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Synthesis, structure and catalytic behaviour in oxidation of cyclohexene of $K_4H_2[SiW_5Mo_6M(H_2O)O_{39}]\cdot xH_2O$ ($M=Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+})

Chun-Yan Hua[a,b], Wei Li[c], Li-Yi Dai[a,b]* and Yong-Kui Shan[a,b]

[a]*Department of Chemistry, E.C.N.U., Shanghai, 200062, P. R. China*

[b]*Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai, 200433, P. R. China*

[c]*School of Chinese Medicine, SDUTCM, Shandong, 250014, P. R. China*

A series of the title complexes were synthesised. The general molecular formula $K_4H_2[SiW_5Mo_6M(H_2O)O_{39}]\cdot xH_2O$ denoted as MW_5 ($M=Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) was determined by means of chemical analysis and thermoanalysis. IR-spectra, UV-spectra, XPS-spectra, and thermal decomposition were systematically investigated. The crystal structure of $K_4H_2[SiW_5Mo_6Mn(H_2O)O_{39}]\cdot 22H_2O$ was determined. The compounds were studied in oxidation of cyclohexene with 30% hydrogen peroxide as oxidant, which indicated that these transition-metal-substituted polyoxometalates were more effective than their corresponding parent compounds.

Keywords: polyoxometalate, tungstomolybdosilicate, transition elements, catalytic behavior, cyclohexene

Polyoxometalates are an important class of compounds, having high theoretical interest and practical applications. They are widely used in acid and oxidation catalysis, analytical chemistry, materials science, medicine, and other fields.[1-8] Multicomponent polyoxometalates formed by the lacunary anions of the polyoxometalates as ligand coordinated to transition metal have attracted a lot of attention as selective oxidation catalysis.[9,10] They show remarkable stability, catalytic activity and resistance to oxidative degradation under catalytic reaction conditions, and seem to be the most robust homogeneous oxidation catalysts at the present time. Many such compounds and their synthesis methods have been reported,[11,12] but the compounds containing two and more types of element are very rarely studied. We have prepared multicomponent polyoxometalates containing transition elements to elucidate systematically the relationship between the catalytic activity substrate specificity and mechanism of catalysis of the polyoxometalates with their structures. In this paper, we will report the synthesis, structure and catalytic performance in cyclohexene oxidation of one series of new transition-metal-substituted polyoxometalates.

Experimental

Synthesis method

Tungstomolybdosilicic acid crystals $H_4SiMo_6W_6O_{40}\bullet(20\text{-}25)H_2O$ (10g), which were synthesised according to the literature,[13] were dissolved in 100ml of water and heated to 80°C in the water-bath. The transition metal nitrate in a little more than stoichiometry was added to the tungstomolybdosilicic acid solution. The pH value the of the resultant solution was adjusted to 4.6–4.8 with an aqueous solution of KAc-HAc (KAc:HAc:H_2O =15:3:30). The reaction mixture was stirred for 30 min at constant temperature (80°C), then filtered. The filtrate was allowed to stand in a refrigerator at 0–3°C for 24 hours, the crystals were formed in approximately 80% yield based on the tungstomolybdosilic acid.

Component analysis and characterisation

Transition elements were estimated by DTPA titration (back-titration with standard zinc solution, in pH 9.5 buffer in presence of Zn-agent). Molybdenum and tungsten in the same compound was separated by the method as described elsewhere,[14] then molybdenum was weighed as MoO_3 after precipitation with α-benzoinoxime and tungsten was weighed as WO_3 after precipitation with cinchonine. Potassium was weighed as $KB(C_6H_5)_4$ and silicon was estimated according to reference,[15] the water content was estimated by TG.

Instruments to be used for characterisation are listed as below: NEXUS 670 FT IR spectrophotometer (Nicolet U.S.A.); 265 UV spectrophotometer (Shimadzu); PHI-5100 X-ray photoelectron spectrometer (Perkin Elmer), using an Al/Mg bianode, resolving power 0.8eV (Ag $3d_{5/2}$), target power 390W, sensitivity 40K, binding energies are referred to the C (1s) line 285.6eV; TG-SDTA 851e (Mettler); D8 ADVANCE X-ray powder diffractometer (Bruker), Cu target K_α λ=1.5418Å; SMART-CCD diffractometer (Bruker).

