

Supplementary Information

Synthesis and activation for catalysis of Fe-SAPO-34 prepared using iron polyamine complexes as structure directing agents

Alessandro Turrina,^{1,2,*} A. Iulian Dugulan,³ Jillian E. Collier,⁴ Richard I. Walton,⁵ John L. Casci² and Paul A. Wright^{1,*}

¹ EaStCHEM School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, KY16 9ST, United Kingdom.

² Johnson Matthey Technology Centre, Chilton P.O. Box 1, Belasis Avenue, Billingham, TS23 1LB, United Kingdom.

³ Fundamental Aspects of Materials and Energy Group, Delft University of Technology, 2629 JB Delft, The Netherlands.

⁴ Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, United Kingdom.

⁵ Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom.

* Corresponding Authors. E-mail: alessandro.turrina@matthey.com; paw2@st-andrews.ac.uk.

Table S1. Gel compositions and hydrothermal synthesis conditions used to prepare pure Fe-SAPO-34.

SDA	Iron source	P/Al	Si/Al	SDA/Al	Fe/Al	H ₂ O/Al	TBA ⁺ /Al	temp. (°C)	time (h)
DETA	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
HEEDA	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
TETA	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
232	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
323	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
TEPA	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
TEPA	Iron(III) chloride	0.62	0.25	0.27	0.1	40	-	220	24
PEHA	Iron(II) acetate	0.62	0.25	0.27	0.1	40	-	220	24
Morpholine	Iron(III) nitrate					40	-	190	14
TEA ⁺	Iron(II) acetate	0.8	0.2	0.2	0.1	40	0.11	190	96

(a) Al, P, Si in ratios correspond to Al(OH)₃, H₃PO₄, SiO₂**Table S2.** Crystallographic data for calcined and dehydrated Fe-SAPO-34.

Chemical composition	Al ₁₈ Si _{5.2} P _{12.8} O ₇₂
Data collection	
Wavelength / Å	1.54056
Diffraction geometry	Debye-Scherrer
Sample	Rotating 0.7 mm capillary
Refined region / 2θ°	2.0–70.0
Step size / 2θ°	0.01
Unit cell	
Chemical formula	Al ₁₈ Si _{5.4} P _{12.6} O ₇₂
Crystal system	trigonal
Space group	R3
<i>a</i> / Å	13.75197(30)
<i>b</i> / Å	13.75197(30)
<i>c</i> / Å	14.9742(7)
Volume / Å ³	2452.47(12)
Rietveld refinement	
Refined region / 2θ°	5.0–69.99
Excluded regions / 2θ°	21.16–21.62
Background	Chebyshev 16 terms
<i>R</i> _{wp}	0.0341
<i>R</i> _p	0.0267
<i>R</i> _F ²	0.066
<i>χ</i> ²	1.619

Table S3. Atomic coordinates and thermal parameters for calcined and dehydrated Fe-SAPO-34.

atom	x	y	z	occupancy	<i>U</i> _{iso}	multiplicity
Al1	0.2356(10)	0.2370(11)	0.0289(6)	1	0.0213(18)	9
Al2	0.7678(11)	0.7656(11)	0.8329(11)	1	0.0213(18)	9
O1	-0.0174(15)	0.2483(12)	-0.0551(9)	1	0.0223(33)	9
O2	0.1171(8)	0.2467(12)	0.0520(12)	1	0.0223(33)	9
O3	0.1877(9)	0.0968(10)	0.0566(12)	1	0.0223(33)	9
O4	0.3132(9)	0.0146(9)	0.1074(11)	1	0.0223(33)	9
O5	0.9852(15)	0.7280(11)	0.91775(11)	1	0.0223(33)	9
O6	0.8827(9)	0.7600(12)	0.7924(12)	1	0.0223(33)	9
O7	0.8037(11)	0.9063(11)	0.8187(12)	1	0.0223(33)	9
O8	0.6838(8)	0.9929(8)	0.7590(6)	1	0.0223(33)	9
P1	-0.0051(9)	0.2191(9)	0.0411(10)	0.7	0.0213(18)	9
P2	0.9947(9)	0.7709(10)	0.8221(6)	0.7	0.0213(18)	9
Si1	-0.0051(9)	0.2191(9)	0.0411(10)	0.3	0.0213(18)	9
Si2	0.9947(9)	0.7709(10)	0.8221(6)	0.3	0.0213(18)	9

Table S4. Selected bond lengths and angles for calcined and dehydrated Fe-SAPO-34.

