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New Simple Synthesis Route for Decatungstate Hybrids: Novel Thermo-Regulated Phase Transfer Catalysts for Selective Oxidation of Alcohols

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Abstract A generalized synthesis method for decatungstate hybrids from bisulfate-based acidic ionic liquids was reported. *N*-butylpyridinium decatungstate $[bPy]_4W_{10}O_{32}$ and 1-butyl-3-methylimidazolium decatungstate $[bmIm]_4W_{10}O_{32}$ were synthesized and have been demonstrated to be good thermo-regulated phase transfer catalysts in an organic-solvent-free selective oxidation of alcohols under mild conditions. Advantages of heterogeneous and homogeneous catalysis are combined here, provided good self-separated and ease-of-recycling catalysts.

Keywords Synthesis · Decatungstate · Phase transfer · Selective oxidation · Self-separation · Recyclable

1 Introduction

The ability to combine, in a single material, inorganic and organic components at molecular level has represented an exciting direction for developing novel multifunctional materials. In recent years, polyoxometalate hybrids, as a new kind of novel functional materials, have received increased attentions because of their advantages including structure diversity, good stability, extensively alterable molecular properties, ease of controlling acidity, reduction potential and solubility [1–3]. An interesting concept of reaction-controlled phase-transfer catalysis by polyoxometalate $Q_3[PO_4(WO_3)_4]$ (Q: organic cation) was firstly reported for propylene epoxidation to propylene oxide by Xi et. al. in 2001. This insoluble catalyst forms soluble active species by the action of H_2O_2, and when the H_2O_2 is used up, the catalyst precipitates for easy recycling [2]. Another interesting example is $Q_3[PW_{12}O_{40}]$ working as reaction induced self separation catalysts for various esterification reactions. The reported catalysts could be dissolved completely in reactant, but insoluble in the product ester [3]. Decatungstate hybrid, as one kind of polyoxometalate hybrids, has been studied widely in catalytic oxidation [4–7] and photochemistry [8–10]. Tzirakis et. al. [4] have outlined the progress in the field of decatungstate catalysis, especially on organic synthesis by oxidation. Another good review devoted on photochemistry and photocatalysis of decatungstate [8]. However, only a little report on decatungstate hybrid as a self-separated catalyst has been found in previous studies. Hexadecyl trimethyl ammonium decatungstate $(n\text{-}C_{16}H_{33}(CH_3)_3N)W_{10}O_{32}$ was reported to oxidize hexanol and octanol to their acids in the presence of H_2O_2, the catalyst is insoluble in water, but dissolved in organic solvent and H_2O_2 at 90–100 °C, when H_2O_2 is used up, catalyst will precipitate out[5]. To find good task-specific decatungstate hybrids, one should choose the proper organic group and the suitable synthesis methods as well.

The typical synthesis method for decatungstate hybrid is through the reaction of sodium tungstate with quaternary ammonium based salt such as (tetrabutylammonium bromide $(C_4H_9)_4N)Br$, tributylammonium bromide $((C_4H_9)_3NH)Br$ [9], *n*-cetyl trimethyl ammonium bromide $(n\text{-}C_{16}H_{33}(CH_3)_3N)Br$ [5] and 1-butyl-3-methylimidazolium bromide [bmIm]Br [6, 7] in the presence of HCl solution.

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Therefore, the existing synthesis method for decatungstates is affected by many factors, such as the environment temperature, pressure, pH values of the solutions, starting concentrations and so on. Meanwhile, the presence of HCl solution will lead to corrosion, environmental and safety problems. Therefore, it is still a great challenge to explore new synthetic method for new decatungstate hybrids. Zou et al. reported a modified synthesis method for ethyl methyl imidazolium decatungstate $[C_6H_{11}N_2]_4W_{10}O_{32}$ by the reaction of Na_2WO_4 and Na_2HPO_4 in the ionic liquid $[Emim][BF_4]$ with stirring for 10 h at 90 °C. The advantage of the modified method is to keep reaction under the pH value of the reaction mixture; however, the yield (18 % based on W) is quite lower and slow evaporation process (1–2 days) under room temperature is needed [11].

