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Catalytic Epoxidation Activity of Keplerate Polyoxomolybdate Nanoball toward Aqueous Suspension of Olefins under Mild Aerobic Conditions

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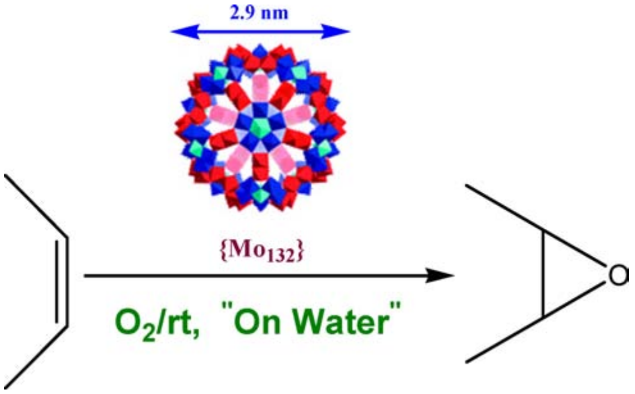
Supporting Information

ABSTRACT: Catalytic efficiency of a sphere-shaped nanosized polyoxomolybdate $\{Mo_{132}\}$ in the aerobic epoxidation of olefins in water at ambient temperature and pressure in the absence of reducing agent is exploited which resulted good-to-high yields and desired selectivity.

Metal-catalyzed aerobic oxidation represents the most elegant and environmentally friendly route for a large-scale production of invaluable oxidation products.[1] The utilization of molecular oxygen for a catalytic oxidation without reducing reagents or radical initiators is a rewarding goal. This is due to the highest content of active oxygen in molecular oxygen and lack of byproducts, contrary to various other oxidants. However, only a few ideal homogeneous epoxidations of olefins with molecular oxygen at 1 atm without reducing agents or radical initiators have been developed to resolve difficulty with either persuasion of the catalysts to act as a stoichiometric oxidant or degradation of their organic ligands.[2] Moreover, the poor product selectivity obtained in aerobic processes is one of the major drawback for using molecular oxygen as the terminal oxidant for the formation of epoxides.[3] In addition, the limited number of catalysts available for direct activation of molecular oxygen, effectively restricts its use. Thus, the innovation and improvement of selective catalytic epoxidation methods where molecular oxygen is employed as terminal oxidants without any reducing reagents or radical initiators is highly desirable.[1] Nevertheless, a major challenge is to accomplish such a process in nontoxic solvents, particularly in aqueous media. It is known that water as a solvent induces attractive patterns of reactivity and selectivity compared with those observed in common organic solvents, which makes green chemistry an active field.[4] Recently, reactions of water-insoluble organic compounds that take place in aqueous suspensions ("on water") have received a great deal of attention because of their high efficiency and straightforward synthetic protocols.[5] Nevertheless, such reactions are still rare and lack generality.

Metal−oxygen cluster molecules, polyoxometalates (POMs) are attractive compounds for a wide range of chemistry because of their high ability to control the molecular properties (composition, size, shape, acidity, and redox potential).[6] They have been of extreme interest as oxidation catalysts due to both their resistance toward oxidation and compatibility with various oxygen sources.[7] Giant polyoxomolybdates, especially $\{Mo_{132}\}$, a spherical ball-like cluster, are nanoscale architectures with more than 500 atoms and the highest Euclidean symmetry,[8] which gained significant interest as cation carriers or nano-sponges and for various other material science applications in the solid state.[8d,9] However, their catalytic properties in the oxidation of organic reactions really lag behind.[10] In continuation of our ongoing research on the development of novel oxidation methods for oxidation of organic compounds[11] and especially in sustainable media,[12] herein we report a simple, mild, and efficient aerobic epoxidation procedure catalyzed by Keplerate $\{Mo_{132}\}$ nanoball, $[(NH_4)_{42}[Mo^{VI}_{72}\ Mo^{V}_{60}O_{372}$-$(CH_3COO)_{30}(H_2O)_{72}]$,[8a] that takes place "on water" in the absence of reducing agent or radical initiators (Scheme 1). The catalyst was reused in the procedure for many times without any loss of activity.

