

## Aluminium Salt of Phosphomolybdic Acid Fabricated by Nanocasting Strategy: An Efficient System for Selective Oxidation of Benzyl Alcohols

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**ABSTRACT.** Preparation of AIPMo<sub>12</sub>O<sub>40</sub> (AIPMo) salts, supported on mesostructured SBA-15 silica, by the reaction deposition strategy causes the formation of isolated AIPMo nanocrystals inside the nanotubular channels. The remarkable characteristic of the SBA-15 structure is that all the cylindrical pores are connected by some small channels. This makes the whole pore system in SBA-15 three-dimensional. We have used 2D hexagonal SBA-15 silicas as hard templates for the nanofabrication of AIPMo salt nanocrystal. The oxidation of alcohols occurs effectively and selectively with H<sub>2</sub>O<sub>2</sub> as the oxidant. AIPMo salt nanocrystal was used as the catalyst.

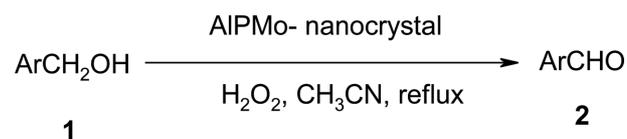
**Key words:** Nanocasting, Mesoporous silica SBA-15, Green chemistry, Polyoxometalates (POMs)

### INTRODUCTION

High-surface area inorganic materials have attracted widespread attention in diverse areas such as heterogeneous catalysis,<sup>1</sup> adsorption,<sup>2</sup> gas sensing,<sup>3</sup> energy storage,<sup>4</sup> drug delivery<sup>5</sup> biomedical applications,<sup>6</sup> electrochemistry,<sup>7</sup> etc. The application of the nanocasting technique to the fabrication of inorganic compounds implies that the fabrication of these products takes place in the nanospaces provided by the pores of a porous solid (hard template). After the synthesis of the material, the template framework is selectively removed and the inorganic product is obtained. Basically, the nanocasting route comprises three steps: i) Infiltration of the porosity of the template with a solution containing the precursors of the inorganic compound; ii) Heat treatment under a controlled atmosphere of the impregnated template to convert the infiltrated precursor into the inorganic material and iii) removal of the template framework by dissolution (i.e. silica) or by oxidation at high temperatures (i.e. carbon). Due to the fact that the synthesis takes place in a confined nanospace, the sintering of the particles is restricted and the preparation of highsurface area materials (nanostructures or nanoparticles) is achieved. In this way, numerous inorganic compounds of high-surface area can be obtained, although high-temperatures are required to synthesize them. Moreover, this synthetic strategy clearly suggests that the structure of the synthesized inorganic compounds can be tailored depending on the pore characteristics of

the selected template.<sup>8</sup> Polyoxometalates (POMs) belong to a large class of nanosized metal-oxygen cluster anions. The chemistry of polyoxometalates (heteropoly acids (HPAs) and heteropoly salts), started by Berzelius back in 1826, has now reached maturity. But it is still a rapidly developing field interconnected with many disciplines.<sup>9</sup> Catalysis by polyoxometalates has attracted much attention because of their strong acidity and redox properties. An additional attractive aspect of polyoxometalates in catalysis is their inherent stability toward oxygen donors.<sup>10</sup>

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 chromium (VI) trioxide,<sup>11</sup> nitric acid,<sup>12</sup> dimethyl sulfoxide/HBr,<sup>13</sup> and hypervalent iodine compounds.<sup>14</sup> 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 environmental promoted oxidation of benzylic alcohols.



**Scheme 1.**

As part of a continuing effort to understand catalytic properties of heteropoly acids, (HPAs),<sup>15-18</sup> herein, we wish to report H<sub>2</sub>O<sub>2</sub>/AIPMo<sub>12</sub>O<sub>40</sub> (AIPMo) salt nanocrystal system for the aerobic oxidative of alcohols (*Scheme 1*).

## EXPERIMENTAL

All materials were commercial reagent grade. Infrared spectra (400–4000 cm<sup>-1</sup>) were recorded from KBr pellets on a Nicolet *Impact 400 D* spectrometer. <sup>1</sup>H NMR spectra were carried out with a Bruker-Avance AQS 300 MHz. The melting points were determined using an electrothermal digital melting point apparatus and were uncorrected. 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. The patterns were run with monochromatic Cu K $\alpha$  (1.5406 Å) radiation with a scan rate of 2° min<sup>-1</sup>. The micrographs were recorded using a SEM (HITACHI COM-S-4200) operated at an accelerating voltage of 30 kV. Thermogravimetric analysis was carried out on a Labsys-Setaram TGA-DSC instrument in flowing N<sub>2</sub> with a heating rate of 20 °C min<sup>-1</sup> up to 1000 °C.