We proposed a new simple method of synthesis decatungstate directly from bisulfate-based acid functional ionic liquids under mild conditions. Suitable amount of sodium tungstate Na_2WO_4 and bisulfate-based ionic liquids $Q^+[HSO_4]^-$ are mixed and heated to reaction temperature (less than 90 °C) under stirring for 8 h, and the corresponding decatungstate $Q_4W_{10}O_{32}$ was obtained with higher yields. The process is efficient and simple in operation without necessary to control pH value. And the acidity provided by the anion bisulfate in ionic liquids, provided enough acidity for the synthesis of decatungstate. A new decatungstate $[bPy]_4W_{10}O_{32}$ has been synthesized and demonstrated effective for the selective oxidation of alcohol.

Selective oxidation of alcohols to the corresponding aldehydes or ketones has attracted much attention as a promising strategy for environmentally benign organic synthesis. Such reactions usually suffer from drawbacks such as poor conversion and selectivity in order to avoid the formation of carboxylic acid caused by over-oxidation. Hydrogen peroxide is probably an ideal oxidant after molecular oxygen due to environmental and economic considerations. However, since H_2O_2 is generally supplied as an aqueous solution, the use of H_2O_2 is often a problem in cases in which substrates are immiscible in water. Therefore, the adding of a co-solvent to achieve sufficient interaction of H_2O_2 with both catalyst(s) and water-immiscible substrate(s) are often required in a conversional method, which will further lead to the difficulty in separation of solvent. For example, ionic liquids have been well documented as the co-solvent in the previous oxidation system [6, 7, 12]. Kumar et. al. [6, 7] report the catalytic oxidation by decatungstate hybrid $[bmIm]_4W_{10}O_{32}$ in the presence of ionic liquid $[bmim]_4BF_4$. Here ionic liquid works as solvent to increase the solubility of catalyst and substrate to form homogeneous reaction media. However, the recovery of catalyst and tedious work for separation of the reagent and products from the catalyst are general problems encountered in this homogeneous reaction media. Hence various heterogeneous methods have been designed to overcome these problems by immobilizing the homogeneous catalysts on solid supports to combine the homogeneous and heterogeneous catalysis in one step [13, 14].

The feature of task-specific decatungstate hybrids is that cationic functional group shows good solubility to organic matters and provides acid site to accelerate reaction rate; decatungstate anion can react with H_2O_2 to form polyoxotungstate which works as the active species of catalytic oxidation reaction. Then decatungstate hybrids is solid in nature, can be dissolved in organics and H_2O_2, while insoluble in water at room temperature and will become soluble with increasing temperature to 60 °C. Then, thermal control makes the solid–liquid–solid phase transformation possible.

In this study, the decatungstate hybrid works as a thermo-regulated phase transfer catalyst, i.e., it is immiscible with the substrate mixture initially, however, become soluble to form a homogeneous phase at reaction condition (60–80 °C). After the completion of the reaction, the catalyst can be self precipitated out at room temperature. The advantages of homogenous and heterogeneous catalysis were combined in one step here.

2 Experimental

2.1 Preparation of Decatungstate Hybrid

According to our previous work [15], bisulfate-based ionic liquids (*N*-butylpyridinium bisulfate $[bPy][HSO_4]$ and 1-butyl-3-methylimidazolium bisulfate $[bmIim][HSO_4]$) were synthesized firstly. The structures and synthesis scheme of the decatungstates were shown in Fig. 1, and detail method was described below:

$Na_2WO_4 \cdot 2H_2O$ (0.825 g, 2.5 mmol) and ionic liquid $[bPy][HSO_4]$ (2.60 g, 10.0 mmol) were mixed under stirring in 25 ml round bottom flask and heated to 65 °C slowly, and proceeded at 65 °C with vigorous stirring at the rate of 1,000 r/min for 8 h, and a yellow solid decatungstates $[bPy]_4W_{10}O_{32}$ was obtained. The decatungstate was then washed with water thoroughly and then dried at room temperature, giving a yield of 87.1 %.

Similar method was used for the synthesis of $[bmIm]_4W_{10}O_{32}$ with high yield (83.5 %) from ionic liquid $[bmIm][HSO_4]$ at the reaction temperature of 83 °C for 8 h. Therefore, it has provided a novel synthesis method for decatungstate hybrids directly from the corresponding bisulfate-based ionic liquids. On account of the diversity of cations in ionic liquids, this synthetic method will greatly enrich the decatungstate hybrid family.

