

Oxidation of cyclopentene catalyzed by tungsten-substituted molybdophosphoric acids

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Abstract—A series of Keggin type tungsten-substituted molybdophosphoric acids ($H_3PMo_{12-n}W_nO_{40} \cdot xH_2O$) were synthesized and characterized by ICP-AES, FT-IR, TG-DSC, and XRD. The tungsten substitution extent significantly affected their catalytic activity in the oxidation of cyclopentene and the selectivity of the resultant products. The tungsten-substituted molybdophosphoric acids with tungsten substitution numbers in a range of 3-6.8 exhibited high catalytic activity in the oxidation of cyclopentene. After reaction for 8 h, the conversion of cyclopentene was up to 97%; the oxidation products mainly consisted of glutaraldehyde, *cis*-1,2-cyclopentanediol and *trans*-1,2-cyclopentanediol with the yields of ca. 23%, 27%, and 45%, respectively.

Key words: Tungsten-substituted Molybdophosphoric Acid, Cyclopentene, Glutaraldehyde, *cis*-1,2-Cyclopentanediol, *trans*-1,2-Cyclopentanediol

INTRODUCTION

Valuable derivatives of cyclopentene, such as glutaraldehyde and 1,2-cyclopentanediol, can be produced through the selective oxidation of cyclopentene, which is a by-product produced in a large quantity in oil refining. The derivatives of cyclopentene have important practical applications in many fields, e.g., glutaraldehyde is extensively used for disinfection, sterilization, leather tanning, and petroleum exploitation processes [1]; 1,2-Cyclopentanediol is an important feedstock to produce glutaric acid, which is an important intermediate for production of polyamide and polyurethane [2].

Several tungsten oxide-containing catalysts were reported as potential catalysts for oxidation of cyclopentene in both homogeneous and heterogeneous catalysis systems. For example, tungstic acid was used as a homogeneous catalyst in the oxidation of cyclopentene with aqueous hydrogen peroxide [3]; tungsten oxides [4], W-doped MCM-41 [5] or SBA-15 [1], and SiO_2 [6,7] or TiO_2 - SiO_2 [8] supported WO_3 were used as heterogeneous catalysts for oxidation of cyclopentene.

Recently, heteropolyacids have been widely investigated as catalysts for acid-catalyzed and oxidation reactions. The advantages of Keggin type heteropolyacid catalysts are the low volatility, low corrosiveness, nontoxicity, high Brønsted acid strength, and high oxidation activity. The catalytic property of heteropolyacids can be tuned by changing their central heteroatoms, framework polyatoms, and charge-compensating cations because the substitution of these atoms changes their acid and redox properties [9-13]. For example, as compared with molybdophosphoric acid, vanadium-substituted molybdophosphoric acids showed high activity and selectivity for the lactonization of 1,4-butanediol to γ -butyrolactone [14], the oxidation of methacrolein to methacrylic acid [11], isobutene to methacrylic acid and methacrolein [15], nitrobenzene to nitrophenol [16], and benzene to phenol [17].

In our present work, a series of tungsten-substituted molybdophos-

phoric acids were synthesized and characterized. The effect of tungsten substitution extent on the catalytic activity of the heteropolyacids in the oxidation of cyclopentene with H_2O_2 was investigated.

EXPERIMENTAL

1. Materials

$Na_2WO_4 \cdot 2H_2O$ (99%), $Na_2MoO_4 \cdot 2H_2O$ (99%), $Na_2HPO_4 \cdot 12H_2O$ (99%), H_2SO_4 (98%), diethyl ether, aqueous hydrogen peroxide (50%), 2-propanol (99.7%), and cyclopentene (98%), all reagent grade, were purchased from National Shanghai Chemical Co. Ltd. and used as received. Distilled water was used throughout all of the experiments.

