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Green oxidation of alcohols in water by a polyoxometalate nano capsule as catalyst

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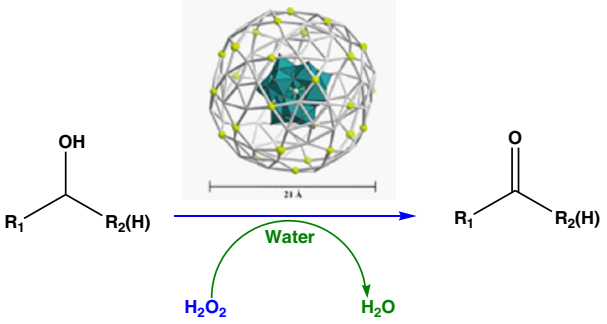
ABSTRACT

In this work a water soluble polyoxometalate nano capsule, $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$, with high stability was evaluated for the oxidation of various alcohols into the corresponding aldehydes and ketones by hydrogen peroxide. This environmentally and economically valuable catalyst allowed for using water as solvent and has not required any organic solvents. In the presence of very low amounts of catalyst high to excellent yields and selectivity were obtained.

One of the most frequently used reactions in organic synthesis is the oxidation of the hydroxyl groups into the corresponding carbonyl compounds. The oxidation of alcohols is traditionally carried out with stoichiometric and even over-stoichiometric amounts of metal oxides or metal salts [1,2]. These oxidants are not only relatively expensive, but they also generate copious amounts of heavy-metal waste. Moreover, the reactions are often performed in environmentally undesirable solvents, typically chlorinated hydrocarbons. In an effort to provide a more environmentally benign "green" process, a variety of catalytic alcohol oxidations that used dioxygen (O_2) or hydrogen peroxide (H_2O_2) have been investigated [3]. These oxidants are atom efficient and produce water as the only by-product [4]. Although the advantages of using hydrogen peroxide as oxidant in alcohol oxidation are evident, reports on this particular subject are still scarce [5].

Polyoxometalates (POMs), as metal–oxygen cluster species have obtained extensive attention [7–9]. They have been of extreme interest as oxidation catalysts due to their unique ensemble of properties, including metal oxide-like structure, thermal and hydrolytic stability, tunable acidities and redox potentials, alterable solubility in various media, their resistance toward oxidation, and compatibility with various oxygen sources. Many examples of homogeneous and heterogeneous systems make use of different types of POMs in organic solvents [10–14]. Unfortunately, most of these methods need to hard conditions such as high temperature, hazardous or toxic solvents and so on, and also one or more equivalents of non-environment oxidizing agents. From an economic and environmental viewpoint, mild condition, green solvents and nontoxic oxidation agents are extremely valuable. Especially in POMs, few efficient and catalytic oxidation processes with hydrogen peroxide and green solvents such as water that proceed under mild conditions are known [15–17].

When oxidations could be performed in water, they would be considerably safer, cheaper, and more environmentally friendly than other processes in use [5,6]. Moreover, when a water-soluble catalyst is used in a biphasic system, most products can be separated by simple decantation, and the catalyst solution could be recycled. Nevertheless, such reactions are still rare and lack generality. In contrast, the use of



Scheme 1. Selective oxidation of various alcohols with $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ in water.

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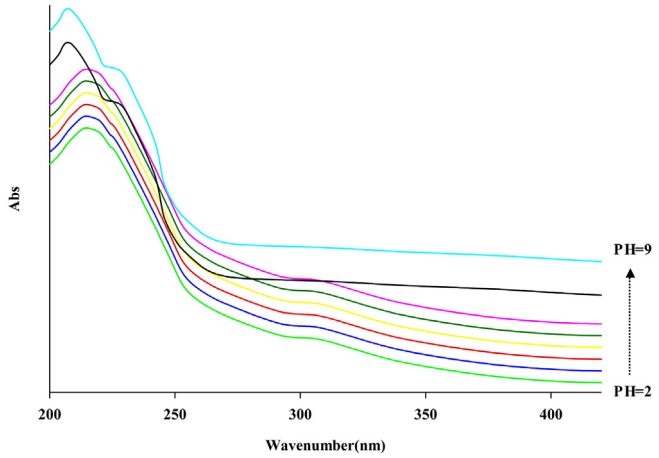


