Supporting information for

Immobilization of Keggin Polyoxovanadoniobate in Crystalline Solids as Effective Heterogeneous Catalysts towards Selective Oxidation of Benzyl-Alkanes

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Table S1 Crystallographic Data for Compounds **1**–**2**.[a]

Compounds	**1**	**2**
Formula	$C_{24}H_{128}Cu_6N_{24}Nb_{12}O_{59}PV_2$	$C_{14}H_{100.5}Co_{2.5}N_{14}Nb_{12}O_{63}PV_2$
M_r	3326. 5	2868. 7
Crystal system	tetragonal	triclinic
Space group	*P4/mnc*	*P-1*
a (Å)	14.5498(3)	12.8884(4)
b (Å)	14.5498(3)	14.1118(5)
c (Å)	22.9484(11)	14.5289(5)
α (deg)	90	93.443(1)
β (deg)	90	105.107(1)
γ (deg)	90	117.046(1)
V (Å^3)	4858.1(3)	2222.65(13)
Z	2	1
$D_{calc.}$ (g cm^{-3})	2.274	1.953
Refns. Collected/Unique	48594/2563	22166/8414
R_{int}	0.0657	0.0256
$R_1[I>2\sigma(I)]$	0.0489	0.0635
$wR_2[I>2\sigma(I)]$	0.1132	0.0914
R_1(all data)	0.0652	0.1704
wR_2(all data)	0.1216	0.1965
GOF on F^2	1.105	1.065
CCDC	1478107	1478108

[a] $R_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$; $wR_2=\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$

Table S2 Selected bond lengths for **1**.

Bond types	Bond lengths	Bond types	Bond lengths	Bond types	Bond lengths
Nb1-O2	2.074(5)	V1-O2_a	1.953(5)	Cu1-N2	1.963(14)
Nb1-O3	2.537(7)	V1-O2	1.953(5)	Cu2-O13_h	2.52(2)
Nb1-O5	1.876(6)	V1-O10	1.644(12)	Cu2-N3_h	2.035(17)
Nb1-O8	1.898(7)	P1-O3_f	1.582(7)	Cu2-N4_h	2.012(12)
Nb1-O11	1.754(6)	P1-O3_g	1.582(7)	Cu2-O13_i	2.52(2)
Nb1-O2_a	2.064(5)	P1-O3	1.582(7)	Cu2-N3_i	2.035(17)
Nb1-O3_c	2.516(7)	P1-O3_a	1.582(7)	Cu2-N4_i	2.012(12)
Nb2-O8	1.939(7)	P1-O3_d	1.582(7)	Cu2-O13_j	2.52(2)
Nb2-O12	1.743(7)	P1-O3_e	1.582(7)	Cu2-N3_j	2.035(17)
Nb2-O5_c	1.975(6)	P1-O3_b	1.582(7)	Cu2-N4_j	2.012(12)
Nb2-O5_e	1.975(6)	P1-O3_c	1.582(7)	Cu2-O13	2.52(2)
Nb2-O8_f	1.939(7)	Cu1-N1	1.969(11)	Cu2-N3	2.035(17)
V1-O2_c	1.953(5)	Cu1-N2_k	1.963(14)	Cu2-N4	2.012(12)
V1-O2_b	1.953(5)	Cu1-N1_k	1.969(11)		

Symmetry transformations used to generate equivalent atoms: a = = -y,x,z; b = -x,-y,z; c = y,-x,z; d = -x,-y,-z; e = y,-x,-z; f= x,y,-z; g =-y,x,-z; h =-x,1-y,z; i = -x,1-y,-z; j =-x,y,-z; k=-1/2+y,1/2+x,1/2-z.

Table S3 Selected bond lengths for **2**.