### SBA-15

SBA-15 was first synthesized by Zhao *et al.* in 1998,<sup>19</sup> using amphiphilic triblock copolymers, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (Pluronic P123), as template. In a typical synthesis, 1.00 g of P123 was dissolved in a mixture of HCl/H<sub>2</sub>O (30.00 g of 2 M HCl to 7.50 g H<sub>2</sub>O). 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.

### AIPMo/SBA

The CsHPMo was inserted in the SBA-15 silica matrix by the two-step reaction deposition method. The parent AIPMo 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 Aluminium 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<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> 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.

### Bulk-AIPMo

Preparation of aluminium dodecatungstophosphate (AIPW<sub>12</sub>O<sub>40</sub>) was reported in 1982 by Ono by the reaction of aluminium nitrate and dodecatungstophosphoric acid in a quantitative yield.<sup>20</sup> We prepared aluminium dodecamolybdophosphate (AIPMo<sub>12</sub>O<sub>40</sub>, Denoted as AIPMo hereafter) by the addition of aluminium nitrate or by aluminium carbonate to the aqueous solution of molybdato-phosphoric acid, which, on complete evaporation of water, gave the desired compound as yellow (AIPMo) powders in a quantitative yield.

### AIPMo Nanoparticles

The silica matrix was gradually removed from the *AIPMo/SBA* materials by a treatment with H<sub>2</sub>O. *AIPMo/SBA* composite 0.50 g was continuously stirred in 20 ml of H<sub>2</sub>O for 10 min at room temperature. The *AIPMo (aq)* was recovered by decantation after centrifugation (7000 rpm) and finally the material was evacuated at 333 K.

### Oxidation of Benzylic Alcohols, General Procedure

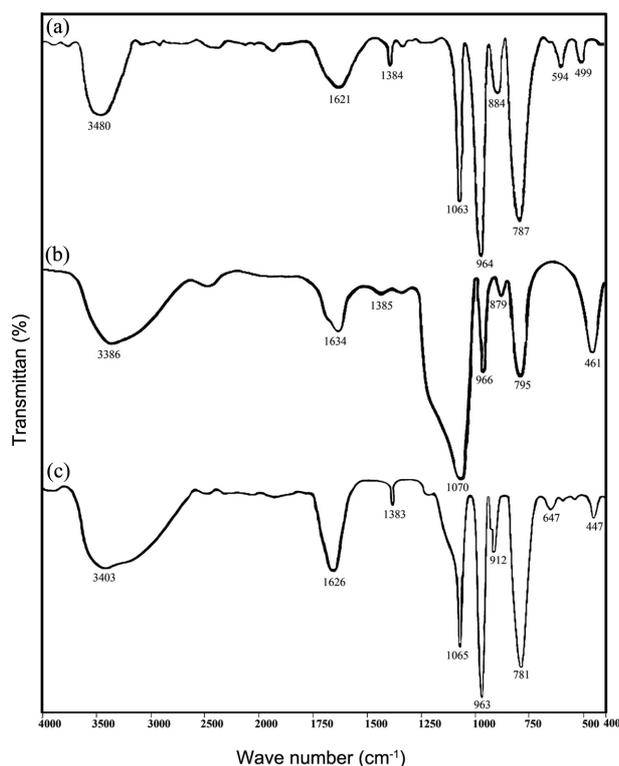
A 25-ml round bottomed flask with 2 ml of CH<sub>3</sub>CN equipped with a magnetic stirrer and reflux condenser was charged with 0.01 mmol catalyst and 5 mmol aqueous hydrogen peroxide (30%). The mixture was stirred and then 1 mmol alcohol was added. The biphasic mixture was stirred at 90 °C for the required time. Progress of the reaction was followed by the aliquots withdrawn directly from the reaction mixture analysed 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 distillation or silica gel column chromatography (hexane/ethyl acetate, 10/1).

## RESULTS AND DISCUSSION

### Characterization of the Catalyst

The prepared catalyst was characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), SEM, EDS, TEM, TG and atomic absorption spectroscopy techniques.