X-ray data collection and structure determination

The data for single crystal of MnW_5($0.35\times0.25\times0.20mm^3$)were collected at 293(2) K on a Bruker SMART-CCD single crystal diffractometer using a Mo anode (λ=0.071073nm) and graphite monochromator. Intensity data with 2θ values in the range 4-54.1° were collected using ω scans. Routine Lorent and polarisation corrections were applied. A total of 1164 reflections with $I\geq2\sigma(I)$ among 2865 unique reflections collected were used for structure determination. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 using the SHELXTL program package.[16] All hydrogen atoms other than those of some water molecules were directly located from the difference Fourier map and included in the structure, but not refined. Crystallographic data are listed in Tables 1, 2 and 3.

Examination of catalytic activity for oxidation of cyclohexene

Oxidation of cyclohexene was run at 10°C in a two-neck glass vessel (50ml), jacketed for circulation of water, immersed in a thermostated water bath with a magnetic stirrer and equipped with a reflux condenser. Cyclohexene (9.8mmol), $CHCl_3$ (10ml) and catalysts (0.073 mmol) were added successively into the reactor. 30% H_2O_2 (8mmol) was added after the mixture had been heated to 10°C. The products were analysed on an Angilent HP 6850 Series gas chromatography equipped with an IFP detector and HP-1 column (L=30m, Φ=0.32mm) after 4 hours of reaction.

Results and discussion

Synthesis and composition analysis

There are two principal synthesis methods of polyoxometalates with transition metals, which have been reported.[11,12] One is by the

Table 1 The experimental conditions and crystallographic data for $K_4H_2[SiW_5Mo_6Mn\ (H_2O)O_{39}]\bullet 22H_2O$

Empirical formula	$K_4H_2[SiW_5Mo_6Mn(H_2O)O_{39}]\cdot 22H_2O$
Space group	P4/mnc
a/nm	1.4119
b/nm	1.4119
c/nm	1.2496
αβγ/°	90
V/nm^3	2.4909(12)
Calculated density(Dc)/g.cm^{-3}	3.817
Z	2
T/K	293(2)
Absorption coefficient(μ)/mm^{-1}	15.922
λ(Mo Kα)/nm	0.071073
No. independent reflections	9554
No. observations	1164($I\geq2\sigma(I)$)
The final R[a]	0.0462
wR[b]	0.1232
Goodness of fit on F_2	1.165

[a] $R=\sum||F_0|-|F_c||/\sum|F_0|$

[b] $wR=[\sum w(|F_0|-|F_c|)^2/\sum w|F_0|^2]^{1/2}$

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* Correspondence. E-mail: lydai@chem.ecnu.edu.cn

Table 2 Selected bond lengths (Å) for $K_4H_2[SiW_5Mo_6Mn(H_2O)O_{39}]\cdot 22H_2O$

M1-O3	1.656(9)	M2–O1	1.681(18)	Si1–O6#3	1.682(16)
M1-O5	1.886(12)	M2–O2	1.923(11)	Si1–O6#4	1.682(16)
M1-O2	1.893(11)	M2–O2#2	1.923(11)	Si1–O6	1.682(16)
M1-O4	1.895(11)	M2–O4#1	1.927(12)	Si1–O6#5	1.682(16)
M1-O5#1	1.897(12)	M2–O4#3	1.927(12)	Si1–O6#1	1.682(16)
M1-O6#1	2.355(16)	M2–O6#1	2.353(15)	Si1–O6#2	1.682(16)
M1-O6	2.359(16)	M2–O6#3	2.353(15)	Si1–O6#6	1.682(16)
				Si1–O6#7	1.682(16)

M=5/12 W+6/12 Mo+1/12 Mn

Table 3 Selected bond angles (°) for $K_4H_2[SiW_5Mo_6\ Mn(H_2O)O_{39}]\cdot 22H_2O$

