Supplementary information for:

Identification of Synergistic Cu/V Red-ox Pair in VCu:AlPO-5; a Comparison with VCu:ZSM-5

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XANES

Vanadium references

Table S1 shows the different XANES features and energy positions for the vanadium reference compounds used in this study.

Table S1 Energy positions and different spectral features of the different vanadium reference compounds.

Reference	Pre-edge peak position/ eV	Pre-edge height/a.u	Pre-edge area/a.u	Pre-edge width/eV	R-factor[a]	E_0/eV	ΔE/eV
Na_3VO_4	5470.17	0.48	3.5(2)	4.8(1)	0.59	5480.76	10.6
NH_4VO_3	5469.51	0.47	3.7(1)	5.1(2)	0.79	5480.283	10.8
V_2O_5	5470.3	0.38	3.5(1)	5.6(2)	0.42	5480.103	9.8
V_2O_4	5471	0.45	3.7(2)	5.2(1)	0.43	5479.12	8.12
V_2O_3	5469.72	0.38	2.4(1)	6.3(1)	0.11	5474.45	4.73
VO	-	-	-	-	-	5471.42	-

Pre-edge area and width are obtained from peak-fitting in Athena along with corresponding [a]R-factors

*1000.

Temperature Programmed Reduction (C_3H_6-TPR)

Vanadium edge

Table S2 and S3 shows the spectral features and energy positions for VCu:AlPO-5 and VCu:ZSM-5 respectively during C_3H_6-TPR.

Table S2 Energy positions and different spectral features for VCu:AlPO-5 at the V K-edge during C_3H_6-TPR

Reaction temp/°C	Pre-edge position/eV	Pre-edge height/a.u	Pre-edge area/a.u	Pre-edge width/eV	R-factor[a]	E_0/eV	ΔE/eV
RT	5470.3	0.38	2.57(8)	4.3(1)	0.59	5482.74	12.44
215	5470.2	0.39	2.6(1)	4.3(1)	0.43	5482.54	12.34
225	5470.2	0.39	2.56(8)	4.2(1)	0.52	5482.64	12.44
255	5470.2	0.39	2.6(1)	4.2(1)	0.5	5482.54	12.34
290	5470.1	0.39	2.4(2)	4.1(1)	1.12	5482.36	12.26
310	5470.2	0.37	2.45(8)	4.2(1)	0.51	5482.55	12.35
390	5470.3	0.31	2.4(1)	4.8(2)	0.77	5480.89	10.59
450	5470.2	0.25	1.7(2)	4.9(3)	0.47	5478.56	8.36

[a]R-factor obtained from peak-fit in Athena* 1000

Table S3 Energy positions and different spectral features for VCu:ZSM-5 at the V K-edge during C_3H_6-TPR

Reaction temp/°C	Pre-edge position/eV	Pre-edge height/a.u	Pre-edge area/a.u	Pre-edge width/eV	R-factor[a]	E_0/eV	ΔE/eV
RT	5470.4	0.39	2.41(9)	3.9(1)	0.85	5483.24	12.84
215	5470.3	0.38	2.37(9)	3.9(2)	0.86	5483.09	12.79
225	5470.3	0.37	2.2(2)	3.8(2)	1.93	5482.95	12.65
255	5470.4	0.37	2.4(1)	4.1(2)	0.93	5482.41	12.01
290	5470.5	0.3	2.3(1)	4.9(3)	1.1	5481.39	10.89
315	5470.5	0.29	2.2(1)	4.8(2)	0.79	5481.06	10.56
390	5470.4	0.25	1.9(1)	4.8(2)	0.43	5480.07	9.67
450	5469.9	0.18	1.2(1)	4.6(3)	0.35	5477.77	7.87