Bond types	Bond lengths	Bond types	Bond lengths	Bond types	Bond lengths
Nb1-O1	1.754(8)	Nb4-O5	1.752(7)	V1-O11	1.608(8)
Nb1-O2	1.887(8)	Nb4-O6	2.084(8)	V1-O3	1.912(8)
Nb1-O2P	2.506(12)	Nb4-O15	2.090(10)	V1-O7	1.901(8)
Nb1-O3	2.073(7)	Nb4-O16	1.869(12)	P1-O1P	1.649(13)
Nb1-O7	2.078(9)	Nb4-O20	1.849(10)	P1-O4P_a	1.474(11)
Nb1-O10	1.906(9)	Nb5-O3P	2.456(12)	P1-O1P_a	1.649(13)
Nb1-O4P_a	2.462(11)	Nb5-O6	2.059(8)	P1-O2P_a	1.444(12)
Nb2-O3P	2.500(12)	Nb5-O7	2.039(8)	P1-O3P_a	1.622(13)
Nb2-O4	1.963(9)	Nb5-O8	1.719(9)	P1-O3P	1.622(13)
Nb2-O14	1.730(12)	Nb5-O9	1.868(10)	Co1-N3	1.976(11)
Nb2-O19	1.984(10)	Nb5-O19	1.868(10)	Co1-N4	1.970(9)
Nb2-O20	1.969(10)	Nb6-O1P	2.456(13)	Co1-N5	1.974(12)
Nb2-O2_a	1.983(7)	Nb6-O4	1.875(9)	Co1-N6	1.952(9)
Nb3-O1P	2.485(13)	Nb6-O12	1.701(10)	Co1-N2	1.947(10)
Nb3-O9	1.986(10)	Nb6-O17	1.861(11)	Co1-N1	1.968(9)
Nb3-O10	1.948(9)	Nb6-O3_a	2.057(7)	Co2-N8	1.98(2)
Nb3-O13	1.729(9)	Nb6-O15_a	2.074(11)	Co2-O1W	1.988(17)
Nb3-O17	1.961(11)	V1-O6	1.909(8)	Co2-N7	1.97(2)
Nb3-O16_a	1.947(14)	V1-O15	1.890(10)		

Symmetry transformations used to generate equivalent atoms: a = 1-x,1-y,-z.

Table S4 Selected bond angels for **1**.

Bond types	Bond angles	Bond types	Bond angles	Bond types	Bond angles
O2-Nb1-O3	89.4(3)	O2-V5-O2_c	81.7(3)	N1-Cu1-N1_h	178.1(8)
O2-Nb1-O5	157.2(3)	O2_b-V5-O10	112.4(2)	N1-Cu1-N2	84.1(7)
O2-Nb1-O8	89.6(3)	O2_c-V5-O10	112.4(2)	N2-Cu1-N2_h	176.9(8)

O2-Nb1-O11	99.0(3)	O3-P1-O3_e	109.1(5)	N1-Cu1-N2_h	95.9(7)
O2-Nb1-O2_a	76.0(2)	O3-P1-O3_a	70.9(5)	N1_h-Cu1-N2	95.9(7)
O2-Nb1-O3_c	63.1(3)	O3_b-P1-O3_g	109.1(5)	N3_i-Cu2-N4_k	92.5(6)
O3-Nb1-O5	67.9(3)	O3-P1-O3_d	180	N3_j-Cu2-N4_i	66.5(6)
O3-Nb1-O8	97.6(3)	O3-P1-O3_c	70.9(5)	N4_i-Cu2-N4_j	32.5(7)
O3-Nb1-O11	157.9(3)	O3_a-P1-O3_c	110.2(5)	N3_k-Cu2-N4_i	92.5(6)
O2_a-Nb1-O3	63.0(3)	O3_a-P1-O3_d	109.1(5)	N4_i-Cu2-N4_k	180
O3-Nb1-O3_c	42.2(3)	O3_c-P1-O3_d	109.1(5)	N3_j-Cu2-N4_j	87.5(6)
O5-Nb1-O8	95.7(3)	O3_c-P1-O3_e	69.8(5)	N3_j-Cu2-N3_k	101.6(7)
O5-Nb1-O11	101.5(3)	O5_c-Nb2-O5_e	87.9(3)	N3_j-Cu2-N4_k	113.5(6)
O2_a-Nb1-O5	90.7(3)	O5_c-Nb2-O8_f	157.2(3)	N3_k-Cu2-N4_j	113.5(6)
O3_c-Nb1-O5	98.9(3)	O5_e-Nb2-O8_f	87.4(3)	N4_j-Cu2-N4_k	147.5(7)
O8-Nb1-O11	102.9(3)	O3-P1-O3_f	69.8(5)	N3_k-Cu2-N4_k	87.5(6)
O2_a-Nb1-O8	155.4(3)	O3-P1-O3_g	109.1(5)	N3_k-Cu2-N4	66.5(6)
O3_c-Nb1-O8	66.1(3)	O3_a-P1-O3_b	70.9(5)	N4-Cu2-N4_k	32.5(7)
O2_a-Nb1-O11	99.1(3)	O3-P1-O3_b	110.2(5)	N3_i-Cu2-N4_i	87.5(6)
O3_c-Nb1-O11	157.8(3)	O3_b-P1-O3_f	180	N3_i-Cu2-N3_j	78.4(7)
O2_a-Nb1-O3_c	89.4(3)	O3_d-P1-O3_g	70.9(5)	N3-Cu2-N4	87.5(6)
O8-Nb2-O12	102.7(3)	O3_a-P1-O3_e	180	N3-Cu2-N3_i	101.6(7)
O5_c-Nb2-O8	87.4(3)	O3_a-P1-O3_f	109.1(5)	N3-Cu2-N4_i	113.5(6)
O5_e-Nb2-O8	157.2(3)	O3_c-P1-O3_f	109.1(5)	N3-Cu2-N3_j	180
O8-Nb2-O8_f	88.3(3)	O3_c-P1-O3_g	180	N3-Cu2-N4_j	92.5(6)
O5_c-Nb2-O12	100.1(3)	O3_d-P1-O3_e	70.9(5)	N3-Cu2-N3_k	78.4(7)
O5_e-Nb2-O12	100.1(3)	O3_d-P1-O3_f	110.2(5)	N3-Cu2-N4_k	66.5(6)
O8_f-Nb2-O12	102.7(3)	O3_a-P1-O3_g	69.8(5)	N3_i-Cu2-N4	113.5(6)
O2-V5-O2_b	135.3(3)	O3_b-P1-O3_c	70.9(5)	N4-Cu2-N4_i	147.5(7)
O2_b-V5-O2_c	81.7(3)	O3_b-P1-O3_d	69.8(5)	N3_j-Cu2-N4	92.5(6)
O2-V5-O10	112.4(2)	O3_b-P1-O3_e	109.1(5)	N4-Cu2-N4_j	180
O2_a-V5-O2_c	135.3(3)	O3_f-P1-O3_g	70.9(5)	N3_i-Cu2-N4_j	66.5(6)
O2_a-V5-O2_b	81.7(3)	O3_e-P1-O3_f	70.9(5)	N3_i-Cu2-N3_k	180
O2_a-V5-O10	112.4(2)	O3_e-P1-O3_g	110.2(5)		
O2-V5-O2_a	81.7(3)	N1_h-Cu1-N2_h	84.1(7)		