Scheme 1. Aerobic Epoxidation of Olefins in Water Catalyzed by $\{Mo_{132}\}$ Nanoball



Catalytic experiments were initiated with the oxidation of cyclooctene (0.5 mmol) with O_2 (1 atm) in the presence of 1 mol % of $\{Mo_{132}\}$ in double-distilled water at 25 °C. It led to 14, 24, 37, and 100% cyclooctene oxide (GC yield based on toluene as internal standard) after 30, 40, 60, and 120 min, respectively, without any reducing reagent. To confirm the ineffectiveness of a reducing agent, isobutyraldehyde as a commonly used reducing agent was added, and no improve-

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ment in the reaction rate was observed (35% after 60 min). Our investigation on the catalyst loading demonstrated a high atom efficiency of the title nanopolyoxomolybdate. Only after 2 h did cyclooctene convert completely using a few minutes of catalyst (0.2 mol %), and cyclooctene oxide was secured exclusively in 96% yield by an easy isolation with ethyl acetate as a safe solvent. More interestingly, the use of an excess amount of cyclooctene (1 mmol) rather than catalyst (1×10^{-5} mmol, 0.001 mol %) gave 57% epoxide yield after 24 h, illustrating a high turnover number of 57000 for this nanostructured catalyst.[2b] This desired conversion rate can be rationalized in terms of the reaction conditions as a heterogeneous suspension of organic droplets in water ("on water").[5b] However, the excellent dispersity of $\{Mo_{132}\}$-type cluster in aqueous solution, generating discrete single-molecular clusters should be taken into account for such an activity.[13] It should be noted that, when the catalyst was replaced by MoO_3, $Na_2MoO_4 \cdot 4H_2O$, or $(NH_4)_6MO_7O_{24} \cdot 4H_2O$ as simple salts of Mo(VI), no oxidation product was observed with longer reaction times up to 24 h. The time course of oxygen uptake by cyclooctene verified these results (Figure 1).

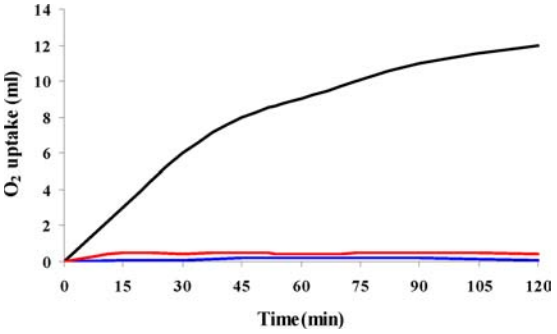


Figure 1. Time course of oxygen uptake by cyclooctene in the presence of $\{Mo_{132}\}$ (black line), $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$ (blue line), and $NaMoO_4 \cdot 2H_2O$ (red line) in water.

Since the structure of POMs is pH dependent,[14] the epoxidation of cyclooctene was run at different pH values. When the pH value was adjusted to less than or equal to 8, exactly the same conversions and selectivity were obtained. Nevertheless, at higher pH values no oxidation activity was observed because the $\{Mo_{132}\}$ cluster became less stable; consequently, the clusters are broken as established by a UV–vis study (see Figure 2). Note that all polyoxometalates decompose at high pH values, while smaller species are formed.[14]

To establish the general applicability of the method, various olefins were subjected to the oxidation protocol using O_2 (1 atm) and 0.2 mol % of $\{Mo_{132}\}$ at 25 °C (Table 1). As summarized in Table 1, different olefins are generally good substrates for this nanocatalyst, forming solely the related epoxides within desired reaction times. Our method led to complete conversion of cyclooctene, cyclohexene, norbornene, styrene, α-methylstyrene, and indene (entries 1, 2, 5, 6, 7, and 9) within 2–4 h. No allylic oxidation occurred, and only a trace amount of benzaldehyde was detected (2%) resulting from a ring-opening reaction of styrene oxide (entry 6). The reaction also proceeded smoothly with less reactive 1-octene (entry 10), and 90% of the corresponding epoxide was secured as a sole product within 4 h. However, the poor reactivities of 1,1,2-tribustituted- and those of *E*-olefins (entries 3, 4, 8, 16) were observed, demonstrating the steric hindrance around the active site of the catalyst. It is worth mentioning that the catalyst was able to oxidize electron-deficient 2-cyclohxene-1-one to the related epoxide in moderate yield (40%, entry 14).

