

SUPPORTING INFORMATION

A HYSORE Investigation of Bimetallic Titanium – Vanadium Microporous Catalysts: Elucidating the Nature of the Active Sites.

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SI1: Synthesis of Catalysts

Materials Specification

Aluminum hydroxide ($\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) and phosphoric acid (85wt% aqueous solution, Sigma Aldrich) were used as the respective aluminium and phosphorus precursors. Vanadium(IV) oxide sulfate hydrate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) and titanium isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, Sigma Aldrich) were used as the metal sources. The specific structure directing agent for AFI frameworks - N,N-dicyclohexylmethylamine (Sigma Aldrich) was used.¹

Typical Synthesis for “M₁M₂” AIPO-5

0.0980 mols (9.601g, Aldrich) of H_3PO_4 was added to 10ml of deionised water and allowed to stir by magnetic stirrer in a PTFE beaker. 4.071g (0.0522mol, Aldrich) of $\text{Al}(\text{OH})_3$ was added slowly and was left stirring for 30minutes with the addition of a further 10ml of water.

Metal precursors were added dropwise, and in the case of the bimetallic AIPO-5's also simultaneously, these two solutions were added slowly to the main reaction mixture. The reaction mixture was left stirring for 30minutes (opaque solution).

N-methyldicyclohexylamine (0.044mol, 8.682g, Aldrich) was added slowly with the remaining 18ml of water. This gel (viscous solution) was left stirring for 60 minutes (~1000rpm) to fully homogenise.

The reaction mixture was divided between Teflon-lined autoclaves (capacity 40ml), sealed and heated for 2hours at 453 K. The autoclaves were immediately quenched in cold water, the product was filtered and washed with water and dried in the oven (343 K). Phase purity was confirmed by powder X-ray diffraction.

Calcination was carried out at 848 K for 16 hours in a tube furnace with a flow of air using a temperature ramp of 5 degrees per minute. The resulting calcined aluminophosphate was checked again for phase purity and stored in a desiccator to minimise the reduction of the active sites through water adsorption, before use in catalysis. Confirmation of the structural integrity after the reduction treatment was checked by powder X-ray diffraction and the patterns and cell parameters compared to the calcined samples (see figures and tables below in SI2).

For EPR experiments calcined samples were dehydrated in vacuum by gradually raising the temperature to 390 K over a period of 2h and kept at that temperature for 1h. The dehydrated samples were then treated with 200 mbar of H_2 at 673 K for 2h, followed by evacuation at this temperature.

Table of specific gel compositions

Table SI 1.1. Gel Compositions of AlPO-5 series.

Catalyst	Gel Composition	ICP experimental metal loading /wt%
VTiAlPO-5	0.485Al₂O₃:0.75P₂O₅:0.015V₂O₅:0.03TiO₂:0.8R:50H₂O (0.97Al:1.5P:0.03V:0.03Ti:0.8R:50H ₂ O)	0.84 (V) 0.99 (Ti)
VAIPO-5	0.48Al₂O₃:0.75P₂O₅:0.02V₂O₅:0.8R:50H₂O (0.96Al:1.5P:0.04V:0.8R:50H ₂ O)	0.96
TiAlPO-5	0.48Al₂O₃:0.75P₂O₅:0.03TiO₂:0.8R:50H₂O (0.96Al:1.5P:0.04Ti:0.8R:50H ₂ O)	1.34

“R” denotes the structure directing agent Methylidicyclohexylamine¹

SI2: Powder XRD and cell parameter refinement values

All powder X-ray diffraction patterns were taken using a Siemens D5000 Powder X-Ray Diffraction Diffraktometer Kristalloflex, using a scan rate of 4 degrees per minute and an increment of 0.02 degrees. The data were collected over a minimum period of 5 hours with the final pattern displayed as accumulation of the repeat scans.

Cell parameter values were refined using the CellRef program with starting values and space groups as quoted in the “Collection of Simulated XRD powder patterns for zeolites”² and “Atlas of Zeolites framework types”³ handbooks.

The six patterns below show that the VTiAlPO-5, VAiPO-5 and TiAlPO-5 samples are phase pure for the AFI framework and maintain structural integrity upon treatment in the reducing hydrogen atmosphere.