O3–M1–O5	100.5(7)	O1–M2–O2	100.1(7)	O6#3–Si1–O6	109.9(5)
O3–M1–O2	99.2(7)	O1–M2–O2#2	100.1(7)	O6#3–Si1–O1#5	108.7(11)
O5–M1–O2	160.2(7)	O2–M2–O2#2	88.6(8)	O6–Si1–O6#5	109.9(5)
O3–M1–O4	101.2(7)	O1–M2–O4#1	98.3(7)	O6#4–Si1–O6#1	108.7(11)
O5–M1–O4	89.8(5)	O2–M2–O4#1	89.5(5)	O6#4–Si1–O6#2	109.9(5)
O2–M1–O4	86.8(5)	O2#2–M2–O4#1	161.5(7)	O6#1–Si1–O6#	2109.9(5)
O3–M1–O5#1	99.3(7)	O1–M2–O4#3	98.3(7)	O6#4–Si1–O6#6	109.9(5)
O5–M1–O5#1	86.9(8)	O2–M2–O4#1	161.5(7)	O6#1–Si1–O6#6	109.9(5)
O2–M1–O5#1	89.4(5)	O2#2–M2–O4#3	89.5(5)	O6#2–Si1–O6#6	108.7(11)
O4–M1–O5#1	159.4(7)	O4#1–M2–O4#3	86.5(7)	O6#3–Si1–O6#7	109.9(5)
O3–M1–O6#1	154.9(6)	O1–M2–O6#1	155.3(4)	O6#5–Si1–06#7	109.9(5)
O5–M1–O6#1	96.4(7)	O2–M2–O6#1	64.4(6)		
O2–M1–O6#1	64.8(6)	O2#2–M2–O6#4	98.7(6)		
O4–M1–O6#1	97.2(7)	O4#1–M2–O6#1	64.1(6)		
O5#1–M1–O6#1	63.0(6)	O4#3–M2–O6#1	97.7(7)		
O3–M1–O6	156.7(6)	O1–M2–O6#3	155.3(4)		
O5–M1–O6	63.1(6)	O2–M2–O6#3	98.7(7)		
O2–M1–O6	98.1(7)	O2–M2–O6#3	64.4(6)		
O4–MI–O6	64.3(6)	O4#1–M2–O6#3	97.7(7)		
O5#1–M1–O6	96.3(7)	O4#3–M2–O1#3	64.1(6)		

Symmetry transformations used to generate equivalent atoms:
#1 −*y*,*x*,*z* #2 *y*,−*x*,*z* #3 *x*,*y*,−*z* #4 *y*,−*x*,−*z* #5 −*x*,−*y*,−*z* #6 −*y*,*x*,−*z* #7 −*x*,−*y*,*z*
#8 −*y*+1/2,−*x*+1/2,−*z*+1/2 #9 −*y*+1/2,−*x*+1/2,*z*−1/2 #10 −*y*+1/2,−*x*+1/2,*z*+1/2
#11 −*x*+1,−*y*+1,−z

reaction of lacunary polyoxometalate anions and the transition metal ions. The other is in site reaction of the simple salt containing the component element. In general, the former method was adopted for the stable lacunary polyoxometalate anions which can be separated in the solid state. The latter is used in the case that lacunary anions are not obtainable. It is demonstrated by our study that $[SiMo_6W_6O_{40}]^{4-}$ would degradate and produce $SiMo_6W_5$ lacunary anion in suitable condition,[17] but it is not stable enough to be separated. If the solution contains the transition ions, the lacunary anions would immediately coordinate with them to lead to stable tetrabasic polyoxometalates as soon as the lacunary anions are formed, which stops further degradation of polyoxometalates. The method is successful in preparation of the polyoxometalates complexes containing lacunary anions which can not be separated in the solid state. The results of composition analysis are listed in Table 4 and indicate that the general formula of their anions is: $[SiW_5Mo_6M(H_2O)O_{39}]^{6-}$ (M=Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}).

IR spectra: The main IR absorption bands of the new compound are observed between 400 and 1100 cm^{-1} and their IR spectra data are summarised in Table 5. These results show that they retain the basic characteristics of the Keggin structures. It indicates that the Keggin structure of tungstomolybdosilicic acid is unchanged after coordination with transition metal ions.

