Electronic Supplementary Information (ESI)
For

A Nanosized $\{Zn_2Ru_3\}$ Coordination Cage Templated by Various Polyoxometalates

Lei Wang,[a] Jun-Feng Liu,[a,b] Weiting Yang,[a] Fei-Yan Yi,[a] Song Dang,[a] and Zhong-Ming Sun*[a]

[a]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, P.R. China.
[b] University of Chinese Academy of Sciences, Beijing 100049, P. R. China.
E-mail: szm@ciac.ac.cn

Contents

1. Experimental Section

1.1 Materials and methods

1.2 Synthesis

1.3 Catalytic Studies

1.4 Structure Determinations

2. The Structural Views of Four Compounds

3. Characterization Section

3.1 The PXRD analysis

3.2 The IR spectrum

3.3 The EDS analysis

3.4 TG-DTA analysis

1. Experimental Section

1.1 Materials and methods

All chemicals used during this investigation were reagent grade and used as received. The synthesis of *m*-H_2L_{Ru} was according to our reported method.[1] The POMs ($H_4PVMo_{11}O_{40}$ and $H_5PV_2Mo_{10}O_{40}$) was synthesized according to reported method.[2] Elemental analyses of C, H and N was carried out with a VarioEL analyzer. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu *K*α radiation (λ = 1.5418Å). Thermogravimetric analysis (TGA) was carried out on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) from room temperature in air atmosphere with a heating rate of 10 °C/min. The infrared (IR) spectrum was measured within the 650-4000 cm^{-1} region on a Nicolet iS10 spectrometer with ITR mode. The EDS spectrums were collected by the Bruker AXS XFlash detector 4010 associated in the FE-SEM (Hitachi S4800) at an accelerating voltage and current of 20 kV and 15 μA. Gas chromatographic (GC) analyses were performed using a GC7900P (techcomp Limited, Shanghai, China) equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). Inlet and detector temperatures were set constant at 180 °C. *n*-Dodecane was used as an internal standard to calculate reaction conversions.

1.2 Synthesis

For compound SiW-1, a solid mixture of $Zn(OAc)_2{\cdot}4H_2O$ (10 mg, 0.02 mmol), ***m*-H_2L_{Ru}** (2.5 mg, 0.003 mmol) and $H_4SiW_{12}O_{40}{\cdot}xH_2O$ (28 mg, 0.01 mmol) was dissolved in a vial containing 2.5 ml DMF and HAc (60 μL). The mixture was allowed to stand in a capped vial at 358 K for 6 d. Red block crystals of **SiW-1** were washed with DMF and air under air. CHN analysis calcd (%) for **SiW-1**: C 26.07, H 2.37, N 6.67; found: C 26.64, H 2.22, N 6.72. IR (cm^{-1}): 3478 (w), 1645 (s), 1604 (m), 1542 (w), 1463 (w), 1442 (w), 1355 (s), 1205 (w), 1091 (m), 1012(m), 968 (s), 916 (s), 781 (s), 754(s), 657 (w).

For compound PVM-2, a solid mixture of $Zn(OAc)_2{\cdot}4H_2O$ (10 mg, 0.02 mmol), ***m*-H_2L_{Ru}** (2.5 mg, 0.003 mmol) and $H_4PVMo_{11}O_{40}$ (28 mg, 0.01 mmol) was dissolved in a vial containing 2.5 ml DMF and HAc (60 μL). The mixture was allowed to stand in a capped vial at 358 K for 6 d. Red block crystals of **PVM-2** were washed with DMF and air under air. CHN analysis calcd (%) for **PVM-2**: C 32.86, H 3.14, N 8.61; found: C 32.92, H 2.97, N 8.73. IR (cm^{-1}): 3402 (w), 1649 (s), 1541 (w), 1444 (m), 1355 (s), 1224 (m), 1057 (s), 934(s), 856 (m), 778 (s), 744 (s), 707(w), 559 (w).