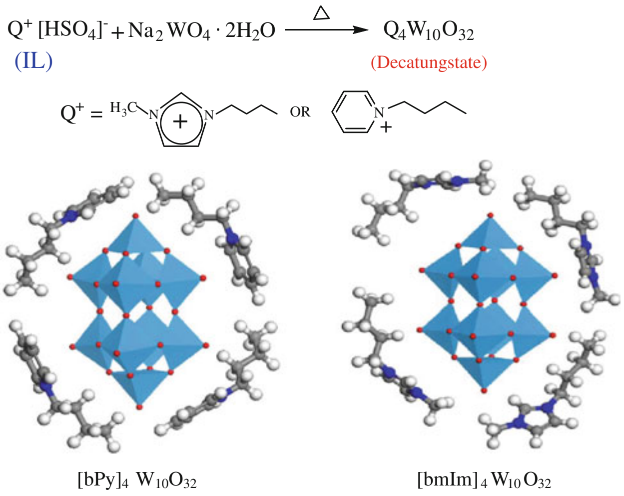


Fig. 1 Structures and synthesis scheme of decatungstate hybrids

2.2 Characterization of Decatungstates

The decatungstate hybrids were fully characterized by Elemental analysis, ^{1}H NMR, ^{13}C NMR, FT-IR, UV and TGA. The C, N and H elemental analyses were performed on an Elementar Vario EL element analyzer. IR spectra (FTIR) were recorded on a PE Spectrum TM GX FTIR spectrometer using liquid film. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were obtained on Varian Mercury-plus 300BB instruments as solutions in deuterium substituted reagent. Chemical shifts were reported in parts per million (ppm, d). UV spectra were obtained using a PerkinElmer's Lambda 900 UV/VIS/NIR spectrophotometer in acetonitrile. The thermal decomposition points of decatungstate hybrids were determined by TGA (Perkin-Elmer Pyris 1 TGA instrument, 10 K/min heating rate under nitrogen).

$[bPy]_4W_{10}O_{32}$: ^{1}H NMR(600 MHz, DMSO, TMS) δ: 0.900(m, 3H, CH_3), 1.302(m, 2H, CH_2), 1.931(m,2H,CH_2), 4.697(s, 2H, CH_2), 8.213(s, 2H, CH), 8.609(m, 2H, CH), 9.134(s, H, CH); ^{13}C NMR(600 MHz, DMSO, TMS) δ: 13.470, 18.813, 32.944, 60.836, 128.353, 144.938, 145.356; IR ν: 3058, 2962, 1631, 1487, 957, 887, 792 cm^{-1}; UV (in acetonitrile): the absorptions at 260 nm and 320 nm are proven to be the $[W_{10}O_{32}]^{4-}$ structure and agree well with the previous literature[16]. Anal. calcd for $C_{36}H_{56}N_4W_{10}O_{32}$(wt%): C 14.92, N1.93, H 1.93; found: C14.94, N1.88, H1.91. the weight loss in the range of 310–460 °C is ascribed to the loss of dissociative cations $[bPy]^+$. The loss-weight of 18.3 % is accordant with the calculated value of 18.8 %.

$[bmIm]_4W_{10}O_{32}$: ^{1}H NMR(600 MHz, DMSO, TMS) δ: 0.903(s, 3H, CH_3), 1.266(s, 2H, CH_2), 1.777(s, 2H, CH_2), 3.885(s, 2H, CH_2), 4.201(s, 3H, CH_3), 7.705(s, 2H, CH_2), 7.774(s, 1H, CH),9.089(s, H,CH); ^{13}C NMR(600 MHz, DMSO, TMS) δ: 13.380, 18.863, 31.501, 35.858, 48.670, 122.364, 123.734, 136.497; IR ν: 3150, 3108, 2957, 2929, 2869, 1571, 1455, 1160, 958, 893, 796, 650 cm^{-1}; UV (in acetonitrile): 260 nm, 320 nm; Elemental Anal.calcd for $C_{32}H_{60}N_4W_{10}O_{32}$(wt%): C 13.23, N3.86, H 1.93; found: C13.29, N3.85, H1.85. the weight loss in the range of 330–470 °C is ascribed to the loss of dissociative cations $[bmIm]^+$. The loss-weight of 18.7 % is accordant with the calculated value of 19.1 %.

