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Short communication

Coumarin-surfactant modified polyoxometalate as highly efficient catalysts for the selective oxidation of benzyl alcohol with air

Qian Xu[a], Shuyi Li[a], M. Katherine Banks[b], Weijian Xu[a,*], Ruoxi Wu[b,*]

[a] School of Chemistry and Chemical Engineering, Hunan University, Hunan 410082, PR China
[b] Zachry Department of Civil Engineering, Texas A&M University, College Station, TX 77843, United States

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ABSTRACT

Two novel polyoxometalate-based catalysts were prepared by modifying Keggin POM $H_4PMo_{11}VO_{40}$ with a coumarin-surfactant through electrostatic interactions. The results indicate that $(Coumarin)_3HPMo_{11}VO_{40}$ exhibits excellent catalytic activity in the selective oxidation of benzyl alcohol using air as the oxidant, where the conversion of benzyl alcohol is 99%, and the selectivity for benzaldehyde is 100%. The excellent catalytic performance can be attributed to π-π* conjugate effects with the reactant, and the structural characteristics of the large BET specific surface area and pore size of the catalyst.

1. Introduction

Benzaldehyde (BzH) is an important chemical intermediate used in a variety of fields. Production of BzH traditionally includes hydrolysis of benzyl chloride and oxidation of toluene. However, the hydrolysis of benzyl chloride often results in a trace amount of chlorine in the product, which greatly limits the application of BzH in the manufacture of odorants, flavors, and pharmaceutical intermediates. As for the oxidation method, the selectivity for BzH is relatively low. In order to develop chlorine-free BzH, selective oxidation of benzyl alcohol (BzOH) to BzH has been investigated [1–4]. Polyoxometalates (POMs) as catalysts have demonstrated high activity in the oxidation of BzOH using hydrogen peroxide (H_2O_2) as the oxidant [5–8]. However, the difficulty in controlling the reaction's oxidative degree due to the super oxidation properties of hydrogen peroxide leads to the inevitable generation of benzoic acid as a by-product. Furthermore, unmodified POM has several disadvantages, such as poor solubility, low selectivity, difficulty in recovery, and poor stability.

To improve its catalytic performance and recovery efficiency, POM was modified by organic molecules to produce different structures and functions [9,10]. Because of POM's multi-electron structure, it can be modified by ion-exchange electrostatic interactions [11–13]. Cationic surfactants are common positive charge-substituted molecules and can easily be introduced into POM to generate a surfactant-POM with an amphipathic molecular structure [14–16]. However, these POM hybrid materials still exhibit some drawbacks, including low BET specific surface area and small pore diameter of the catalysts. Both of these factors result in insufficient contact between catalysts and reactants, reducing the catalytic efficiency. Therefore, it is necessary to develop new strategies to design POM hybrid catalysts with a high BET specific surface area, large pore diameter, and high recyclability.

Here in, a new surfactant containing coumarin functional groups was synthesized and introduced into $H_4PMo_{11}VO_{40}$ with a Keggin structure. Two catalysts $(Coumarin)_3HPMo_{11}VO_{40}$ and $(Coumarin)_4PMo_{11}VO_{40}$) were synthesized and their catalytic ability in the oxidation of BzOH was investigated. The results indicate that $(Coumarin)_3HPMo_{11}VO_{40}$ exhibits better catalytic performance of the two, and the effects of the solvent, the amount of catalyst, reaction temperature, and oxidant on the reaction were studied. The catalyst is well dispersed in DMSO while being automatically separated by UV light (365 nm) after reaction due to photodimerization between the coumarin-surfactants. This study provides a new perspective for the preparation of POM hybrid materials with a large specific surface area, an appropriate pore size, and which features homogeneous catalytic and heterogeneous separation using surfactants containing functional groups through the electrostatic effect. Furthermore, the oxidation of BzOH using air as the oxidant offers practical industrial significance.

2. Experimental

The preparation process of the catalyst is shown in Scheme. 1, taking $(Coumarin)_4PMo_{11}VO_{40}$ as an example and other details of synthesis and characterization of the materials are shown in Supporting Information (SI). The adsorption kinetics of BzOH in the catalysts was carried by literature [14].