For compound PV_2M-3, a solid mixture of $Zn(OAc)_2{\cdot}4H_2O$ (10 mg, 0.02 mmol), ***m*-H_2L_{Ru}** (2.5 mg, 0.003 mmol) and $H_5PV_2Mo_{10}O_{40}$ (28 mg, 0.01 mmol) was dissolved in a vial containing 2.5 ml DMF and HAc (60 μL). The mixture was allowed to stand in a capped vial at 358 K for 6 d. Red block crystals of **PV_2M-3** were washed with DMF and air under air. CHN analysis calcd (%) for **PV_2M-3**: C 32.66, H 2.96, N 8.36; found: C 33.17, H 2.86, N 8.27. IR (cm^{-1}): 3467 (w), 1653 (s), 1599 (m), 1543 (w), 1444 (m), 1353 (s), 1218 (m), 1093 (w), 1054 (m), 966 (w), 916 (s), 876 (w), 788(s), 752 (s), 704 (w), 604 (w).

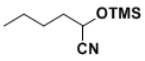
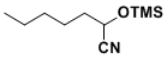
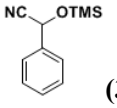
For compound PM-4, a solid mixture of $Zn(OAc)_2{\cdot}4H_2O$ (10 mg, 0.02 mmol), ***m*-H_2L_{Ru}** (2.5 mg,

0.003 mmol) and $H_7PMo_{12}O_{40}\cdot xH_2O$ (28 mg, 0.01 mmol) was dissolved in a vial containing 2.5 ml DMF and HAc (60 μL). The mixture was allowed to stand in a capped vial at 358 K for 6 d. Red block crystals of **PM-4** were washed with DMF and air under air. CHN analysis calcd (%) for **PM-4**: C 32.02, H 2.91, N 8.20; found: C 32.64, H 3.12, N 8.39. IR (cm^{-1}): 3458 (w), 1639 (m), 1638 (s), 1543 (m), 1492 (w), 1350 (s), 1223 (m), 1068 (m), 932 (s), 811 (w), 763 (s), 729 (w), 704 (w), 678 (m).

1.3 Catalytic Studies

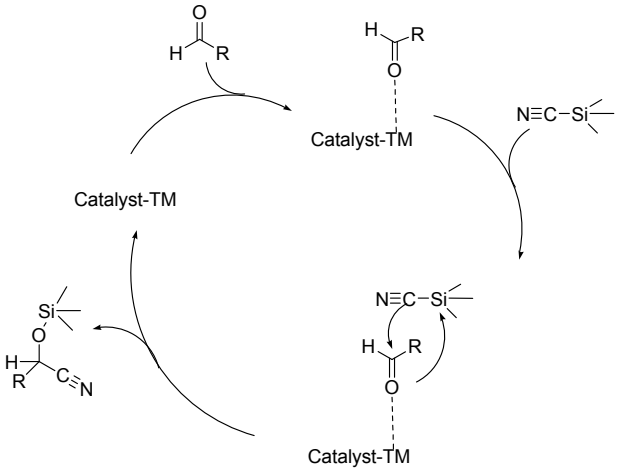
The hybrids **SiW-1**, **PVM-2**, **PV_2M-3** and **PM-4** were used as solid catalysts for the cyanosilylation of trimethylsilyl cyanide (TMSCN) with aldehydes. In a typical experiment, a predetermined amount of hybrids was added to the glass tube containing a solution of aldehydes (0.44 mmol) and TMSCN (0.53 mmol) and *n*-Dodecane (0.1 mmol) as an internal standard in CH_3CN (0.2 ml). The reaction was initiated by the addition of hybrids (0.5 - 0.7 mmol‰). The reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, analyzing by GC with reference to *n*-Dodecane, and further confirming product identity by GC. After the catalysis reaction, the remaining solids were collected by centrifuge at 4000 r/min, washed with CH_3CN for three times and air under air for the further examinations.

