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

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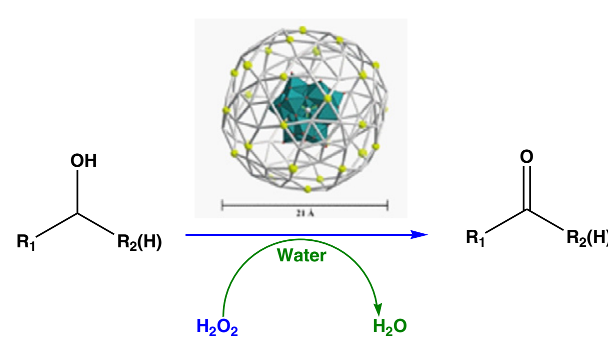
ABSTRACT

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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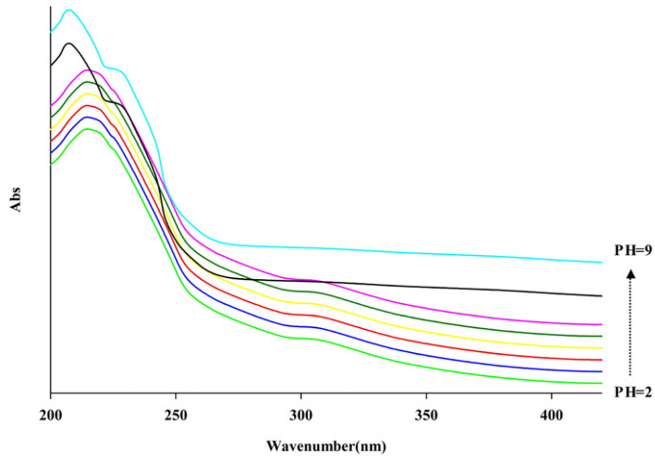

Fig. 1. Screening the stability of $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ nano capsule in the oxidation of benzyl alcohol at different pH's by UV–vis.

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 $\{(M^{VI})M^{VI}{}_5\}_{12}(\text{linker})_{30}$ (M = Mo or W), called Keplerates, are multi-functional 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]

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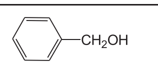
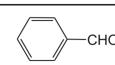
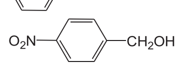
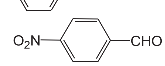
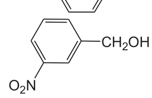
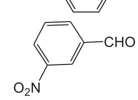
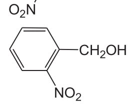
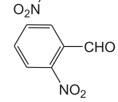
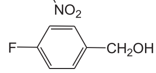
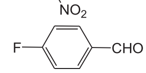
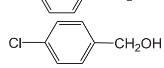
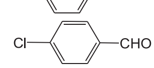
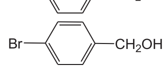
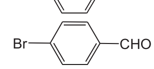
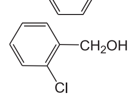
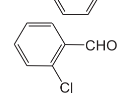
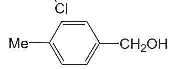
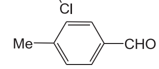
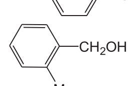
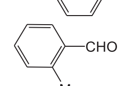
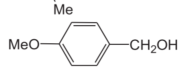
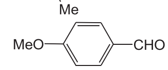
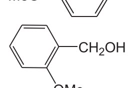
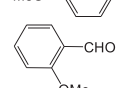
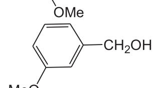
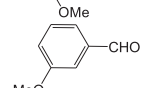
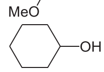
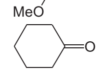
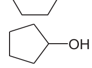
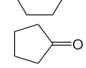
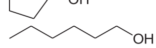
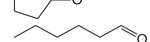
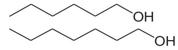
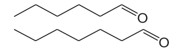
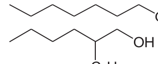
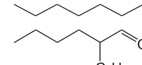
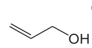
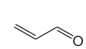
1			30
2			20
3			25
4			30
5			60
6			90
7			105
8			70
9			40
10			50
11			100
12			120
13			150
14			120
15			130
16			25
17			25
18			120
19			20

[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.