The red shift of bands in IR spectra of these new compounds, in comparison with one of the corresponding potassium tungstomolybdosilicates, is similar to the results for other complexes.[18] This is because when the transition metal ions M^{2+} coordinated instead of Mo^{6+}, the anions become more negative and lead to a looser structure. It is worth noticing that the $\nu\ _{as}$M–Ob–M bands in all synthesised compounds disappeared, and the $\nu\ _{as}$M–Oc–M bands are split, which agreed with the

Table 4 Results of component analysis for the new compounds synthesised

Element content complex	M	Si	Mo	W	H_2O	K%
$MnW_5\cdot 22H_2O$	(1.98)1.95	(1.01)1.02	(20.75)20.60	(33.13)32.92	(14.92)15.47	(5.64)5.23
$CoW_5\cdot 22H_2O$	(2.12)2.12	(1.01)1.01	(20.72)20.72	(33.09)33.07	(14.90)14.87	(5.63)5.60
$NiW_5\cdot 21H_2O$	(2.13)2.12	(1.02)1.02	(20.85)20.86	(33.31)33.32	(14.35)14.37	(5.67)5.64
$CuW_5\cdot 23H_2O$	(2.27)2.27	(1.00)1.00	(20.55)20.58	(32.83)32.83	(15.42)15.44	(5.58)5.54
$ZnW_5\cdot 24H_2O$	(2.32)2.31	(0.99)0.98	(20.41)20.42	(32.59)32.57	(15.95)15.94	(5.54)5.50
$CdW_5\cdot 23H_2O$	(3.94)3.93	(0.98)0.98	(20.20)20.34	(32.26)32.25	(15.16)15.17	(5.49)5.47

*theoretical values in brackets

Table 5 IR spectra data of the new compounds (cm^{-1})

complex	ν asM–Od	ν asSi–Oa	ν asM–Ob–M	ν asM–Oc–M	ν_σSi–Oa
$KSiMo_6W_6$	966	916	863	781	538
MnW_5	946	894		802 747 705	536
CoW_5	952	897		797 736 965	534
NiW_5	950	900		797 712	538
CuW_5	949	898		794 736 685	537
ZnW_5	948	897		795 747 703	535
CdW_5	940	885		795 724	536

Table 6 The conversion of substrates and the selectivity of products in the oxidation of cyclohexene

Catalysts	Yield/%			Selectivity/%			
	Cyclo-hexenone	Cyclo-hexenol	Cyclo-hexene oxides	Cyclo-hexenone	Cyclo-hexenol	Cyclo-hexane oxides	Cyclo-hexene conversion/%
CoW_5	1.8	4.6	3.4	18.3	46.9	34.7	9.8
NiW_5	1.6	0.0	1.6	50.0	0.0	50.0	3.2
CuW_5	0.5	2.8	0.0	15.1	84.8	0.0	3.3
MnW_5	3.0	2.3	0.9	48.4	37.1	14.5	6.2
ZnW_5	0.0	0.0	1.0	0.0	0.0	100.0	1.0
CdW_5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$KSiMo_6W_6$	0.0	0.0	0.0	0.0	0.0	0.0	0.0

results of molybdsilicate complexes with rare earth elements.[17] It is reasonable to attribute it to the distortion of the intra six-membered ring M–Oc–M–Oc–M–Oc one M_3O_{13} group is different from that of the intra six-membered M–Ob–M–Oc–M–Ob ring of a different M_3O_{13} group in the Keggin structure, resulting in decrease of the relative intensity and simultaneous splitting of the corresponding IR bands. The weak ν_{as}M–Ob–M bands of the Keggin structure in tungstomolybdosilicic acid become weak enough to be covered by ν_{as}Si–O of the new compounds, while the stronger band (ν_{as}M–Oc–M) is split into two or three bands in the IR spectra. It can be seen that the split of the ν_{as}M–Oc–M band is different in the compounds with different transition elements, *e.g.* IR band ν_{as}M–Oc–M of the compounds with Ni^{2+} and Cd^{2+} is split into two, but of the others split into three. The minimum value of this split is 71 cm^{-1} and maximum is 109 cm^{-1} (see Table 5). The results demonstrate that the ion radius, and electronic structure of transition element may have an effect on the structure and characteristics of bonds of multicomponent polyoxometalates with transition elements.

