Structure of the Catalytic Active Sites in Vanadium Doped Alumino Phosphate Microporous Materials. New Evidence from Spin Density Studies.

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SUPPORTING INFORMATION

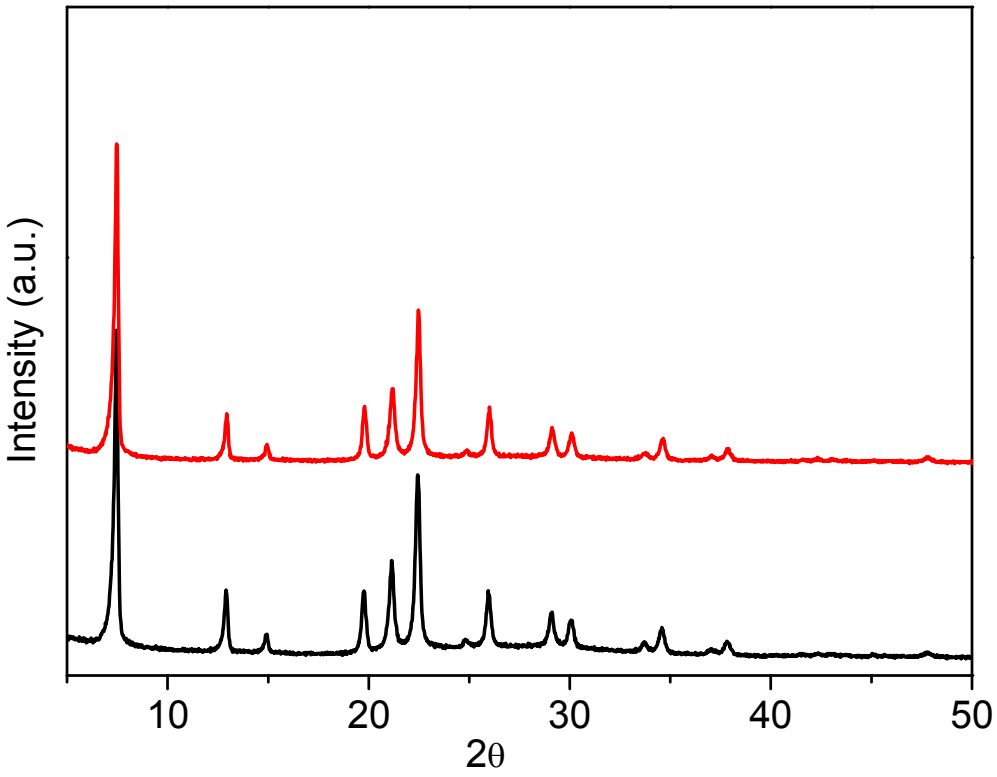

Figure S1 XRD patterns of VAPO-5 sample after calcination (bottom) and after repeated oxidation/reduction cycles (top).

