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Nanocasted Cs Salt of Phosphomolybdic Acid: A New System for Selective Oxidation of Alcohols

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Since the discovery of many types of mesoporous silicas, such as SBA-15, KIT-6, FDU-12, and SBA-16, porous crystalline transition metal oxides have been synthesized using the mesoporous silicas as hard templates. The authors have used 2D hexagonal SBA-15 silicas as hard templates for the nanofabrication of $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ (CsHPMo) salt nanocrystal. The oxidation of alcohols occurs effectively and selectively with H_2O_2 as the oxidant. CsHPMo salt nanocrystal was used as the catalyst.

Keywords green chemistry, heteropoly acids, HPAs, mesoporous silica SBA-15, nanocasting

INTRODUCTION

The synthesis of porous materials has attracted and still attracts intensive attention, and significant advances have been made with respect to structural, compositional, and morphological control. Porous materials are normally classified into three types by pore diameter (i.e. microporous [below 2 nm], mesoporous [2–50 nm], and macroporous [exceeding 50 nm]).^[1] The fabrication of porous materials, especially the creation of mesoporous materials, has been extensively investigated over the last years. Template methods,^[2] which imply a more or less direct replication of the pore system from the template, seem to be one of the most promising synthetic pathways to create porous materials, especially if materials with ordered porosity are the goal. The principle of the nanocasting pathway with hard template, which involves three main steps: (a) formation of the template, (b) the casting step, and (c) removal of the template. Clearly, a three-dimensional pore network is necessary in the template to create a stable replica. In addition, the templates should be easily and completely removed to obtain the true replicas.^[3] In recent decades, uses of heteropoly acids (HPAs) as catalysts for fine organic synthetic processes have been developed and are

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important for industries related with fine chemicals,^[4] including flavors, pharmaceuticals, and food industries.^[5]

Solid HPAs have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts.^[6]

Oxidation of alcohols into the corresponding aldehydes and ketones is one of the most fundamental transformations in organic synthesis. Usually the oxidation of benzylic alcohols has been carried out using oxidants such as vanadium polyoxometalate $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}]3H_2O,^{[7]} Mn(OAC)_3/$ catalytic 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),^[8] ceric ammonium nitrate (CAN)/Brönsted acidic ionic liquid,^[9] and supported platinum by iron oxide.^[10]

In recent years, replacement of toxic oxidants in organic reactions has become of high priority in environmentally benign chemistry. Among other reagents, hydrogen peroxide is a cheap and easily available oxidizing reagent, and it is considered as the most desirable oxidant in terms of environmentally promoted oxidation of benzylic alcohols have been reported. As part of a continuing effort to understand catalytic properties of HPAs,^[11–14] herein we studied the H₂O₂ /Cs_{2.5}H_{0.5}PMo₁₂O₄₀ (CsHPMo) salt nanocrystal system for the aerobic oxidative of alcohols (Scheme 1).

EXPERIMENTAL

All materials were commercial reagent grade. Infrared spectra (400–4000 cm⁻¹) were recorded from KBr pellets on a Nicolet Impact 400 D spectrometer (Sahreza Branch, Islamic Azad University). Reaction courses and product mixtures were monitored by thin-layer chromatography. The X-ray powdered diffraction patterns were performed on a Bruker-D8 advance with automatic control (Central Laboratory of the University of Isfahen X-ray Lab). The patterns were run with

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FIG. 1. Ordered mesoporous silica (SBA-15 material). (a) High-resolution FESEM image of the pore structure of SBA-15; (b) representation of the pore arrangement.

monochromatic Cu K α (1.5406 Å) radiation with a scan rate of 2° min⁻¹. The micrographs were recorded using a SEM (HI-TACHI COM-S-4200, Tarbiat Hodares University) operated at an accelerating voltage of 30 kV. Transmission electron microscopy (TEM) images were recorded digitally with a Gatan slow-scan charge-coupled device camera on a JEOL 2011 electron microscope operating at 200 kV (Shiraz University).

SBA-15

SBA-15 was first synthesized by Zhao et al.^[15] in 1998, using amphiphilic triblock copolymers, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123), as template. In a typical synthesis, 1.00 g of P123 was dissolved in a mixture of HCl/H₂O (30.00 g of 2 M HCl to 7.50 g H₂O). After dissolution 2.08 g of TEOS or 1.96 g of sodium silicate was added. The slurry was hydrothermally treated at

100°C for 48 h after stirring at 40°C for 16 h. The product was filtered off and dried at 800°C for 10 h (Figure 1).