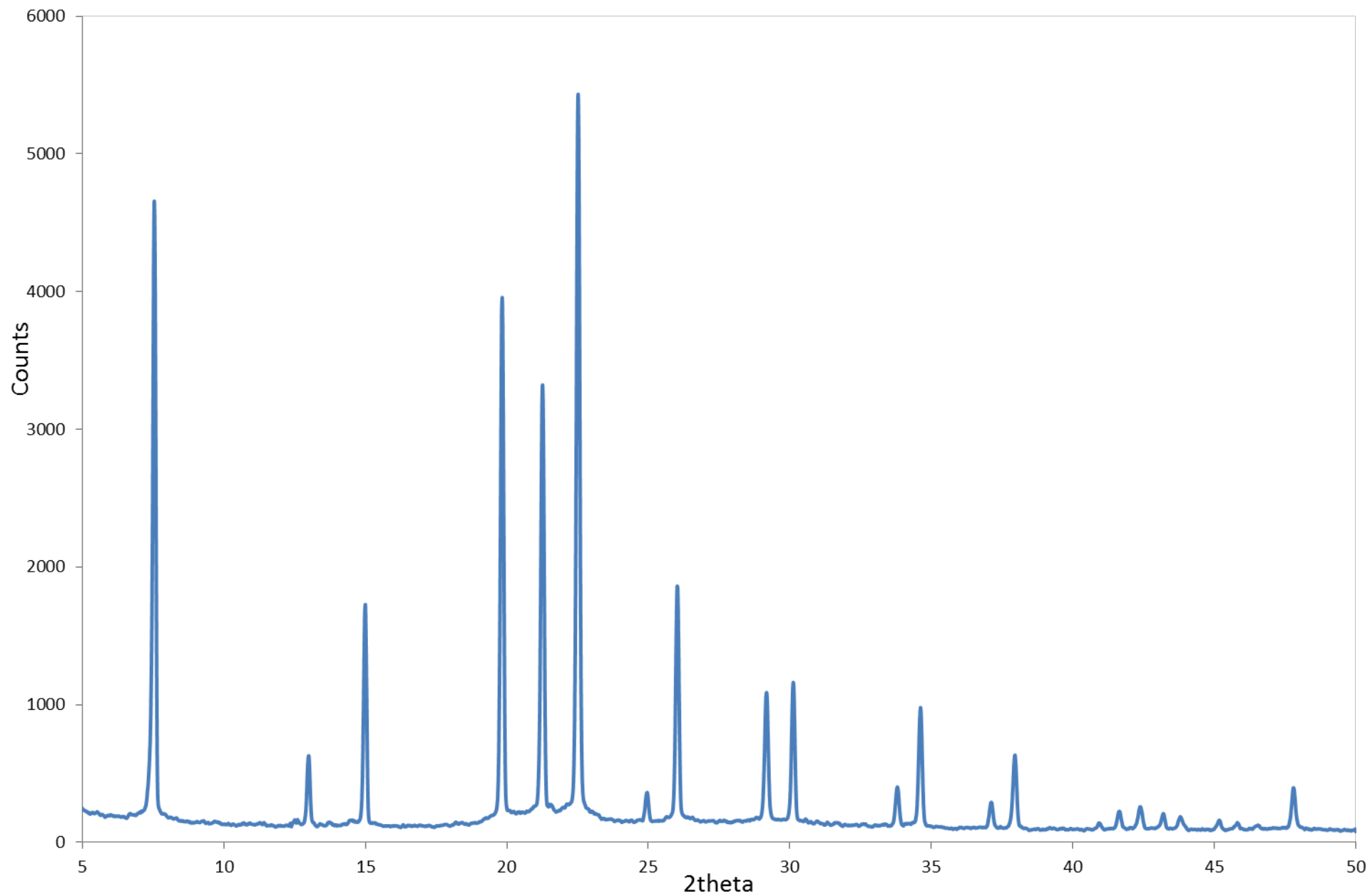


Figure SI 2.1: Calcined Powder X-ray Diffraction Pattern for VTiAlPO-5

Table SI 2.2: CellRef refinement values for calcined VTiAlPO-5.

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.675	13.675	8.4881	90	90	120	1374.7
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.6752	13.6752	8.4556	90	90	120	1369.4
0	0	0.0634	0	0.0043	0	0	0	

				2T-			
H	K	L	2T(Obs)	Zero	2Th(Cal)	Dif	
0	1	0	7.51	7.51	7.4644	0.0456	
1	1	0	13.0457	13.0457	12.9471	0.0986	
0	2	0	15.01	15.01	14.9607	0.0493	
1	2	0	19.8761	19.8761	19.8338	0.0423	
0	0	2	21.3046	21.3046	21.0121	0.2925	
1	2	1	22.51	22.51	22.4734	0.0366	
1	1	2	24.9207	24.9207	24.7584	0.1623	
2	2	0	26.0368	26.0368	26.0632	-0.0264	
1	2	2	29.1618	29.1618	29.0513	0.1105	
0	4	0	30.1886	30.1886	30.1842	0.0044	
2	2	2	33.76	33.76	33.7144	0.0456	
2	3	1	34.6529	34.6529	34.6776	-0.0247	
0	4	2	37.1082	37.1082	37.0683	0.0399	
0	5	0	38.0011	38.0011	37.9875	0.0136	
2	4	1	41.6618	41.6618	41.7464	-0.0846	
1	5	0	42.3761	42.3761	42.498	-0.1219	
0	1	4	43.2243	43.2243	43.4859	-0.2616	
1	5	2	47.8671	47.8671	47.8708	-0.0037	

