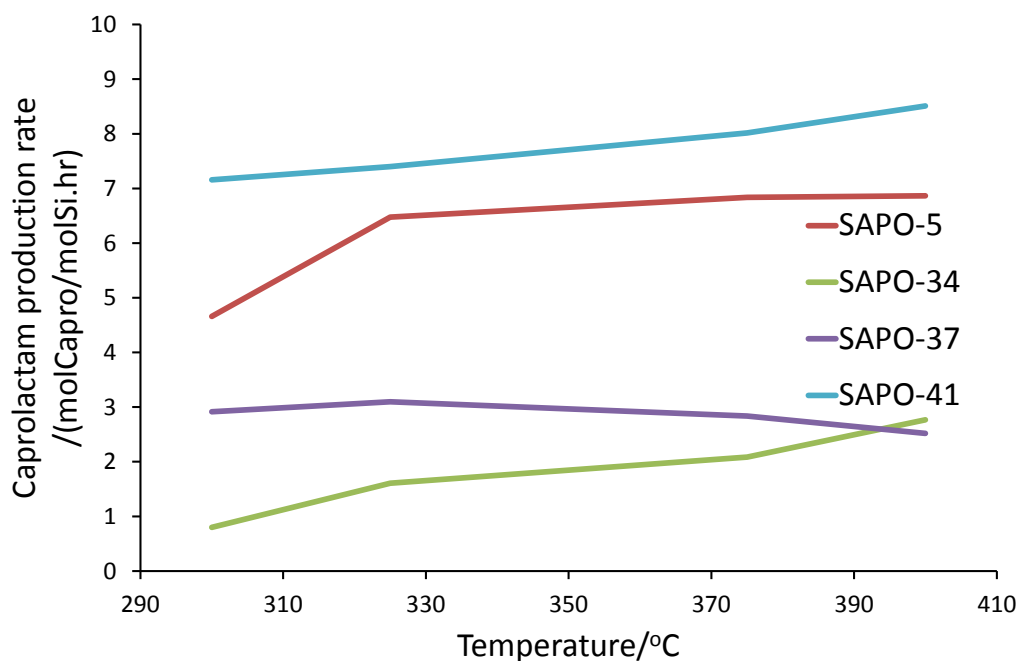


Figure S18: ϵ -Caprolactam production rates, per mole of silicon dopant, per hour for vapor-phase Beckmann rearrangement. Conditions: Liquid feed of 10 wt% cyclohexanone oxime in ethanol, WHSV of 0.4 hr⁻¹, 33.3 mL of He carrier gas, 1 h on stream.

Beckmann rearrangement mechanism

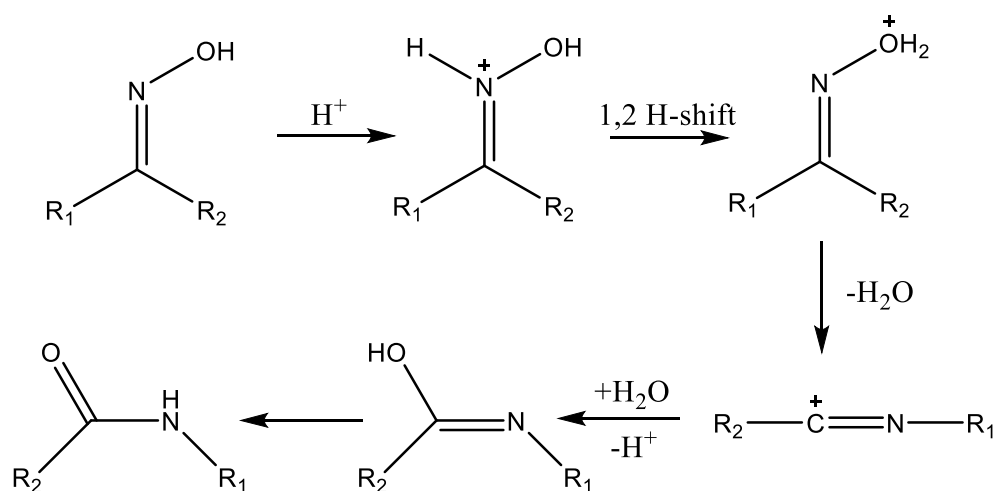


Figure S19: Acid-catalyzed Beckmann rearrangement mechanism.

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