Table S1 Cyanosilylation of TMSCN with various aldehydes by precursor

Entry	Catalyst	Product	Conversion (%) [a]	Yield (%) [b]
1	**$TBA_4SiW_{12}O_{40}$**	 **(3a)**	none	none
2	**$H_4SiW_{12}O_{40}$**	**3a**	>99	94
3	**$H_4PVMo_{11}O_{40}$**	**3a**	>99	93
4	**$H_5PV_2Mo_{10}O_{40}$**	**3a**	>99	94
5	**$H_7PMo_{12}O_{40}$**	**3a**	>99	92
6	***m*-H_2L_{Ru}**	**3a**	>99	94
7	**$TBA_4SiW_{12}O_{40}$**	 **(3b)**	none	none
8	**$H_4SiW_{12}O_{40}$**	**3b**	>99	94
9	**$H_4PVMo_{11}O_{40}$**	**3b**	98	93
10	**$H_5PV_2Mo_{10}O_{40}$**	**3b**	97	92
11	**$H_7PMo_{12}O_{40}$**	**3b**	97	91
12	***m*-H_2L_{Ru}**	**3b**	99	94
13	**$TBA_4SiW_{12}O_{40}$**	 **(3c)**	none	none
14	**$H_4SiW_{12}O_{40}$**	**3c**	98	92
15	**$H_4PVMo_{11}O_{40}$**	**3c**	98	93
16	**$H_5PV_2Mo_{10}O_{40}$**	**3c**	98	91
17	**$H_7PMo_{12}O_{40}$**	**3c**	99	93
18	***m*-H_2L_{Ru}**	**3c**	98	92

[a] GC conversion based on aldehydes. [b] GC yield averaged by two parallel experiments.

Reaction conditions: aldehydes (0.44 mmol), TMSCN (0.53 mmol), *n*-Dodecane (0.1 mmol), 2 wt% catalysts (2.0 mg), 298 K and 2 min.



Scheme 1. Possible mechanism for the cyanosilylation reaction.

1.4 Structure Determinations

Suitable single crystals of compounds **SiW-1**, **PVM-2**, **PV_2M-3** and **PM-4** were selected for single-crystal X-ray diffraction analysis. The data were collected on a Bruker AXS SMART APEX II diffractometer in the range of 2.15 to 27.48 º at the temperature of 293(2) K for **SiW-1** and 1.30 to 26.05 º at the temperature of 273(2) K for **PVM-2** by using graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å), respectively. The data of **PV_2M-3** and **PM-4** were collected on a Bruker Saturn70 diffractometer in the range of 3.73 to 59.67 º at the temperature of 293(2) K and 3.73 to 74.46 º at the temperature of 293(2) K by using graphite-monochromated Cu-*K*α radiation (λ = 1.54178 Å), respectively. Data processing was accomplished with the **SAINT** processing program.[3] A total of 61140 reflections were collected, of which 6120 reflections were unique for **SiW-1**. A total of 42000 reflections were collected, of which 5167 reflections were unique for **PVM-2**. A total of 12642 reflections were collected, of which 3842 reflections were unique for **PV_2M-3**. A total of 18661 reflections were collected, of which 5298 reflections were unique for **PM-4**. All the structures were solved by direct method and refined by full matrix least-squares technique with the **SHELXTL** 97 crystallographic software package.[4] All non-H atoms of frameworks were located from a difference Fourier map and refined anisotropically. All the H atoms of ***m*-H_2L_{Ru}** ligands were also added geometrically. The remained solvent molecules (DMF and H_2O) were disordered and could not be modeled properly, the program **SQUEEZE**[5] was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The amount of the disorder DMF and H_2O have been determined by the TG-DTA and CHN. For **SiW-1**, **PVM-2**, **PV_2M-3** and **PM-4**, they contain 9DMF, 11DMF, 9DMF and 9DMF, respectively. All of the crystal data and structure refinement details for all compounds are given in Table S3-4.

Table S3 The crystal data and structure refinement details for **SiW-1**, **PVM-2**, **PV_2M-3** and **PM-4**