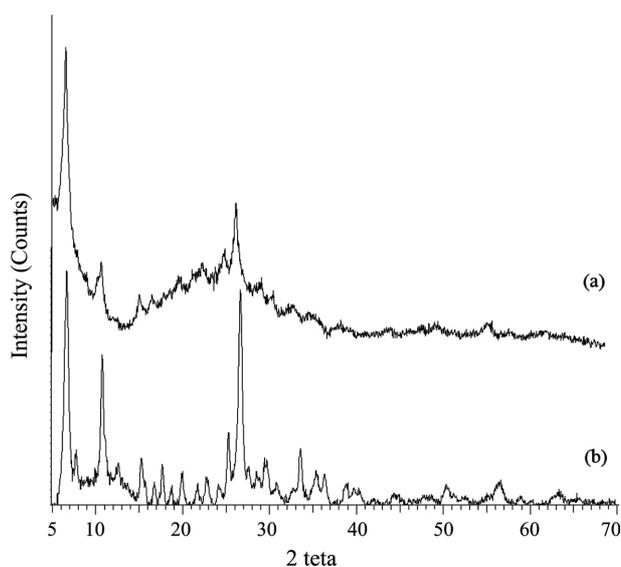
FT-IR spectra have proved to be a powerful technique for studying surface interaction between HPA and organic and inorganic supports. The infrared spectrum of the bulk-AIPMo exhibited strong vibrations at 1063  $\nu_{\text{as}}$ (P-Oa), 964  $\nu_{\text{as}}$ (W-Oa), 884  $\nu_{\text{as}}$ (W-O-W), and 787 cm<sup>-1</sup>  $\nu_{\text{as}}$ (W-Oc-W) respectively (*Fig. 1a*), while that of AIPMo nanocasts



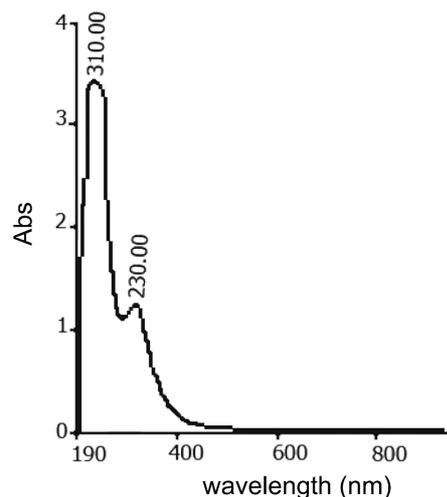
**Fig. 1.** FTIR spectra of (a) bulk-AIPMo<sub>12</sub>O<sub>40</sub>; (b) AIPMo<sub>12</sub>O<sub>40</sub>/SBA-15; (c) AIPMo<sub>12</sub>O<sub>40</sub> nanocast.

(Fig. 1c) exhibited them at 1065  $\nu_{\text{as}}(\text{P-Oa})$ , 963  $\nu_{\text{as}}(\text{W-Oa})$ , 912  $\nu_{\text{as}}(\text{W-O-W})$ , and 781  $\text{cm}^{-1}$   $\nu_{\text{as}}(\text{W-Oc-W})$   $\text{cm}^{-1}$ . Fig. 1b represents the FT-IR transmission spectra of calcined AIPMo/SBA-15. It shows a typical infrared spectrum of silica<sup>21</sup> with bands assigned at 1634  $\text{cm}^{-1}$  with a broad band at 1070  $\text{cm}^{-1}$ . The FT-IR spectra of AIPMo/SBA-15 indicate that most of characteristic bands of the parent Keggin structure, which could be found in HPA fingerprint region (1250-500  $\text{cm}^{-1}$ ), are not shown or do not appear in the same assignable position of the bands corresponding to SiO<sub>2</sub> host material (Fig. 1b).

X-ray powder analysis is widely used to study the structure of heteropoly complexes. The XRD patterns of the as-prepared AIPMo<sub>12</sub>O<sub>40</sub>/SBA-15 composite and the AIPMo<sub>12</sub>O<sub>40</sub> nanocasts are shown in Fig. 2. The XRD peaks for the AIPMo phase inside the AIPMo/SBA-15 composites (Fig. 1a) and AIPMo nanocasts (Fig. 2b) could be attributed to bcc cubic structure, which was commonly associated with the pure alkaline heteropoly salts.<sup>22</sup> Thus, the removal of the silica matrix did 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 composites completely disappeared for nanocasted materials.



