Supplementary File

Hydrothermal synthesis of two supramolecular inorganic organic hybrid phosphomolybdates based on Ni (II) and Co(II): structural diversity and heterogeneous catalytic activities

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Table S1: Selected bond lengths (Å) and angles (°) for 1 and 2

(ia) Selected Bond length of complex **1**

Mo1-Mo2	2.5754(11)	Mo4-O18	2.095(3)
Mo1 -O4	2.299(3)	Mo5-O3	2.283(3)
Mo1 -O5	1.932(3)	Mo5-O18	2.091(3)
Mo1 -O6	1.676(3)	Mo5-O21	2.048(3)
Mo1 -O7	2.096(3)	Mo5-O22	1.943(3)
Mo1 -O8	2.052(3)	Mo5-O23_a	1.673(3)
Mo1-O14	1.978(3)	Mo5 -O24	1.970(3)
Mo2-O2	2.295(3)	Mo6 -O2	2.277(3)
Mo2 -O5	1.927(3)	Mo6 -O22	1.943(3)
Mo2 -O27	2.099(3)	Mo6 -O24	1.981(3)
Mo2 -O30	2.047(4)	Mo6-O25	1.671(3)
Mo2-O31	1.678(4)	Mo6-O26	2.045(4)
Mo3 -Mo4	2.5863(11)	Mo6 -O27	2.092(3)
Mo3 -O4	2.281(3)	Ni1-O13	2.165(3)
Mo3 -O7	2.092(3)	Ni1-O14	2.141(3)
Mo3-O11	2.047(3)	Ni1 -O24	2.145(3)
Mo3 -O12	1.678(4)	Ni1–O13_a	2.165(3)
Mo3 -O15	1.944(4)	Ni1 -O24_a	2.145(3)
Mo4 -O3	2.284(3)	Mo3 -O13_a	1.977(3)
Mo4 -O13_a	1.971(3)	Ni1–O14_a	2.141(3)

Symmetry Code: a = 1-x,1-y,2-z.

(ib)Selected Bond angles of complex **1**

Mo2-Mo1-O4	88.75(7)	O3-Mo4-O18	73.44(10)
Mo2-Mo1-O5	48.05(8)	O3-Mo4-O13_a	81.01(11)
Mo2-Mo1-O6	99.63(10)	O15-Mo4-O18	156.05(14)
Mo2-Mo1-O7	134.17(7)	O16-Mo4-O17	96.99(17)
Mo2-Mo1-O8	134.89(11)	Mo6-Mo5-O21	134.38(11)
O4-Mo1-O5	82.87(11)	O22-Mo5-O24	95.57(12)
O4-Mo1-O6	170.82(14)	O24-Mo6-O25	101.93(17)
O5-Mo1-O6	105.52(15)	O25-Mo6-O26	96.36(16)
O5-Mo1-O7	155.66(11)	O13-Ni1-O14	85.16(10)
O6-Mo1-O7	97.97(15)	O13-Ni1-O24	83.78(11)
Mo1-Mo2-O2	89.23(7)	O13-Ni1-O13_a	180.00
Mo1-Mo2-O5	48.20(9)	O13-Ni1-O14_a	94.84(10)
Mo1-Mo2-O14	49.39(8)	O24-Ni1-O24_C	180.00
Mo1-Mo2-O27	135.19(7)	O13_a-Ni1-O14_a	85.16(10)
Mo1-Mo2-O30	132.37(8)	O13_a-Ni1-O24_a	83.78(11)
O27-Mo2-O30 Mo4-Mo3-O4	77.89(11) 89.23(7)	Mo4-O3-Mo5 Mo1-O4-Mo3	99.59(11) 99.35(11)
Mo4-Mo3-O11	133.23(10)	Mo3_a-O13-Ni1	135.33(13)
Mo4-Mo3-O15	48.36(9)	Mo4_a-O13-Ni1	134.49(14)
O4-Mo3-O11	78.89(12)	Mo3-O15-Mo4	83.35(15)
O7-Mo3-O11	85.65(11)	Mo4-O18-Mo5	112.85(13)
O11-Mo3-O15	85.20(13)	Mo5-O24-Ni1	134.05(14)
O12-Mo3-O15	105.16(16)	Mo6-O24-Ni1	135.10(13)
Mo3-Mo4-O3	88.92(7)	Mo2-Mo1-O14	49.37(8)
Mo3-Mo4-O18	134.05(7)	O4-Mo1-O7	73.32(11)
O4-Mo1-O8	79.50(10)	O14-Mo2-O27	86.64(11)
O4-Mo1-O14	80.45(10)	O27-Mo2- O30	84.63(11)
O5-Mo1-O8	87.12(14)	O30-Mo2- O31	99.25(16)
O5-Mo1-O14	95.45(12)	O4-Mo3- O12	17.20(15)
O6-Mo1-O8	96.94(13)	O3-Mo5- O18	73.54(10)
O6-Mo1-O14	102.11(13)	O18-Mo5- O21	84.07(13)
O7-Mo1-O8	83.73(13)	O21-Mo5- O22	86.51(14)
O7-Mo1-O14	85.65(11)	O2-Mo6- O22	83.68(10)