Symmetry transformations used to generate equivalent atoms: a = = -y,x,z; b = -x,-y,z; c = y,-x,z; d = -x,-y,-z; e = y,-x,-z; f= x,y,-z; g =-y,x,-z; h =-1/2+y,1/2+x,1/2-z; i = -x,1-y,z; j =-x,1-y,-z; k =x,y,-z.

Table S5 Selected bond angels for **2**.

Bond types	Bond angles	Bond types	Bond angles	Bond types	Bond angles
O1-Nb1-O2	99.3(4)	O13-Nb3-O16_a	101.9(6)	O6-V1-O7	82.3(4)
O1-Nb1-O2P	160.9(4)	O16_a-Nb3-O17	88.6(5)	O3-V1-O15	82.3(4)
O1-Nb1-O3	99.0(4)	O5-Nb4-O6	97.5(3)	O11-V1-O15	111.6(4)
O1-Nb1-O7	101.0(4)	O5-Nb4-O15	99.0(4)	O1P_a-P1-O2P	71.5(7)
O1-Nb1-O10	102.1(4)	O5-Nb4-O16	104.5(5)	O2P_a-P1-O4P	61.0(6)
O1-Nb1-O4P_a	162.8(4)	O5-Nb4-O20	103.2(4)	O3P_a-P1-O4P	73.1(7)
O2-Nb1-O2P	70.9(4)	O6-Nb4-O15	74.2(3)	O2P-P1-O4P	119.0(7)
O2-Nb1-O3	92.1(3)	O6-Nb4-O16	155.2(5)	O1P_a-P1-O2P_a	108.5(7)
O2-Nb1-O7	157.4(3)	O6-Nb4-O20	90.6(4)	O1P_a-P1-O3P_a	100.8(7)
O2-Nb1-O10	95.6(4)	O15-Nb4-O16	91.1(5)	O4P-P1-O4P_a	180
O2-Nb1-O4P_a	96.6(4)	O15-Nb4-O20	154.6(5)	O2P-P1-O2P_a	180