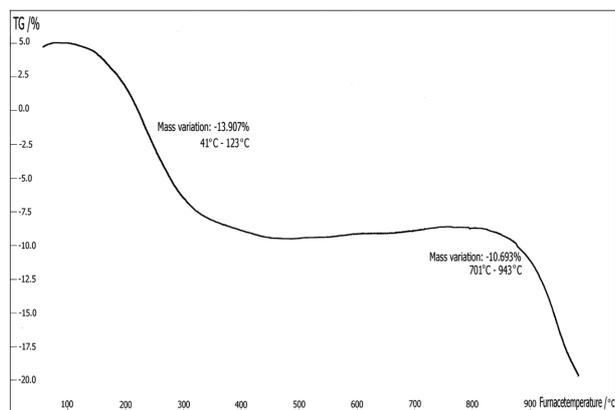
**Fig. 2.** XRD patterns of (a) AIPMo<sub>12</sub>O<sub>40</sub>/SBA-15; (b) AIPMo<sub>12</sub>O<sub>40</sub> nanocast.



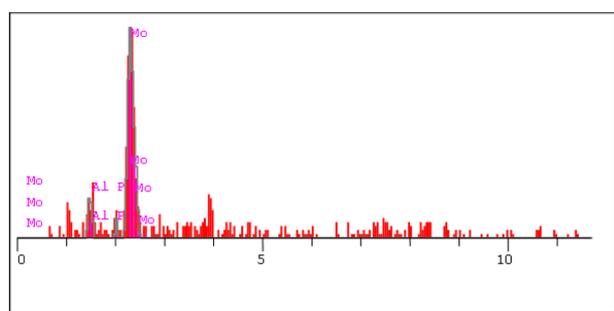
**Fig. 3.** UV-vis spectra of AIPMo<sub>12</sub>O<sub>40</sub> nanocasts.

Fig. 3. shows the UV-vis spectra of AIPMo<sub>12</sub> nanocast. Two main absorptions are present in the bulk-PMO<sub>12</sub> spectrum: the first is centered at 255 nm, and is attributed to the oxygen-tungsten charge-transfer absorption band for Keggin anions.<sup>23</sup> The second broad absorption in the bulk-H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> is centered at 360 with a shoulder at 345 nm. For the encapsulated AIPMo<sub>12</sub> nanocast, these bands are clearly observed in 230 and 310 nm, respectively.

The thermal stability 1000 °C (Fig. 4). The TGA curve indicates that the weight loss of AIPMo can be divided into two steps. The first weight loss is 13.907% from 41 to 123 °C, involving the release of three lattice water molecules. The second step beginning about 701-943 °C (10.693%)



**Fig. 4.** TG analysis of AIPMo<sub>12</sub>O<sub>40</sub> nanoparticles.



Element	Line Intensity (c/s)	Conc (wt%)
Al	2.80	6.148 wt%
Si	0.43	0.898 wt%
P	0.86	1.717 wt%
Mo	15.44	91.237 wt%
Total:		100.000

**Fig. 5.** EDS measurements carried out during SEM observations.

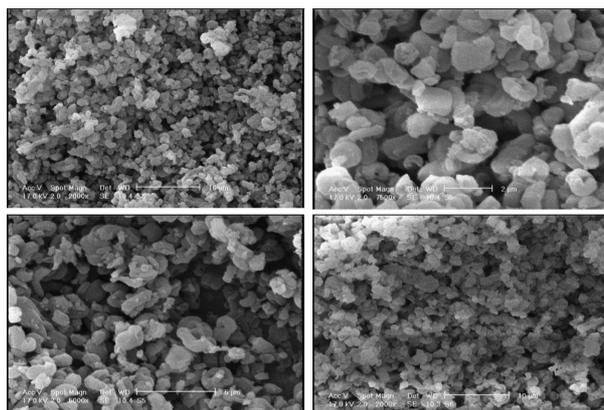
belongs to the decomposition of POM and release WO<sub>3</sub>.

The AIPMo nanoparticles have been found to be high purity by EDS measurements. EDS results (*Fig. 5*) indicated that the as-prepared samples contained Al, Mo, P and O elements. The percentage of silica matrix removed from the AIPMo/SBA composite is about 99%. 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  $\pm 0.09$ . These analyses indicate that the value of Al/Mo ratio is 3 which agrees well with calculated formula AIPMo<sub>12</sub>O<sub>40</sub>.