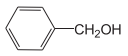
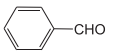
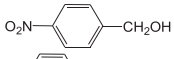
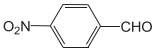
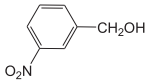
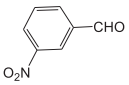
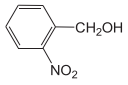
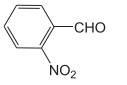
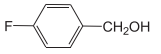
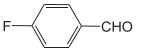
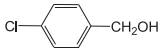
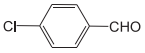
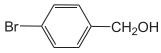
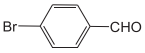
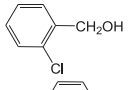
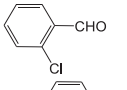
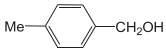
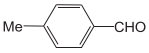
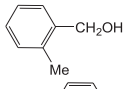
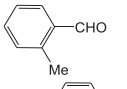
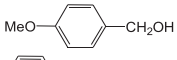
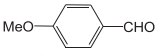
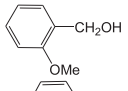
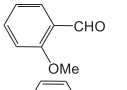
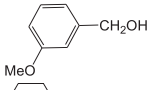
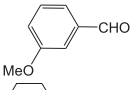
Fig. 1. Screening the stability of $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ nano capsule in the oxidation of benzyl alcohol at different pH's by UV–vis.

an organic solvent, such as toluene or acetonitrile, necessitates a tedious distillation and cumbersome recovery of the catalyst.

Spherical porous molybdenum-oxide-based capsules of the type $\{(M^{VI})M^{VI}_5\}_{12}(linker)_{30}$ (M = Mo or W), called Keplerates, are multifunctional nano-objects which have allowed the study of several new phenomena and have been the basis of many applications due to their unique structural features and properties [18–27]. Among them, the $\{Mo_{72}Fe_{30}\}$-type species – comprising 12 molybdenum-oxide-based pentagonal units linked by 30 Fe^{III} spacers that span an icosidodecahedron – have attracted considerable attention since their initial report in 1999 [7–9]. The unique spherical Keplerates of the type $\{Mo_{72}Fe_{30}\}$ have received a lot of attention because of their magnetic properties as well, although their catalytic properties in the oxidation of organic reactions really lag behind [28–32].

In this work, a core–shell hybrid made of Keggin-type heteropolyoxomolybdates encapsulated into $\{Mo_{72}Fe_{30}\}$-type Keplerates, $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ [25–27] (Scheme 1) was used as catalyst for the oxidation of alcohols by H_2O_2 in water and especially in a sustainable medium [33,34]. After preparation of POM nano

Table 1
Selective oxidation of various alcohols to the corresponding carbonyl compounds in the presence of POM nano capsule catalyst.[a]

Entry	Substrate	Product	Time (min)[b]
1			30
2			20
3			25
4			30
5			60
6			90
7			105
8			70
9			40
10			50
11			100
12			120
13			150
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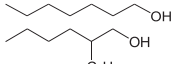
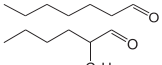
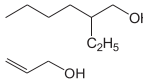
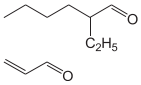
17			25
18			120
19			20

[a] Reaction conditions: alcohol (1 mmol), catalyst (1 μmol), water (3 mL), and 30% H_2O_2 (4.5 mmol) at 45 °C.
[b] Yields are quantitative and refer to GC yields.

capsules, $PMo_{12}O_{40} \subset \{(Mo)Mo_5\}_{12}\{Fe^{III}\}_{30}$, according to the literature, their synthesis was confirmed by elemental analysis, TG, FTIR, XRD, and UV–vis spectroscopy (Figs. S1–S4) [27]. Catalytic experiments were initiated by the oxidation of benzyl alcohols (1 mmol), as a model compound, with H_2O_2 (4.5 mmol) in the presence of 1 μmol POM nano capsule in bidistilled water at 45 °C [35]. Only after 45 min, using a few amounts of catalyst (1 μmol), benzyl alcohol completely converted and benzaldehyde was produced exclusively in 100% yield by an easy isolation with ethyl acetate as a safe solvent.

Since the structure of POMs is pH dependent, the oxidation of enzyl alcohol was run at different pH values (Fig. 1). When the pH value was adjusted to less than or equal to 6.6, exactly the same conversions and selectivity were obtained. Nevertheless, since the $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ nano capsule became less stable at higher pH values, low oxidation activity was observed; consequently, the clusters are broken as established by UV–vis study. Note that all POMs decompose at high pH values, while smaller species are formed [27].