2.3 Typical Reaction Procedure for Selective Oxidation of Alcohols

In a typical reaction procedure, the catalyst (0.07 mmol) and alcohol (30 mmol) were added in 25 ml round bottom flask equipped with magnetic stirrer. The reaction mixture was heated to reaction temperature (40–80 °C) slowly with stirring under reflux, followed by dropwise addition suitable amount of hydrogen peroxide 30 wt% aqueous solution. The reaction proceeded at reaction temperature under reflux with vigorous stirring at the rate of 1,000 r/min for a period of time. After the reaction mixture was cooled to room temperature, the catalyst would precipitate out and separated from the reaction mixture by centrifugation, followed by washing with water, then filtration and dry for the next run. Qualitative and quantitative analyses of organic products were conducted with a MAT-90 GC/MS and GC SP2100 equipped with a FID detector, respectively. The conversion of alcohols was based on the content of alcohols in the product, and the selectivity was based on (moles of aldehyde or ketone produced/total moles of the reacted alcohol) as determined by GC using an internal standard.

Oxidant efficiency is determined by iodometric titration method described in the supporting materials of one Ref. [17]. After the catalytic reaction for 1 h, the reaction mixture was diluted with methanol to a total volume of 20 ml. The mole of remaining oxidant was determined as follows. A portion (1.0 ml) of the diluted methanol solution was added to 1 M H_2SO_4 aqueous solution (20 ml) containing 1 mmol potassium iodide and a small amount of starch. The mixture turned purple due to generation of I_2. Then, the mixture was titrated with 0.02 M $Na_2S_2O_3$ aqueous solution until the color disappeared.

3 Results and Discussion

Benzaldehyde is an industrially useful target, and is easily over-oxidized to benzoic acid. Selective oxidation of benzyl alcohol was studied over different catalysts and the results were listed in Table 1. The presence of weak acidic ionic liquids such as $[bmIm]HSO_4$ and $[bPy]HSO_4$ don't have catalytic roles in the reaction, and no obvious

Table 1 Effect of different catalysts on selective oxidation of benzyl alcohol

Entry	Catalyst	Conv. (%)	Sel. (%)
1	–	4.8	100
2	[bmIm]HSO_4	5.0	100
3	[bPy]HSO_4	5.1	100
4	[$(CH_2)_4SO_3$HmIm]HSO_4	37.9	93.7
5	[$(CH_2)_4SO_3$HPy]HSO_4	40.1	91.6
6	[bmIm]$_4W_{10}O_{32}$	66.3	92.7
7	[bPy]$_4W_{10}O_{32}$	66.1	97.8

Conditions: 0.07 mmol Cat., 30 mmol H_2O_2, 30 mmol benzyl alcohol, 40 °C, 10 h, stirring under reflux

improvement in the conversion (5.0–5.1 %) can be observed as compared with blank test. (See Entry 1–3). Interestingly, ionic liquids 1-(4-butylsulfonic acid)-3-methylimidazolium bisulfate [$(CH_2)_4SO_3$HmIm]HSO_4 and *N*-(4-butylsulfonic acid) pyridinium bisulfate [$(CH_2)_4SO_3$HPy]HSO_4 with two Brönsted acid sites have catalytic activity to the oxidation reaction, which can be ascribe to their stronger acidity. As demonstrated in our previous studies, stronger acidity is favorable in the oxidation reaction by H_2O_2, and will accelerate the reaction rate [18, 19]. The presence of decatungstates hybrids [bPy]$_4W_{10}O_{32}$ and [bmIm]$_4W_{10}O_{32}$ as the catalyst both result in much improvement in the conversion of substrate. Compared with the catalytic performance of [bmIm]$_4W_{10}O_{32}$, slight lower conversion (66.1 %) but higher selectivity to benzoic aldehyde (97.8 %) was obtain with [bPy]$_4W_{10}O_{32}$ as the catalyst. Therefore, decatungstate [bPy]$_4W_{10}O_{32}$ was demonstrated a better catalyst of selective oxidation of benzyl alcohol.