[a] R-factor obtained from peak-fit in Athena* 1000

Copper edge

XANES of Cu:AlPO-5 and Cu:ZSM-5

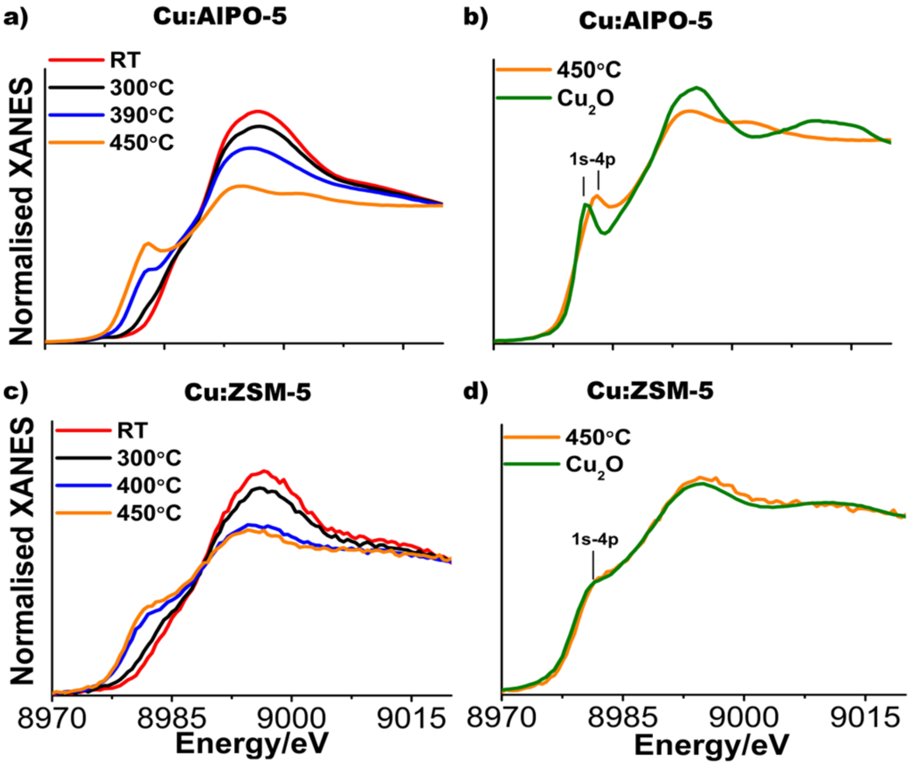

Figure S1 XANES during C_3H_6-TPR for Cu:AlPO-5 and Cu:ZSM-5, b) Comparison of reduced Cu:AlPO-5 at 450°C with $Cu_2(I)O$ data collected at SNBL, d) Comparison of reduced Cu:ZSM-5 at 450°C with $Cu_2(I)O$ data collected at MaxLab.

EXAFS

Vanadium and Copper edge

Table S4 EXAFS least squares refinements of VCu:AlPO-5 and VCu:ZSM-5 at the Cu K-edge from *in situ* C_3H_6-TPR[a].

Sample	Reaction stage	Shell	N	R/Å	$2\sigma^2$/Å^2	E_F/eV	R/%
VCu:AlPO-5	RT[b]	Cu-O	3.5(3)	1.950(7)	0.009(2)	-1.3(3)	36.20
	Prop[c]	Cu-O	0.9(1)	1.849(7)	0.005(1)	-5.4(4)	30.46
	300 °C	Cu-O	2.4(1)	1.965(3)	0.015(1)		
	Prop[c]	Cu-O	0.6(1)	1.804(6)	0.007(2)	-3.1(3)	35.67
	400 °C	Cu-O	0.7(1)	1.957(7)	0.013(1)		
		Cu…Cu	1.4(1)	2.511(3)	0.021(1)		
	Prop[d]	Cu-O	-	1.85(1)	-	-5.0(5)	37.87
	450°C	Cu…Cu	4.9(6)	2.517(4)	0.031(3)		
VCu:ZSM-5	RT[b]	Cu-O	4.4(2)	1.930(4)	0.013(1)	-7.9(3)	27.49
	Prop[c]	Cu-O	0.4(1)	1.86(2)	0.004(1)	-5.1(5)	33.03
	300 °C	Cu-O	3.3(2)	1.953(6)	0.012(1)		
	Prop[c]	Cu-O	0.7(1)	1.832(5)	0.004(1)	-6.7(4)	35.53
	400 °C	Cu-O	1.4(1)	2.006(7)	0.014(2)		
		Cu…Cu	1.9(3)	2.51(1)	0.042(4)		
	Prop[d]	Cu-O	0.3(1)	1.85(4)	0.017(1)	-6.2	41.76
	450 °C	Cu…Cu	6.6(1)	2.53(1)	0.038(1)		