2. Catalyst Preparation

Tungsten-substituted molybdophosphoric acids were prepared by a modified classical ether extraction method. The preparation of a tungsten-substituted molybdophosphoric acid with a desired formula of $H_3PMo_{11}WO_{40} \cdot xH_2O$ is presented as an example: 8.95 g of $Na_2HPO_4 \cdot 12H_2O$ and 66.54 g of $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 50 ml and 100 ml of distilled water, respectively. The above-mentioned solutions were mixed and heated at 90 °C for 30 min under stirring. Then a 50 ml aqueous solution containing 8.25 g of $Na_2WO_4 \cdot 2H_2O$ was added to the above mixed solution. The resultant solution reacted at 90 °C for 30 min. After reaction, the reaction solution was cooled to room temperature and the pH value of the solution was adjusted to 1.5-2 by adding 98% H_2SO_4 dropwise under vigorous stirring. The solution was heated to 90 °C and reacted for 8 h under stirring. After reaction, the solution was cooled to room temperature, standing over night. 100 ml of diethyl ether was added to the solution with intense, thorough shaking. After that, 20 ml of H_2SO_4 (1 : 1, v/v) was added to the solution batchwise with shaking and extracting until three layers appeared in the solution. In this extraction process, the oil-like yellow heteropolyacid-etherate compound presented at the bottom layer; the middle layer was canary yellow and probably contained tungstic and molybdic species; the top layer was diethyl ether. After separation, a stream of air was passed through the oil-like yellow heteropolyacid-etherate compound to free it of

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Table 1. Compositions of the resultant tungsten-substituted molybdophosphoric acids determined by ICP-AES and TG-DSC and the calculated formulas

Sample numbers	Desired mole ratios of P : Mo : W	Mole ratios of P : Mo : W determined by ICP-AES	Endothermic peak 1		Endothermic peak 2		Exothermic peak		Calculated formulas
			T (°C)	-H ₂ O (%)	T (°C)	-H ₂ O (%)	T (°C)	-H ₂ O (%)	
A	1 : 12 : 0	1 : 12 : 0	74.9	6.44	116.7	4.36	416.0	1.52	H ₃ PMo ₁₂ O ₄₀ ·12H ₂ O
B	1 : 11 : 1	1 : 10.6 : 1.1	98.2	10.54	117.0	6.82	435.0	1.45	H ₃ PMo _{10.6} W _{1.1} O ₄₀ ·22H ₂ O
C	1 : 9 : 3	1 : 8.7 : 3.0	91.9	8.35	121.8	6.15	457.0	1.30	H ₃ PMo _{8.7} W ₃ O ₄₀ ·19H ₂ O
D	1 : 7 : 5	1 : 6.5 : 4.8	85.1	4.66	127.1	4.57	469.0	1.25	H ₃ PMo _{6.5} W _{4.8} O ₄₀ ·12H ₂ O
E	1 : 5 : 7	1 : 4.8 : 6.8	88.8	7.58	158.0	3.54	496.0	1.15	H ₃ PMo _{4.8} W _{6.8} O ₄₀ ·15H ₂ O
F	1 : 3 : 9	1 : 3.3 : 8.5	72.0	4.33	161.8	2.57	518.9	1.07	H ₃ PMo _{3.3} W _{8.5} O ₄₀ ·11H ₂ O
G	1 : 1 : 11	1 : 1.2 : 10.6	68.1	4.33	169.1	2.91	561.1	1.01	H ₃ PMo _{1.2} W _{10.6} O ₄₀ ·12H ₂ O

diethyl ether. The remaining yellow substance (the coarse tungsten-substituted molybdophosphoric acid) was dissolved in 25 ml of distilled water, concentrated to the appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallize further. The yellow crystal that formed was filtered, washed with water, and air dried.

The synthesis method of the other tungsten-substituted molybdophosphoric acids was similar to the above-mentioned one. Only the mole ratio of the reactants was changed according to that of P : Mo : W in the desired formula H₃PMo_{12-n}W_nO₄₀·XH₂O.

3. Characterization

The bulk elemental composition of the as-prepared tungsten-substituted molybdophosphoric acids was examined by inductive coupled plasma atomic emission spectroscopy (ICP-AES) (VISTA-MPX CCD simultaneous ICP-AES). Thermal gravimetry and differential scanning calorimetry (TG-DSC) curves of the samples were acquired by using a thermoanalysis instrument (NETZSCH STA 449C) under dynamic nitrogen atmosphere at a heating rate of 10 °C/min. Fourier transform infrared spectra (FT-IR) of the samples were recorded on a Nicolet-Nexus 470 FTIR spectrometer at room temperature by the KBr pellet technique. Powder X-ray diffraction analysis was performed on a Shimada DX-D1 powder diffractometer by using CuK α radiation at a wavelength of 0.154 nm, 30 kV and 30 mA.

