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. Casci[2] 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_2O/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) clhoride	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 $Al(OH)_3$, H_3PO_4, SiO_2

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
Diffractometer 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	*R*3
a / Å	13.75197(30)
b / Å	13.75197(30)
c / 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	Chebyschev 16 terms
R_{wp}	0.0341
R_p	0.0267
R_F^2	0.066
X^2	1.619

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

atom	*x*	*y*	*z*	occupancy	*Uiso*	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)

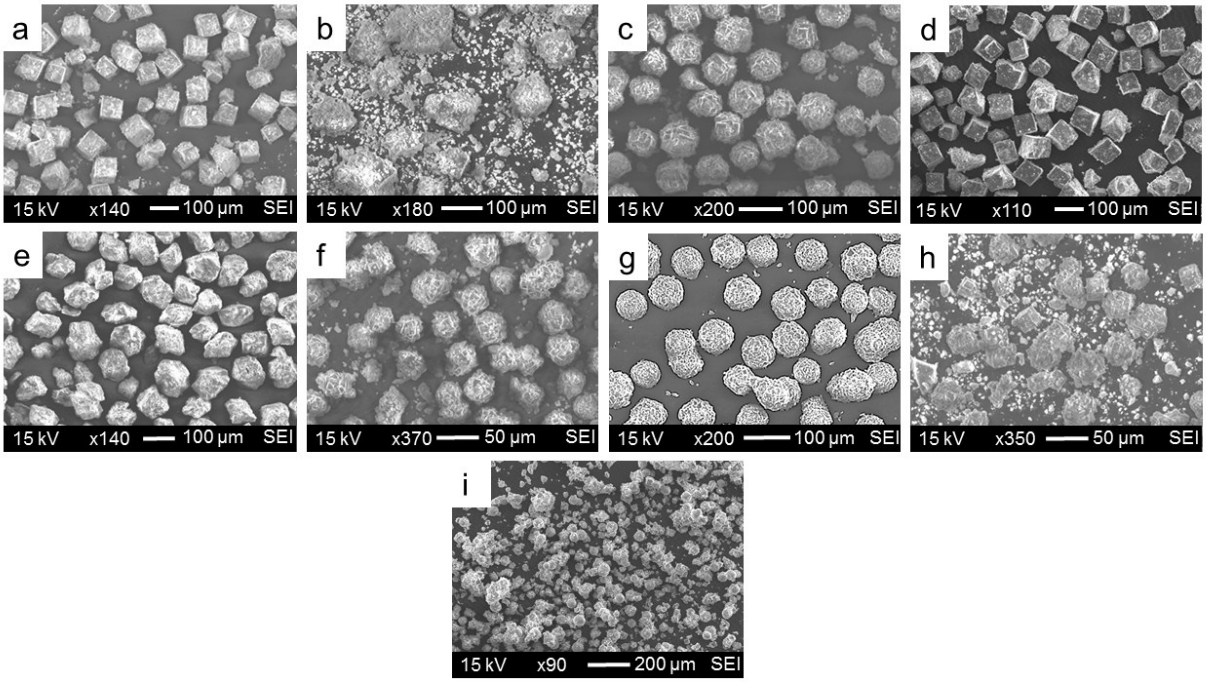

Figure S1. SEM images of of as-prepared Fe-SAPO-34 obtained using (a) DETA, (b) HEEDA, (c) TETA, (d) 232, (e) 323, (f) TEPA, (g) PEHA, (h) morpholine and (i) TEA^{+}

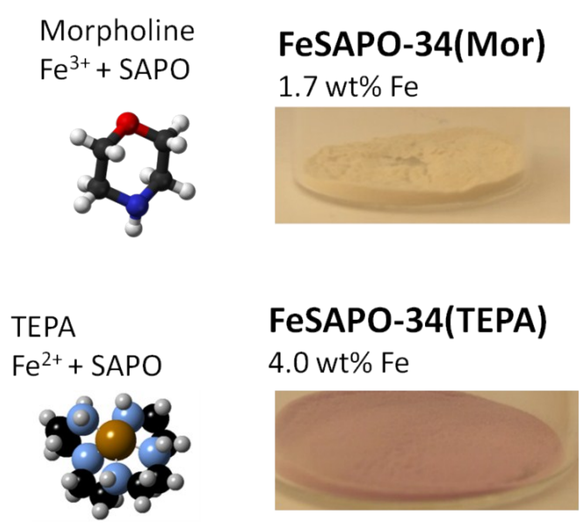

Figure S2. Comparison of colours of powders of Fe-SAPO-34 materials prepared (above) with morpholine and (below) with tetraethylenepentamine as organic additives.