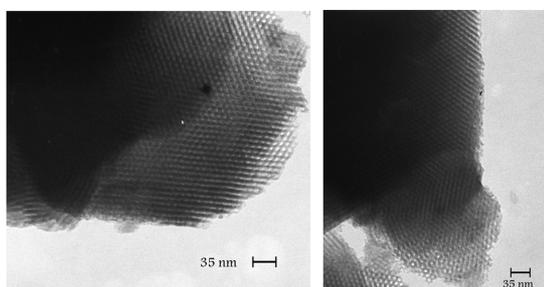
The SEM picture of CsHPMo is shown in *Fig. 6*. AIPMo exhibited nearly the dense aggregate of rock-like morphology. There is no definite shape shown for any particles but the edges appear to be spherical.

## TEM

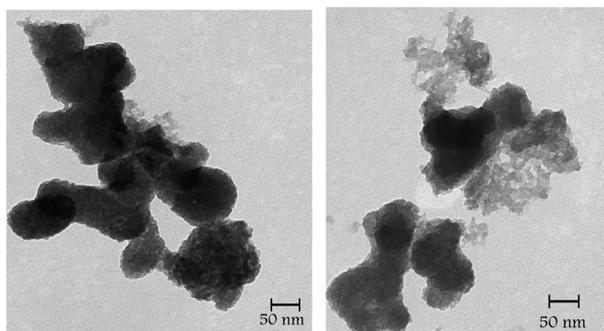
*Fig. 7* shows the TEM images of PW<sub>12</sub>/MCF and



**Fig. 6.** SEM micrographs of the sample AIPMo<sub>12</sub>O<sub>40</sub> nanoparticles.



(a)



(b)

**Fig. 7.** TEM micrographs of (a) AIPMo<sub>12</sub>O<sub>40</sub>/SBA-15; (b) AIPMo<sub>12</sub>O<sub>40</sub> nanocasts.

AIPMo<sub>12</sub>O<sub>40</sub> nanoparticles. The sample for the TEM measurement was suspended in ethanol and supported on a carbon coated copper grid. Isolated 5-9 nm nanoparticles of AIPMo/SBA-15 were clearly observed by TEM (*Fig. 7a*) in the curved nanotubular channels inside the silica microfibrils.

Physical Properties of SBA-15, bulk- AIPMo, AIPMo/BA-15 and nanocasted AIPMo materials are listed in *Table 1*. As expected, the BET surface areas, total pore volumes and mesopore sizes of SBA-15<sup>22</sup> material decreased from 873 to 299 m<sup>2</sup>g<sup>-1</sup>, from 1.4 to 0.37 cm<sup>3</sup>g<sup>-1</sup>,

**Table 1.** The texture parameters of parent AIPMo/SBA-15 and AIPMo nanocast in comparison with the bulk CsHPW materials

Materials	Texture parameters (N <sub>2</sub> adsorption)		
	Surface area (m <sup>2</sup> /g) <sup>a</sup>	Pore volume (cm <sup>3</sup> /g) <sup>a</sup>	Pore diameter (nm)
SBA-15 [22]	873	1.4	6.4
Bulk-AIPMo	2.65	0.014	21.164
AIPMo/SBA-15	299.29	0.368	4.92
AIPMo nanocasts	63.45	0.083	17.00

<sup>a</sup>Total pore volume measured at  $p/p_0 = 0.99$ .

and from 6.4 to 4.9 nm, respectively, after the functionalization with AIPMo. These changes reflect that part of the mesopore volume in the SBA-15 matrix is filled with AIPMo nanocrystals, resulting in pore diameters that are less than that of silica channels.

### Oxidation of Benzylic Alcohols

The catalytic activity of the prepared catalyst was tested using Benzyl alcohols as reference alcohol. Oxidation was carried out with H<sub>2</sub>O<sub>2</sub>/Urea (UHP) as an oxidant and in the presence of catalytic amounts of AIPMo nanocast. The optimum conditions used for the oxidation of benzyl alcohol by this catalytic system was catalyst, oxidant, and substrate in a mol ratio of 1:15:0.03, respectively (Table

**Table 2.** Effect of different conditions in the oxidation of benzyl alcohol with catalytic amount of AIPMo nanocast.<sup>a</sup>