O8-Mo1-O14	159.30(10)	O2-Mo6- O24	80.80(11)
Mo1-Mo2-O31	99.21(11)	O26-Mo6- O27	84.78(12)
O2-Mo2-O31	170.51(13)	Mo4-Mo3-O4	89.23(7)

Symmetry Code: a = 1-x,1-y,2-z.

(iia)Selected Bond length of complex **2**

Mo1-O1	1.928(6)
Mo1-O2	1.709(5)
Mo1–O3	2.277(4)
Mo1–O1_a	1.928(6)
Mo2-O1	1.938(5)
Mo2 -O3	2.317(6)
Mo2-O4	1.717(6)
Mo2-O5	1.714(5)
Mo2-O6	1.914(5)
Mo2-O8_a	2.188(5)
Mo3-O8	2.330(4)
Mo3 -O9	1.729(6)
Mo3 -O10	1.8912(17)
Mo3 -O11	2.292(6)
Mo3 -O12	1.702(5)
Mo3 -O6_a	1.925(5)
Co1 -O15	2.075(6)
Co1-O13_b	2.131(7)
Co1-O14_b	2.094(5)
Co1-O15_b	2.075(6)
Co1 -O13	2.131(7)
Co1-O14	2.094(5)
P1 -O3	1.559(6)
P1 -O11_a	1.535(5)
P1 -O8	1.548(5)

Symmetry Code: a = 1-x,y,1/2-z , b =1-x,-y,-z

(iib)Selected Bond angles of complex **2**

O1-Mo1-O2	101.9(3)	O1_a -Mo1-O2_a	101.9(3)
O1-Mo1-O3	73.0(2)	O1_a -Mo1-O3_a	73.0(2)
O1-Mo1-O1_a	146.91(18)	O2_a-Mo1 -O3_a	88.49(19)
O1-Mo1-O2_a	98.5(3)	O1-Mo2-O3	71.9(2)
O1-Mo1-O3_a	81.8(2)	O1-Mo2-O4	95.3(2)
O2-Mo1-O3	88.49(19)	O1-Mo2-O5	100.3(2)
O1_a-Mo1-O2	98.5(3)	O1-Mo2-O6	152.7(2)
O2-Mo1-O2_a	103.2(2)	O1-Mo2 -O8_a	81.84(18)
O2-Mo1-O3_a	167.0(2)	O3 -Mo2 -O4	164.1(2)
O1_a -Mo1-O3	81.8(2)	O3-Mo2-O5	87.7(2)
O2_a-Mo1-O3	167.0(2)	O3-Mo2-O6	89.0(2)
O3-Mo1-O3_a	80.59(15)	O3-Mo2-O8_a	72.86(19)
O4-Mo2-O5	104.3(3)	O4-Mo2-O6	99.4(2)
O4-Mo2-O8_a	96.4(2)	O5-Mo2-O6	98.2(2)
O5-Mo2-O8_a	158.9(3)	O6-Mo2-O8_a	73.86(18)
O8-Mo3-O9	84.7(2)	O8-Mo3-O10	85.2(2)
O8-Mo3-O11	86.57(17)	O8-Mo3-O12	167.95(19)
O6_a-Mo3-O8	70.37(18)	O9 -Mo3-O12	102.5(3)
O10-Mo3-O12	103.0(2)	O6_a-Mo3-O11	76.4(2)
O13_b-Co1-O15_b	84.7(3)	O14_b-Co1-O15_b	88.3(2)
O13-Co1-O14	91.3(2)	O13 -Co1-O15	84.7(3)
O13-Co1-O13_b	180.00	O13-Co1-O14_b	88.7(2)
O13-Co1-O15_b	95.3(3)	O14-Co1-O15	88.3(2)
O13_b-Co1-O14	88.7(2)	O14-Co1-O14_b	180.00
O14-Co1-O15_b	91.7(2)	O13_b-Co1-O15	95.3(3)
O14_b-Co1-O15	91.7(2)	O15-Co1-O15_b	180.00
Co1-O14-H5	116(12)	Co1-O15-H8	116(12)
Co1-O15-H7	127(14)	Mo1-O1-Mo2	120.8(3)