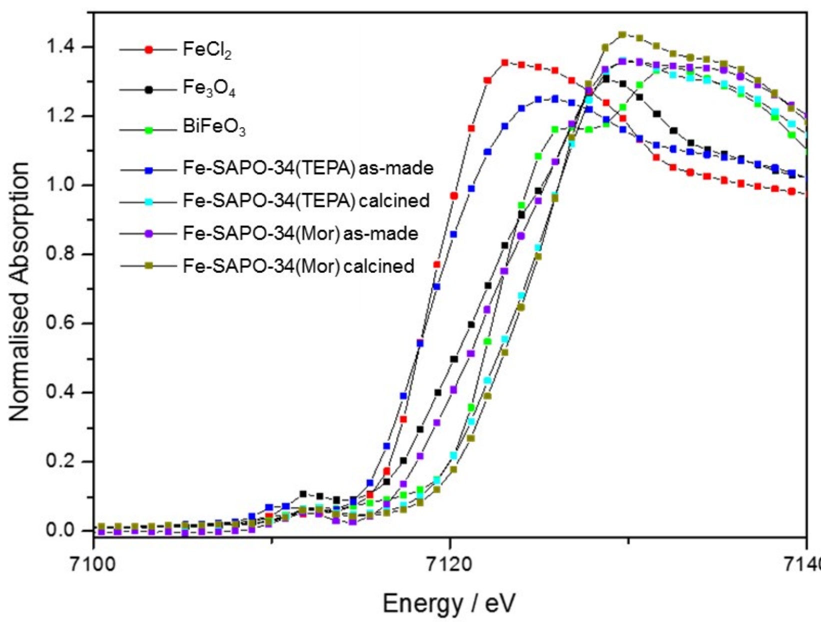

Figure S3. Fe K-edge XANES spectra recorded at room temperature of as-made and calcined Fe-SAPO-34(Mor) and Fe-SAPO-34(TEPA). Spectra from $FeCl_2$, Fe_2O_3 and $BiFeO_3$ were collected as references.

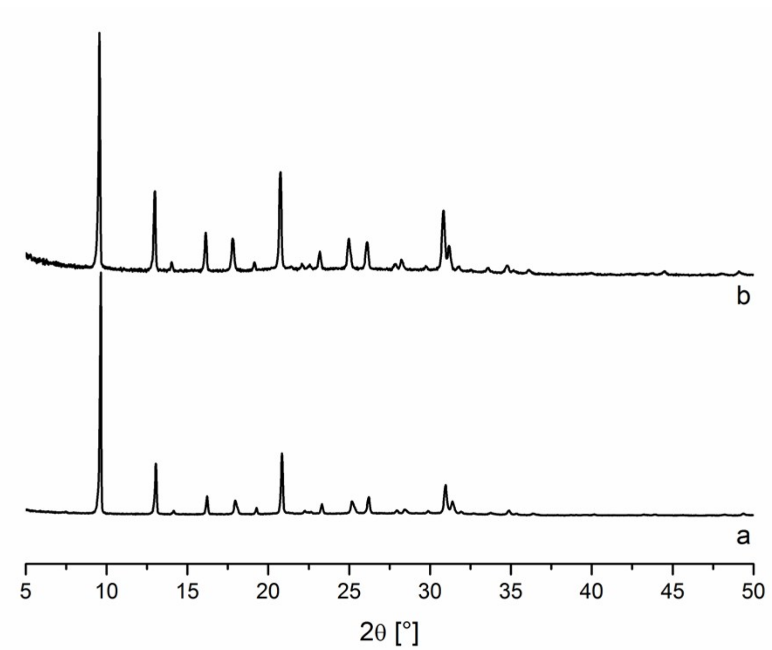

Figure S4. PXRD patterns of (a) calcined Fe-SAPO-34(Mor) and (b) calcined Fe-SAPO-34(TEPA).