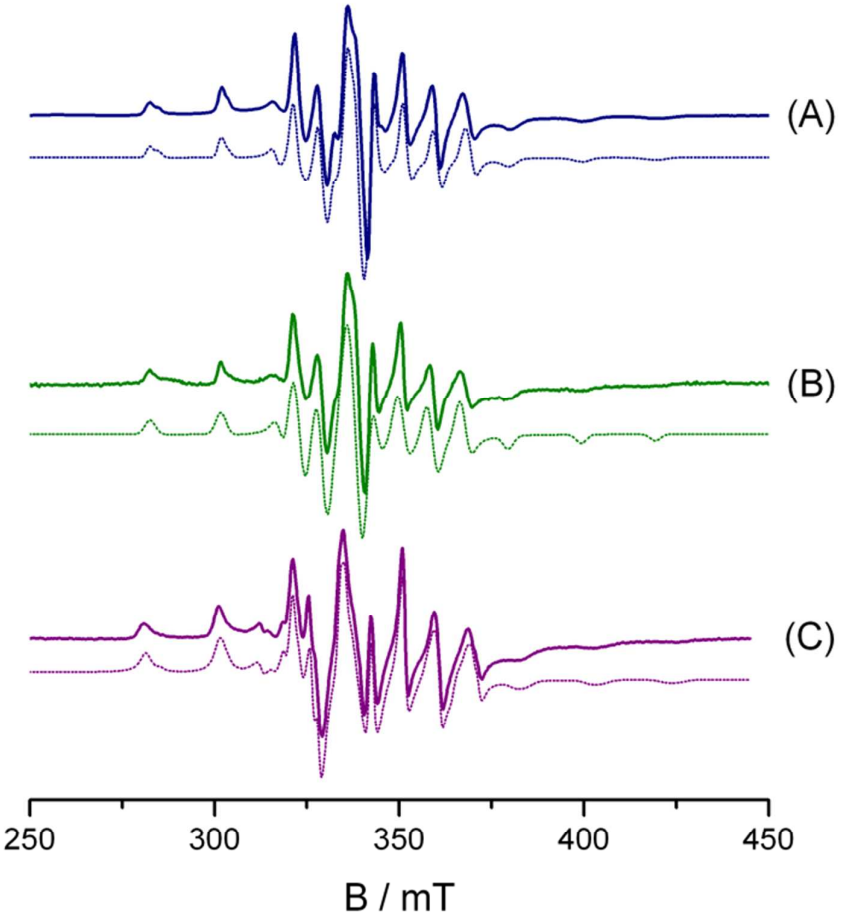

Figure S2. Experimental (solid lines) and computer simulations (dotted lines) X-band CW EPR spectra of (A) as-synthesized, (B) calcined sample dehydrated at T = 423K for 1 hour and (C) reduced in hydrogen atmosphere at T = 673K for 2 hours. All spectra were recorded at T = 77K, 10 mW microwave power and a modulation amplitude 0.15 mT The spin-Hamiltonian parameters extracted from the computer simulations are listed in Table S1.

Table S1. Spin-Hamiltonian parameters of VO^{2+} centers in VAPO-5 upon different treatments. The parameters are obtained from computer simulation of the field swept EPR spectra reported in Figure S1 and Figure S2. The hyperfine coupling constants are expressed in MHz.

		g_1 ±0.01	g_2 ±0.01	g_3 ±0.001	A_1 ±5	A_2 ±5	A_3 ±1	Ab (%)
as-synthesized	Species 1	1.978	1.9734	1.9358	209	183	534	58
	Species 2	1.978	1.9643	1.9375	207	178	515	42
Calcined sample dehydrated at 423K	Species 1	1.978	1.9734	1.9358	209	183	534	60
	Species 2	1.978	1.9643	1.9375	207	178	515	40
Calcined sample reduced in H_2 at 673K	Species 1	1.9901	1.9825	1.9378	224	198	541	56
	Species 2	1.9852	1.9704	1.9274	215	168	530	44