Symmetry Code: a =1-x,y,1/2-z; b = 1-x,-y,-z

Table S2. Hydrogen Bonds (Å, °) for Complex 1

A-B···C	Distance between A-B (Å)	Distance between B···C (Å)	Distance between A···C (Å)	Bond angle (°)
N1-H1···O10	0.91(5)	1.78(6)	2.641(6)	158(5)
N2-H2C···O35	0.9000	2.4400	2.941(14)	115.00
N2-H2C···O36	0.9000	2.0300	2.866(12)	153.00
N2-H2D···O28	0.9000	1.7700	2. 671(6)	175.00
C2-H2A···O6	0.9700	2.4200	3.345(7)	159.00
C3-H3B···O30	0.9700	2.5800	3.406(7)	143.00
C4-H4A···O31	0.9700	2.2300	3.094(7)	148.00
C5-H5B···O11	0.9700	2.5600	3.334(7)	137.00
C6-H6A···O19	0.9700	2.3900	3.293(7)	154.00
C6-H6B···O10	0.9700	2.3800	3.186(6)	140.00
C6-H6B···O32A	0.9700	2.4300	3.013(11)	119.00
C9-H9A···O21	0.9700	2.5400	3.324(7)	138.00
C10-H10A···O5	0.9700	2.5300	3.135(8)	120.00
C13-H13A···O19	0.9700	2.5600	3.466(8)	155.00
C15-H15B···O1	0.9700	2.5500	3.218(14)	126.00

Table S3. Hydrogen Bonds (Å, °) for Complex 2

A-B···C	Distance between A-B (Å)	Distance between B···C(Å)	Distance between A···C(Å)	Bond angle(°)
N1–H1···O11	0.90(15)	1.86(16)	2.732(8)	161(18)
N1–H1D···O7	0.94(19)	1.9(2)	2.736(12)	153(12)
N2 -H2N···O16	0.79(8)	2.53(16)	2.802(11)	102(13)
N2 -H2N···O18	0.79(8)	1.99(8)	2.744(10)	158(14)
O13- H3··· O2	0.84(19)	1.88(16)	2.689(9)	161(17)
O13- H4··· O9	0.85(12)	2.55(14)	3.267(7)	142(11)
O14- H5··· O1	0.86(18)	1.96(17)	2.735(8)	150(15)
O15- H7··· O7	0.85(10)	1.90(12)	2.684(7)	154(16)

O15- H8··· O2	0.9(2)	2.57(17)	3.053(7)	117(14)
O15- H8··· O17	0.9(2)	2.0(2)	2.866(11)	162(17)
O16- H16··· O9	0.85(10)	1.90(17)	2.609(9)	154(17)
C1- H1A··· O4	0.9700	2.4300	3.258(10)	144.00
C2- H2B···O6	0.9700	2.5200	3.450(9)	161.00
C2- H2B··· O12	0.9700	2.4500	3.176(9)	132.00
C4- H4A···O7	0.9700	2.5900	3.251(9)	125.00
C4- H4B···O4	0.9700	2.5500	3.350(9)	140.00
C5- H5B···O4	0.9700	2.4100	3.275(11)	148.00

Table S4. Oxidation of styrene over POM based complexes 1 and 2[t].

catalyst	**Conversion (%)**	**Main product**	**Selectivity (%)**
1.	81.141	Benzaldehyde	84.47
2.	54.85	Benzaldehyde	89.148

[t]Reaction condition: 0.50 g substrate, 0.55 g 30% H_2O_2, 10 ml MeCN, 0.02 g catalyst, 60ºC temperature, maximum time 24 h.