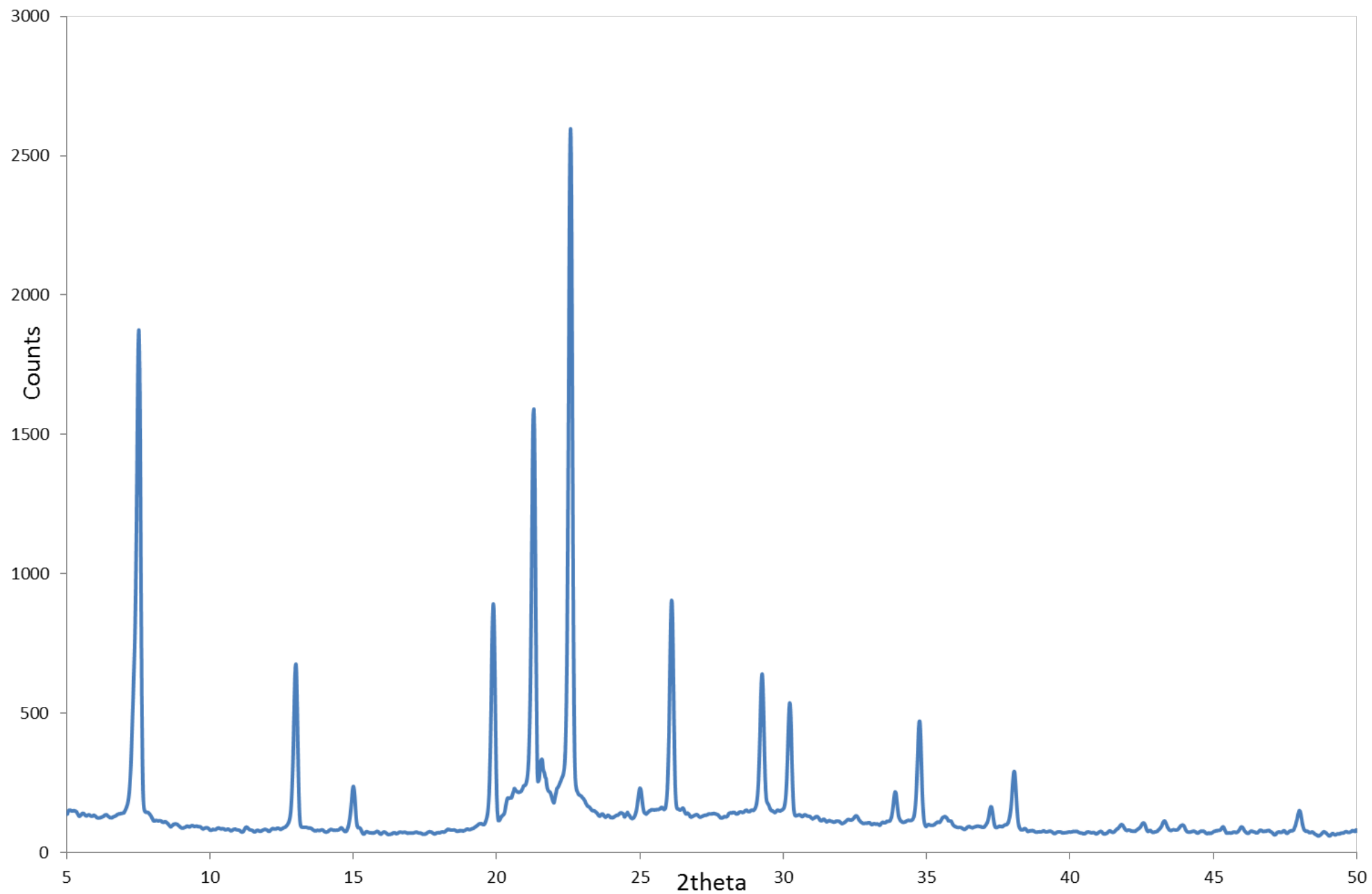


Figure SI 2.2: Reduced Powder X-ray Diffraction Pattern for VTiAlPO-5

Table SI 2.3: CellRef refinement values for reduced VTiAlPO-5.

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.6493	13.6493	8.3469	90	90	120	1346.7
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.6496	13.6496	8.3469	90	90	120	1346.8
0	0	0.0282	0	0.0018	0	0	0	

H	K	L	2T(Obs)	2T-Zero	2Th(Cal)	Dif
0	1	0	7.5446	7.5446	7.4784	0.0662
1	1	0	12.9911	12.9911	12.9715	0.0196
0	2	0	15.0446	15.0446	14.9889	0.0557
1	2	0	19.9107	19.9107	19.8714	0.0393
0	0	2	21.3393	21.3393	21.289	0.0503
1	2	1	22.5446	22.5446	22.5648	-0.0202
1	1	2	24.9554	24.9554	25.0088	-0.0534
2	2	0	26.1161	26.1161	26.1129	0.0032
1	3	1	29.3304	29.3304	29.2657	0.0647
0	4	0	30.2232	30.2232	30.2422	-0.019
2	2	2	33.9286	33.9286	33.9332	-0.0046
1	4	0	34.7321	34.7321	34.7774	-0.0453
0	4	2	37.3214	37.3214	37.2819	0.0395
1	2	3	38.0357	38.0357	38.0614	-0.0257
1	5	0	42.6786	42.6786	42.5816	0.097
0	0	4	43.3482	43.3482	43.361	-0.0128
1	5	1	43.9286	43.9286	44.007	-0.0784
2	5	0	48.0357	48.0357	48.0666	-0.0309

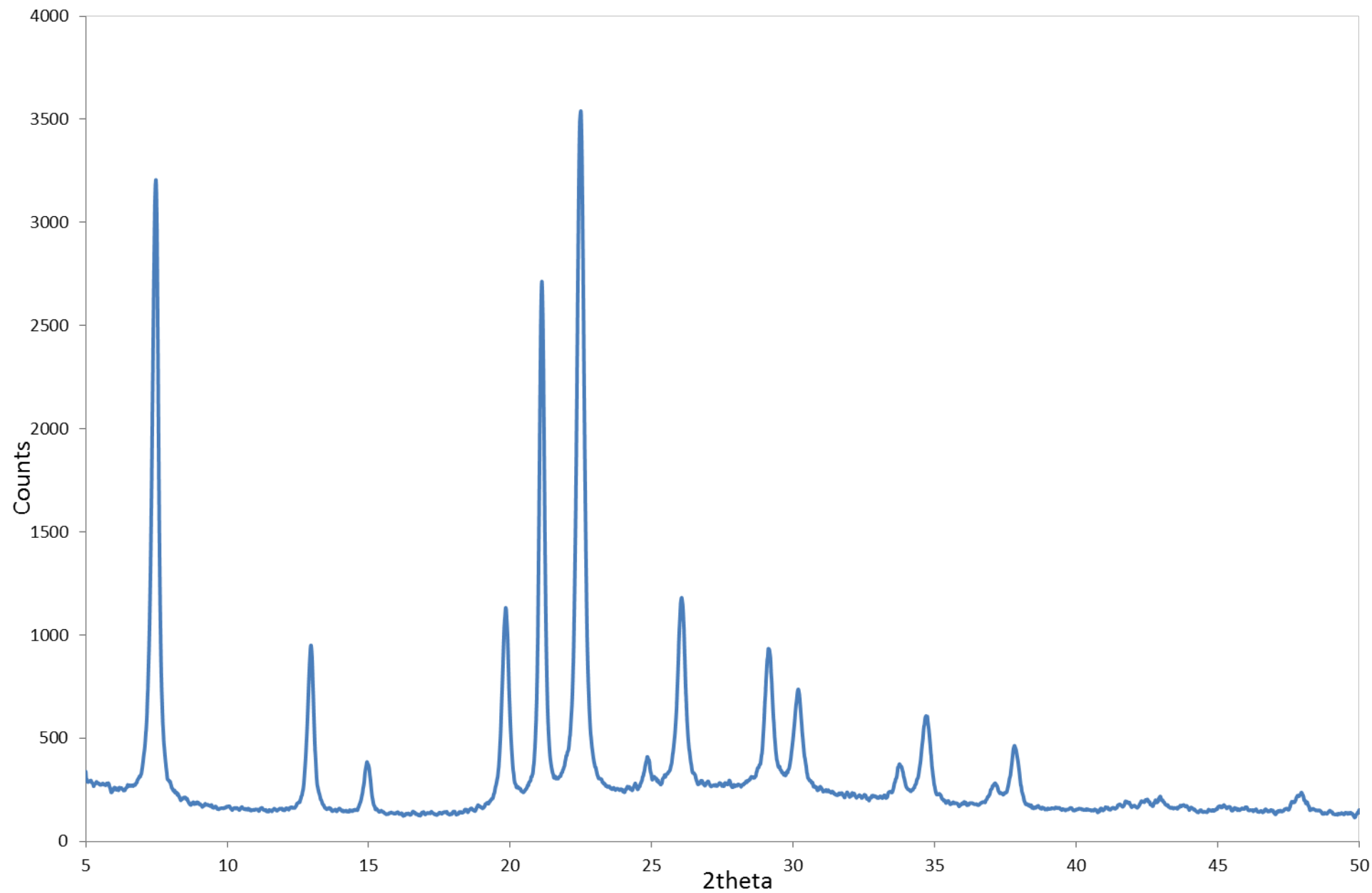


Figure SI 2.3: Calcined Powder X-ray Diffraction Pattern for TiAlPO-5

Table SI 2.4: CellRef refinement values for calcined TiAlPO-5:

	0	1.5418	13.6704	13.6704	8.4134	90	90	120	1361.7
	0	0	1	0	1	0	0	0	
Final values : (Standard errors on 2nd line)									
Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.	
0	1.5418	13.6707	13.6707	8.4134	90	90	120	1361.7	
0	0	0.0074	0	0.0006	0	0	0		
H	K	L	2T(Obs)	2T-	Zero	2Th(Cal)	Dif		
0	1	0	7.4764	7.4764	7.4668	0.0096			
1	1	0	12.9643	12.9643	12.9514	0.0129			
0	2	0	14.9667	14.9667	14.9656	0.0011			
1	2	0	19.8487	19.8487	19.8404	0.0083			
0	0	2	21.1296	21.1296	21.1188	0.0108			
1	2	1	22.4968	22.4968	22.5044	-0.0076			
1	1	2	24.8551	24.8551	24.852	0.0031			
2	2	0	26.068	26.068	26.072	-0.004			
1	2	2	29.1476	29.1476	29.1347	0.0129			
0	4	0	30.1843	30.1843	30.1944	-0.0101			
2	2	2	33.7876	33.7876	33.7903	-0.0027			
1	4	0	34.7188	34.7188	34.7221	-0.0033			
0	4	2	37.1176	37.1176	37.1403	-0.0227			
1	2	3	37.8572	37.8572	37.8592	-0.002			

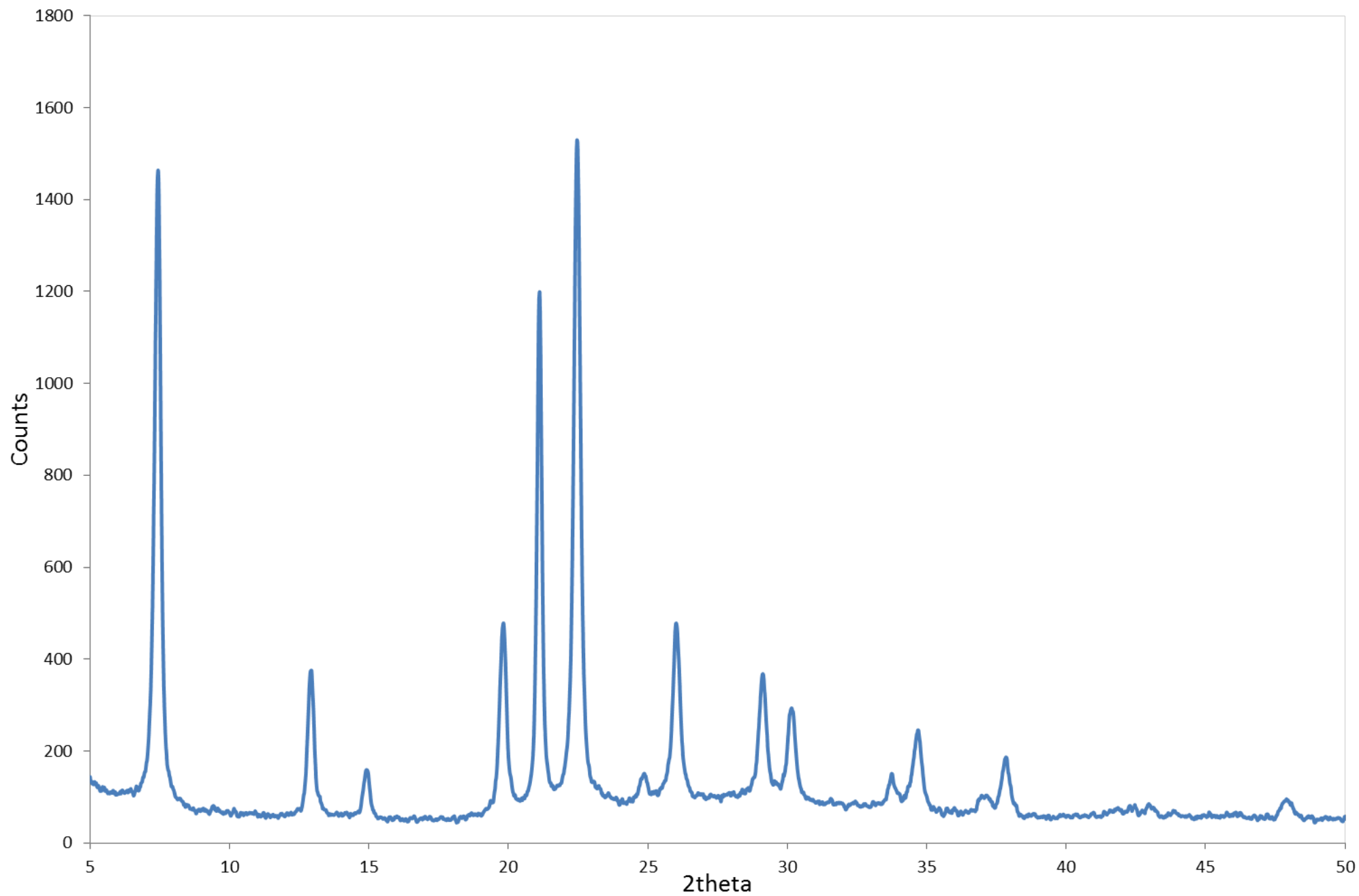


Figure SI 2.4: Reduced Powder X-ray Diffraction Pattern for TiAlPO-5

Table SI 2.5: CellRef refinement values for reduced TiAlPO-5:

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.7069	13.7069	8.3865	90	90	120	1364.5
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.6946	13.6946	8.405	90	90	120	1365.1
0	0	0.0298	0	0.0039	0	0	0	