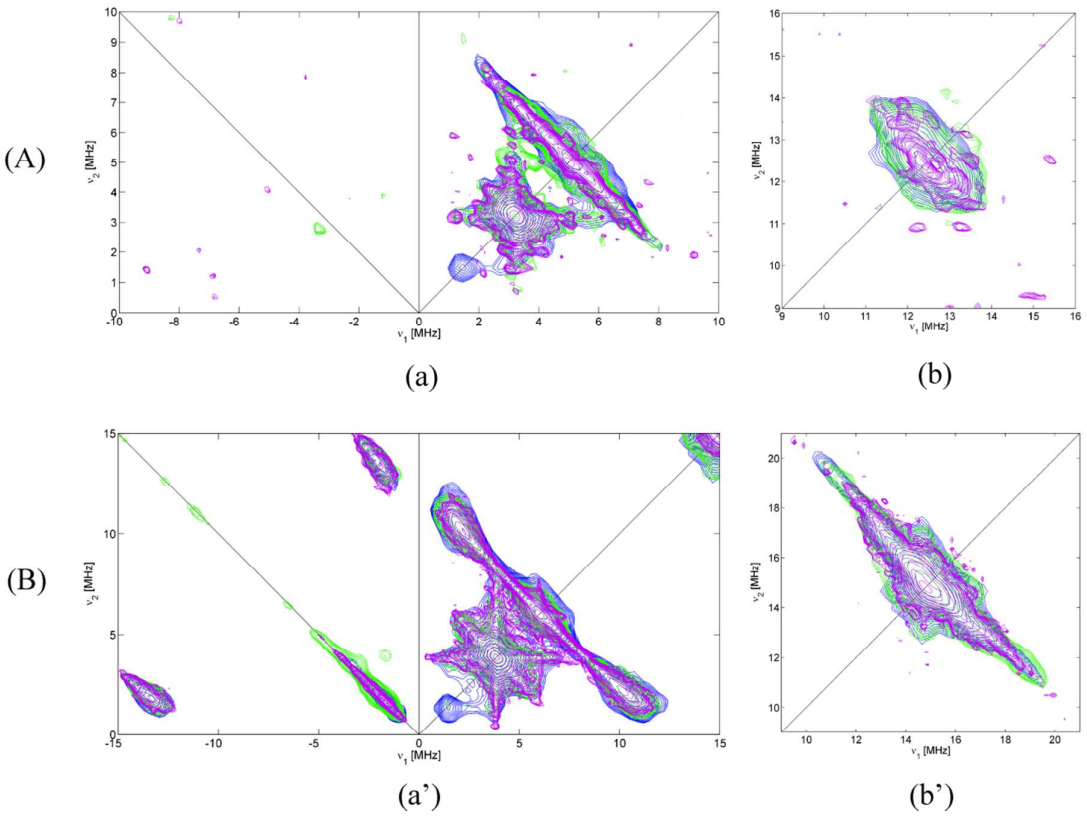

Figure S3. Experimental X-band HYSCORE spectra of as-synthesized (blue line), calcined (green line) and reduced (magenta line) VAPO-5 samples recorded at (A) B_0 = 292.1 mT and (B) B_0 = 348.8 mT, corresponding to the $g_{\|}$, m_I = -7/2 observer position and to the so-called "powder like" position, respectively. The spectra are recorded at T = 20K . Spectra in panel A are recorded at τ value τ = 96 ns, while in panel B spectra recorded at three different τ values (96, 136, 250 ns) are summed together after Fourier transform. The spectra refer to the ^{27}Al and ^{31}P couplings region (spectra (a) and (a')) and to the ^{1}H coupling region (spectra (b) and (b')).

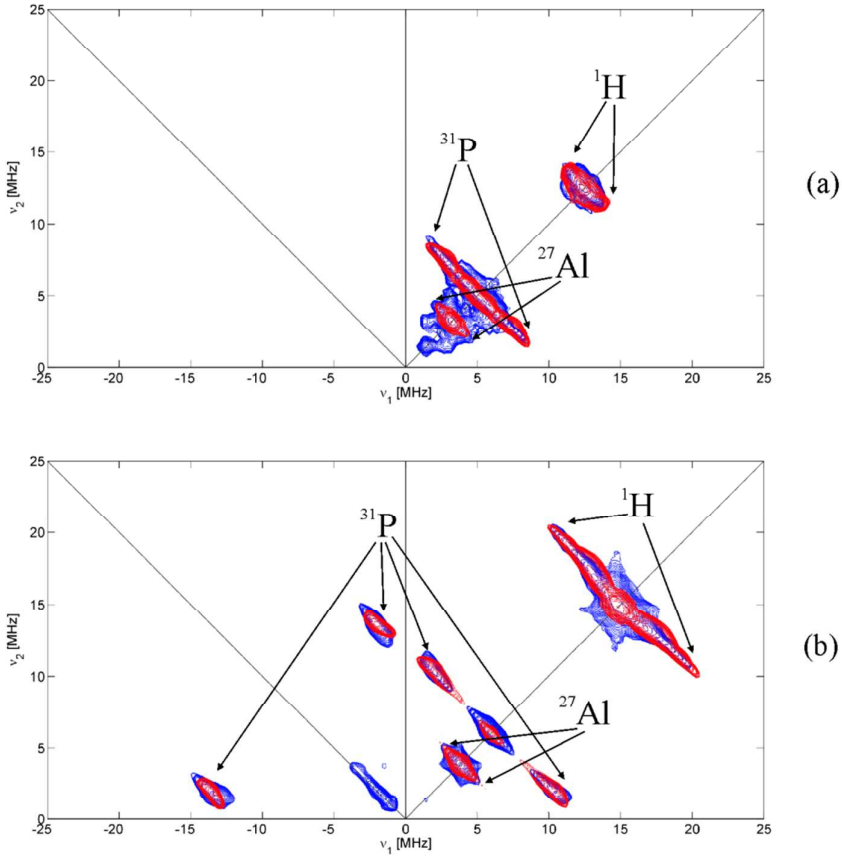

Figure S4. Experimental (blue) and computer simulation (red) X-band HYSCORE spectra of as prepared VAPO-5 recorded at (a) B_0 = 292.1 mT and (b) B_0 = 348.8 mT, corresponding to the $g_{\|}$, m_I = -7/2 observer position and to the so-called "powder like" position, respectively. The spectra were recorded at T = 20K. The spectra in (a) were recorded at τ=96 ns, while in (b) spectra recorded at three different interpulse τ delay (τ= 96, 136 and 250 ns) are summed together after Fourier transform. The spin Hamiltonian parameters extracted from the computer simulations are listed in Table 1 of the main text.