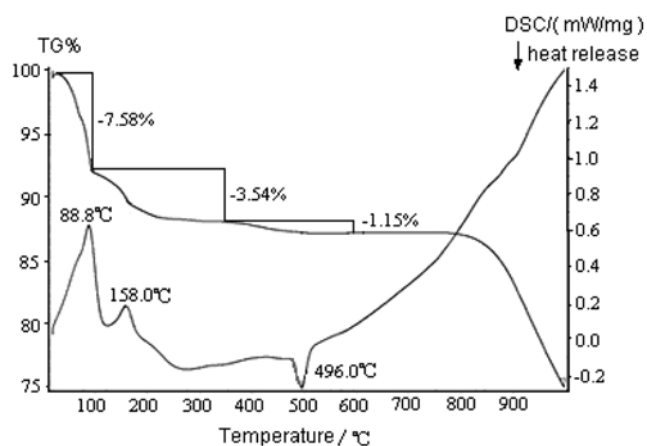
4. Catalysis Test

The activity test was performed in a closed 250 ml three-neck flask at 35 °C with magnetic stirring using aqueous H₂O₂ as an oxidant and 2-propanol as a solvent. In the catalytic reaction, the amounts of catalyst, aqueous H₂O₂, cyclopentene, and 2-propanol were 0.5 mmol, 24 ml, 18 ml, and 88 ml, respectively. The determination of the resultant products was performed on a gas chromatograph coupled with a mass spectrophotometer (TRACE DSQ-TRACE GC ULTRA) by comparing their mass spectra with NIST library data. The quantitative analyses of the unreacted cyclopentene and the products were performed on a gas chromatograph (FID) with a capillary column (SE-54).

RESULTS AND DISCUSSION

1. Characterization of Tungsten-substituted Molybdophosphoric Acids

1-1. Elemental Analysis

**Fig. 1. TG-DSC curves of the sample with a mole ratio of P : Mo : W of 1 : 4.8 : 6.8.**

The main element contents of the tungsten-substituted molybdophosphoric acids analyzed by ICP-AES are listed in Table 1. ICP-AES analysis indicated that the mole ratios of P : Mo : W of the samples were nearly in agreement with the desired ones.

1-2. TG-DSC Analysis

The contents of water present in the tungsten-substituted molybdophosphoric acids were analyzed by TG-DSC technique. The TG-DSC analysis of the sample with a mole ratio of P : Mo : W of 1 : 4.8 : 6.8 was taken as a representative example. As shown in Fig. 1, in the first weight-loss stage, free crystallized water, 7.58% of the total sample weight, was lost and an endothermic peak correspondingly emerged at 88.8 °C. The H⁺-combined water, 3.54% of the total sample weight, was lost in the second weight-loss stage accompanied by an endothermic peak at 158 °C. In the third weight-loss stage, the structural water, 1.15% of the total sample weight, was lost and an exothermic peak at 496 °C appeared in the DSC curve, characterizing the collapse of the heteropolyacid [18]. The as-prepared tungsten-substituted molybdophosphoric acids are hydrated crystals.

From Table 1, we also found that the temperatures of the second endothermic peaks, corresponding to the weight loss of H⁺-combined water, increased from 116.7 to 169.1 °C, while the tungsten atom number in the formulas increased from 0 to 10.6. It is well known that when the desorption temperature of the H⁺-combined

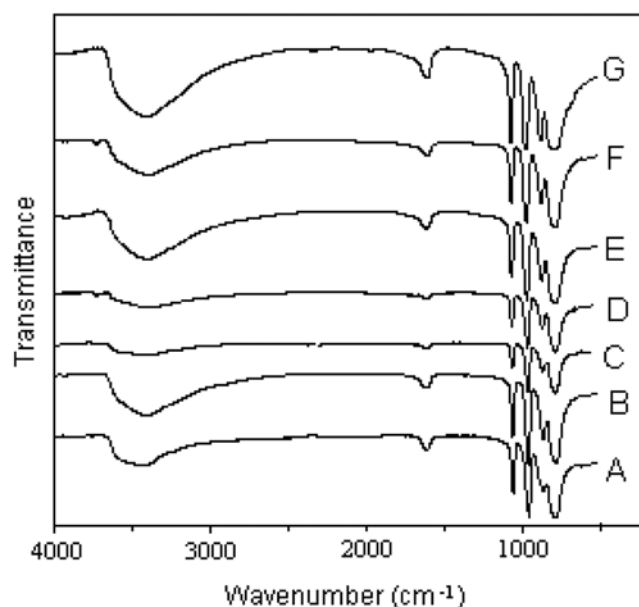


Fig. 2. FT-IR spectra of the heteropolyacids.

water is high, the acid strength is high [19] and that the acid strength of tungstophosphoric acid is higher than that of molybdophosphoric acid [9,10,20]. Therefore, an increase of tungsten content in the tungsten-substituted molybdophosphoric acids raises their acid strength.