bond length / Å		bond angle / °	
Al1-O	1.731(8)	O-Al1-O	109.4(8)
Al2-O	1.731(9)	O-Al2-O	109.4(8)
Al-O(Avg.)	1.731(9)	O-Al-O (Avg.)	109.4(8)
P1(Si1)-O	1.546(12)	O-P1(Si1)-O	109.5(9)
P2(Si2)-O	1.544(12)	O-P2(Si2)-O	109.4(9)
P(Si)-O(Avg.)	1.545(12)	O-P(Si)-O (Avg.)	109.5(9)
T-O(Avg.)	1.638(11)	O-T-O (Avg.)	109.5(9)

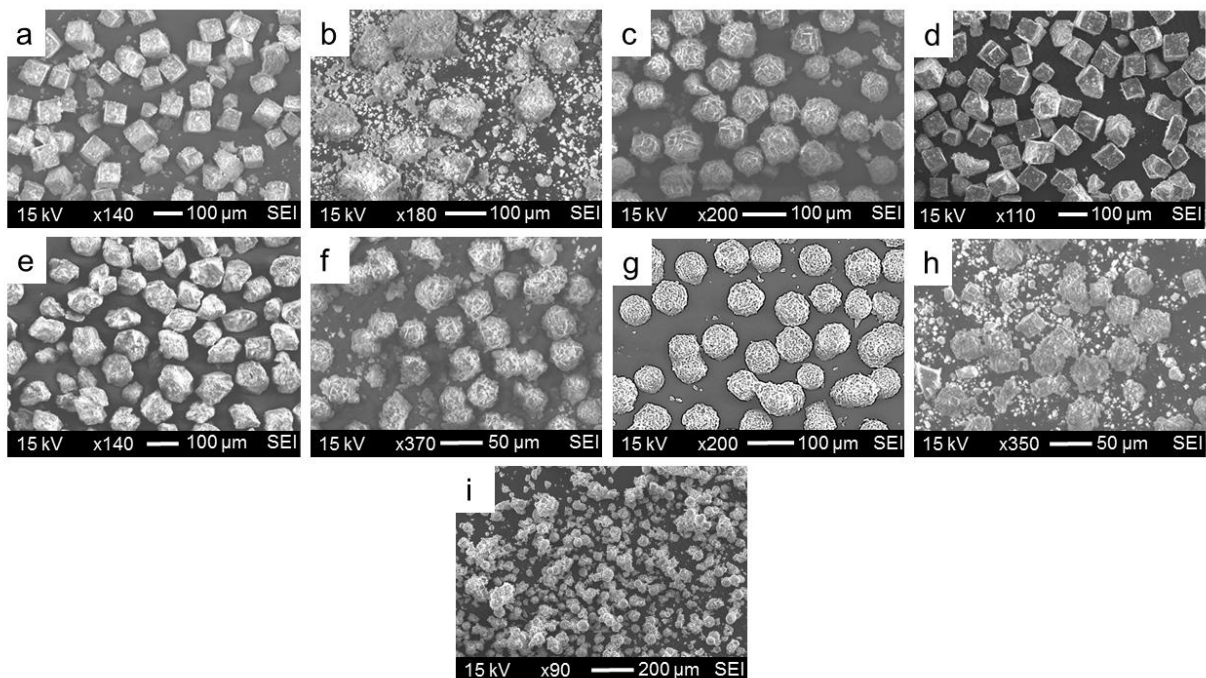


Figure S1. SEM images of of as-prepared Fe-SAPO-34 obtained using (a) DETA, (b) HEEDA, (c) TETA, (d) 232, (e) 323, (f) TEPA, (g) PEHA, (h) morpholine and (i) TEA⁺

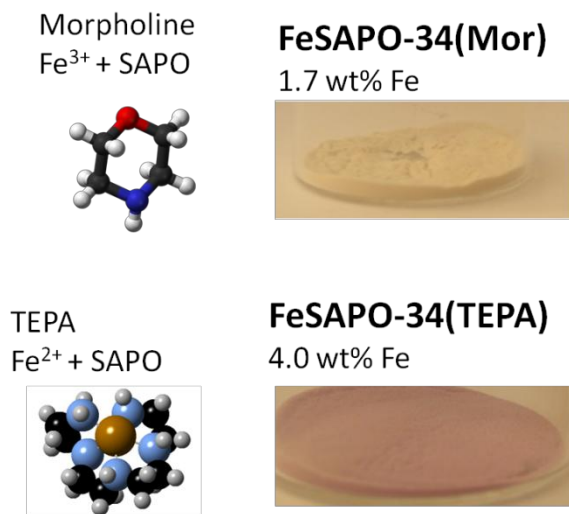


Figure S2. Comparison of colours of powders of Fe-SAPO-34 materials prepared (above) with morpholine and (below) with tetraethylenepentamine as organic additives.