The reaction conditions of selective oxidation of benzyl alcohol by [bPy]$_4W_{10}O_{32}$ have been optimized systematically, and the effect of reaction temperature was studied as shown in Entry 1–5 of Table 2. Conversion of benzyl alcohol increased with reaction temperature; however the selectivity to benzoic aldehyde decreased. It is observed that the decatungstates [bPy]$_4W_{10}O_{32}$ itself is immiscible in the reaction mixture, so the adding of decatungstates makes the mixture in suspension form, however, it will turn to a homogeneous phase when increasing the temperature to 60 °C. Further increasing the temperature won't lead to obvious increase in the substrate conversion, but much decrease in the selectivity to benzoic aldehyde. Therefore, higher temperature will accelerate reaction rate so as to increase the conversion, however, deeper oxidation products will appear. The suitable reaction temperature is 60 °C.

Table 2 Selective oxidation of benzyl alcohol by [bPy]$_4W_{10}O_{32}$

Entry	Temp. (°C)	Time (h)	Catalyst (mmol)	H_2O_2 (mmol)	Conv. (%)	Sel. (%)
1	20	10	0.07	30	18.9	100
2	40	10	0.07	30	56.4	98.6
3	60	10	0.07	30	79.2	96.1
4	80	10	0.07	30	85.7	92.2
5	100	10	0.07	30	87.9	89.4
6	60	5	0.07	30	67.4	98.3
7	60	10	0.07	30	79.2	96.1
8	60	15	0.07	30	89.6	95.7
9	60	20	0.07	30	92.5	88.5
10	60	25	0.07	30	94.3	83.7
11	60	15	0.05	30	59.1	96.5
12	60	15	0.06	30	74.3	96.1
13	60	15	0.07	30	89.6	95.7
14	60	15	0.08	30	92.9	94.6
15	60	15	0.09	30	93.5	93.5
16	60	15	0.08	24	87.2	95.3
17	60	15	0.08	30	92.9	94.6
18	60	15	0.08	36	95.2	92.9
19	60	15	0.08	45	96.7	91.5
20	60	15	0.08	60	96.9	89.5

Note 30 mmol benzyl alcohol used as the substrate

With the increase of reaction time, the conversion increases while the selectivity to benzoic aldehyde decreases due to the overtime oxidation of substrate (see Entry 6–10 in Table 2). The conversion and selectivity to benzoic aldehyde can reach 89.6 and 95.7 %, respectively when reacting for 15 h. Overtime oxidation does not result in much increase in substrate conversion.

Increasing catalyst [bPy]$_4W_{10}O_{32}$ amount will lead to the increase in conversion and decrease in the selectivity (see Entry 11–15 in Table 2). The conversion and selectivity with 0.08 mmol decatungstates would reach 92.9 and 94.6 %, respectively. Further increasing the catalyst amount would not improve the conversion greatly, but decrease the selectivity due to the increased oxidation activity.

Conversion of substrate increased while selectivity decreased with increasing the oxidant amount. (See Entry 16–20 in Table 2) When molecular ratio of $n(H_2O_2)/n(\text{benzyl alcohol}) = 1$, the conversion could be 92.9 % and selectivity to benzyl aldehyde can reach to 94.6, so we can see that the H_2O_2 utilization efficiency is quite high. While increasing $n(H_2O_2)/n(\text{benzyl alcohol})$ to 1.5, the conversion and selectivity were 96.7 and 91.5 %, respectively, higher product yield was obtained and the oxidant efficiency can reach 81.5 %. Further increasing the ratio $n(H_2O_2)/n(\text{benzyl alcohol})$ won't lead to the obvious increase in conversion; however the product selectivity would decrease due to deep oxidation. Therefore, the ratio of $n(H_2O_2)/n(\text{benzyl alcohol}) = 1.5$ is suitable.