1-3. FT-IR Analysis

Fig. 2 shows the FT-IR spectra of the as-prepared tungsten-substituted molybdophosphoric acids, and the data are listed in Table 2. Over a range of 700–1,100 cm^{-1} , the absorption bands at 1,064–1,079, 963–983, 872–890, and 788–798 cm^{-1} , corresponding to the four characteristic skeletal vibrations of the Keggin oxoanions, were observed in the FT-IR spectra of each sample. These absorption bands are attributed to the vibrations of $\nu_{as}(\text{P}-\text{O}_a-(\text{M})_3)$, $\nu_{as}(\text{M}=\text{O}_d)$, $\nu_{as}(\text{M}-\text{O}_b-\text{M})$ in corner shared octahedra, and $\nu_{as}(\text{M}-\text{O}_c-\text{M})$ in edge shared octahedra ($\text{M}=\text{Mo}, \text{W}$), respectively [21–23]. These characteristic bands are regarded as experimental evidences for the existence of heteropolyacid molecules. Furthermore, the FTIR characteristic peaks of the Keggin structure of the tungsten-substituted molybdophosphoric acids were similar to each other, indicating that the Keggin structure was not changed after tungsten substitution. The bands of $\nu_{as}(\text{P}-\text{O}_a-(\text{M})_3)$, $\nu_{as}(\text{M}=\text{O}_d)$, $\nu_{as}(\text{M}-\text{O}_b-\text{M})$, and $\nu_{as}(\text{M}-\text{O}_c-\text{M})$ ($\text{M}=\text{Mo}, \text{W}$) shifted to high frequency with the increase of the amount of tungsten, which can be explained as being due to the substitution of molybdenum with tungsten.

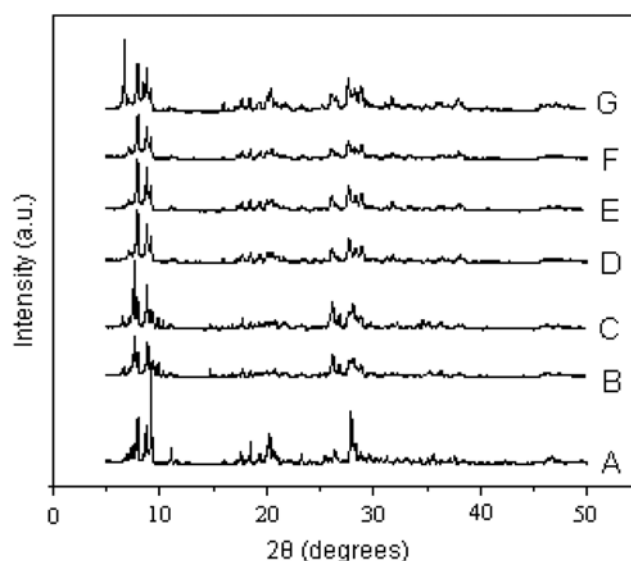


Fig. 3. X-Ray diffraction patterns of the heteropolyacids.

The bands at ca. 1,610 cm^{-1} and 3,440 cm^{-1} attributed to the bending and stretching vibrations of crystallized water [24] were present in all of the FT-IR spectra, revealing that the resultant tungsten-substituted molybdophosphoric acids were hydrated.

1-4. XRD Analysis

As shown in Fig. 3, the X-ray diffraction patterns of the tungsten-substituted molybdophosphoric acids are primarily distributed in four ranges of 2θ , which are 6–12°, 16–23°, 25–30°, and 31–38°, revealing that the synthesized samples belong to the set of Keggin type heteropolyacids [24]. The XRD pattern of heteropolyacid reflects its secondary structure, which strongly depends on its environment. The variation in the intensities of diffraction peaks should be due to the framework polyatom substitution and the hydration.