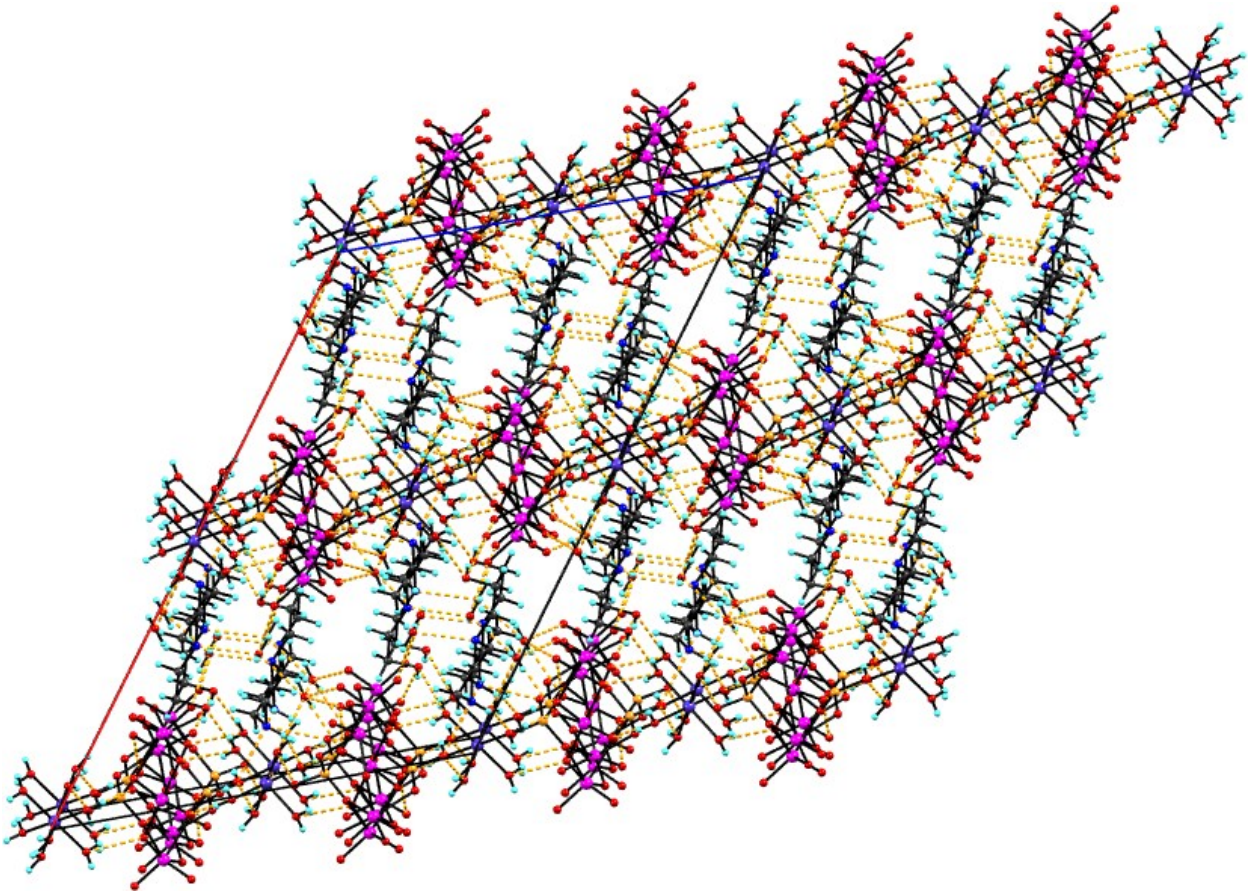

Fig.S1 The supra-molecular H-bonded 3D network along crystallographic *b* axis in complex **2**.