CsHPMo/SBA

The CsHPMo was inserted in the SBA-15 silica matrix by the two-step reaction deposition method. The parent CsHPMo sample was obtained by dispersing the surfactant free SBA-15 (0.5 g) in 10 mL of n-propanol followed by an addition of 0.20 g of cesium carbonate (Aldrich). The contents were stirred for 4 h, filtered, and dried under vacuum. The dry solids were treated for 12 h with a solution containing an excess of $H_3PMo_{12}O_{40}$ dissolved in *n*-propanol under continuous stirring, after which they were filtered and washed with an excess of *n*-propanol. The resulting solids were dried at 383 K for 2 h and calcined at 573 K for another 2 h (Figure 2).

CsHPMo Nanoparticles

The silica matrix was gradually removed from the CsH-PMo/SBA materials by a treatment with HF. CsHPMo/SBA composite 0.50 g were continuously stirred in 20 mL of an aqueous HF solution for 3 h at room temperature (Figure 2). The solid was recovered by decantation after centrifugation (7000 rpm). The water addition/centrifugation sequence was repeated three times and finally the material was evacuated at 333 K.

Oxidation of Benzylic Alcohols, General Procedure

A 25-mL round-bottomed flask with 5 mL of CH_3CN equipped with a magnetic stirrer and reflux condenser was charged with 0.02 mmol catalyst and 5 mmol aqueous hydrogen peroxide (30%). The mixture was stirred and then 1 mmol



FIG. 2. (a) Preparation of the CsHPMo/SBA-15; (b) preparation of the CsHPMo nanoparticles.



FIG. 3. FTIR spectra of $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$.

alcohol was added. The biphasic mixture was stirred at 90°C for the required time. Progress of the reaction was followed by the aliquots withdrawn directly from the reaction mixture analyzed by GC using internal standard. After completion of the reaction, the mixture was treated with a 10% sodium hydrogen sulfite solution to decompose the unreacted hydrogen peroxide and then with 10% sodium hydroxide. The product was extracted with *n*-butyl-ether. The pure product was obtained by distilla-

tion or silica gel column chromatography (hexane/ethyl acetate, 10/1).

RESULTS AND DISCUSSION

Physicochemical Characterization

Figure 3 shows the FTIR spectra of the $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$. From the FTIR spectra, it was found that for 110°C dried

| Chemical composition of parent CsHPMo/SBA-15 and its nanocast | | | | | | | | | |
|---|------------------------------------|---------------------|--------------|--------------------------------|--------------------------------|------------------------------|------------|---|---|
| | | Cs/Mo ₁₂ | | | | SiO ₂ removed (%) | | | |
| Entry | Sample | EDX | AA | ICP | NAA | EDX | AA | ICP | NAA |
| 1 2 | CsHPMo/SBA-15 CsHPMo (nanocast) | 2.41 2.46 | 2.43 2.38 | $2.5 \pm 0.08 \\ 2.4 \pm 0.03$ | $2.5 \pm 0.05 \\ 2.4 \pm 0.01$ | 0 98.02 | 0 98.10 | $\begin{array}{c} 0\\ 98\pm0.05\end{array}$ | $\begin{array}{c} 0\\ 98\pm0.01\end{array}$ |

TABLE 1



FIG. 4. XRD patterns of Cs_{2.5}H_{0.5}PMo₁₂O₄₀.



FIG. 5. (a) EDX measurements carried out during SEM observations; (b) SEM micrographs of the sample $Cs_{2.5}H_{0.5}PM_{012}O_{40}$ nanoparticles.

samples the Keggin bands are observed at 1098, 960, 903, and 806 cm⁻¹ for Cs_{2.5}H_{0.5}PMo₁₂O₄₀. These were assigned to ν_{as} (P–O_a), ν_{as} (Mo–O_a), ν_{as} (Mo–O–Mo), and ν_{as} (Mo–O_c–Mo), respectively.^[16]

Figure 4 shows the XRD pattern of $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ dried at 110°C. It can be observed that $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ nanoparticles are crystalline. Thus, the removal of the silica matrix does not affect the crystal structure. The wide amorphous halo centered at $2\theta = 23^{\circ}$ in the spectra of SBA-15 silica in as-prepared composite^[17] completely disappeared for $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ nanocasted material.

The as-prepared CsHPMo particles have been found to be high purity by EDX measurements. EDX results (Figure 5) indicated that the as-prepared samples contain Cs, Mo, P, and O elements. The percentage of silica matrix removed from the CsHPMo/SBA composite is about 98%. The good distribution of all elements analyzed is in agreement with the atomic adsorption analysis, neutron activation analysis (NAA), and ICP results with deviation in the range of ± 0.09 (Table 1). These analyses

| TABLE 2 |
|--|
| Oxidation of benzylic alcohols with H ₂ O ₂ catalyzed by CsHPMo nanocrystals in CH ₃ CN at reflux conditions ^a |