2. Catalytic Activity Test

GC/MS analysis showed that the main products in the oxidation of cyclopentene catalyzed by tungsten-substituted molybdophosphoric acids were glutaraldehyde, *cis*-1,2-cyclopentanediol, and *trans*-1,2-cyclopentanediol. The ion peaks at m/z 27, 29, 39, 41, 44, 57, 72, 82 in the mass spectra (not shown) were attributed to glutaraldehyde. The major ion peaks present at m/z 27, 29, 41, 43, 55, 57, 83, 84, 101 were attributed to both *cis*-1,2-cyclopentanediol and *trans*-1,2-cyclopentanediol, whose peaks appeared at different time in the GC analysis.

Fig. 4 shows the conversion of cyclopentene catalyzed by tung-

Table 2. FT-IR data of $\text{H}_3\text{PMo}_{12-n}\text{W}_n\text{O}_{40}\cdot\text{XH}_2\text{O}$ (cm^{-1})

Samples	$\nu_{as}(\text{P}-\text{O}_a-(\text{M})_3)$	$\nu_{as}(\text{M}=\text{O}_d)$	$\nu_{as}(\text{M}-\text{O}_b-\text{M})$	$\nu_{as}(\text{M}-\text{O}_c-\text{M})$
$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 12\text{H}_2\text{O}$	1064	963	872	788
$\text{H}_3\text{PMo}_{10.6}\text{W}_{1.4}\text{O}_{40}\cdot 22\text{H}_2\text{O}$	1067	967	873	790
$\text{H}_3\text{PMo}_{8.7}\text{W}_{3.3}\text{O}_{40}\cdot 19\text{H}_2\text{O}$	1069	969	875	792
$\text{H}_3\text{PMo}_{6.5}\text{W}_{5.5}\text{O}_{40}\cdot 12\text{H}_2\text{O}$	1072	973	878	794
$\text{H}_3\text{PMo}_{4.8}\text{W}_{7.2}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	1075	976	882	796
$\text{H}_3\text{PMo}_{3.3}\text{W}_{8.7}\text{O}_{40}\cdot 11\text{H}_2\text{O}$	1077	980	885	797
$\text{H}_3\text{PMo}_{1.2}\text{W}_{10.8}\text{O}_{40}\cdot 12\text{H}_2\text{O}$	1079	983	890	798

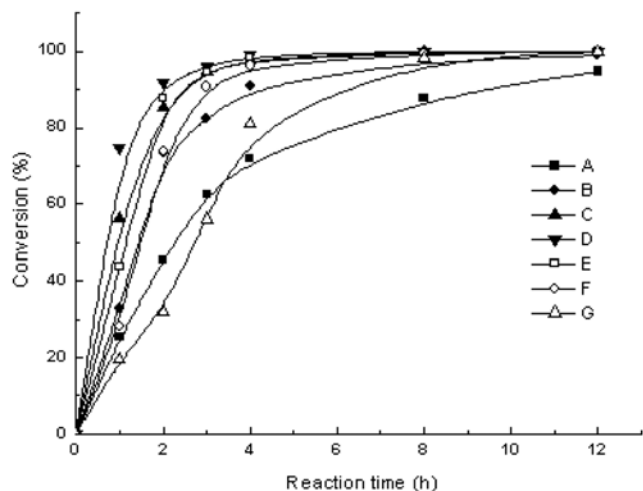


Fig. 4. The conversion of cyclopentene catalyzed by the heteropolyacids.

sten-substituted molybdophosphoric acids. When tungsten-substituted molybdophosphoric acids catalyzed oxidation of cyclopentene, the conversion of cyclopentene was up to 97% after reaction for 8 h. Tungsten-substituted molybdophosphoric acids exhibited good catalytic activity in the oxidation of cyclopentene. The initial conversions during the first 2 h showed that the catalytic oxidation activities of tungsten-substituted molybdophosphoric acids were in an order of $\text{H}_3\text{PMo}_{6.5}\text{W}_{4.8}\text{O}_{40} \cdot 12\text{H}_2\text{O} > \text{H}_3\text{PMo}_{8.7}\text{W}_3\text{O}_{40} \cdot 19\text{H}_2\text{O} > \text{H}_3\text{PMo}_{4.8}\text{W}_{6.8}\text{O}_{40} \cdot 15\text{H}_2\text{O} > \text{H}_3\text{PMo}_{10.6}\text{W}_{1.1}\text{O}_{40} \cdot 22\text{H}_2\text{O} > \text{H}_3\text{PMo}_{3.3}\text{W}_{8.5}\text{O}_{40} \cdot 11\text{H}_2\text{O} > \text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O} > \text{H}_3\text{PMo}_{1.2}\text{W}_{10.6}\text{O}_{40} \cdot 12\text{H}_2\text{O}$. The catalytic activity increased with increasing the tungsten substitution number from 0 to 4.8. Further increasing tungsten substitution number from 4.8 to 10.6 led to the decrease of the catalytic activity.