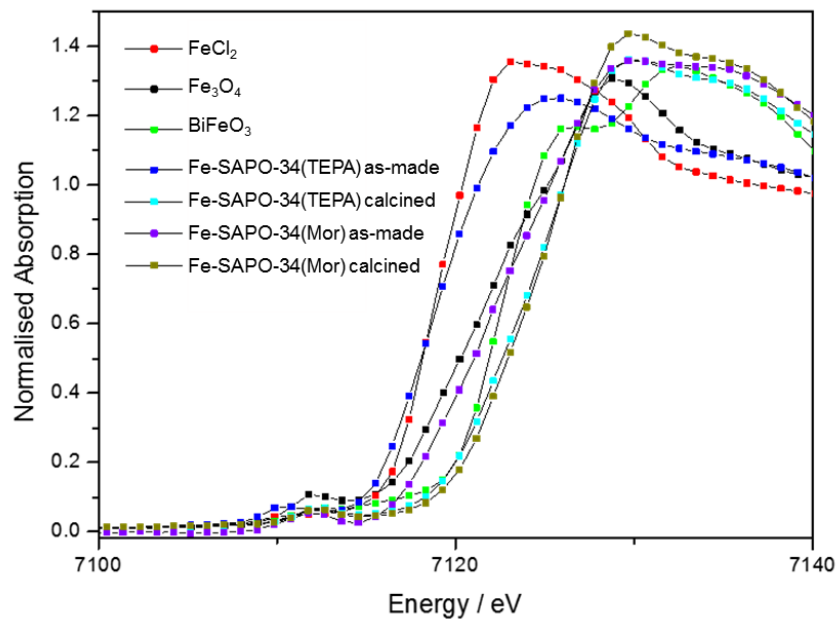


Figure S3. Fe K-edge XANES spectra recorded at room temperature of as-made and calcined Fe-SAPO-34(Mor) and Fe-SAPO-34(TEPA). Spectra from FeCl₂, Fe₂O₃ and BiFeO₃ were collected as references.

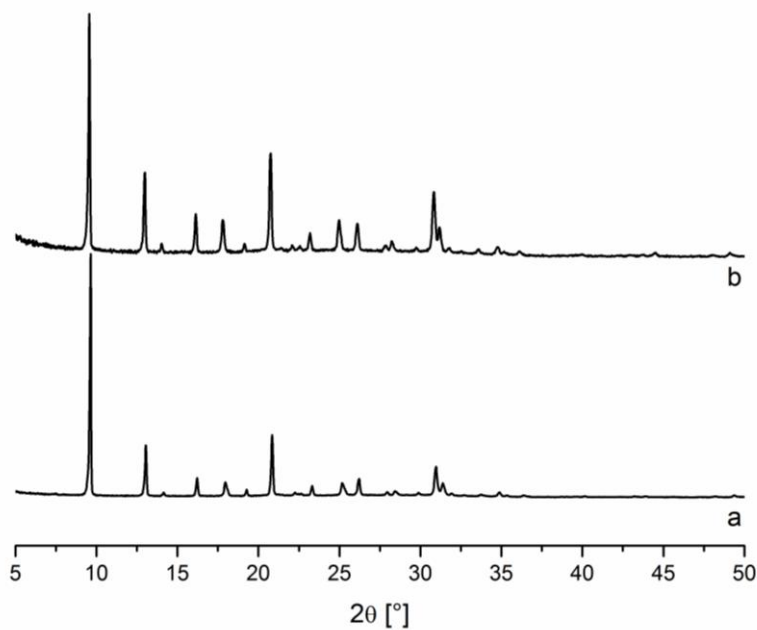


Figure S4. PXRD patterns of (a) calcined Fe-SAPO-34(Mor) and (b) calcined Fe-SAPO-34(TEPA).