Table 3 Recycling of decatungstate catalyst $[bPy]_4W_{10}O_{32}$

Cycles	Conv.(%)	Sel.(%)
1st	96.7	91.5
2nd	96.5	90.7
3rd	95.4	89.2
4th	93.8	88.6

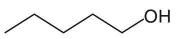
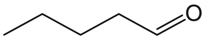
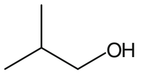
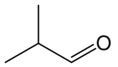
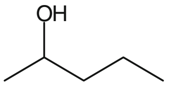
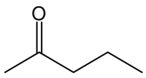
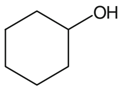
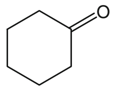
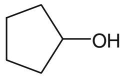
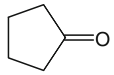
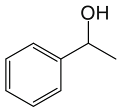
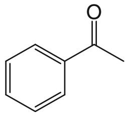
Conditions: 0.08 mmol Cat $[bPy]_4W_{10}O_{32}$, 45mmolH_2O_2, 30 mmol benzyl alcohol, 60 °C, 15 h, stirring, under reflux

Therefore, the conversion can reach 96.7 %, and the selectivity to benzoic aldehyde is up to 91.5 % under the following optimum conditions: 30 mmol benzyl alcohol, 0.08 mmol catalyst $[bPy]_4W_{10}O_{32}$, $n(H_2O_2)/n$(benzyl alcohol) = 1.5, 60 °C and 15 h.

More attention has been given to reusability of catalysts in the reaction systems for the development of cost-effective protocols. Therefore, recycling experiments were examined for the selective oxidation of benzyl alcohol with hydrogen peroxide catalyzed by $[bPy]_4[W_{10}O_{23}]$. After reaction, the catalyst will be self precipitated out when cooling reaction mixture down to room temperature. Then the catalyst can be washed by water thoroughly and dried for the next run. The substrate conversion and the selectivity to benzoic aldehyde were listed in Table 3. It could be seen that the catalytic activity was slightly decreased in the second, third, and forth run, which might be ascribed to the mechanical loss of decatungstates. Thus the catalyst $[bPy]_4[W_{10}O_{23}]$ can be reused at least up to four cycles without apparent loss in catalytic activity, so it is an effective, recyclable and environmental friendly catalyst.

The organic-solvent-free selective oxidation of different alcohols has been studied under the same catalytic conditions, including primary, secondary, alicylic, and benzylic alcohols. The results were listed in Table 4. The conversion and selectivity for alicylic and benzylic alcohol is comparatively higher than that of aliphatic alcohol. For aliphatic alcohol, the primary alcohols with long chain are the most difficult to be oxidized, can be converted to aldehyde with the conversion of 38.2 % and the selectivity of 78.3 %. Under the same conditions secondary alcohol is easier to be oxidized than primary aliphatic alcohol. So the decatungstate hybrid is quite effective catalyst for oxidation of alcohols, especially to alicylic and benzylic alcohols.

Table 4 Selective oxidation of alcohols catalyzed by $[bPy]_4W_{10}O_{32}$

substrate	Product	Conv. (%)	Sel. (%)
		38.2	78.3
		59.6	92.2
		65.0	90.4
		86.5	98.3
		88.3	98.7
		87.6	92.8

Conditions: 0.06mmol $[bPy]_4W_{10}O_{32}$, 125mmol 30%H_2O_2, 50mmol substrate, 80°C, 8h, stirring, under reflux.

4 Conclusions

We demonstrated a common, effective and simple synthesis route for decatungstate hybrids with high yield from bisulfate-based acidic ionic liquid in mild conditions. On account of the diversity of cations in ionic liquids, this would be a method to greatly enrich the decatungstate hybrids family. New decatungstate $[bPy]_4W_{10}O_{32}$ was demonstrated as an effective self-separated catalyst in selective oxidation of alcohols especially alicylic and benzylic alcohols. In this catalytic oxidation system, decatungstate hybrid works as catalyst, and is immiscible with reaction mixture under room temperature, however can be dissolved in mixture to form a homogenous phase under reaction condition. When the reaction is completed, the catalyst can be self precipitated out at room temperature. The advantages of homogenous and heterogeneous catalysis were combined in this system. The decatungstate hybrid can be easily reused after washing by water and drying. There is no obvious decrease in catalytic activity after 4 times recycling.

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