Electronic spectra: The UV absorption bands of polyoxometalate ligands are in the range 200–450 nm. These bands are caused by charge transfer from terminal oxygen atom (Od) to molybdenum or tungsten in the MO_6-octahedron (M=Mo,W; M←Od). For $KSiMo_6W_6$, MnW_5, CoW_5, NiW_5, CuW_5, ZnW_5 and CdW_5, the characteristic bands (M←Od) are 219.6 nm, 218.6 nm, 220.2 nm, 219.2 nm, 218.0 nm, 218.4nm and 217.4nm, respectively. From these results, we can conclude that the effect of different transition element ions on the electronic structure of the polyoxometalate ligands is not very notable. The M←Ob,c charge transfer (from bridge oxygen atom to Mo or W) bands can not be observed, due to the lengthened O–M bonds. This phenomenon is coincident with the red shift of the corresponding band in IR spectra of the new compounds.

XPS spectra: The binding energies of electrons in the inner shell of the transition element in polyoxometalates are higher than that of their oxides, *e.g.* in NiO, the binding energies of electrons in inner shells $2P_{3/2}$ and $2P_{1/2}$ of Ni are 853.30 eV and 871.70 eV respectively, but they become 855.77 eV and 873.89 eV in new complex (NiW_5). The increase of binding energies demonstrates that the electron density around the transition element decreases and a part of the negative charge on transition element moves to the polyoxometalate ligands. At the same time, it demonstrates that the electronegativity of the polyoxometalate ligand is stronger than that of the O^{2-} ion.

Thermal decomposition of the complexes: Thermal behaviour of the compounds was studied by means of thermogravimetric (TG), differential thermal analysis (DTA), IR spectroscopy and X-ray powder diffraction at different temperatures. The TG and DTA curves of all new compounds are very similar. It shows that their decomposition processes might be the same, and different transition elements have little effect on it.

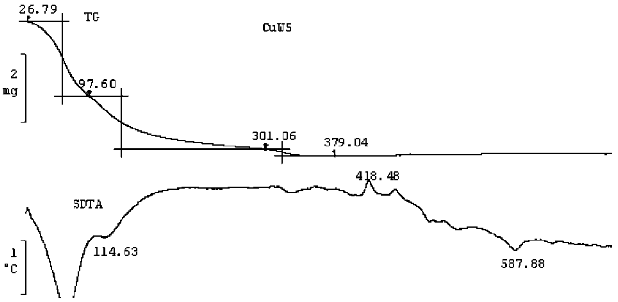

Fig. 1 The TG and DTA curve of CuW_5.

From the TG curve of CuW_5 it can be seen that a gradual loss of weight starts from 27°C and stops up to 380°C, including three stages of weight loss: The first is around 26.8–97.6°C; second, 97.6–301.1°C; and third, 301.1–379.0°C (See Fig. 1). In the first and second stages, the weight loss is fast, and two endothermic peaks are observed on DTA curves at 71.6°C and 114.6°C. The IR spectra of the complex does not change in this range of temperature, but a number of the X-ray powder diffraction peaks of the complex diminishes apparently above 80°C, and there are only two diffraction peaks at 300°C (2θ:10,18). Thus the weight loss is due to elimination of zeolite and crystal water in the first two steps and accompanied by powdering of the crystal. In the third region, the weight loss is small, which is mainly structural water. There is an exothermic peak (418.5°C) on the differential thermal curve. The IR spectra of the sample at 320°C and 350°C are different. At 320°C they retain the IR spectra character of the Keggin structure. The X-ray power diffraction patterns of the sample at 300°C and 350°C are also different, the latter have more diffraction peaks than the former. It shows that the compounds decomposed accompanied by loss of structural water. The decomposition temperature is at 320°C to 350°C. The exothermal peak at 418.5°C on the DTA curves is caused by the crystallisation of a part of the decomposed product. When the complex is further heated, the TG curve shows no change. One stronger endothermic peak at 587.9°C is observed, which is due to the melting of the decomposed products.