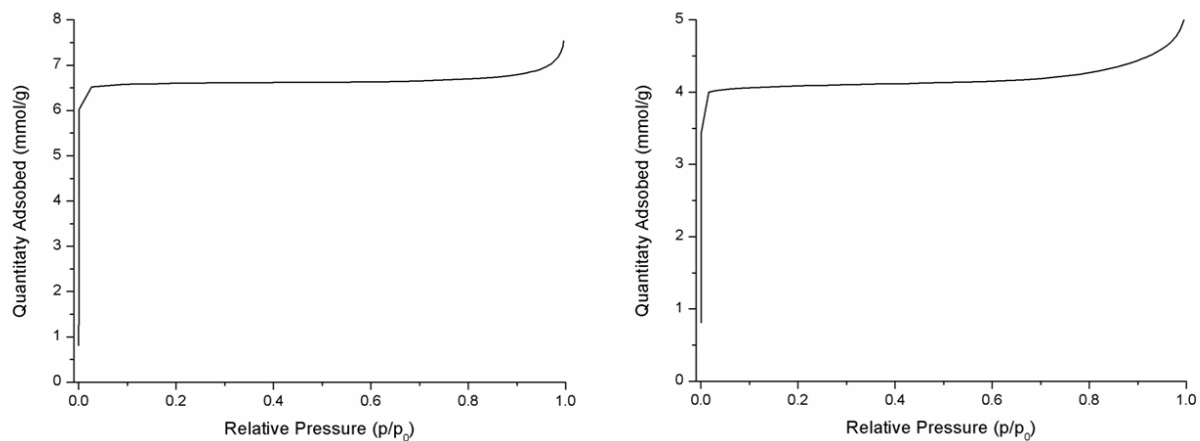


Figure S5. Isotherms for the adsorption of N_2 at 77 K on calcined Fe-SAPO-34(Mor) (left) and Fe-SAPO-34(TEPA) (right).

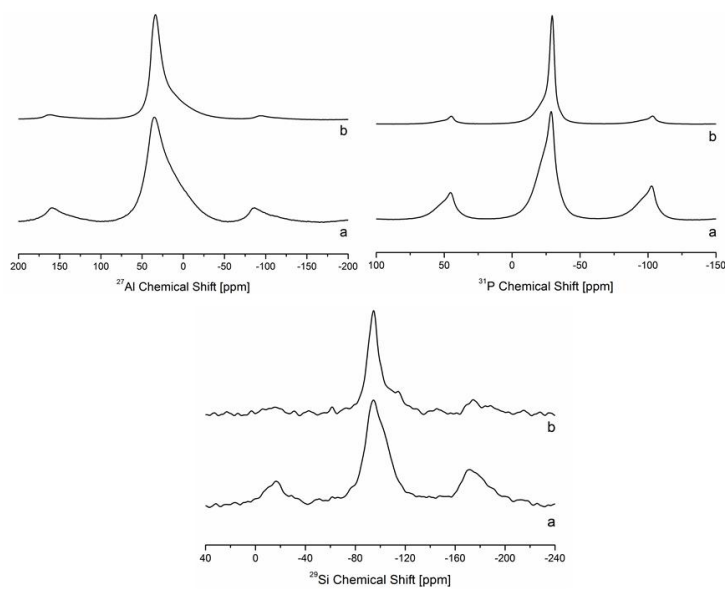


Figure S6. Solid-state MAS NMR spectra for (a) dehydrated calcined Fe-SAPO-34(TEPA) and (b) dehydrated calcined Fe-SAPO-34(Mor). Above left, ^{27}Al ; above right, ^{31}P ; below, ^{29}Si .

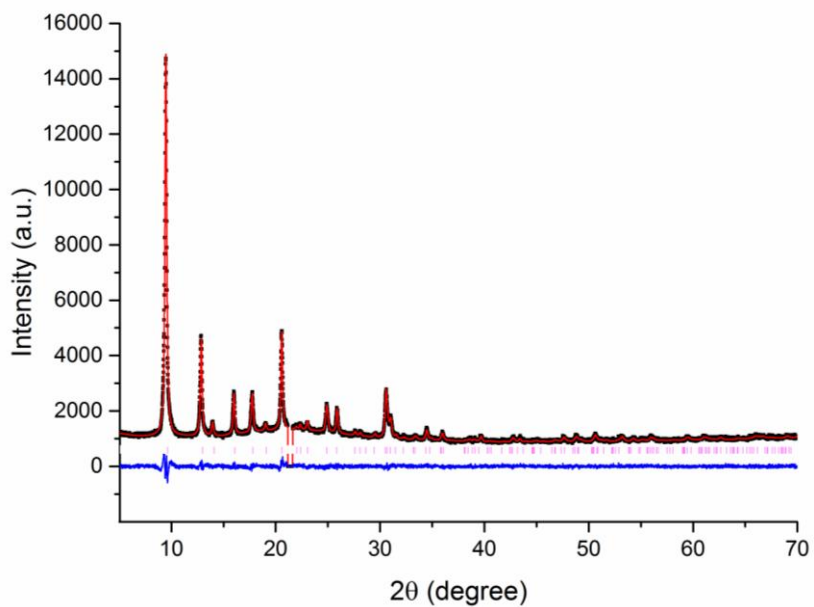


Figure S7. Rietveld refinement for calcined, dehydrated Fe-SAPO-34, against PXRD lab data ($\lambda = 1.54056 \text{ \AA}$). Space group $R3$, $a = 13.75197(30) \text{ \AA}$, $c = 14.9742(7) \text{ \AA}$, $R_{wp} = 3.41 \%$. Black squares = experimental data, red line = simulated data, magenta tick marks = predicted peak positions, blue line = difference profile.