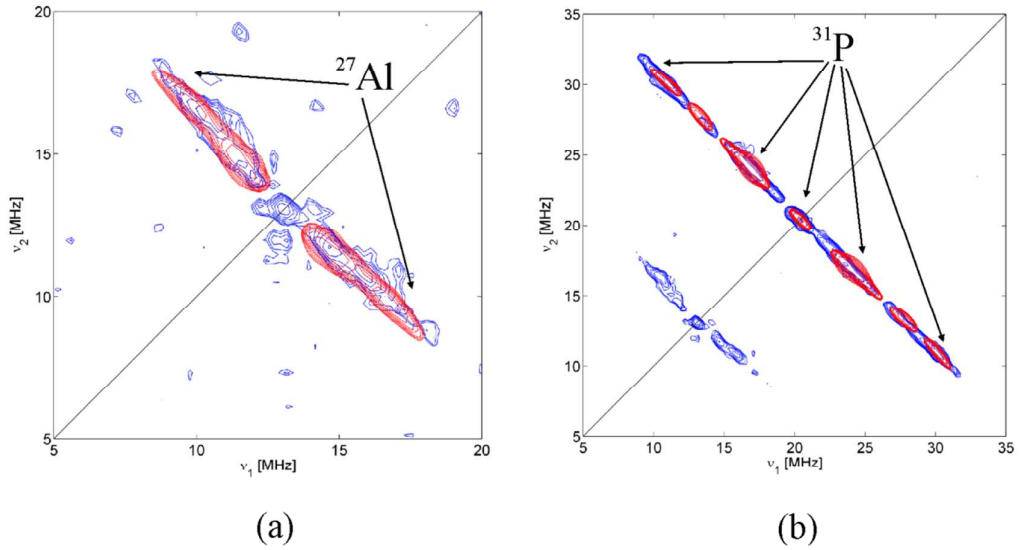

Figure S5. Experimental (blue lines) and computer simulation (red lines) Q-band (a) ^{27}Al HYSCORE and (b) ^{31}P HYSCORE spectra of as-synthesized VAPO-5. The spectra are recorded at B_0 = 1183.8 mT, corresponding to the $g_{\|}$, m_I = -7/2 observer position, and τ value 152 ns. The spectra were recorded at T = 40 K. The spin Hamiltonian parameters extracted from the computer simulations are listed in Table 2 of the main text.

Atomic coordinates of the two DFT optimized V model clusters

VO^{2+} substituted at a framework Al^{3+} site

Cluster

V	0.152919	0.468544	-0.265254
O	-0.412323	1.955344	-0.194546
H	-1.810936	-0.796824	-1.896806
P	2.261820	1.818087	1.678464
P	2.324386	-1.342772	-1.866382
P	-1.542436	-1.822404	1.444419
P	-3.072935	0.829831	-1.066756
H	-3.154653	-0.360408	2.149192
H	3.460199	-2.583033	-0.219362
H	-3.216355	3.128638	-1.822854
H	1.480689	-3.079607	-3.311024
H	-2.604675	-3.261206	-0.116403
H	0.617714	3.630989	1.837418
O	1.042521	-0.518867	-1.681427
O	-0.900798	-2.915332	2.303416
O	-2.950809	2.200531	-1.706794
O	1.880840	0.955303	0.484933
O	2.114663	-2.462411	-2.907894
O	-2.126503	-2.460565	0.158719
O	-4.159709	-0.027238	-1.705963
O	3.468145	-0.461600	-2.414270
O	-2.733002	-1.233318	2.224059
O	-1.690975	0.043831	-1.399935
O	2.039171	0.994678	2.959610
O	2.745269	-1.999065	-0.524688
O	-0.515474	-0.731072	1.091924
O	-3.216493	0.941954	0.445698
H	4.303176	-0.561341	-2.902267
H	4.611026	1.947450	1.368353
H	1.643949	1.188404	3.826581
O	3.717895	2.284220	1.553476
O	1.472506	3.167795	1.825146
H	-4.282446	-0.687491	-2.409077
H	-3.765391	1.719072	0.646117
H	-0.554553	-3.823892	2.304529

Periodic

Cell:

A	B	C	ALPHA	BETA	GAMMA
13.6869	13.7944	8.3486	87.451	92.160	119.724

Coordinates:

V	4.350972065721E-01	3.400688700873E-01	4.295274317666E-01
O	3.512801454008E-01	3.741875420807E-01	3.400541872639E-01
H	4.046476784559E-01	3.696403373261E-01	-2.440465046493E-01
P	4.799631288063E-01	3.193087755200E-01	6.629963360659E-02
P	-4.281636038902E-01	-3.249899125886E-01	1.137433114927E-01
P	-3.154203133465E-01	1.129890745851E-01	8.396094626514E-02
P	-1.073256750364E-01	-4.431317584226E-01	8.727944187035E-02
P	1.319476560290E-01	4.413335926246E-01	1.043973584523E-01
P	3.359390455217E-01	-1.309238947312E-01	9.008710371344E-02
P	-1.141993823159E-01	3.390441041485E-01	-4.055363535924E-01
P	4.492227446728E-01	1.217120020603E-01	-4.404212139096E-01
P	-3.322099619653E-01	-4.525104978900E-01	-4.127779941344E-01
P	3.569065004162E-01	4.891451291670E-01	-3.577358229767E-01
P	-4.548833646851E-01	-1.105930489666E-01	-3.956130550095E-01
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AL	-1.138708488181E-01	3.382963642300E-01	-2.805253427879E-02
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AL	-3.228437714783E-01	-4.606380227257E-01	-4.130328053777E-02
AL	3.568652044783E-01	4.641106880098E-01	1.626079227372E-02
AL	-4.500764179662E-01	-1.265190111417E-01	-2.666059041151E-02
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O	-2.147374015492E-01	-4.391946154739E-01	-4.237757802955E-01
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O	-3.332830800608E-01	2.481921869365E-03	1.849581264306E-02
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Extra-framework vanadyl group in the center of a 6-membered AlPO ring

cluster

H	-0.097363	5.227001	-0.938699
Al	-0.199172	2.715818	-0.901175
O	0.298101	4.361871	-1.101129
H	-0.987276	-1.689422	-2.776920
H	-1.045283	1.590412	-2.990592
P	-2.588782	1.456636	0.476335
P	2.638411	1.583364	-0.011285
H	3.934328	-2.292504	-2.132344
P	-0.155443	-2.571623	-0.757266
H	-3.929603	-2.374277	-1.593437
H	-4.195525	-2.399670	2.339017
Al	-2.727735	-1.584946	0.479195
Al	2.736108	-1.627657	-0.027330
H	3.767352	2.157288	-1.986981
H	0.192320	-4.867456	-0.902513
H	-3.810119	1.996461	-1.459494
H	-4.054263	2.073479	2.207352
O	-3.294144	1.617358	1.808658
O	1.062617	1.862690	0.066617
O	0.909014	-1.734913	0.100104
O	-3.466924	-1.866718	1.997946
O	-1.783300	0.039227	0.491979
O	2.500403	0.088334	0.504156
O	0.471534	-3.943216	-1.014785
O	-1.475643	2.499662	0.270201
O	3.379954	2.435121	0.984725
O	-1.371551	-2.671470	0.156523
O	-0.393190	1.734742	-2.294051
O	-3.563246	1.442575	-0.699857
O	3.135807	1.665845	-1.435239
O	3.293911	-1.770669	-1.633565
O	-0.377527	-1.777625	-2.025116
O	-3.795754	-1.745418	-0.873822
V	0.396303	0.074490	0.904287
O	0.295360	0.050489	2.444262
H	4.432882	-2.531597	1.513901
H	4.268539	2.555127	1.359956
O	3.535398	-2.559048	1.160356

periodic

Cell:

A	B	C	ALPHA	BETA	GAMMA
13.7340	13.7320	8.3073	90.007	90.001	120.051

Coordinates:

AL 4.396439383587E-01 3.272218912087E-01 -4.957104088616E-01
P 4.483333326975E-01 3.274551456545E-01 1.296292560149E-01
P -4.206652421922E-01 -3.334634725256E-01 1.369279464563E-01
P -3.208273712861E-01 1.131511524358E-01 1.361328880134E-01
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P 1.248103833651E-01 4.477292647736E-01 1.374037871196E-01
P 3.499462690095E-01 -1.149805901134E-01 1.360968000029E-01
P -1.280474081261E-01 3.332394052541E-01 -3.589917750394E-01
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AL -4.354597728962E-01 -3.332813885167E-01 -4.973860616462E-01

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