O2P-Nb1-O3	65.9(3)	O16-Nb4-O20	95.3(5)	O2P-P1-O3P_a	68.6(7)
O2P-Nb1-O7	86.7(4)	O3P-Nb5-O6	65.8(4)	O2P-P1-O4P_a	61.0(6)
O2P-Nb1-O10	95.4(4)	O3P-Nb5-O7	92.0(4)	O3P-P1-O4P	106.9(7)
O2P-Nb1-O4P_a	34.7(4)	O3P-Nb5-O8	157.5(5)	O1P_a-P1-O3P	79.2(7)
O3-Nb1-O7	74.9(3)	O3P-Nb5-O9	97.6(4)	O2P_a-P1-O3P	68.6(7)
O3-Nb1-O10	156.0(3)	O3P-Nb5-O19	65.1(4)	O1P_a-P1-O4P_a	108.7(6)
O3-Nb1-O4P_a	87.1(3)	O6-Nb5-O7	75.4(3)	O1P-P1-O2P	108.5(7)
O7-Nb1-O10	89.8(3)	O6-Nb5-O8	99.0(4)	O1P-P1-O3P	100.8(7)
O4P_a-Nb1-O7	64.8(4)	O6-Nb5-O9	157.8(3)	O1P-P1-O4P	108.7(6)
O4P_a-Nb1-O10	69.6(4)	O6-Nb5-O19	91.7(4)	O1P-P1-O1P_a	180
O3P-Nb2-O4	91.3(4)	O7-Nb5-O8	100.4(4)	O1P-P1-O2P_a	71.5(7)
O3P-Nb2-O14	159.4(5)	O7-Nb5-O9	91.2(4)	O1P-P1-O3P_a	79.2(7)
O3P-Nb2-O19	62.8(4)	O7-Nb5-O19	156.9(4)	O1P-P1-O4P_a	71.3(6)
O3P-Nb2-O20	65.4(4)	O8-Nb5-O9	100.9(4)	O2P-P1-O3P	111.4(7)
O2_a-Nb2-O3P	94.9(4)	O8-Nb5-O19	100.6(5)	O3P_a-P1-O4P_a	106.9(7)
O4-Nb2-O14	100.7(5)	O9-Nb5-O19	94.4(5)	O2P_a-P1-O3P_a	111.4(7)
O4-Nb2-O19	87.9(4)	O1P-Nb6-O4	96.1(4)	O2P_a-P1-O4P_a	119.0(6)
O4-Nb2-O20	155.4(4)	O1P-Nb6-O12	158.5(5)	O3P-P1-O3P_a	180
O2_a-Nb2-O4	87.3(3)	O1P-Nb6-O17	63.3(5)	O1P_a-P1-O4P	71.3(6)
O14-Nb2-O19	100.6(5)	O1P-Nb6-O3_a	90.8(4)	O3P-P1-O4P_a	73.1(7)
O14-Nb2-O20	103.9(5)	O1P-Nb6-O15_a	64.1(4)	N4-Co1-N5	85.2(4)
O2_a-Nb2-O14	102.4(4)	O4-Nb6-O12	101.8(5)	N4-Co1-N6	92.9(4)
O19-Nb2-O20	87.9(4)	O4-Nb6-O17	94.8(5)	N5-Co1-N6	92.3(4)
O2_a-Nb2-O19	157.0(4)	O3_a-Nb6-O4	89.9(3)	N1-Co1-N2	93.0(4)
O2_a-Nb2-O20	87.3(3)	O4-Nb6-O15_a	154.0(4)	N1-Co1-N3	85.5(4)
O1P-Nb3-O9	92.5(4)	O12-Nb6-O17	103.1(5)	N1-Co1-N4	176.3(4)
O1P-Nb3-O10	96.3(4)	O3_a-Nb6-O12	100.9(4)	N1-Co1-N5	92.4(5)
O1P-Nb3-O13	158.7(4)	O12-Nb6-O15_a	101.5(5)	N1-Co1-N6	90.0(4)
O1P-Nb3-O17	61.6(5)	O3_a-Nb6-O17	154.0(4)	N2-Co1-N3	91.5(4)
O1P-Nb3-O16_a	66.3(5)	O15_a-Nb6-O17	90.9(5)	N2-Co1-N4	89.6(4)
O9-Nb3-O10	86.4(4)	O3_a-Nb6-O15_a	74.5(3)	N2-Co1-N5	174.1(4)
O9-Nb3-O13	100.7(4)	O3-V1-O6	138.5(3)	N2-Co1-N6	85.3(4)
O9-Nb3-O17	87.9(5)	O3-V1-O7	83.0(3)	N3-Co1-N4	91.8(4)
O9-Nb3-O16_a	157.4(5)	O3-V1-O11	111.3(4)	N3-Co1-N5	91.3(5)
O10-Nb3-O13	101.2(4)	O7-V1-O15	137.5(4)	N3-Co1-N6	174.4(4)
O10-Nb3-O17	156.9(5)	O6-V1-O11	110.2(4)	N7-Co2-N8	87.3(9)
O10-Nb3-O16_a	88.2(4)	O6-V1-O15	83.0(4)	O1W-Co2-N7	88.8(8)
O13-Nb3-O17	101.9(5)	O7-V1-O11	110.9(4)	O1W-Co2-N8	92.3(8)

Symmetry transformations used to generate equivalent atoms: a = 1-x,1-y,-z.

Scheme. S1 The proposed formation process for polyanion $PNb_{12}O_{40}(VO)_2$.