2T-							
H	K	L	2T(Obs)	Zero	2Th(Cal)	Dif	
0	1	0	7.4554	7.4554	7.4538	0.0016	
1	1	0	12.9018	12.9018	12.9287	-0.0269	
0	2	0	14.9107	14.9107	14.9394	-0.0287	
1	2	0	19.8214	19.8214	19.8054	0.016	
0	0	2	21.1607	21.1607	21.1402	0.0205	
2	1	1	22.5	22.5	22.4444	0.0556	
1	1	2	24.8661	24.8661	24.8583	0.0078	
2	2	0	26.0714	26.0714	26.0257	0.0457	
1	3	1	29.1518	29.1518	29.1529	-0.0011	
0	4	0	30.1339	30.1339	30.1405	-0.0066	
2	2	2	33.75	33.75	33.7677	-0.0177	
1	4	0	34.7321	34.7321	34.6595	0.0726	
0	4	2	37.0536	37.0536	37.1082	-0.0546	
1	2	3	37.8125	37.8125	37.9316	-0.1191	
2	5	0	47.9464	47.9464	47.8988	0.0476	

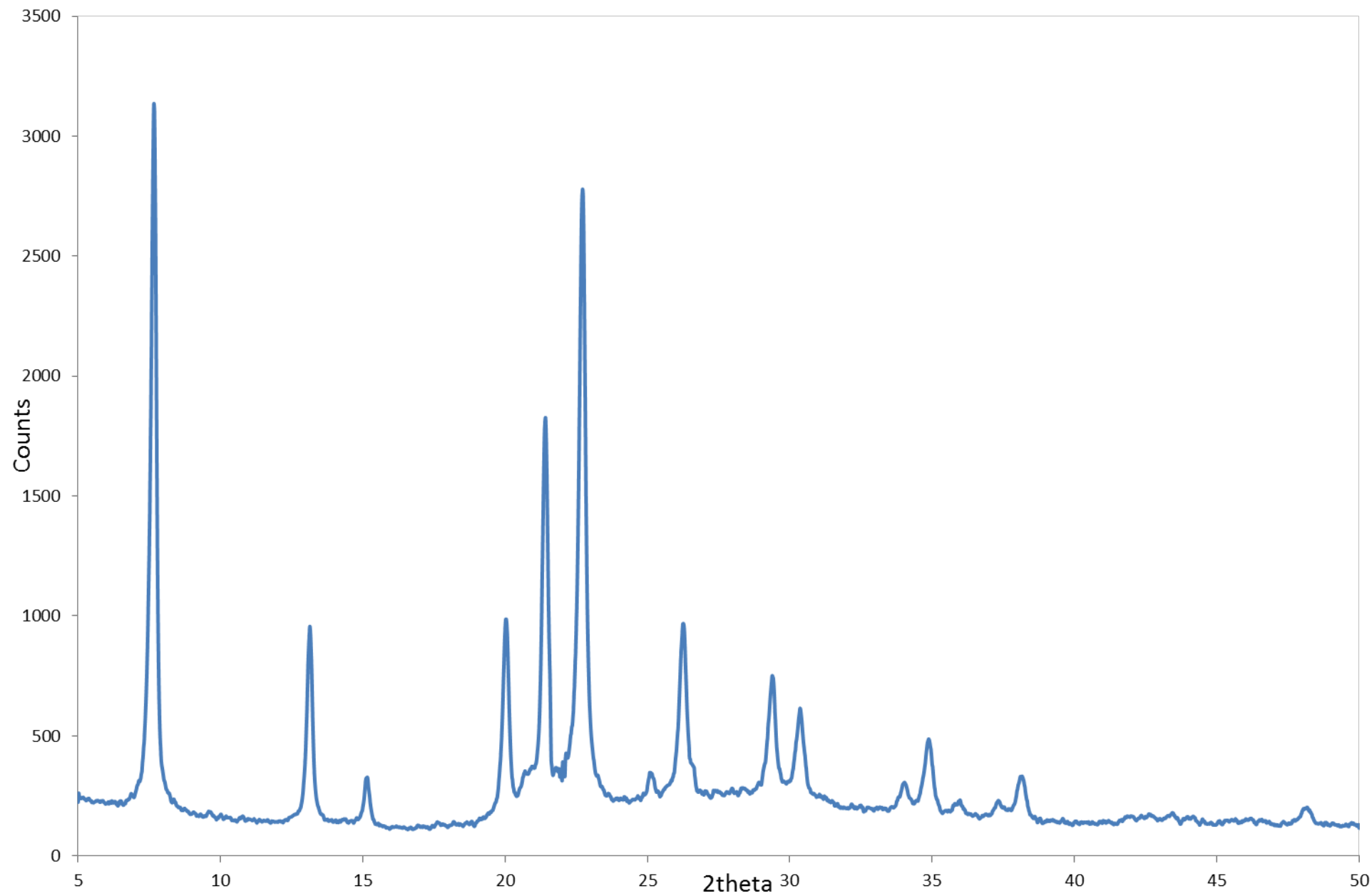


Figure SI 2.5: Calcined Powder X-ray Diffraction Pattern for VAlPO-5

Table SI 2.6: CellRef refinement values for calcined VAIPO-5:

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.5634	13.5634	8.338	90	90	120	1328.4
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.5652	13.5652	8.3404	90	90	120	1329.2
0	0	0.0499	0	0.0023	0	0	0	

				2T-			
H	K	L	2T(Obs)	Zero	2Th(Cal)	Dif	
0	1	0	7.5893	7.5893	7.525	0.0643	
1	1	0	13.1696	13.1696	13.0525	0.1171	
0	2	0	15.1786	15.1786	15.0827	0.0959	
1	2	0	20.0446	20.0446	19.9963	0.0483	
0	0	2	21.3839	21.3839	21.3057	0.0782	
1	2	1	22.6786	22.6786	22.6865	-0.0079	
1	1	2	25.1786	25.1786	25.0663	0.1123	
2	2	0	26.2946	26.2946	26.2783	0.0163	
1	2	2	29.375	29.375	29.3818	-0.0068	
0	4	0	30.3571	30.3571	30.4349	-0.0778	
2	2	2	34.0179	34.0179	34.0746	-0.0567	
1	3	2	34.9107	34.9107	34.9455	-0.0348	
0	4	2	37.4107	37.4107	37.4522	-0.0415	
1	2	3	38.125	38.125	38.1925	-0.0675	
1	2	4	48.2589	48.2589	48.2152	0.0437	