Crystal structure: The crystal structure is built up from $[SiW_5Mo_6Mn(H_2O)O_{39}]^{6-}$ anions, K^+-ions and H_2O molecules, and is isostructural in space group P4/mnc with $K_4H_2PMo_9V_3O_{40}\cdot 10H_2O$[19] and $H_6PV_3Mo_9O_{40}\cdot 30H_2O$.[20] The site symmetry of the molecule in the crystal is 4/m, which is incompatible with the tetrahedral symmetry of the Keggin molecule. The central SiO_4 group must be disordered, as indicated by the fact that Si is surrounded by a cube of O atoms at 0.1682nm, with each O site half-occupied to satisfy the needs of the 4/m symmetry in crystallography (see Fig. 2), so that the M metal ions (Mo, W, Mn) are coordinated by seven O atoms and the Si ion is coordinated by eight O atoms as observed in Fig. 2. The result is inescapable that these tetrahedral structures contain normal Keggin molecules disordered as a whole in two positions related by a 90° rotation about the molecular four-fold axis. This model was originally proposed for these crystal structures by Sergienko *et al.*,[21] and was later confirmed by Pope *et al.*[22]

The $[SiW_5Mo_6Mn(H_2O)O_{39}]^{6-}$ group has the Keggin structure and consists of a central SiO_4- tetrahedron surrounded by twelve MO_6-octahedra. The twelve octahedra may be subdivided into four Mo_3O_{13} groups. In these groups each MO_6-octahedron is linked to its neighbour on either side by a shared edge making one corner

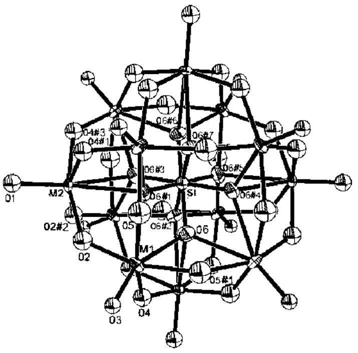

Fig. 2 The crystal structure of MnW_5.

common to the three octahedra. The four groups are then linked to each other by sharing corners and to the SiO_4-tetrahedron by the three-coordinate oxygen atoms. The M-O distances can be divided into three groups according to the number of atoms that the oxygen is coordinated to: (1) coordinated to only one M-atom, the distances vary between 1.65–1.68 Å; (2) coordinated to two M-atoms, the distances vary between 1.88–193 Å; (3) coordinated to one Si atom and to three M-atoms, the distances vary between 2.35–2.36 Å. This Keggin anion lies in the crystal with its five W, six Mo and one Mn sites oriented randomly to one of the 12 positions and with the statistical weight of 5/12, 6/12 and 1/12, respectively. The deformation of the Keggin structure anion $[SiMo_6W_6O_{40}]^{4-}$ caused by the replacement of one tungsten atom could not be studied in detail because of its randomness.

Cyclohexene oxidation activity: Table 6 summarises the activity of various catalysts used in cyclohexene oxidation. On all catalysts, cyclohexenone, cyclohexenol and cyclohexene oxides are produced as the major products. It is clear that among the catalysts studied the precursor $KSiMo_6W_6$ synthesised by the conventional method (synthesised by direct precipitation of $H_4SiMo_6W_6O_{40}\cdot 20–25H_2O$[13] with a little more than stoichiometric potassium carbonate) showed the poorest activity while the catalytic activity was obviously increased (except for CdW_5) when the transition metals were introduced into the Keggin structure. It can also be concluded that the improvement of catalytic activity in oxidation of cyclohexene on the title polyoxometalates may be related to the displacement of transition metal ions, which caused some differences in ion radius, electronic charge and electronic structure of the outer sphere between transition-metal-substituted polyoxometalates and $KSiMo_6W_6$, and which play significant roles in the redox processes as new, more effective active sites for the formation of peroxide groups. As can be seen, CuW_5 exhibits high performance for selective oxidation of cyclohexene to cyclohexenol (84.8%), ZnW_5 for cyclohexene oxides (100%), and NiW_5 for cyclohexenone and cyclohexene oxides (50/50), which is likely associated with the change in the redox properties of the polyanions. In conclusion, the corresponding tetra-basic polyoxometalates show obvious yet irregular catalytic activity and selectivity.

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