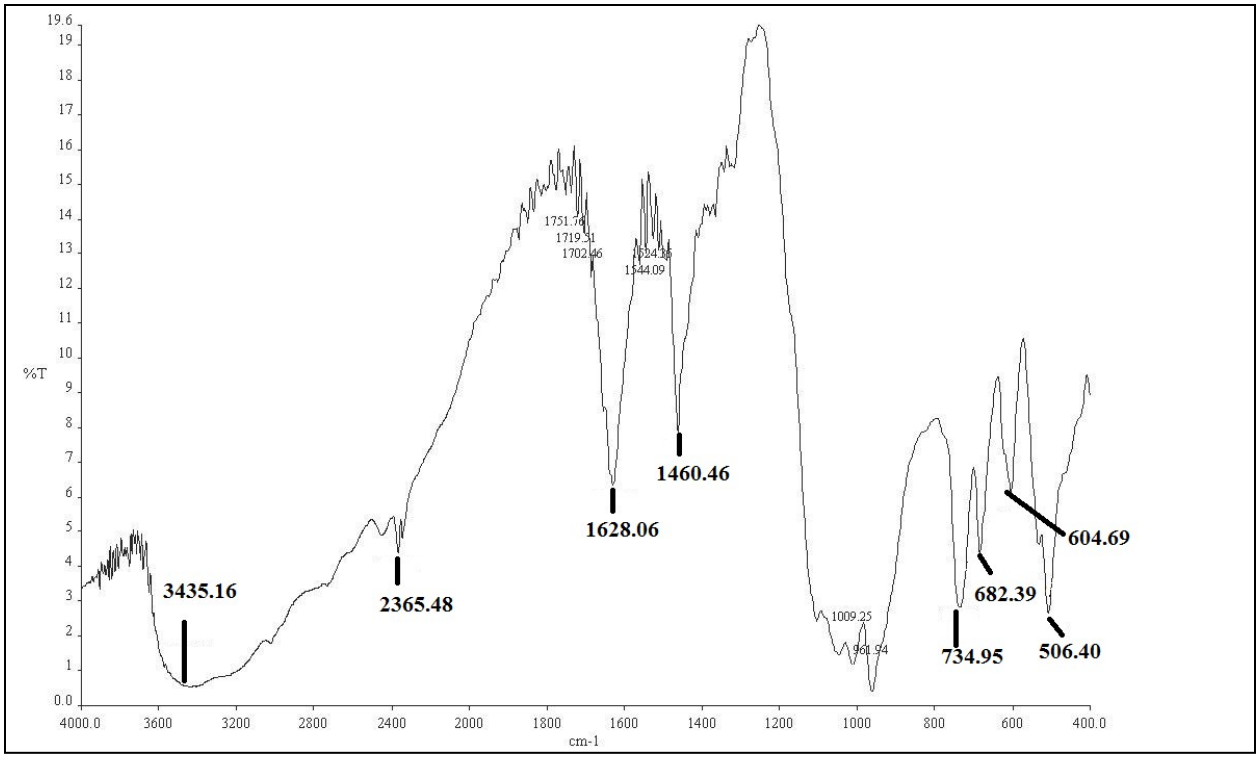

Fig.S2 (a)IR spectra of complex **1(Ni POM)**.

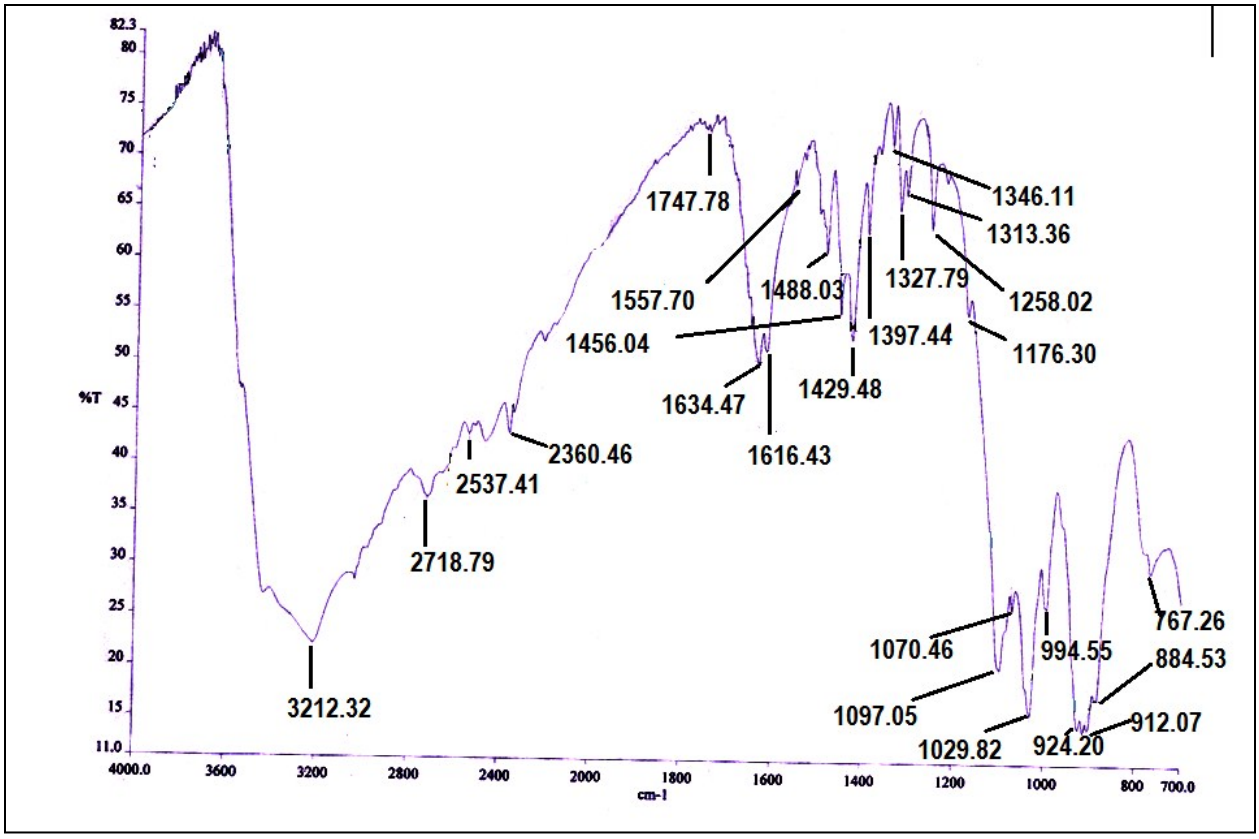

Fig.S2 (b)IR spectra of complex **2(Co- POM)**.