Name	**SiW-1**	**PVM-2**	**PV_2M-3**	**PM-4**
Empirical formula	C96H66N18O58Ru3SiW12Zn2(C3H7NO)9	C96H66Mo11N18O58PRu3VZn2(C3H7NO)11	C96H66Mo10N18O58PRu3V2Zn2(C3H7NO)9	C96H66Mo12N18O58PRu3Zn2(C3H7NO)9
Formula weight	5724.71	4794.31	4601.24	4695.16
Temperature	293(2) K	273(2) K	293(2) K	293(2) K
Wave length	0.71073 Å	0.71073 Å	1.54178 Å	1.54178 Å
Crystal system, Space group	Trigonal, *R*-3c	Trigonal, *R*-3c	Trigonal, *R*-3c	Trigonal, *R*-3c
Unit cell dimensions	*a* = 23.7147(6) Å *b* = 23.7147(6) Å *c* = 49.252(2) Å *α* = 90 ° *β* = 90 ° *γ* = 120 °	*a* = 23.5835(10) Å *b* = 23.5835(10) Å *c* = 48.792(4) Å *α* = 90 ° *β* = 90 ° *γ* = 120 °	*a* = 23.6950(4) Å *b* = 23.6950(4) Å *c* = 48.6610(10) Å *α* = 90 ° *β* = 90 ° *γ* = 120 °	*a* = 23.6889(3) Å *b* = 23.6889(3) Å *c* = 48.7070(9) Å *α* = 90 ° *β* = 90 ° *γ* = 120 °
Volume	23987.6(15) $Å^3$	23501(2) $Å^3$	23660.6(7) $Å^3$	23670.7(6) $Å^3$
Z, calculated density	6, 2.105 Mg/m^3	6, 1.683 Mg/m^3	6, 1.653 Mg/m^3	6, 1.690 Mg/m^3
Absorption coefficient	9.243 mm^{-1}	1.574 mm^{-1}	10.584 mm^{-1}	10.889 mm^{-1}
F(000)	13956	11544	11430	11658
Theta range for data collection	2.15 to 27.49 °	1.30 to 26.05 °	3.73 to 59.67 °	3.73 to 74.46
Limiting indices	-30≤*h*≤30,-30≤*k*≤30,-62≤*l*≤60	-29≤*h*≤25,-29≤*k*≤26,-60≤*l*≤59	-25≤*h*≤11,-20≤*k*≤15,-52≤*l*≤53	-25≤*h*≤22,-27≤*k*≤28,-60≤*l*≤51
Reflections collected/ unique	61140 / 6120 [*R*(int) = 0.0730]	42000 / 5167 [*R*(int) = 0.1000]	12642 / 3842 [*R*(int) = 0.0558]	18661 / 5298 [*R*(int) = 0.0269]
Completeness	99.8 %	100.0 %	99.0 %	98.2 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6120 / 0 / 288	5167 / 0 / 289	3842 / 0 / 290	5298 / 0 / 288
Goodness-of-fit on F^2	1.139	0.946	1.081	1.043
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0740, wR_2 = 0.1768	R_1 = 0.0568, wR_2 = 0.1525	R_1 = 0.0497, wR_2 = 0.1215	R_1 = 0.0515, wR_2 = 0.1322
R indices (all data)	R_1 = 0.0790, wR_2 = 0.1805	R_1 = 0.0948, wR_2 = 0.1682	R_1 = 0.0593, wR_2 = 0.1260	R_1 = 0.0555, wR_2 = 0.1354

Extinction coefficient	0.000025(3)	0.000076(9)	none	0.0000046(8)
Largest diff. peak and hole	3.564 and -1.708 e. Å^{-3}	0.855 and -1.753 e. Å^{-3}	0.571 and -0.663 e. Å^{-3}	0.725 and -1.207 e. Å^{-3}

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S4 Selected bond and angle for **SiW-1, PVM-2, PV$_2$M-3** and **PM-4**

Zn(1)-O(1W)	1.92(2)	Zn(1)-O(1)#1	1.941(13)
Zn(1)-O(1)	1.941(13)	Zn(1)-O(1)#2	1.941(13)
Ru(1)-N(3)#3	2.042(12)	Ru(1)-N(3)	2.042(12)
Ru(1)-N(1)#3	2.072(14)	Ru(1)-N(1)	2.072(14)
Ru(1)-N(2)#3	2.080(13)	Ru(1)-N(2)	2.080(13)
O(1W)-Zn(1)-O(1)#1	115.6(4)	O(1W)-Zn(1)-O(1)#2	115.6(4)
O(1W)-Zn(1)-O(1)	115.6(4)	O(1)#1-Zn(1)-O(1)#2	102.7(5)
O(1)#1-Zn(1)-O(1)	102.7(5)	O(1)-Zn(1)-O(1)#2	102.7(5)

Symmetry transformations used to generate equivalent atoms: #1 -y+2,x-y+2,z; #2 -x+y,-x+2,z; #3 y-2/3,x+2/3,-z+1/6