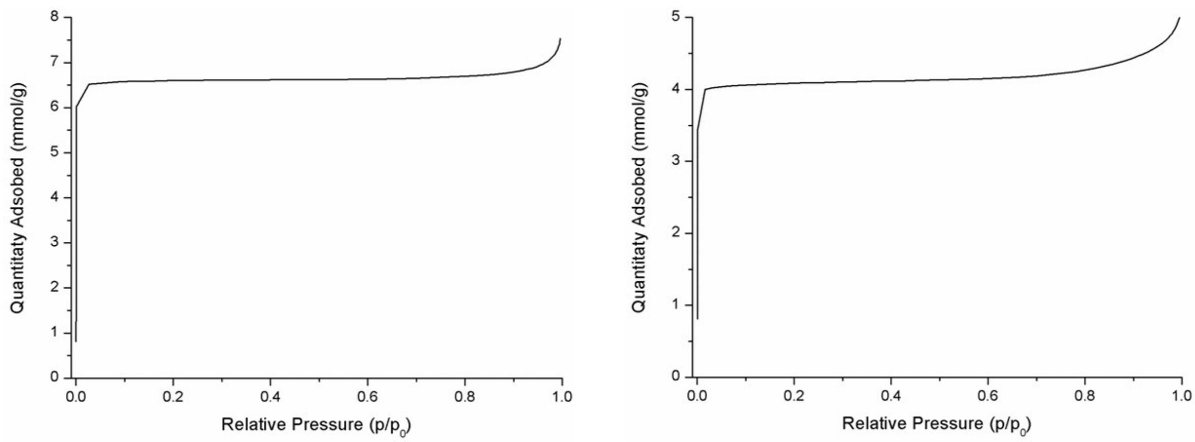

Figure S5. Isotherms for the adsorption of N_2 at 77 K on calcined Fe-SAPO-34(Mor) (left) and Fe-SAPO-34(TEPA) (right).

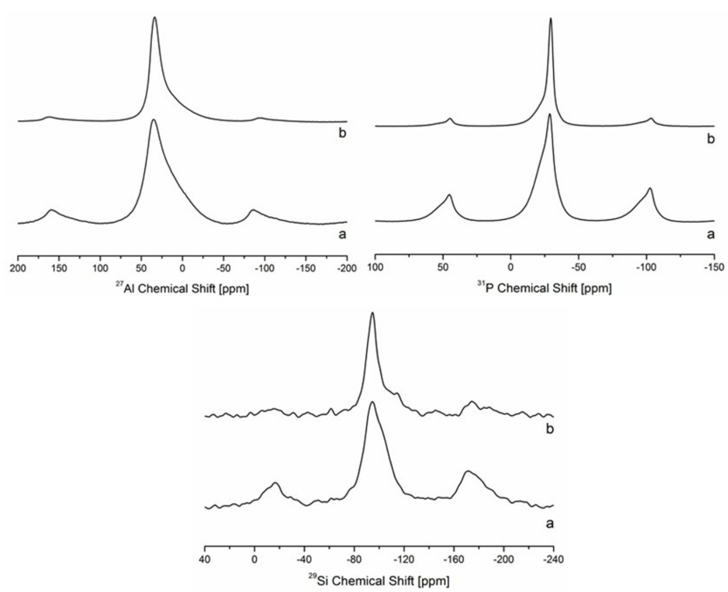

Figure S6. Solid-state MAS NMR spectra for (a) dehydrated calcined Fe-SAPO-34(TEPA) and (b) dehydrated calcined Fe-SAPO-34(Mor). Above left, ^{27}Al; above right, ^{31}P; below, ^{29}Si.

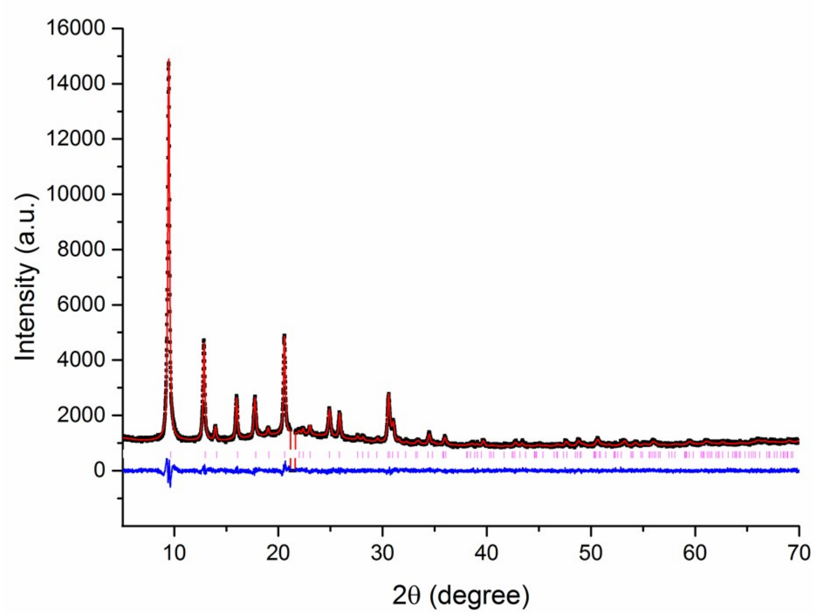

Figure S7. Rietveld refinement for calcined, dehydrated Fe-SAPO-34, against PXRD lab data (λ = 1.54056 Å). Space group *R*3, *a* = 13.75197(30) Å, c = 14.9742(7) Å, R_{wp} = 3.41 %. Black squares = experimental data, red line = simulated data, magenta tick marks = predicted peak positions, blue line = difference profile.