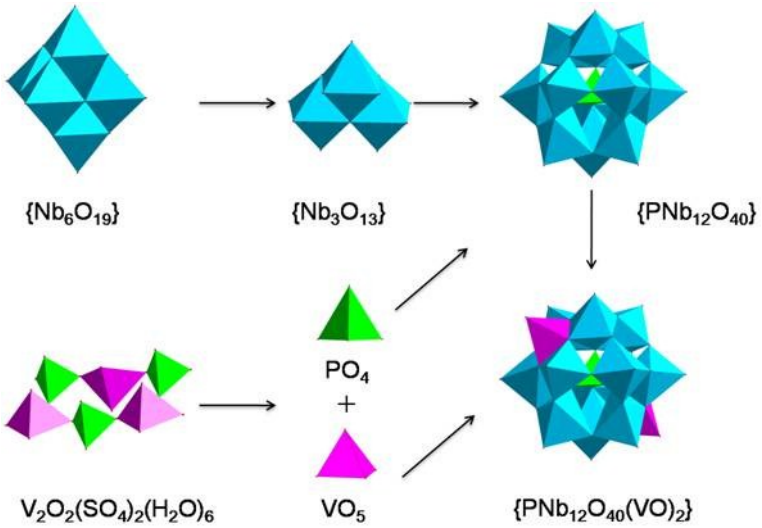


Fig. S1 Digital photograph of **1** (left) and **2** (right).

Fig. S2 The PXRD patterns of **1**(left) and **2** (right).

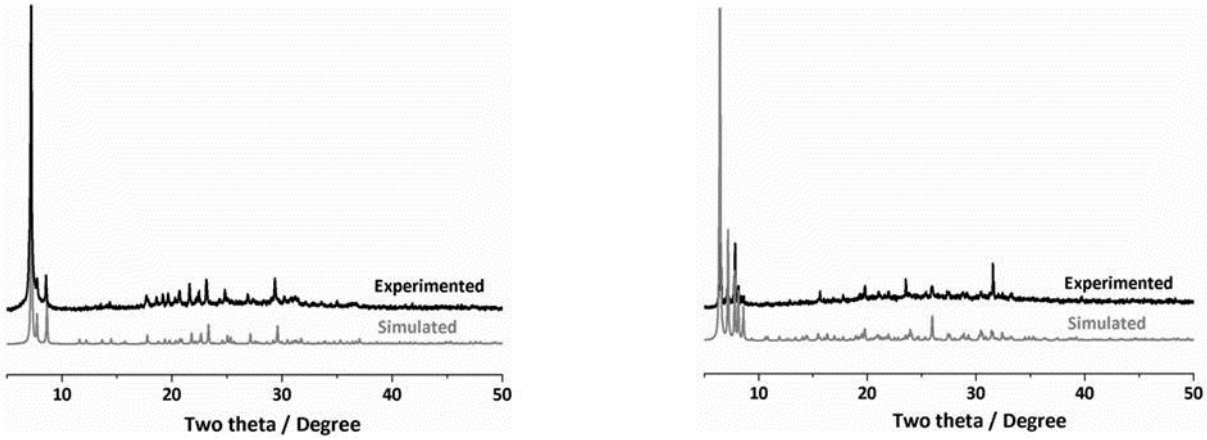


Fig. S3 IR spectra of **1**(left) and **2** (right).

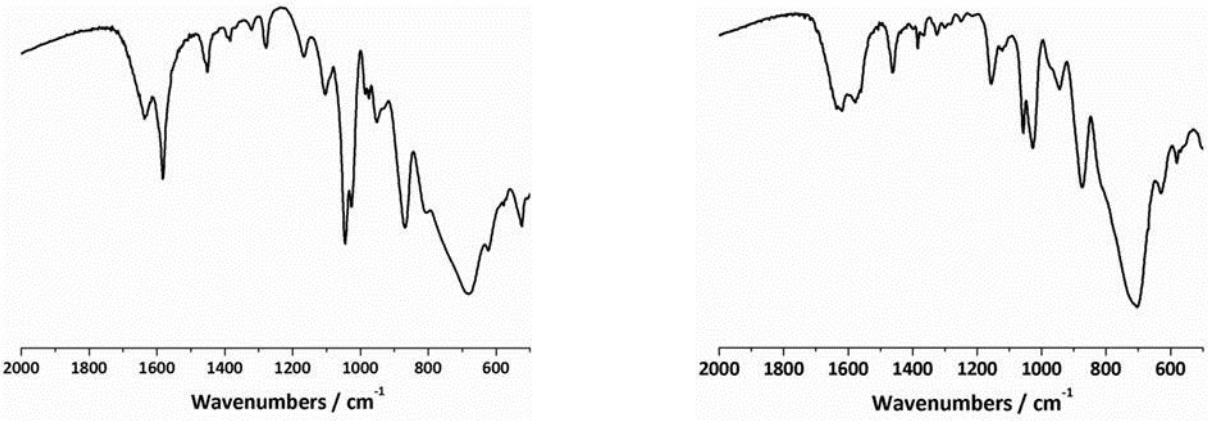


Fig. S4 The TG curves for **1** (left) and **2** (right). According to the TG analysis, a total of eleven and twenty lattice water molecules in 1 and 2 can be determined, respectively.