Zn(1)-O(2)	1.941(6)	Zn(1)-O(2)#1	1.941(6)
Zn(1)-O(2)#2	1.941(6)	Zn(1)-O(1W)	1.980(11)
Ru(1)-N(2)#3	2.052(7)	Ru(1)-N(1)#3	2.055(6)
Ru(1)-N(2)	2.052(7)	Ru(1)-N(3)#3	2.072(7)
Ru(1)-N(1)	2.055(6)	Ru(1)-N(3)	2.072(7)
O(2)-Zn(1)-O(2)#1	100.7(2)	O(2)-Zn(1)-O(1W)	117.21(19)
O(2)-Zn(1)-O(2)#2	100.7(2)	O(2)#1-Zn(1)-O(1W)	117.21(19)
O(2)#1-Zn(1)-O(2)#2	100.7(2)	O(2)#2-Zn(1)-O(1W)	117.21(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+y+1,-x+2,z; #2 -y+2,x-y+1,z; #3 y,x,-z+3/2

Zn(1)-O(1W)	1.951(10)	Zn(1)-O(1)#1	1.963(6)
Zn(1)-O(1)	1.963(6)	Zn(1)-O(1)#2	1.963(6)
Ru(1)-N(1)	2.059(6)	Ru(1)-N(3)#3	2.065(7)
Ru(1)-N(1)#3	2.059(6)	Ru(1)-N(2)	2.068(7)
Ru(1)-N(3)	2.066(7)	Ru(1)-N(2)#3	2.068(7)
O(1W)-Zn(1)-O(1)#1	114.91(16)	O(1)#1-Zn(1)-O(1)	103.52(19)
O(1W)-Zn(1)-O(1)	114.91(16)	O(1)#1-Zn(1)-O(1)#2	103.52(19)
O(1W)-Zn(1)-O(1)#2	114.91(16)	O(1)-Zn(1)-O(1)#2	103.52(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+y+1,-x+1,z; #2 -y+1,x-y,z; #3 y+1/3,x-1/3,-z+1/6

Zn(1)-O(1)	1.948(6)	Zn(1)-O(1)#6	1.948(5)
Zn(1)-O(1)#7	1.948(5)	Zn(1)-O(1W)	1.951(9)
Ru(1)-N(1)#1	2.052(6)	Ru(1)-N(1)	2.052(6)
Ru(1)-N(3)	2.054(6)	Ru(1)-N(3)#1	2.054(6)
Ru(1)-N(2)	2.071(6)	Ru(1)-N(2)#1	2.071(6)

O(1)-Zn(1)-O(1)#6	103.5(2)	O(1)-Zn(1)-O(1W)	114.93(17)
O(1)-Zn(1)-O(1)#7	103.5(2)	O(1)#6-Zn(1)-O(1W)	114.93(17)
O(1)#6-Zn(1)-O(1)#7	103.5(2)	O(1)#7-Zn(1)-O(1W)	114.93(17)

Symmetry transformations used to generate equivalent atoms: #1 y,x,-z+3/2; #2 x-y,x,-z+1; #3 y,-x+y,-z+1

2. The Structural Views of Four Compounds

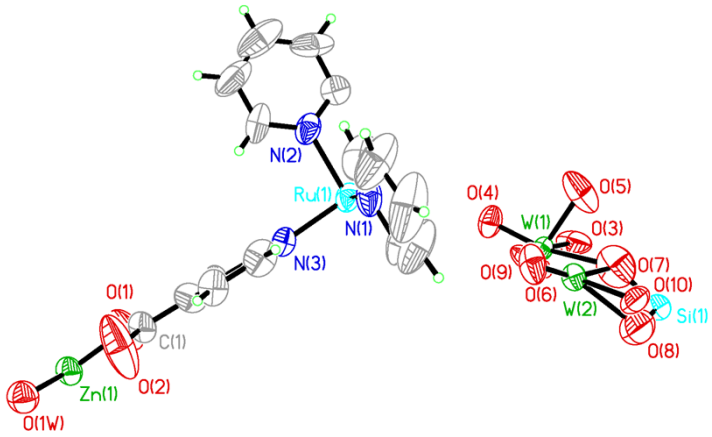


Fig. S1 Asymmetric unit of the **SiW-1** showing the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level.