Using the best reaction conditions and to establish the general applicability of the method, various alcohols were subjected to the oxidation protocol using H_2O_2 and $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$. By these very mild reaction conditions – 1 μmol nano capsule catalyst, 4.5 mmol H_2O_2, 45 °C, and 0.5–2.5 h oxidation reaction in water – to a reasonable extent various benzylic alcohols produced target aldehydes and/or ketones in excellent yields (Table 1). This catalytic system efficiently worked both in the presence of electron-donating or electron-withdrawing substituent as well as in less sterically favored positions on the aromatic rings (Table 1, entries 1 to 13). Our catalytic process was also amenable to cyclic alcohols (Table 1, entries 14 and 15) and high yields were observed for linear alcohols and allyl alcohol (Table 1, entries 16 to 18). By increasing the time of reaction, complete conversion was obtained for most substrates with the exception of aromatic alcohols with electron donating groups (Table 1, entries 11 to 13) that only provided high yields at moderate times. As everyone could see in Table 1, this catalytic system possesses novelty regarding selectivity only for aldehydes and ketones. It was shown that secondary and primary linear and aromatic alcohols were oxidized selectively (greater than 99%) to ketones and aldehydes, respectively, with no further oxidation of aldehydes to carboxylic acids.

For comparison the catalytic activity of $H_3PMo_{12}O_{40}$ and $H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ in the oxidation of benzyl alcohol at the same conditions were also investigated. Results for $H_3PMo_{12}O_{40}$ showed only 20% conversion after 60 min and for $H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ demonstrated that 120 min oxidation reaction is needed for complete conversion of alcohol.

In this procedure, the POM nano capsule catalyst was reused several times without any loss of activity. Recovery of the catalyst was easy and efficient. When the reaction was completed, hydrophobic organic products were isolated by adding ethyl acetate as a safe solvent. Then aqueous solution of catalyst was reused directly for the next round of reactions without further purification. The solid catalyst $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ could also be obtained easily by removing the water followed by washing with ethyl acetate or ethanol and drying under vacuum. The ease of recovery, combined with the intrinsic stability of the $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$, allows for the catalyst to be recovered efficiently over 10 times in the oxidation of benzyl alcohol (Fig. 2). Only after the ninth run was a negligible decrease in catalyst performance (<2%) observed. Therefore, these POM catalysts showed high stability, activity and selectivity in oxidation reaction runs.

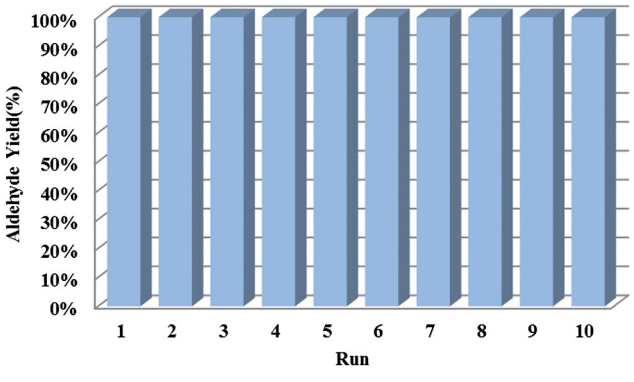


Fig. 2. Recyclability of the POM nano capsule catalyst in the oxidation of benzyl alcohol with hydrogen peroxide in water according to the procedure mentioned in Table 1.

Comparison between FTIR, XRD, and UV–vis spectra of the used catalyst with those of fresh one (Figs. S1–S3) illustrated that the structure and morphology of the catalyst remained completely intact. Therefore, the title methodology is environmentally benign because of the use of hydrogen peroxide as an oxygen source, water as a reaction media, reusability of an active catalyst, very low catalyst loading, easy isolation of hydrophobic organic products, and as a final point no need for toxic reagents or solvents. These advantages make this catalytic method readily amenable to scalability.

In summary, green oxidation of different alcohols into aldehydes and ketones by a water soluble POM nano capsule was developed. High to excellent yields were obtained in the oxidation reactions by $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ as catalyst. This catalytic system is valuable because of easy and safe procedure and also from the environmental point of view. As a result, this method could have high potential for industrial purposes.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.03.030.

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