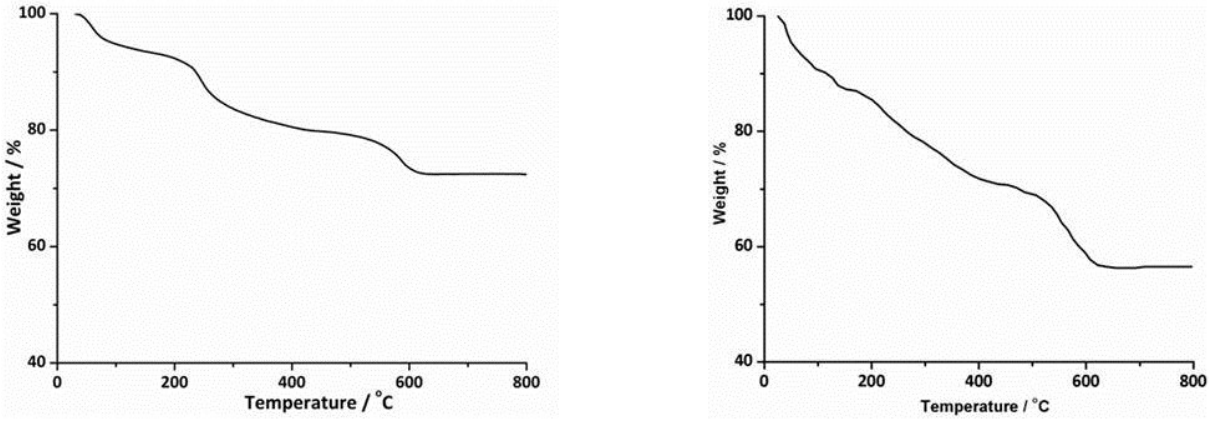


Fig. S5 The XPS survey spectrum for **1** (left) and **2** (right). The binding energies were obtained with reference to the C 1s at 284.8 eV. The plot displays signals attributable to Nb3d, V2p, Cu/Co2p, P2p, C1s, N1s.

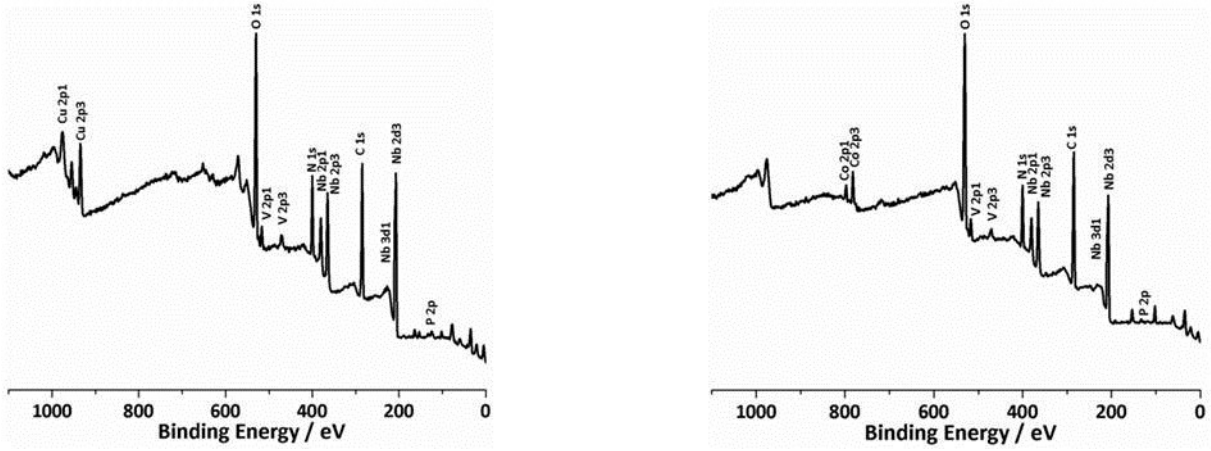


Fig. S6 The XPS V2p spectra of **1** (left) and **2** (right).