Fig. S2 Asymmetric unit of the **PVM-2** shown in the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level.

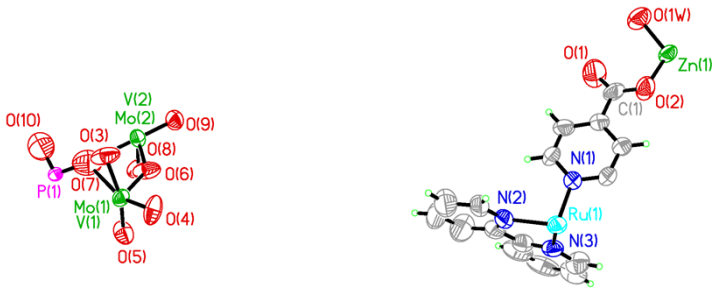


Fig. S3 Asymmetric unit of the **PV_2M-3** shown in the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level.

Fig. S4 Asymmetric unit of the **PM-4** shown in the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level.

3. Characterization Section

3.1 The Powder X-ray power diffraction (PXRD) analysis

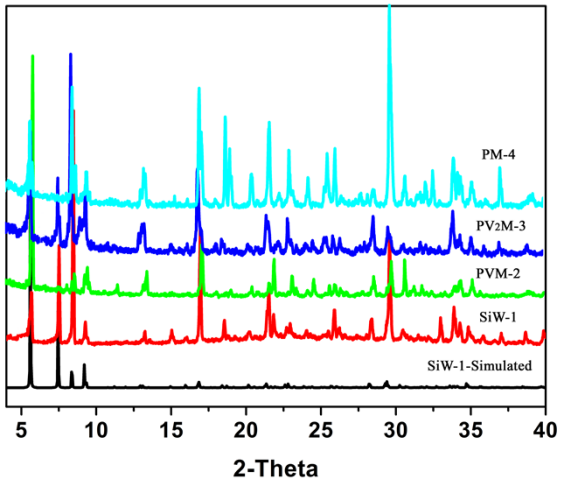


Fig. S5 The PXRD patterns of **SiW-1, PVM-2, PV_2M-3 and PM-4** in the range of 4 to 40 degree