Entry	Solvent	Yield% <sup>b</sup>
1	H <sub>2</sub> O	70
2	CH <sub>3</sub> CN	90
3	CH <sub>2</sub> Cl <sub>2</sub>	45
4	Cyclohexane	50
5	C <sub>6</sub> H <sub>6</sub>	55
6	n-Hexane	65
7	CCl <sub>4</sub>	40
8	CH <sub>3</sub> CN (25°C)	10
9	CH <sub>3</sub> CN (60°C)	55
10	CH <sub>3</sub> CN	25
11	CH <sub>3</sub> CN <sup>c</sup>	60
12	CH <sub>3</sub> CN <sup>d</sup>	75
13	CH <sub>3</sub> CN <sup>e</sup>	85
14	CH <sub>3</sub> CN	90
15	CH <sub>3</sub> CN <sup>f</sup>	55
16	CH <sub>3</sub> CN <sup>g</sup>	75

<sup>a</sup>Reaction condition: benzyl alcohol (1 mmol), catalyst (0.03 mmol), H<sub>2</sub>O<sub>2</sub>/Urea (15 mmol) under reflux conditions after 35 min.

<sup>b</sup>Isolated yield.

<sup>c</sup>catalyst (0.02 mmol) was used.

<sup>d</sup>catalyst (0.025 mmol) was used.

<sup>e</sup>H<sub>2</sub>O<sub>2</sub>/Urea (12 mmol) was used.

<sup>f</sup>The bulk-AIPMo (0.03 mmol) was used as catalyst.

<sup>g</sup>The AIPMo/SBA-15 (0.03 mmol) was used as catalyst.

2). In the catalytic reactions the choice of solvent is crucial. The influence of the various solvent on the yield of the reaction was investigated using benzyl alcohol as the substrate. From these studies it was concluded that CH<sub>3</sub>CN was the most favorable solvent (Table 2). The performance of the AIPMo/SBA-15 composite and AIPMo (bulk) are shown in Table 2. It is important that both removal of silica and nanocasting synthesis caused the increase of reactivity (Table 2, entries 15, 16).

To study the scope of this procedure the oxidation of other alcohols was next studied (Table 3). To test the role of electron influence of phenyl substituents on the efficiency of oxygenation, 4-MeO-benzyl alcohol and 4-NO<sub>2</sub>-benzyl alcohol were exposed to the oxidation system. These two substrates obtained 95% and 60% of conversions, respectively, after 30 min. The electron-withdrawing nitro group reduced the reactivity of benzyl alcohol toward oxidation, whereas the methoxy-group on the para-position of the phenyl ring increased the tendency of benzyl alcohol oxidation (Table 3).

The recovery and reusability of the catalyst were investigated. We have noticed that after the addition of CHCl<sub>3</sub> 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 was followed by NAA, XRD and FT-IR spectra) and no appreciable change in activity was noticed after three cycles.

## CONCLUSIONS

The elimination by HF of the silica matrix from the composites occurred by the two-step reaction deposition of AIPMo<sub>12</sub>O<sub>40</sub> (AIPMo) salt nanocrystal. We have used 2D hexagonal SBA-15 silica as templates for the nanofabrication of AIPMo nanoparticles. We have developed an efficient strategy for aerobic oxidation of benzylic alcohols using AIPMo nanoparticles, as an eco-friendly, inexpensive and efficient catalyst. This reaction provides a new environmentally friendly route to the conversion of alcoholic functions to carbonyl groups. Aldehydes do not

**Table 3.** Oxidation of benzylic alcohols with UHP catalyzed by AIPMo nanocrystals in CH<sub>3</sub>CN at reflux conditions.<sup>a</sup>

Entry	Substrate (1)	Ar	Product (2)	Time (min)	Yield (%) <sup>b,c</sup>
1	a	C <sub>6</sub> H <sub>5</sub>	a	35	92
2	b	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	b	30	60
3	c	2-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	c	55	55
4	d	4-HO-C <sub>6</sub> H <sub>4</sub>	d	30	92
5	e	2-HO-C <sub>6</sub> H <sub>4</sub>	e	20	90
6	f	4-MeO-C <sub>6</sub> H <sub>4</sub>	f	30	95
7	g	4-Cl-C <sub>6</sub> H <sub>4</sub>	g	30	90
8	h	2-Cl-C <sub>6</sub> H <sub>4</sub>	h	25	85
9	i	4-F-C <sub>6</sub> H <sub>4</sub>	i	30	80
10	j	4-Br-C <sub>6</sub> H <sub>4</sub>	j	30	75
11	k	2-Me-C <sub>6</sub> H <sub>4</sub>	k	25	90
12	l	2-NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	l	20	75

<sup>a</sup>Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.03 mmol), H<sub>2</sub>O<sub>2</sub>/Urea (15 mmol), CH<sub>3</sub>CN (2 ml) under reflux conditions.