| | | Cs | 0.10 | | |
|-------|---------------|--|--|--------------|--------------------------|
| | | ArCH ₂ OH ——— H 1a-t | \sim A $_2O_2$, CH $_3$ CN, reflux | rCHO 2a-t | |
| Entry | Substrate (1) | Ar | Product (2) | Time (min) | Yield (%) ^{b,c} |
| 1 | a | C ₆ H ₅ | а | 70 | 98 |
| 2 | b | $4-NO_2-C_6H_4$ | b | 90 | 95 |
| 3 | с | $3-NO_2-C_6H_4$ | с | 85 | 87 |
| 4 | d | $2-NO_2-C_6H_4$ | d | 90 | 82 |
| 5 | e | $4-HO-C_6H_4$ | e | 50 | 95 |
| 6 | f | $2-HO-C_6H_4$ | f | 85 | 90 |
| 7 | g | $4-Cl-C_6H_4$ | g | 78 | 92 |
| 8 | h | $2-Cl-C_6H_4$ | h | 90 | 75 |
| 9 | i | 4-MeO-C ₆ H ₄ | i | 50 | 92 |
| 10 | j | 3-MeO-C ₆ H ₄ | j | 80 | 90 |
| 11 | k | 4-F-C ₆ H ₄ | k | 95 | 90 |
| 12 | 1 | $4-Br-C_6H_4$ | 1 | 90 | 92 |
| 13 | m | $4-\text{Me-C}_6\text{H}_4$ | m | 95 | 87 |
| 14 | n | $3-Me-C_6H_4$ | n | 90 | 85 |
| 15 | 0 | $2-NH_2-C_6H_4$ | 0 | 100 | 87 |
| 16 | р | 2-Thienyl | р | 85 | 90 |
| 17 | q | $2-Me-C_6H_4$ | q | 78 | 87 |
| 18 | r | 2-Pyridyl | r | 100 | 90 |
| 19 | S | 1-phenyl ethanol | S | 82 | 75 |
| 20 | t | $C_6H_5CH_2CH_2$ | t | 95 | 82 |

^aReaction conditions: benzyl alcohol derivatives (1 mmol), H₂O₂ (5 mmol), CsHPMo (2 mol %), CH₃CN (5 mL). ^bIsolated yield.

^cAll products were identified by comparison with authentic sample (mp, IR, NMR).



FIG. 6. TEM micrographs of CsHPMo nanocast.

indicate the value of Cs/Mo_{12} ratio is 2.5, which agrees well with calculated formula, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$.

The SEM picture of CsHPMo is shown in Figure 5. CsHPMo exhibited nearly the dense aggregate of rock-like morphology. There is no definite shape shown for any particles but the edges appear to be spherical with diameters about 43 nm. The isolated primary 10–20 nm nanoparticles of CsHPMo were also detected at TEM micrographs (Figure 6).

Oxidation of Benzylic Alcohols

In the catalytic reactions the choice of solvent is crucial. The influence of the various solvents on the yield of the reaction was investigated using of benzyl alcohol as the substrate. From these studies it was deduced that CH₃CN to be the most favorable solvent. To study the scope of this procedure the oxidation of other alcohols was next studied (Table 2, entries 2–20). All benzylic alcohols having electron-donating and withdrawing groups in the aromatic ring that is 4-methoxy and 4-nitro benzyl

alcohols were converted in to their corresponding aldehydes in good isolated yields within 50 and 90 min.

Heterocyclic alcohols, 2-thiophenemethanol, and 2pyridinemethanol were oxidized to the corresponding aldehydes in high yields. No oxidation was observed with S and N hetero atoms. In addition, a mixture of primary and secondary alcohols was next subjected to oxidation. When benzyl alcohol and 1-phenylethanol were allowed to react, the former oxidized to benzaldehyde in 93% yield and the latter gave acetophenone in <7% yield. This clearly reveals that this method can be applied for the chemoselective oxidation of primary hydroxyl groups in the presence of secondary alcohols.

The recovery and reusability of the catalyst has been investigated. We have noticed that after the addition of CHCl₃ to the reaction mixture, this catalyst can be easily recovered quantitatively by simple filtration. The wet catalyst was recycled (the nature of the recovered catalysts has been followed by NAA,

TABLE 3 Investigation of the feasibility of reusing CsHPMo nanocasts in the oxidation of benzylic alcohols with H_2O_2 in CH₃CN after 70 min^a

| Run | Yield (%) |
|-----|-----------|
| 1 | 98 |
| 2 | 98 |
| 3 | 92 |
| 4 | 55 |

XRD, and FT-IR spectra) and no appreciable change in activity was noticed after three cycles (Table 3).

CONCLUSIONS

In conclusion, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ nanocrystals can act as an efficient catalyst for aerobic alcohol oxidation. This reaction provides a new environmentally friendly route to the conversion of alcoholic functions to carbonyl groups. Aldehydes do not undergo further oxidation to carboxylic acids. Furthermore, there is no organic waste from the reaction and the isolation procedure is straightforward requiring only the separation of the organic product from the polyoxometalates and inorganic salts.

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