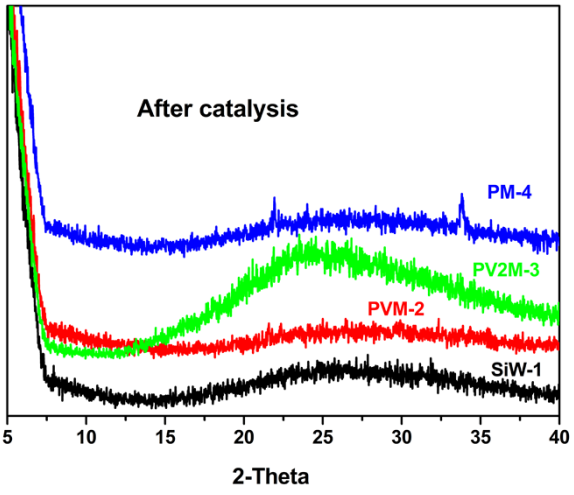


Fig. S6 The PXRD patterns of **SiW-1, PVM-2, PV_2M-3 and PM-4** after catalysis

3.2 The IR spectrum

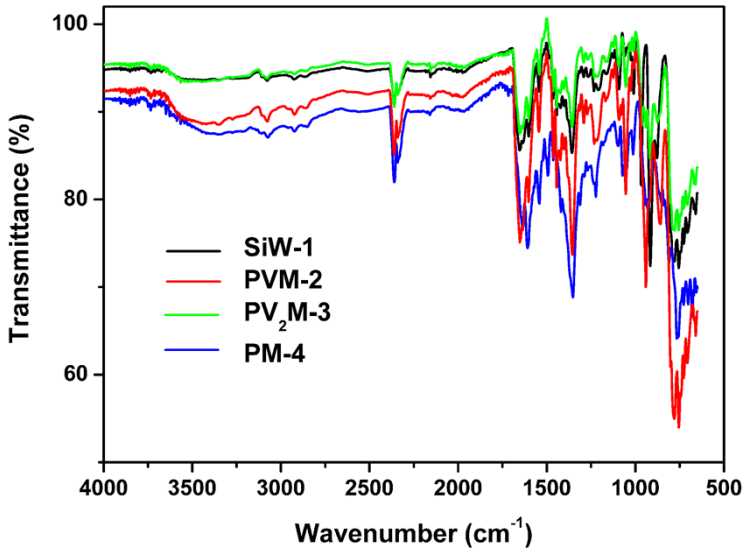


Fig. S7 The FTIR spectrum of **SiW-1, PVM-2, PV_2M-3 and PM-4**

3.3 The EDS analysis

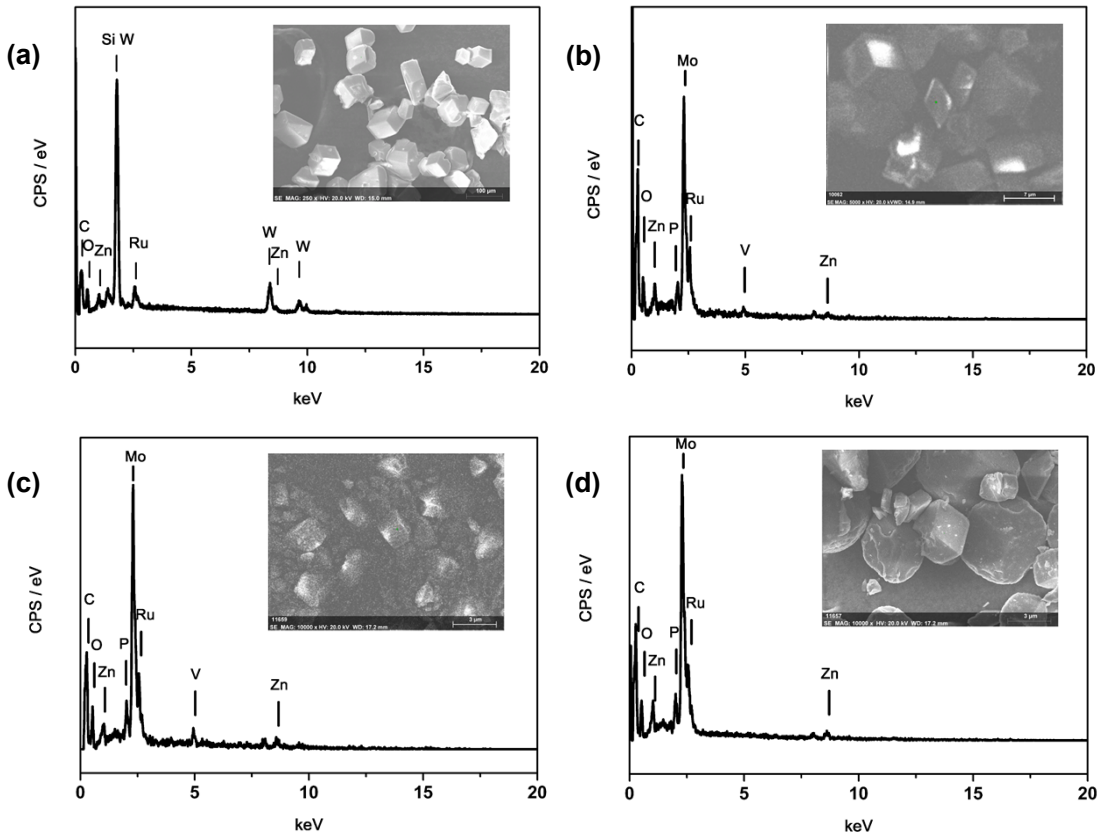


Fig. S8 The EDS of **SiW-1 (a), PVM-2 (b), PV_2M-3 (c) and PM-4 (d)**

Table S3 The atom rate of **SiW-1, PVM-2, PV_2M-3 and PM-4**

	Ru (at. %)	Zn (at. %)	Mo (at. %)	P (at. %)	V (at. %)
SiW-1	1.77	1.28	7.08 (W)	0.82 (Si)	/
PVM-2	3.29	2.48	8.98	0.81	1.72
PV_2M-3	3.60	2.82	10.13	1.36	2.35
PM-4	3.88	2.82	14.10	1.52	/