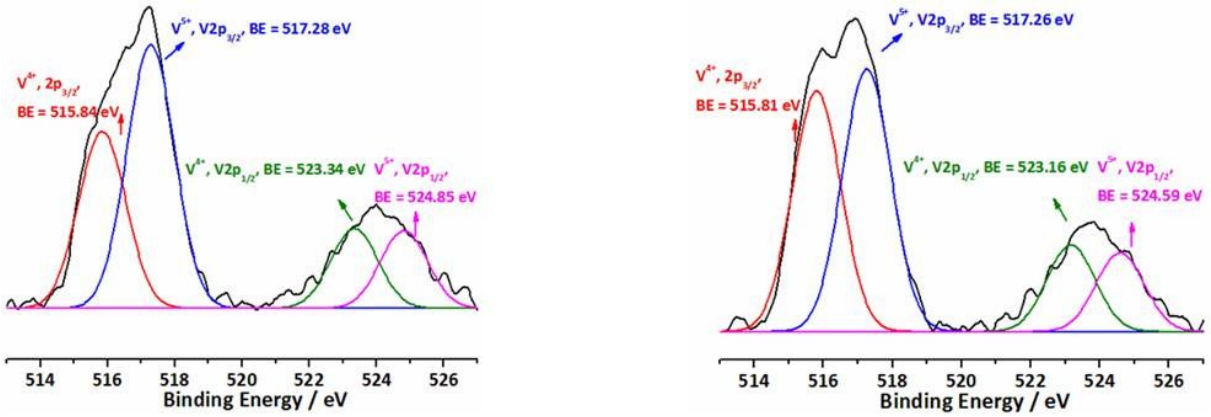
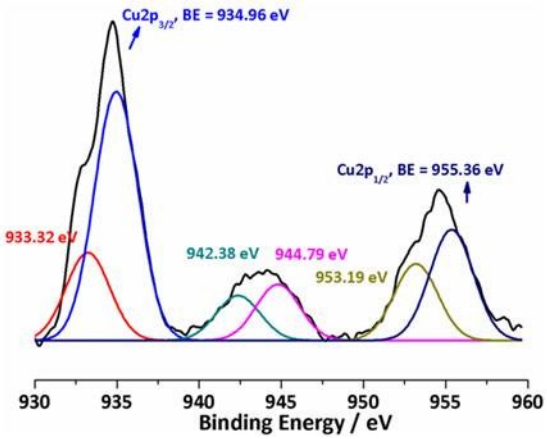


Fig. S7 The XPS Cu2p spectrum of **1** (left) and Co2p spectrum of **2** (right).



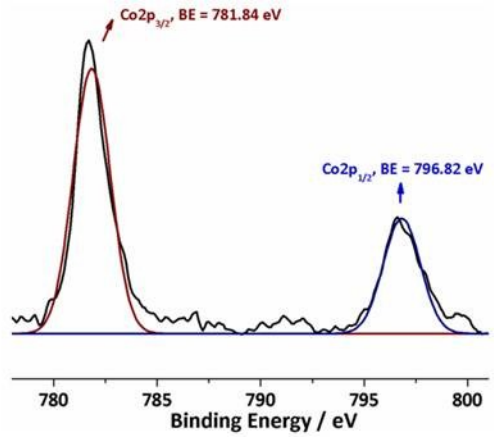


Fig. S8 The solvents optimized for **1** as catalyst for oxidation of ethylbenzene.

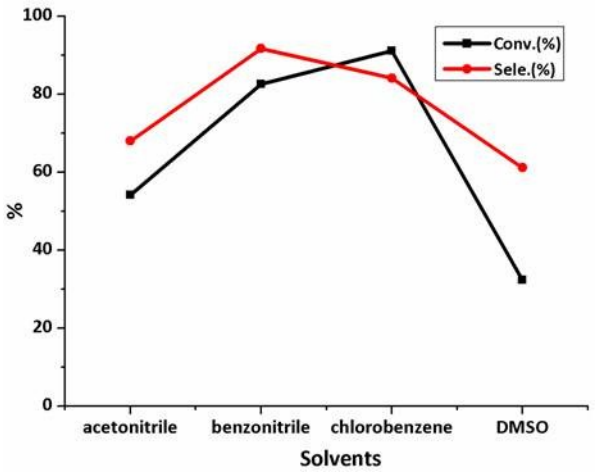


Fig. S9 The amount of catalyst employed optimized for **1** towards oxidation of ethylbenzene.

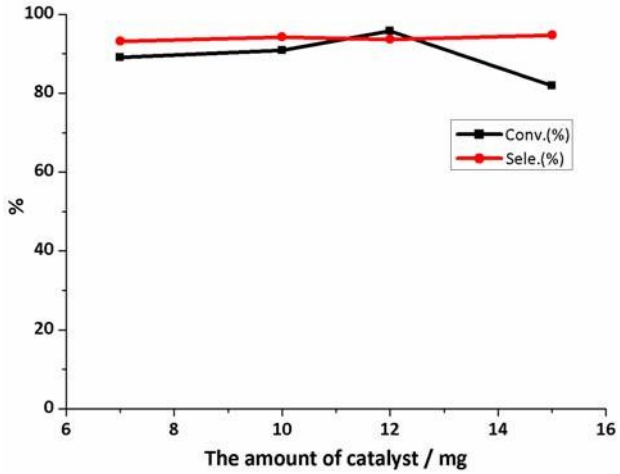


Fig. S10 The reaction temperature optimized for **1** as catalyst for oxidation of ethylbenzene.