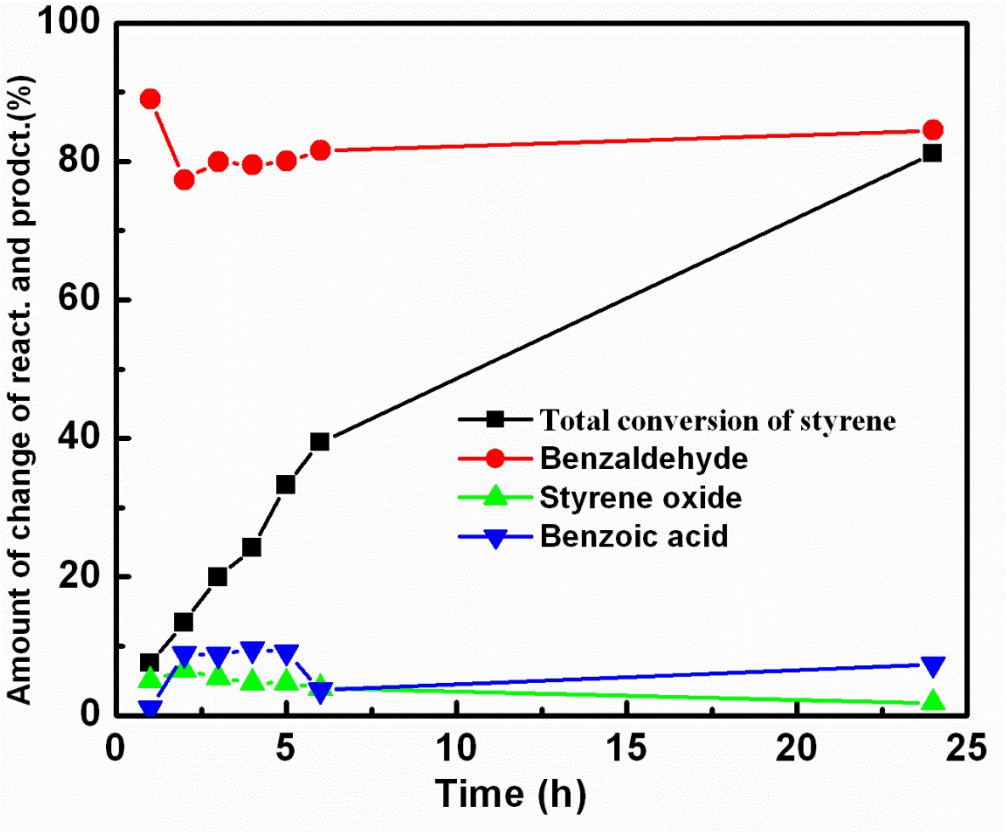

Fig.S3 Styrene conversion and benzaldehyde /styrene oxide formation respect to time for catalyst **1**