[a]The least-squares refinements were carried out at wavenumber k= 2-12 Å^{-1} using a k^3 weighting scheme. The goodness of fit, R, is given in %. The standard deviation in the last digit as calculated by EXCURV98 is given in parentheses. [b]AFAC=0.72 obtained from CuO. [c]AFAC=0.71 obtained from Cu_2O. [d]AFAC=0.92 obtained from Cu foil.

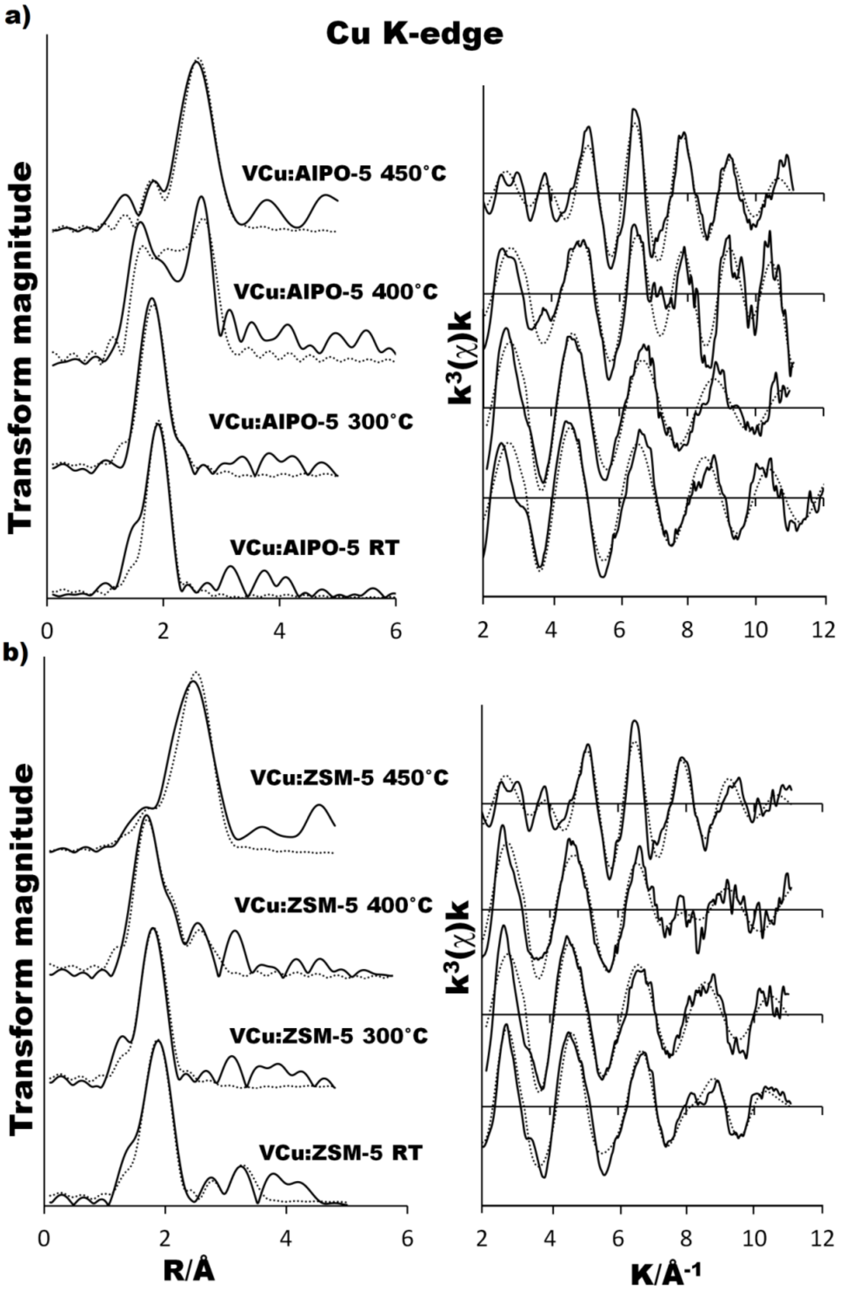

Figure S2 Experimental (--) and theoretical (..) least-squares refined EXAFS $k^3\chi(k)$ and Fourier transforms for a)VCu:AlPO-5 and b)VCu:ZSM-5 at room temperature 25°C and during C_3H_6-TPR.

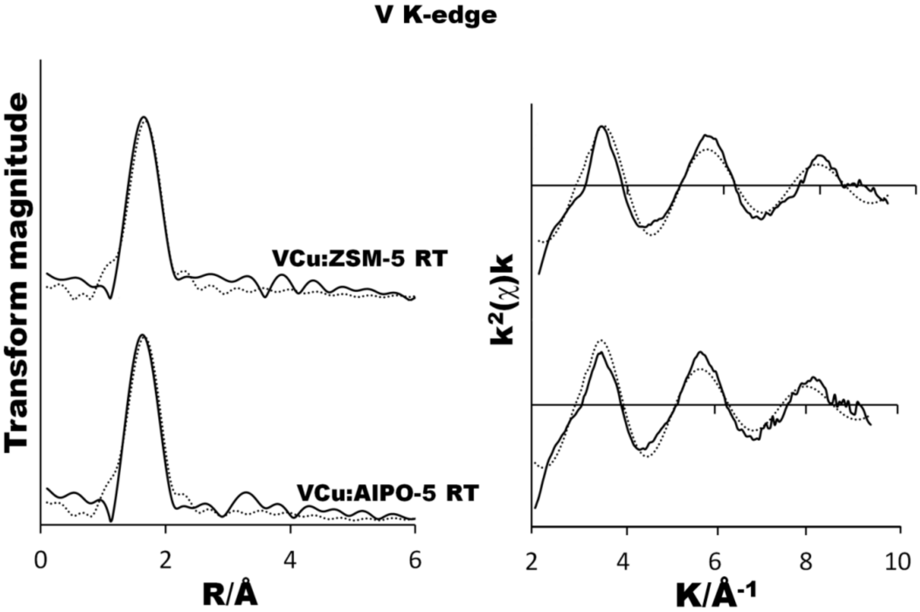

Figure S3 Figure 5 Experimental (-) and theoretical (..) least squares refined EXAFS $k^2\chi(k)$ and Fourier transforms for VCu:AlPO-5 and VCu:ZSM-5 at room temperature 25°C.

Table S5 EXAFS least squares refinements of VCu:AlPO-5 and VCu:ZSM-5 at the V K-edge from in situ C_3H_6-TPR[a]

Sample	Reaction stage	Shell	N	R/Å	$2\sigma^2$/Å^2	E_F/eV	R/%
VCu:AlPO-5	RT[b]	V-O	5.3(5)	1.73(1)	0.007(4)	-3(1)	33.76
VCu:ZSM-5	RT[b]	V-O	4.7(4)	1.73(1)	0.003(3)	-2.6(9)	30.65

[a]The Least-squares refinements were carried out at wavenumber k= 2-9Å^{-1} using a k^2 weighting scheme. The goodness of fit, R, is given in %. The standard deviation in the last digit as calculated by EXCURV98 is given in parentheses.[b]AFAC=0.58 obtained from NH_4VO_3.