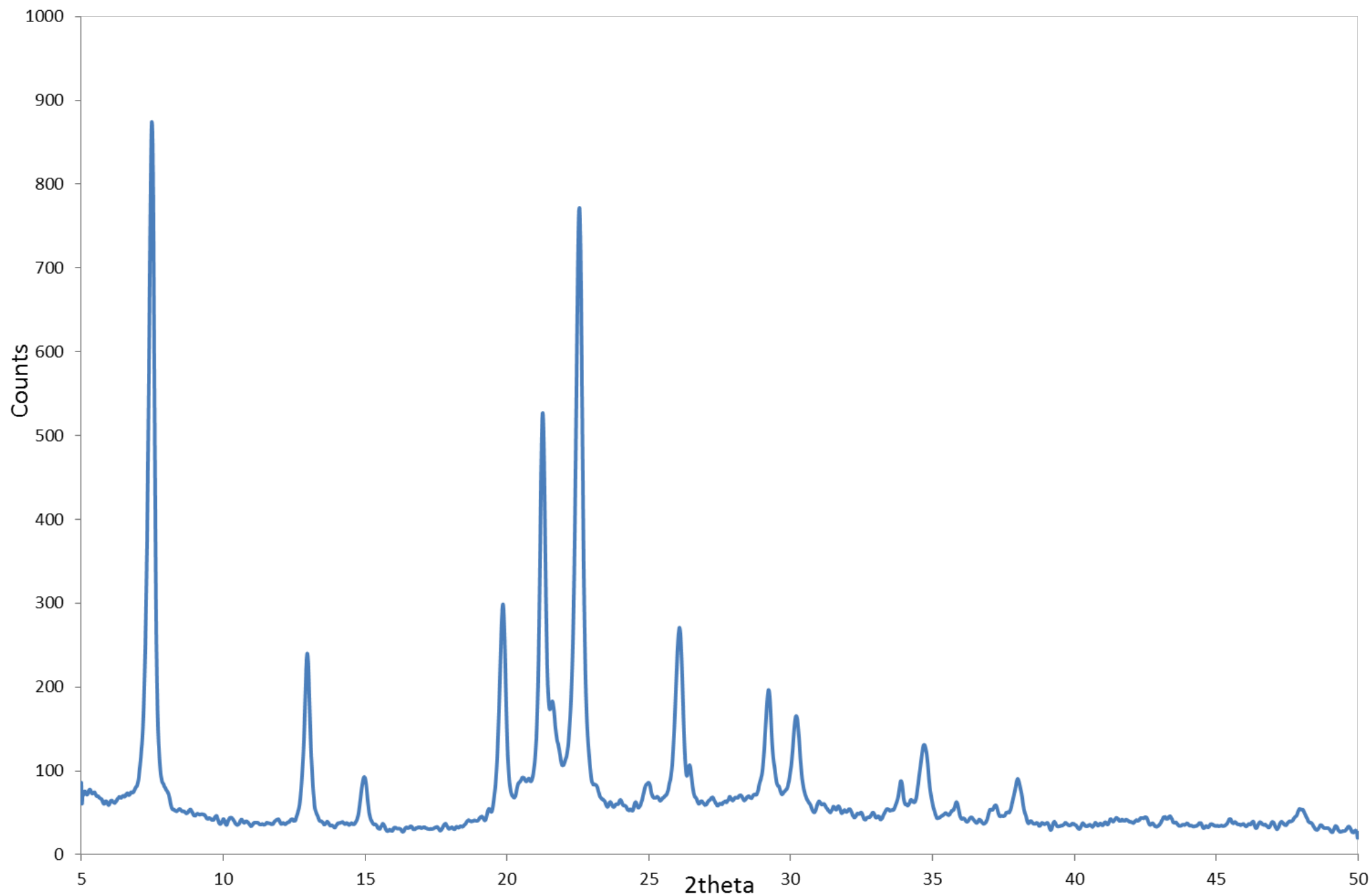


Figure SI 2.6: Reduced Powder X-ray Diffraction Pattern for VA1PO-5

Table SI 2.7: CellRef refinement values for reduced VAIPO-5:

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.6375	13.6375	8.3597	90	90	120	1346.5
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	13.6378	13.6378	8.3597	90	90	120	1346.5
0	0	0.0427	0	0.002	0	0	0	

				2T-			
H	K	L	2T(Obs)	Zero	2Th(Cal)	Dif	
0	1	0	7.5	7.5	7.4849	0.0151	
1	1	0	12.9911	12.9911	12.9827	0.0084	
0	2	0	15	15	15.0019	-0.0019	
1	2	0	19.8661	19.8661	19.8887	-0.0226	
0	0	2	21.25	21.25	21.256	-0.006	
2	1	1	22.5893	22.5893	22.5644	0.0249	
1	1	2	24.9107	24.9107	24.9865	-0.0758	
2	2	0	26.1161	26.1161	26.1183	-0.0022	
1	2	2	29.2411	29.2411	29.27	-0.0289	
0	4	0	30.1786	30.1786	30.2689	-0.0903	
2	2	2	33.9732	33.9732	33.9299	0.0433	
1	3	2	34.7768	34.7768	34.7948	-0.018	
0	4	2	37.2768	37.2768	37.2844	-0.0076	
1	2	3	38.125	38.125	38.0673	0.0577	

Table SI 2.8: Summary of simulated versus refinement values

Structure	$a / \text{Å}$	$c / \text{Å}$	Volume / Å^3	Deviation		
				$a / \text{Å}$	$c / \text{Å}$	Volume / Å^3
<i>Idealised Cell Data</i> ²	13.8	8.6	1418.4			
Experimental AlPO-5	13.69	8.43	1368.2			
VTiAlPO-5 Calcined	13.6752	8.4556	1369.4	0.1248	0.1444	49.0
VTiAlPO-5 Reduced	13.6496	8.3469	1346.8	0.1504	0.2531	71.6
TiAlPO-5 Calcined	13.6707	8.4134	1361.7	0.1293	0.1866	56.7
TiAlPO-5 Reduced	13.6946	8.405	1365.1	0.1054	0.195	53.3
VAIPO-5 Calcined	13.5652	8.3404	1329.2	0.2348	0.2596	89.2
VAIPO-5 Reduced	13.6378	8.3597	1346.5	0.1622	0.2403	71.9