* Corresponding authors.
E-mail addresses: weijxu@hnu.edu.cn (W. Xu), wur@tamu.edu (R. Wu).

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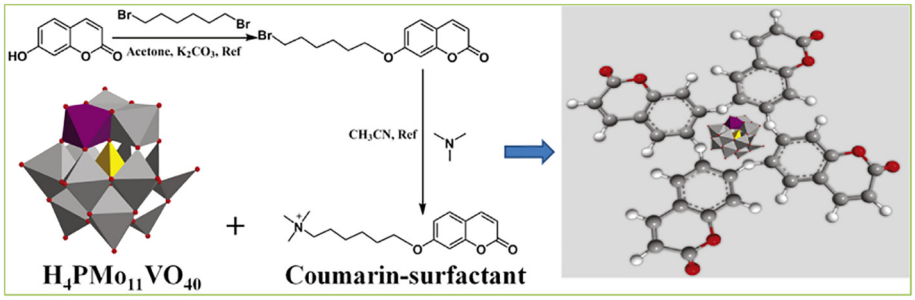

Scheme. 1. Illustration for preparing a net-like trap POM based amphiphilic catalyst.

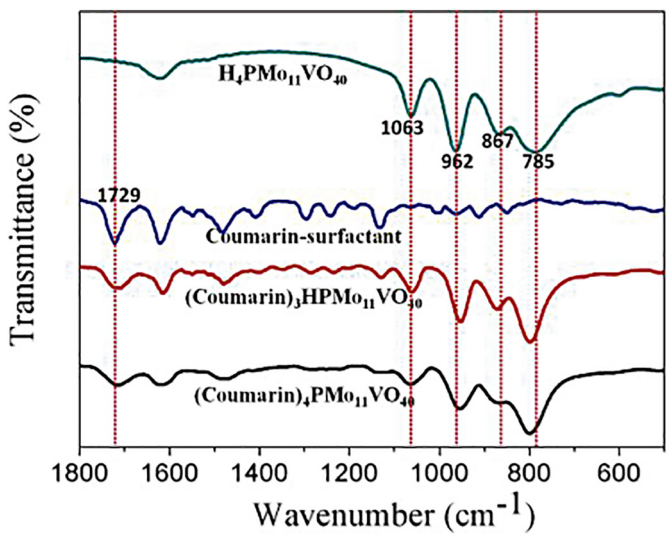

Fig. 1. FT-IR spectra of POM, coumarin-surfactant, $(Coumarin)_3HPMo_{11}VO_{40}$ and $(Coumarin)_4PMo_{11}VO_{40}$.

3. Results and discussion

As shown in Fig. 1, the characteristic vibrational spectrum of $H_4PMo_{11}VO_{40}$ features peaks at 1063 cm^{-1} (ν_{as} P-O_a), 962 cm^{-1} (ν_{as} P = O_d), 867 cm^{-1} (ν_{as} Mo-O_b-Mo), and 785 cm^{-1} (ν_{as} Mo-O_c-Mo). The peaks at 1729, 1609, 1471, 1058, 946, and 788 cm^{-1} in the FT-IR spectrum can be assigned to the coumarin-surfactant. The characteristic absorption peaks of the coumarin-surfactant and POM are shown in both absorption curves of $(Coumarin)_3HPMo_{11}VO_{40}$ and $(Coumarin)_4PMo_{11}VO_{40}$. It can be seen that the absorption peaks of the two catalysts have shifted from that of pure POM, due to the strong ionic interactions between the cationic surfactant and $PMo_{11}VO_{40}^{4-}$. As shown in **Fig. S1**, the largest difference in the ^1H NMR spectra between the coumarin-surfactant and coumarin-POM (both $(Coumarin)_3HPMo_{11}VO_{40}$ and $(Coumarin)_4PMo_{11}VO_{40}$) is the resonance signals of N-CH_3. This is similar to that observed in the FT-IR results, where the chemical shift of the hydrogen protons of N-CH_3 on coumarin-POM are shifted from the coumarin-surfactant due to electrostatic effects. These changes indicate that the modified catalyst maintains the POM's Keggin structure and there is a strong electrostatic force between the surfactant and the POM. The FT-IR and NMR results can preliminarily confirm that the coumarin-surfactant has been introduced to the POM; however, it is necessary to investigate the specific number of surfactants by thermal analysis. The TGA results (**Fig. S2**) show that the mass loss of $(Coumarin)_3HPMo_{11}VO_{40}$ and $(Coumarin)_4PMo_{11}VO_{40}$ is 41.2% and 35.2% (in *w*/w) before 750 °C, which are in accordance with the theoretical calculations (41.6% and 35.6%). Combined with the elemental analysis results (**Table 1**), the predicated chemical formulas of the two catalysts are further confirmed.