Studying reversibility: EXAFS refinements from cycling between propene and oxygen

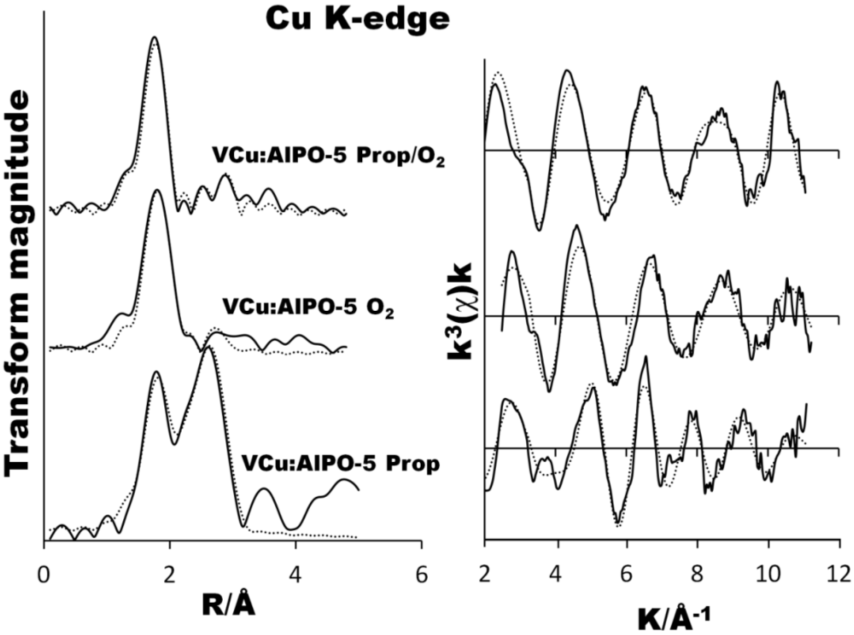

Figure S4 Experimental (--) and theoretical (..) least squares refined EXAFS $k^3\chi(k)$ and Fourier transforms for a)VCu:AlPO-5 at room temperature and from one cycle in propene and O_2 respectively, with the last being in reaction mixture (Prop/O_2).

Table S6 Table 4 EXAFS least squares refinements of VCu:AlPO-5 at the Cu K-edge during cycling between propene and O_2[a].

Sample	Reaction stage	Shell	N	R/ Å	$2\sigma^2$/ Å^2	E_F/ eV	R / %
VCu:AlPO-5	Dehyd[b]	Cu-O	2.6(2)	1.959(3)	0.009(1)	-8.1(4)	32.05
		Cu…V	0.7(1)	2.88(1)	0.03(2)		
	Prop[c]	Cu-O	0.8(1)	1.845(3)	0.007(2)	-6.1(6)	42.55
	Cycle 1	Cu…Cu	4.8(1)	2.509(2)	0.030(1)		
	O_2[b]	Cu-O	2.8(1)	1.928(3)	0.005(1)	-4.5(2)	28.58
	Cycle 1	Cu…V	0.4(1)	2.95(1)	0.013(2)		
	Prop[c]	Cu-O	0.7(1)	1.86(1)	0.013(3)	-6.3(5)	38.35
	Cycle 2	Cu…Cu	6.6(2)	2.519(2)	0.036(1)		
	O_2[b]	Cu-O	2.8(1	1.915(2)	0.009(1)	5.4(4)	30.9