Fig. 5 shows the yield of glutaraldehyde catalyzed by tungsten-substituted molybdophosphoric acids. For all of the tungsten-substituted molybdophosphoric acid catalysts, the yield of glutaraldehyde rapidly increased with prolonging the reaction time to 4 h. Then

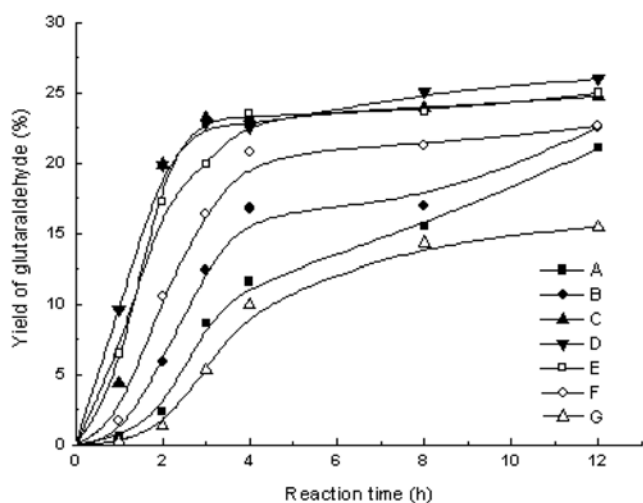


Fig. 5. The yield of glutaraldehyde catalyzed by the heteropolyacids.

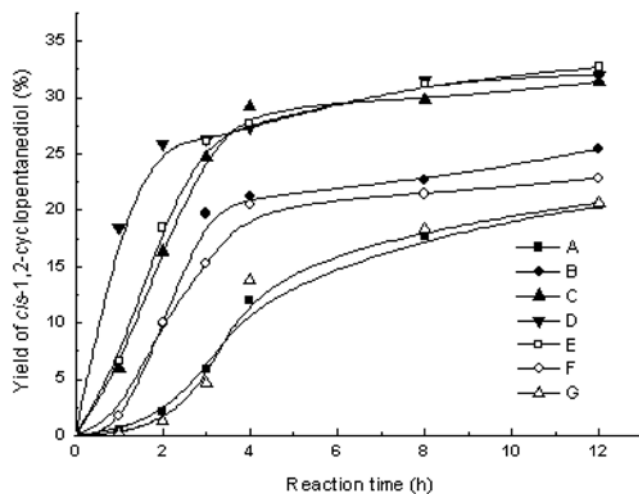


Fig. 6. The yield of *cis*-1,2-cyclopentanediol catalyzed by the heteropolyacids.

the yields slightly increased with further prolonging the reaction time from 4 to 12 h, revealing that glutaraldehyde was one of the final products in the oxidation of cyclopentene. The yield order of glutaraldehyde catalyzed by the tungsten-substituted molybdophosphoric acids is: $\text{H}_3\text{PMo}_{6.5}\text{W}_{4.8}\text{O}_{40} \cdot 12\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{4.8}\text{W}_{6.8}\text{O}_{40} \cdot 15\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{8.7}\text{W}_3\text{O}_{40} \cdot 19\text{H}_2\text{O} > \text{H}_3\text{PMo}_{3.3}\text{W}_{8.5}\text{O}_{40} \cdot 11\text{H}_2\text{O} > \text{H}_3\text{PMo}_{10.6}\text{W}_{1.1}\text{O}_{40} \cdot 22\text{H}_2\text{O} > \text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O} > \text{H}_3\text{PMo}_{1.2}\text{W}_{10.6}\text{O}_{40} \cdot 12\text{H}_2\text{O}$.