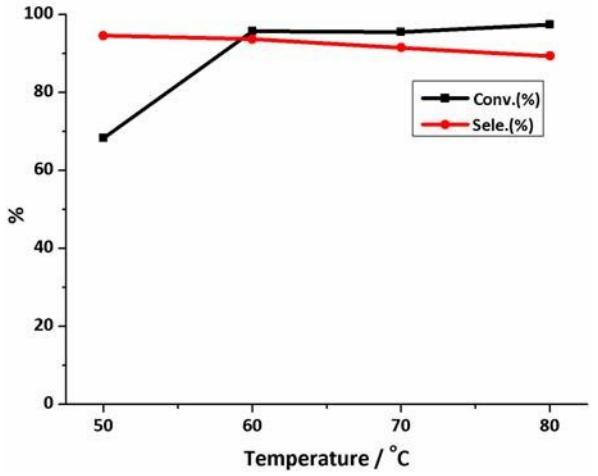


Fig. S11 The reaction time optimized for **1** as catalyst for oxidation of ethylbenzene.

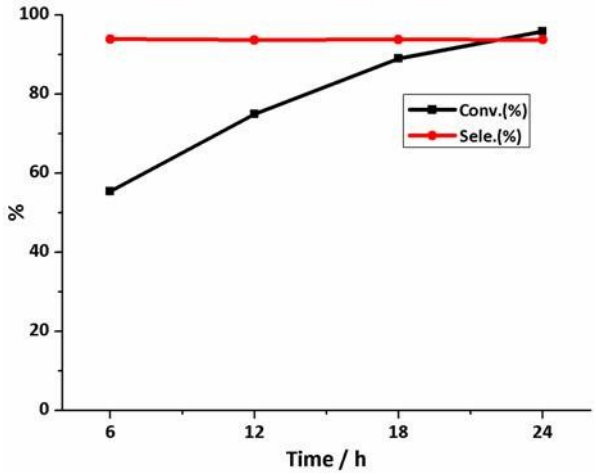


Fig. S12 Conversion and selectivity of diphenylmethane to benzophenone in recycle experiments. Reaction conditions: diphenylmethane (0.125 mmol), catalyst (12 mg), solvent benzonitrile (0.5mL), TBHP (70% in water, 2.5equiv), 60^{o}C, 24 h.

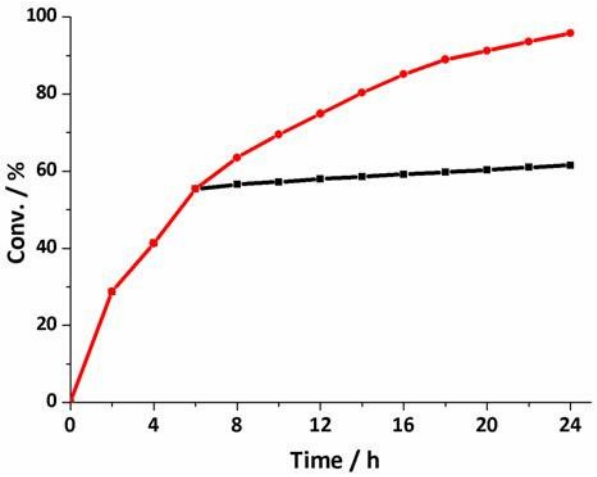


Fig. S13 The XPRD patterns of compound **1** after catalysis.

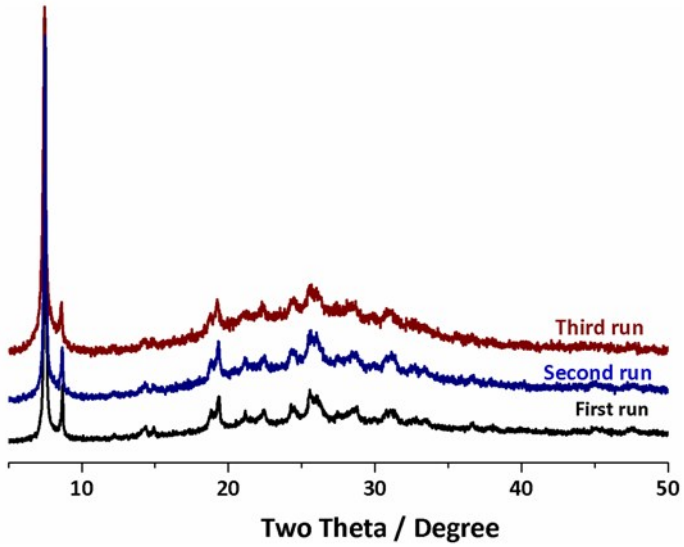


Fig. S14 The IR patterns of compound **1** after catalysis.