		)				9
Cycle 2	Cu…V	0.7(2)	2.90(1)	0.018(2)		
Prop[c]	Cu-O	0.7(1)	1.891(3)	0.008(2)	-7.0(4)	35.81
Cycle 3	Cu…Cu	6.6(1)	2.535(2)	0.035(1)		
O_2[b]	Cu-O	2.8(1)	1.92(1)	0.004(2)	-5.5(3)	29.49
Cycle 3	Cu…V	0.4(1)	2.962(8)	0.014(1)		
Prop/ O_2[b]	Cu-O	2.3(1)	1.946(2)	0.005(1)	-7.3(4)	27.70
	Cu…V	0.4(1)	2.82(1)	0.020(1)		

[a] The least-squares refinements were carried out at wavenumber k= 2-12 $Å^{-1}$ using a k^3 weighting scheme. The goodness of fit, R, is given in %. The standard deviation in the last digit as calculated by EXCURV98 is given in parentheses. [b] AFAC=0.72 obtained from $Cu(OH)_2$. [c] AFAC=0.86 obtained from Cu foil.

Valence fraction obtained from linear combination (LC) during C_3H_6-TPR

Linear combination (LC) fit at the Cu K-edge for VCu:AlPO-5, Cu:AlPO-5, VCu:ZSM-5 and Cu:ZSM-5 are shown in Figure S4a and b. Figure S5c show the valence fractions for vanadium in VCu:AlPO-5 and VCu:ZSM-5 obtained from the threshold energy during C_3H_6-TPR.

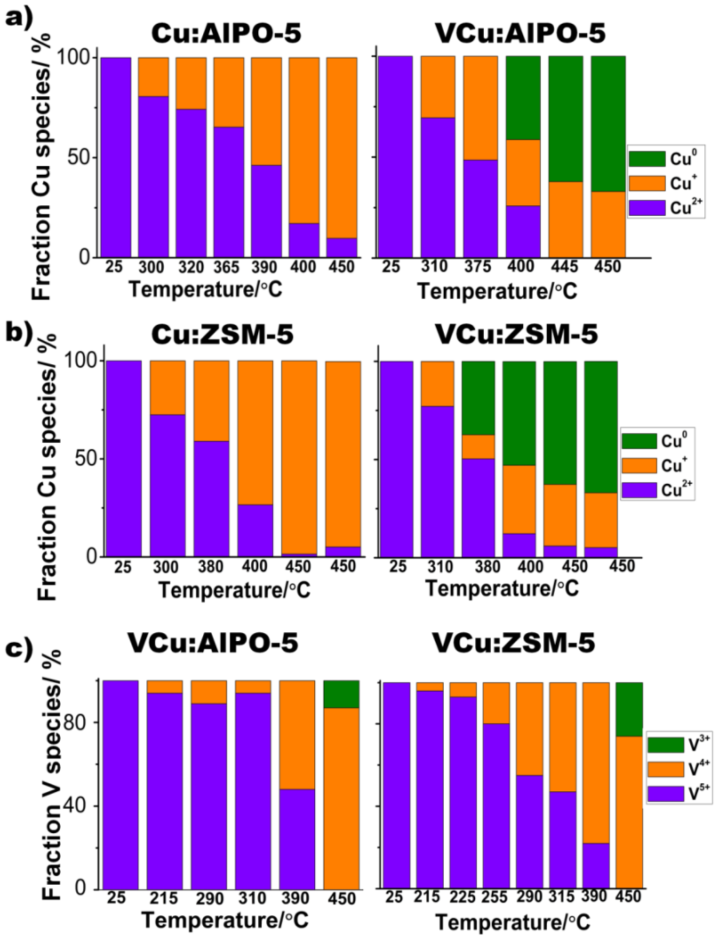

Figure S6 Valence fractions of copper and vanadium during C_3H_6-TPR for a)VCu:AlPO-5 and Cu:AlPO- at the Cu K-edge, b) VCu:ZSM-5 and Cu:ZSM-5 , c) VCu:AlPO-5 and VCu:ZSM-5 at the V K-edge. The valence fractions of copper are obtained from LC fit, while vanadium valence fraction is obtained from E_0.