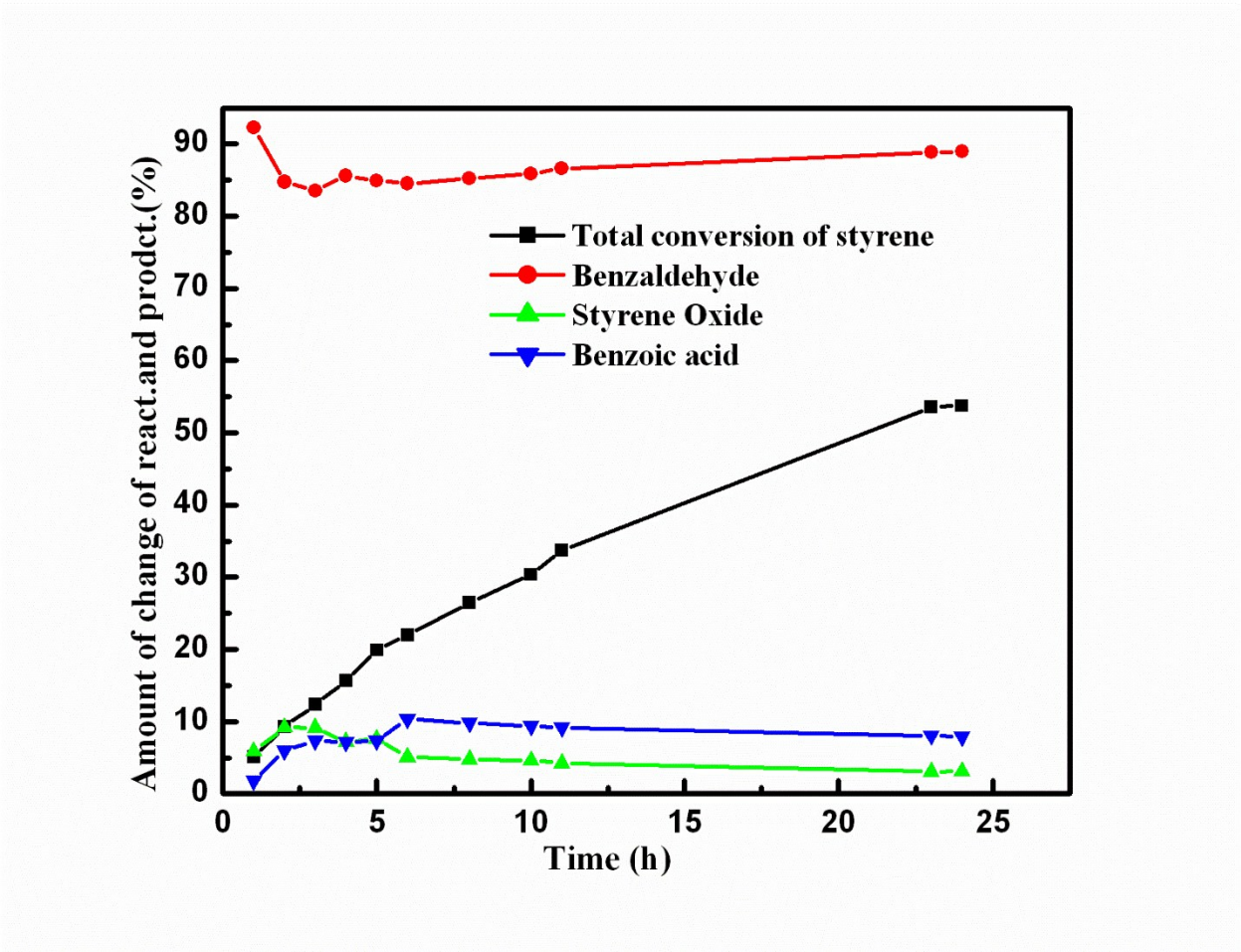

Fig.S4 Styrene conversion and benzaldehyde/styrene oxide formation respect to time for catalyst **2**.