In the selective oxidation of BzOH to BzH, the main side reaction is the overoxidation of BzH to benzoic acid. As shown in Table 1, the catalytic efficiency of $(Coumarin)_3HPMo_{11}VO_{40}$ is higher than $(Coumarin)_4PMo_{11}VO_{40}$. Both catalysts exhibit a larger BET specific surface area than pure $H_4PMo_{11}VO_{40}$ and the same POM hybrid material, as reported in the literature [14] (*i.e.*, $(DDA)_4PMo_{11}VO_{40}$ (1.25), $(HDA)_4PMo_{11}VO_{40}$ (1.12), $(ODA)_4PMo_{11}VO_{40}$ (0.82), and $(DODA)_4PMo_{11}VO_{40}$ (0.68)). This is because organic small molecules with flexible chains can easily enter the channels of $H_4PMo_{11}VO_{40}$. The rigid structure of the coumarin-surfactant does not enable easy access to the $H_4PMo_{11}VO_{40}$ channel-like structure; therefore, these surfactants form a net-like trap configuration, thereby increasing the specific surface area of the catalyst and allowing the capture of the BzOH reaction material. However, $(Coumarin)_4PMo_{11}VO_{40}$ exhibits a small pore diameter (10.36), much less than that of $(Coumarin)_3HPMo_{11}VO_{40}$ and $H_4PMo_{11}VO_{40}$. This small diameter size is not conducive to the timely diffusion of the reactants, reducing the catalytic effect. The small pore size may result from strong intermolecular forces and π-π*conjugate effects between coumarin molecules. Unlike $(Coumarin)_4PMo_{11}VO_{40}$, $(Coumarin)_3HPMo_{11}VO_{40}$ possesses a structural defect, which reduces the intermolecular forces between the courmarin-surfactant.

Fig. S3 shows the cyclic voltammograms (CVs) of sample containing $H_4PMo_{11}VO_{40}$ and coumarin-surfactant, ranging from −0.2 to +1.2 V (*vs* Ag/AgCl), in 0.1 mol L^{-1} phosphate-buffered saline at 100 mV s^{-1} scan rate. Three pairs of redox peaks of initial $H_4PMo_{11}VO_{40}$ are detected, with the peak potentials $E_{1/2}$ = −0.091, 0.211, and 0.515 mV, ($E_{1/2} = (E_{pc} + E_{pa})/2$) [17]. The redox reaction occurs easily on the

Table 1
BET Specific Surface Area, Pore Diameter and Chemical Composition of Catalysts Investigated.

					Content of element[a] (wt%)		
Catalyst	S_{BET} ($m^2 g^{-1}$)	D_{av}[b] (nm)	con(%)[c]	sel(%)[d]	C	H	N
$(Coumarin)_4PMo_{11}VO_{40}$	25.59	10.36	45	100	28.89 (27.81)	4.02 (3.48)	1.79 (1.87)
$(Coumarin)_3HPMo_{11}VO_{40}$	30.51	133.04	99	100	22.25 (21.07)	3.13 (2.93)	1.60 (1.56)
$H_4PMo_{11}VO_{40}$	9.16	56.59	78	90			

[a] Data in parentheses represent the theoretical content of the element in the catalyst.
[b] Average pore diameter.
[c] Conversion of BzOH
[d] Selectivity for BzH. Reaction conditions: catalyst (0.5 μmol), air as oxidant, DMSO (0.5 mL), BzOH (1 mmol), 150 °C, 100 min.