Table SI 2.9: Table of ionic radii values⁴

<i>Element</i>	<i>Radius / pm</i>
Al (3+)	54
P (5+)	38
Ti (3+)	67
Ti (4+)	61
V (4+)	53
V (5+)	46

SI3: Statistical rational of atom placement and active site density in VTiAlPO-5 catalysts

Atom Placement Calculation

The following calculation is focused on a single isolated titanium centre, bonded to four aluminium atoms. The atomic gel ratio is 0.97Al:0.97P:0.03V:0.03Ti. Therefore the probability of titanium being bonded to an aluminium atom is 0.97. In the tetrahedral environment of the AFI framework (figure SI 3.1), the site is bonded to four other atoms (via an oxygen bridge), therefore:

Figure SI 3.1: Schematic of tetrahedral titanium with four atoms bonded via bridging oxygen's

- 1) Titanium bonded to only aluminium atoms = $(0.97)^4 * 100 = \underline{\underline{88.52\%}}$
- 2) Titanium bonded to 3 aluminium and one vanadium = $(4 * (0.97)^4 * 0.03) = \underline{\underline{10.95\%}}$

This calculation is based purely on statistical analysis and does not take into account for energetics, electronic favourability or framework distortions, which are all likely to increase the proportion of titanium and vanadium placed next to each other in the framework.

Active Site Density

The AFI framework comprises of 12-ring channels containing strictly alternating aluminium and phosphorus T-sites. The unit cell (figure SI 3.2) consists of 24 T-site atoms with tetrahedrally coordinated centres. In the case of the VTiAlPO-5, VAlPO-5 and TiAlPO-5 catalysts described in this work, vanadium and titanium ions substitute at these T-sites. In the AFI structure, all of the T-sites are exposed to an outer channel, meaning that all of the T-sites can be equally considered to have an active metal centre substituted as none of them are 'buried' in the bulk material (displayed in figure SI 3.3)

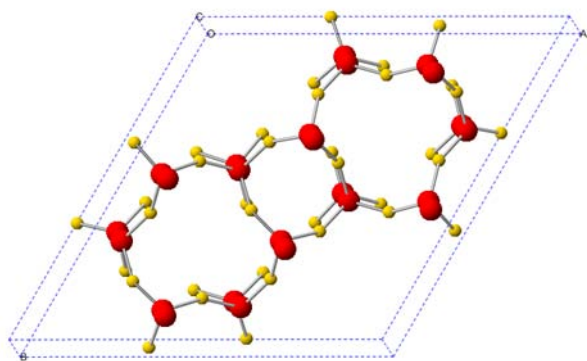


Figure SI 3.2: AFI unit cell representation

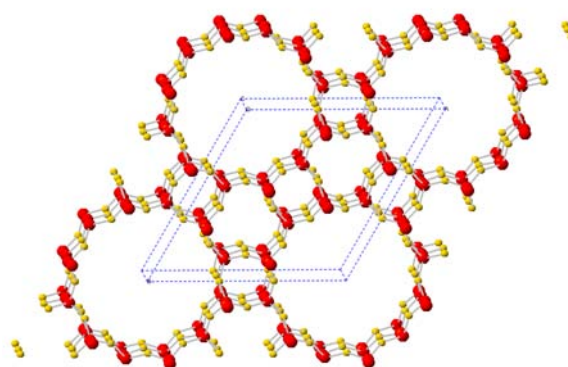


Figure SI 3.3: Unit cells combining to give the porous AFI channel network

Basing the model on a 12-membered central ring (to avoid double counting of any one T-site – compare figures SI 3.4 and SI 3.5), the likelihood of two active sites being next to, or in very close proximity to one-another can be estimated.

The VTiAlPO-5 catalyst tested in this study was synthesised with a 6 atom% loading. Therefore there are 0.72 heteroatoms per 12-membered ring - (12×0.06) – which can be interpreted as greater than a 50:50 chance of a heteroatoms being located in a 12-membered pore of the main AFI channel. Combining 4 layers of these rings gives a cylindrical arrangement, as in figure 3.6, and accounts for active sites that may be next to each other, but as a member of a different 12-ring assembly.

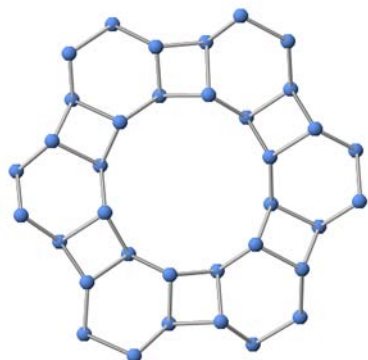


Figure SI 3.4: Central 12-membered ring with interconnecting 6- and 4- rings linking to another assembly of 12-membered rings

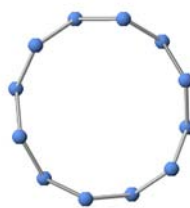


Figure SI 3.5: Isolated 12-membered ring

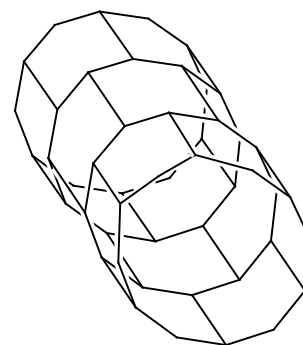


Figure SI 3.6: Representation of 4 layers of 12 membered rings.

There are 48 T-sites in one of these units (4 layers of 12-membered rings). Therefore, by calculating the percentage of these 48 T-sites that are in fact substituted heteroatoms, (ie: vanadium or titanium), then it can be estimated that 2.88 atoms in one of these 48 T-site assemblies in an active centre.

$$\text{Number of heteroatoms in assembly} = 48 \times 0.06 = 2.88$$

SI4: EPR measurements

Experimental details

X-band CW EPR spectra were detected at 10K on a Bruker EMX spectrometer (microwave frequency 9.75 GHz) equipped with a cylindrical cavity. A microwave power of 10 mW, modulation amplitude of 0.1 mT and a modulation frequency of 100 KHz was used.