<sup>b</sup>Isolated yield.

<sup>c</sup>All products were identified by comparison with authentic sample (mp, IR, NMR).

undergo further oxidation to carboxylic acids. The advantages of this catalytic system is mild reaction conditions, short reaction times, moderate to good product yields, easy preparation of the catalysts, non-toxicity of the catalysts, simple and clean work-up of the desired products.

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## REFERENCES

- Raimondi, F.; Scherer, G. G.; Kötzt, R.; Wokaun, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2190.
- Medine, G. M.; Zaikovskii, V.; Klabunde, K. J. *J. Mater. Chem.* **2004**, *14*, 757.
- Reddy, K. M.; Satyanarayana, L.; Manorama, S. V.; Misra, R. D. K. *Mater. Res. Bull.* **2004**, *39*, 1491.
- Aricò, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; van Schalkwijk, W. *Nat. Mater.* **2005**, *4*, 366.
- Yi, D. K.; Selvan, S. T.; Lee, S. S.; Papaefthymiou, G. C.; Kundaliya, D.; Ying, J. Y. *J. Am. Chem. Soc.* **2005**, *127*, 4990.
- Tartaj, P.; Morales, M. D. P.; Veintemillas-Verdaguer, S.; Gonzalez-Carreño, T.; Serna, C. J. *J. Phys. D: Appl. Phys.* **2003**, R182.
- Lee, J.; Yoon, S.; Hyeon, T.; Oh, S. M.; Kim, K. B. *Chem. Commun.* **1999**, 2177.
- Valdés-Solís, T.; Fuertes, A. B. *Mater. Res. Bull.* **2006**, *41*, 2187.
- Kozhevnikov, I. V. *Catalysts for Fine Chemical Synthesis, Catalysis by polyoxometalates*; Wiley: New York, 2002; Vol. 2.
- Neumann, R. *Prog. Inorg. Chem.* **1998**, *47*, 317.
- Hajipour, A. R.; Mallakpour, S. E.; Khoei, S. *Synlett* **2000**, 740.
- Strazzolini, P.; Runcio, A. *Eur. J. Org. Chem.* **2003**, 526.
- Li, C.; Xu, Y.; Lu, M.; Zhao, Z.; Liu, L.; Cui, Y.; Zheng, P.; Ji, X.; Gao, G. *Synlett* **2002**, 2041.
- Surendra, K.; Krishnaveni, N. S.; Reddy, M. A.; Nag-eswar, Y. V. D.; Rao, K. R. *J. Org. Chem.* **2003**, *68*, 2058.
- Fazaeli, R.; Tangestaninejad, S.; Aliyan, H. *Appl. Catal., A: Gen.* **2007**, *318*, 218.
- Fazaeli, R.; Aliyan, H. *Appl. Catal., A: Gen.* **2007**, *331*, 78.
- Fazaeli, R.; Aliyan, H. *Appl. Catal., A: Gen.* **2009**, *353*, 74.
- Fazaeli, R.; Tangestaninejad, S.; Aliyan, H.; Moghadam, M. *Appl. Catal., A: Gen.* **2006**, *309*, 44.
- Sun, M.; Zhang, J.; Cao, C.; Zhang, Q.; Wang, Y.; Wan, H. *Appl. Catal., A: Gen.* **2008**, *349*, 212.
- Baba, T.; Watanabe, H.; Ono, Y. *J. Phys. Chem.* **1983**, *87*, 2406.
- Tanaka, T.; Nishimura, Y.; Kawasaki, S.; Ono, M.; Funabiki, T.; Yoshida, S. *J. Catal.* **1989**, *118*, 327.
- Rao, P. M.; Goldberg-Oppeneimer, P.; Kababya, S.; Vega, S.; Landau, M. V. *J. Mol. Catal. A: Chem.* **2007**, *275*, 214.
- Miao, Y.; Lu, G.; Liu, X.; Guo, Y.; Wang, Y.; Guo, Y. *Microporous Mesoporous Mater.* **2009**, *122*, 55.