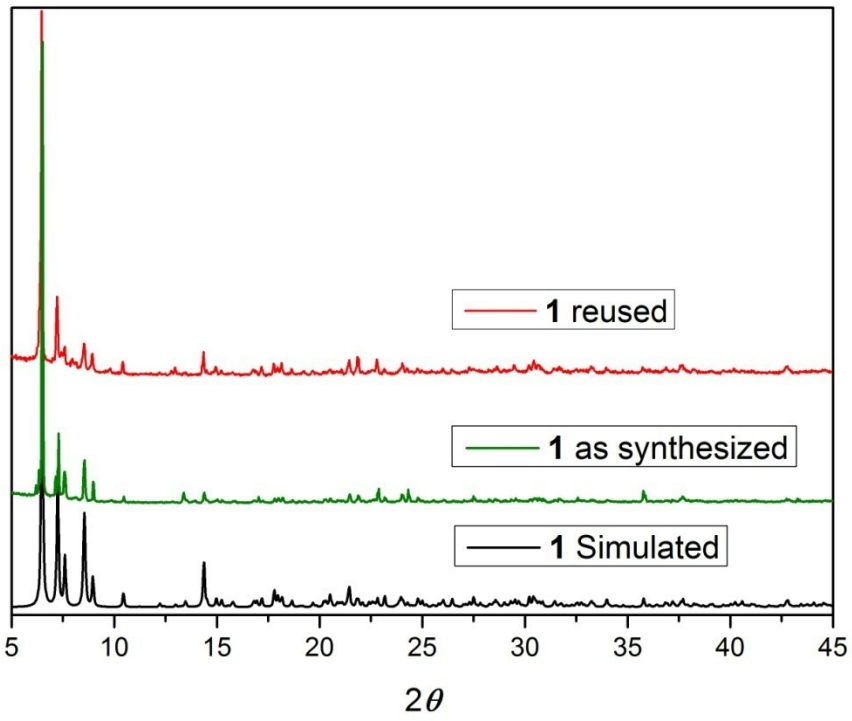

Fig.S5 Powder XRD plot of complex **1.**

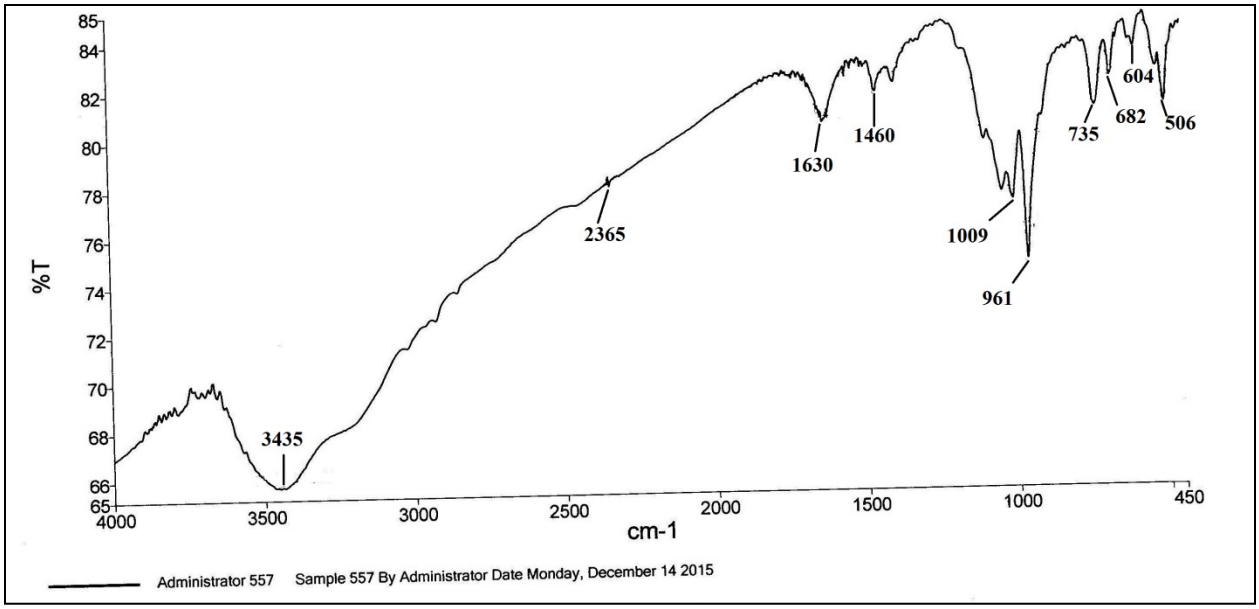

Fig.S6 (a) :IR spectra of reused complex **1(Ni POM)**.

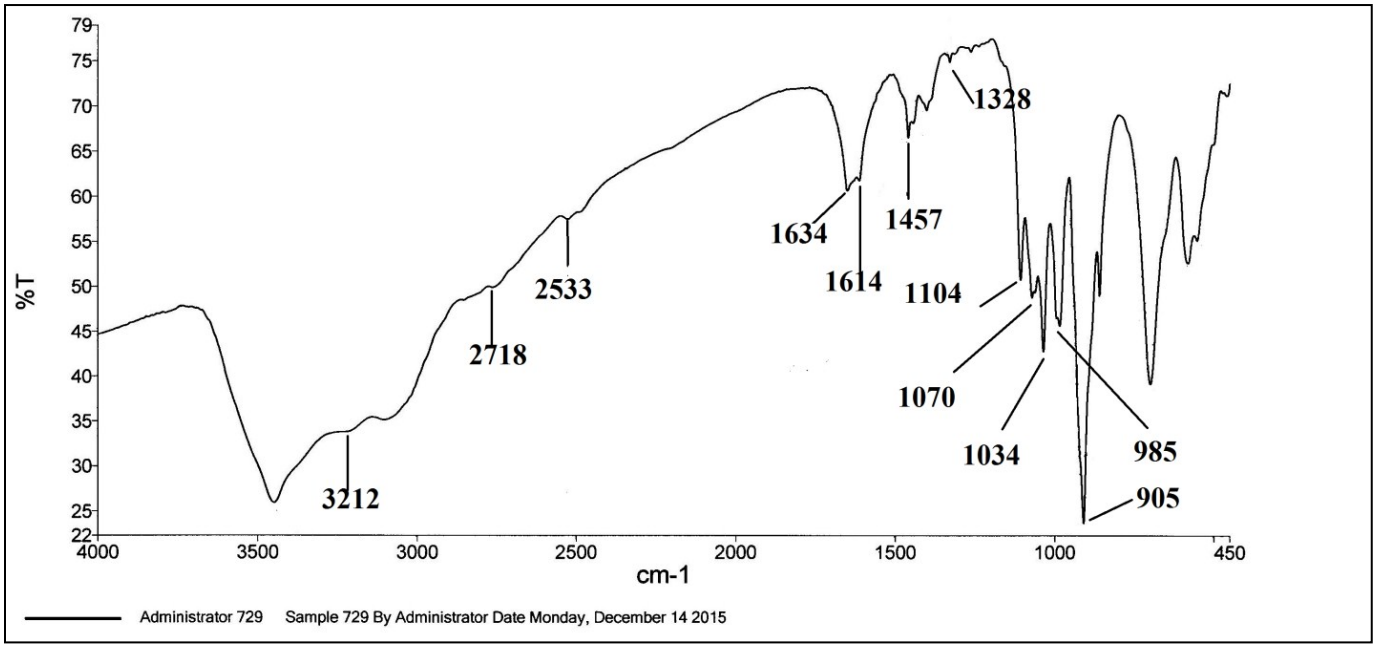

Fig.S6(b) IR spectra of reused complex **2(Co POM)**.