Pulse EPR experiments were performed on an ELEXYS 580 Bruker spectrometer (at the microwave frequency of 9.76 GHz) equipped with a liquid-helium cryostat from Oxford Inc. All experiments were performed at 10 K. The magnetic field was measured by means of a Bruker ER035M NMR gaussmeter.

Electron-spin-echo (ESE) detected EPR experiments were carried out with the pulse sequence: $\pi/2 - \tau - \pi - \tau - \text{echo}$, with microwave pulse lengths $t_{\pi/2} = 16$ ns and $t_{\pi} = 32$ ns and a τ value in the range 200-500 ns.

Hyperfine Sublevel Correlation (HYSCORE) experiments⁵ were carried out with the pulse sequence $\pi/2 - \tau - \pi/2 - t_1 - \pi - t_2 - \pi/2 - \tau - \text{echo}$ with the microwave pulse length $t_{\pi/2} = 16$ ns and $t_{\pi} = 16$ ns. The time intervals t_1 and t_2 were varied in steps of 8 ns starting from 96 ns to 2704 ns. In order to avoid blind spot effects different τ values were chosen, which are specified in the figure captions. An eight-step phase cycle was used for eliminating unwanted echoes. The time traces of the HYSCORE spectra were baseline corrected with a third-order polynomial, apodized with a Hamming window and zero filled. After two-dimensional Fourier transformation, the absolute value spectra were calculated. The spectra were added for the different τ values in order to eliminate blind-spot effects. The HYSCORE spectra were simulated using the EasySpin⁶ Matlab toolbox.

HYSCORE spectra at g_{\parallel} position.

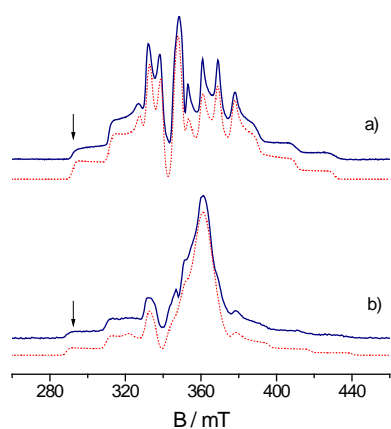


Figure SI4.1 Two Pulse ESE detected EPR spectra of a) calcined and b) reduced TiVAPO, showing the field position at which the HYSCORE spectra of Figure S3 were taken. The spectra were recorded at 10 K with an interpulse delay of 200 ns. The dotted red curves correspond to the computer simulation of the spectra with parameters listed in Table SI4.1.

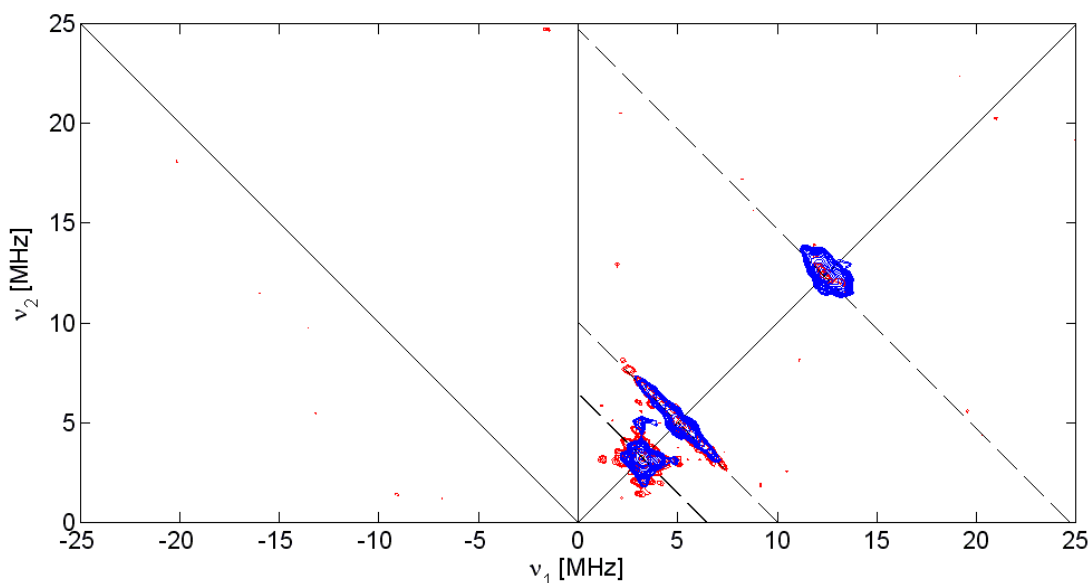


Figure SI4.2 HSCORE spectra taken at the position indicated in Figure S2 (parallel position) of the calcined (blue) and reduced (red) sample. Spectra taken at two τ values (96 ns and 176 ns) were added together after Fourier transform. All spectra were taken at 10 K.

Table SI4.1. Spin-Hamiltonian Parameters of the VO^{2+} species for the calcined and reduced sample. The parameters are obtained from simulation of the CW and ESE-detected EPR spectra reported in Figure 1. Hyperfine couplings are given in MHz.

	g_x	g_y	g_z	A_x	A_y	A_z
	± 0.003	± 0.003	± 0.002	± 15	± 15	± 15
Calcined TiVAIPO-5	1.9729	1.9729	1.9267	194	194	544
Reduced TiVAIPO-5	1.9756	1.9756	1.9196	210	210	559

Despite the difference in the line-width between the spectra of the reduced and calcined sample and the small differences in the spin Hamiltonian parameters (Table S1) the HSCORE spectra taken at a field position where only the VO^{2+} species resonate, demonstrate that the local environment of the VO^{2+} is the same in the oxidized and reduced samples and consistent with the VO^{2+} group substituting a lattice Al^{3+} .

References

1. M. Sanchez-Sanchez, G. Sankar, A. Simperler, R. G. Bell, C. R. A. Catlow and J. M. Thomas, *Catalysis Letters*, 2003, **88**, 163 - 167.
2. M. M. J. Treacy and J. B. Higgins, *Collection of Simulated XRD Powder Patterns for Zeolites*, Elsevier, 2007.
3. C. Baerlocher, L. B. McCusker and D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, 2007.
4. C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, Prentice Hall, 2001.

5. P. Höfer, A. Grupp, H. Nebenführ and M. Mehring, *Chem. Phys. Lett.*, 1986, **132**, 279.
6. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42.