Fig. 6 shows the yield of *cis*-1,2-cyclopentanediol catalyzed by tungsten-substituted molybdophosphoric acids. The yield of *cis*-1,2-cyclopentanediol rapidly increased with prolonging the reaction time to 4 h, then the yield slightly increased with further prolonging the reaction time from 4 to 12 h, revealing that *cis*-1,2-cyclopentanediol was another final product in the oxidation of cyclopentene. The yield order of *cis*-1,2-cyclopentanediol catalyzed by the tungsten-substituted molybdophosphoric acids is: $\text{H}_3\text{PMo}_{6.5}\text{W}_{4.8}\text{O}_{40} \cdot 12\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{4.8}\text{W}_{6.8}\text{O}_{40} \cdot 15\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{8.7}\text{W}_3\text{O}_{40} \cdot 19\text{H}_2\text{O} > \text{H}_3\text{PMo}_{10.6}\text{W}_{1.1}\text{O}_{40} \cdot 22\text{H}_2\text{O} > \text{H}_3\text{PMo}_{3.3}\text{W}_{8.5}\text{O}_{40} \cdot 11\text{H}_2\text{O} > \text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{1.2}\text{W}_{10.6}\text{O}_{40} \cdot 12\text{H}_2\text{O}$.

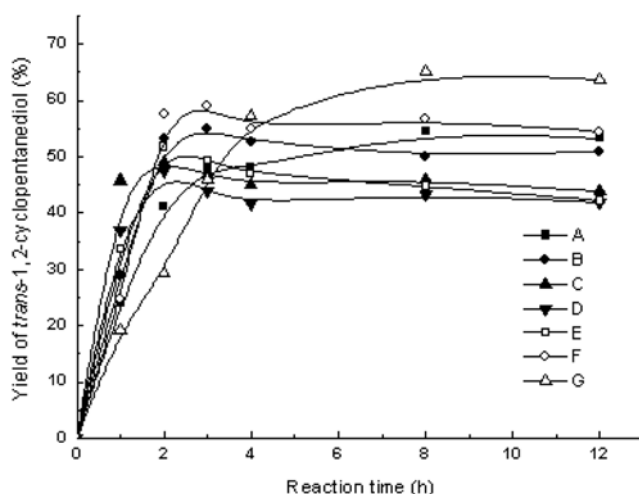
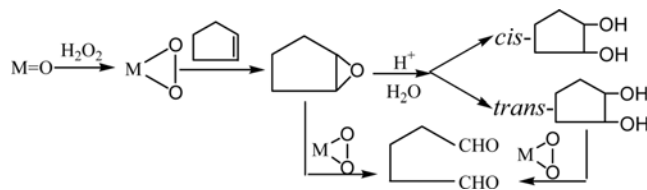


Fig. 7. The yield of *trans*-1,2-cyclopentanediol catalyzed by the heteropolyacids.

The yields of *trans*-1,2-cyclopentanediol catalyzed by tungsten-substituted molybdophosphoric acids are shown in Fig. 7. When the tungsten-substituted molybdophosphoric acids with tungsten substitution numbers in a range of 1.1–8.5 were used as the catalysts, the yields of *trans*-1,2-cyclopentanediol increased with increasing the reaction time to ca. 2 h, then slightly decreased with further prolonging the reaction time. The yield of *trans*-1,2-cyclopentanediol catalyzed by molybdophosphoric acid and the tungsten-substituted molybdophosphoric acid with a tungsten substitution number of 10.6 increased with prolonging the reaction time. As certified by the conversion of cyclopentene, the tungsten-substituted molybdophosphoric acids with tungsten substitution numbers in a range of 1.1–8.5 had higher oxidation activity than the molybdophosphoric acid and the tungsten-substituted molybdophosphoric acid with a tungsten substitution number of 10.6, causing further oxidation of the resultant *trans*-1,2-cyclopentanediol. After reaction for 8 h, the yields of *trans*-1,2-cyclopentanediol catalyzed by the tungsten-substituted molybdophosphoric acids were in the order of $\text{H}_3\text{PMo}_{1.2}\text{W}_{10.6}\text{O}_{40} \cdot 12\text{H}_2\text{O} > \text{H}_3\text{PMo}_{3.3}\text{W}_{8.5}\text{O}_{40} \cdot 11\text{H}_2\text{O} > \text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O} > \text{H}_3\text{PMo}_{10.6}\text{W}_{1.1}\text{O}_{40} \cdot 22\text{H}_2\text{O} > \text{H}_3\text{PMo}_{8.7}\text{W}_3\text{O}_{40} \cdot 19\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{6.5}\text{W}_{4.8}\text{O}_{40} \cdot 12\text{H}_2\text{O} \approx \text{H}_3\text{PMo}_{4.8}\text{W}_{6.8}\text{O}_{40} \cdot 15\text{H}_2\text{O}$. The tungsten-substituted molybdophosphoric acids with tungsten substitution numbers of 3–6.8 showed lower *trans*-1,2-cyclopentanediol yields (ca. 40%) in the oxidation of cyclopentene than the other heteropolyacids. The yield of *trans*-1,2-cyclopentanediol was more than that of *cis*-1,2-cyclopentanediol due to that *trans*-1,2-cyclopentanediol has a more steady structure than *cis*-1,2-cyclopentanediol.