3.4 TG-DTA analysis

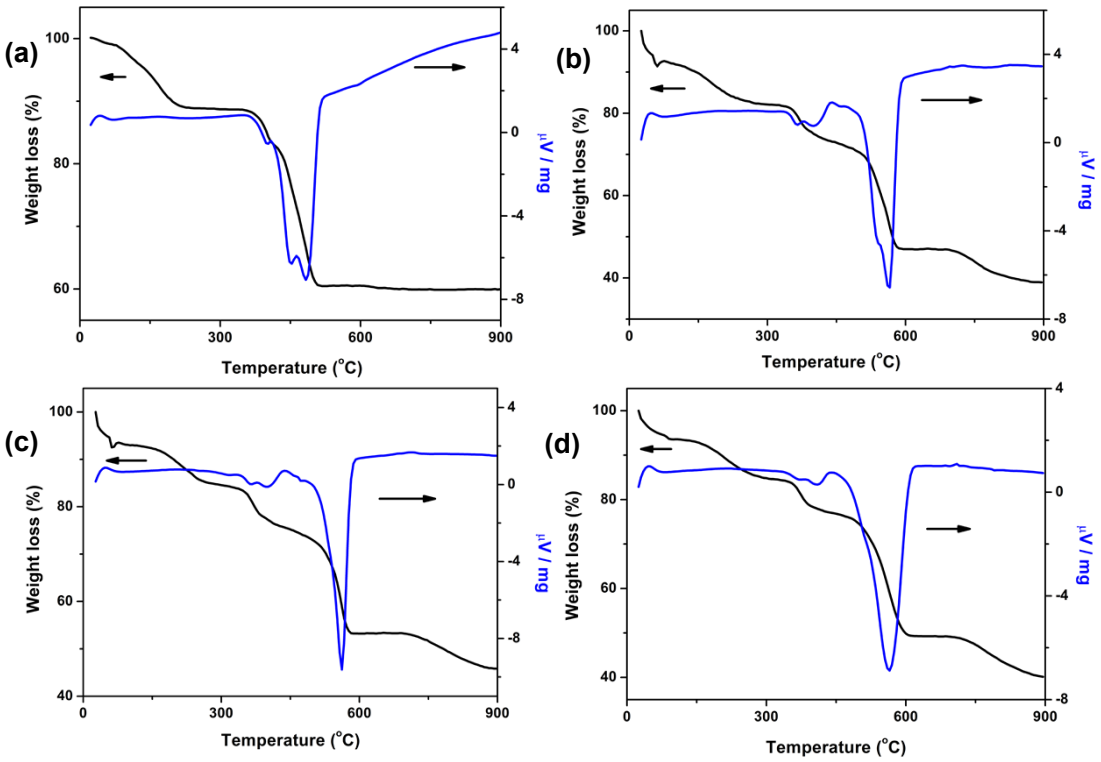


Fig. S9 The TGA-DTA curves of **SiW-1, PVM-2, PV_2M-3 and PM-4** under air atmosphere

The thermogravimetric studies were carried out in air for **SiW-1, PVM-2, PV_2M-3 and PM-4** at a heating rate of 10°C min^{-1} in the temperature range from RT to 900° C (Fig. S9). The TGA curves of above four compounds show similar weight loss with three steps from RT to 600 °C. The weight loss from RT to 250 °C is attributed to the loss of solvent molecules. Further continuous weight from 250 to 600 °C is attributed to the decomposition of organic ligands. For **SiW-1**, the first step weight loss is 11.4 % (calc. 11.6 % with 9 DMF). For **PVM-2**, the first step weight loss is 17 % (calc. 16.8 % with 11 DMF). For **PV_2M-3**, the first step weight loss is 14.4 % (calc. 14.5 % with 9 DMF). For **PM-4**, the first step weight loss is 14.5 % (calc. 14.2 % with 9 DMF).

Reference

1. M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos,V. Shklover, C. H. Fischer, M. Grätzel, *Inorg. Chem.*, **1999**, 38, 6298-6305.
2. G. A. Tsigdinos, C. J. Hallada, *Inorg. Chem.*, **1968**, 7, 437-441.
3. SMART and SAINT software package, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
4. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
5. (a) A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7; (b) A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148.