3. Reaction Route

A plausible oxidation route of cyclopentene catalyzed by tungsten-substituted molybdophosphoric acids is shown in Scheme 1. In the catalytic oxidation process of cyclopentene, H_2O_2 reacted with $\text{M}=\text{O}$ ($\text{M}=\text{Mo}, \text{W}$) bonds of tungsten-substituted molybdophosphoric acids to form peroxy-heteropolyacids as active components [25]. In addition to the formation of glutaraldehyde, *cis*-1,2-cyclopentanediol, and *trans*-1,2-cyclopentanediol, a trace amount of cyclopentene epoxide was also detected in the catalytic oxidation of cyclopentene catalyzed by the heteropolyacids. Therefore, we suggested that cyclopentene was first oxidized by peroxy-heteropolyacids to cyclopentene epoxide. Then the resultant cyclopentene epoxide was rapidly converted to glutaraldehyde, *cis*-1,2-cyclopentanediol, and *trans*-1,2-cyclopentanediol in two ways. One way was to form *cis*-1,2-cyclopentanediol and *trans*-1,2-cyclopentanediol via hydrolysis of cyclopentene epoxide catalyzed by proton acid, and a certain amount of *trans*-1,2-cyclopentanediol was further oxidized by peroxy-heteropolyacids to glutaraldehyde. Another way was to form glutaraldehyde via the oxidation of cyclopentene epoxide by peroxy-heteropolyacids.



Scheme 1. The reaction route of cyclopentene oxidation catalyzed by heteropolyacids.

In the catalytic oxidation process, besides the heteropolyacids having oxidation activity, their protons also play a role as acid catalysts in the conversion of cyclopentene epoxide to *cis*-1,2-cyclopentanediol and *trans*-1,2-cyclopentanediol. The yield of both *cis*-1,2-cyclopentanediol and *trans*-1,2-cyclopentanediol is higher than that of glutaraldehyde, meaning that the acid catalytic activity of the heteropolyacids is higher than their catalytic oxidation activity.

When H_2O_2 is used as an oxidant, the polyatoms of heteropolyacids are able to combine with H_2O_2 to form peroxy bond [25]. Furthermore, Rao et al. [21] reported that tungsten atom has stronger combination ability with oxygen than molybdenum atom. Therefore, it is reasonable to conclude that the combination ability of heteropolyacids with H_2O_2 becomes stronger with increasing the tungsten substitution number from 0 to 4.8, giving higher oxidation activity. However, further increasing the tungsten substitution number from 4.8 to 10.6 excessively strengthens the combination ability of heteropolyacid with H_2O_2 , resulting in the decrease of the capability to release reactive oxygen, subsequently giving a lower catalytic activity. Adequate tungsten substitution extent is essential to the catalytic oxidation activity. This is probably the reason why the heteropolyacids with tungsten substitution numbers ranging from 3 to 6.8 show higher catalytic activity in the selective oxidation of cyclopentene to glutaraldehyde.

CONCLUSIONS

Glutaraldehyde, *cis*-1,2-cyclopentanediol, and *trans*-1,2-cyclopentanediol were the main products in the oxidation of cyclopentene catalyzed by tungsten-substituted molybdophosphoric acids. $\text{H}_3\text{PMo}_{8.7}\text{W}_3\text{O}_{40} \cdot 19\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{6.5}\text{W}_{4.8}\text{O}_{40} \cdot 12\text{H}_2\text{O}$, and $\text{H}_3\text{PMo}_{4.8}\text{W}_{6.8}\text{O}_{40} \cdot 15\text{H}_2\text{O}$ exhibited higher catalytic oxidation activity than the other tungsten-substituted molybdophosphoric acids. After reaction for 8 h, the conversion of cyclopentene was up to 97% and the yields of glutaraldehyde, *cis*-1,2-cyclopentanediol, and *trans*-1,2-cyclopentanediol were around 23%, 27% and 45%, respectively. The substitution extent of tungsten-substituted molybdophosphoric acids affected their catalytic oxidation activity and their protons also participated in the catalytic reaction.

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