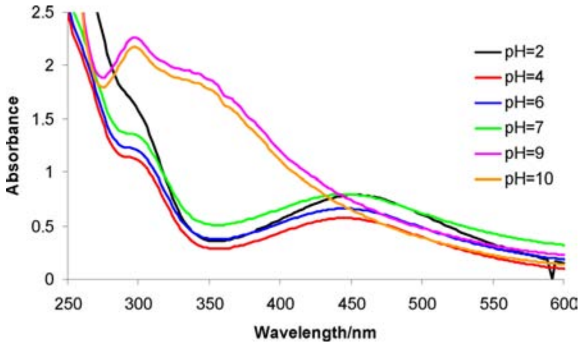


Figure 2. Screening of pH in the aerobic epoxidation of cyclooctene in water catalyzed by $\{Mo_{132}\}$ nanoball.

The method possesses novelty regarding chemoselectivity. The hydroxyl group which is sensitive to oxidation remained completely intact under the influence of the catalyst, producing the pertinent epoxides in high yields (entries 11–13). To confirm our claim, a competitive reaction between cyclooctene and benzyl alcohol was run. After 2 h, cyclooctene oxide was obtained quantitatively as the only product.

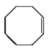
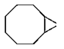
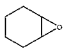
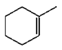
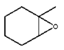
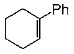
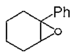
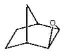
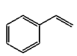
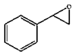
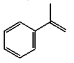
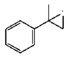
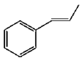
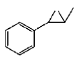
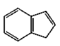
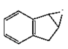
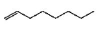
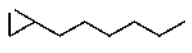
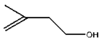
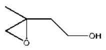
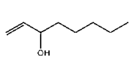
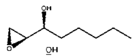
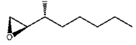
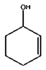
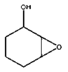
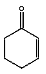
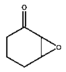
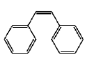
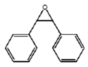
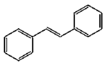
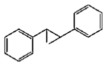
Then we applied this protocol to sulfur-containing olefins. Electron-rich allyl sulfides, diallyl and allyl phenyl sulfide, were converted completely to the corresponding sulfones after 5–6 h while the olefin moiety was tolerated in the reaction. Nevertheless, other sulfides displayed no oxidation activity under the same conditions even after a long period of time.

The stereoselectivity of the method was notable. Norbornene gave exclusively the related *exo*-epoxide (entry 5). Moreover, epoxidation of *cis*- and *trans*-olefins proceeded with absolute stereospecificity (entries 8, 15, and 16). However, 1-octen-3-ol (entry 12) gave an approximately equal yield of diastereoisomers of *erythro*-/*threo*-1,2-epoxy-3-octanol (55:43 ratio).

In addition, epoxidation of *cis*-stilbene was faster than that of the corresponding *trans*-olefin. This result was similar to that observed in the presence of porphyrin systems which proceeded differently from a radical pathway.[15] Moreover, oxygenation of cyclooctene was not inhibited by the presence of radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol (BHT). For example, the conversion and selectivity for cyclooctene oxide after 2 h in the presence of >5 equiv of BHT (rather than catalyst) was ~97 and 100%, respectively, according to GC analysis. These results demonstrate that nonradical processes prevail to a high extent in the present system, although some contribution of free radicals could exist.

Recovery of the catalyst was easy and efficient. When the reaction was complete, hydrophobic organic products were isolated by adding ethyl acetate as a safe solvent. Then an aqueous solution of catalyst was reused directly for the next round of reactions without further purification. The solid catalyst $\{Mo_{132}\}$ 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 $\{Mo_{132}\}$, allows the catalyst to be recovered efficiently over 10 times in the epoxidation of cyclooctene (Figure 3).Only after the ninth run was there a negligible decrease in catalyst performance (<2%). Raman bands of the original skeletal vibration of $\{Mo_{132}\}$ changed only

Table 1. Aerobic Olefin Epoxidation in Water Catalyzed by $\{Mo_{132}\}^{a}$

Entry	Olefin	Product	Yield%[b]	Time (h)
1			96	2
2			92	3
3			60	5
4			33	5
5			95	2
6			93	3
7			94	4
8			45	5
9			89	4
10			90	4
11			96	5
12		 	55^{c} *(erythro)* 43^{c} *(threo)*	5
13			80	5
14			40	5
15			97	5
16			25	5

[a] The reactions were run at 25 °C in 2 mL of an aqueous suspension of olefin (0.5 M), containing 2 μmol of $\{Mo_{132}\}$ as catalyst under 1 atm O_2 (7−10 mL/min). [b] Yield of isolated products. All the reactions were run at least in triplicate, and the yields represent an average of these reactions. The selectivities of epoxides were >99% except for entry 6 which was 98% (2% benzaldehyde). [c] Determined by NMR.

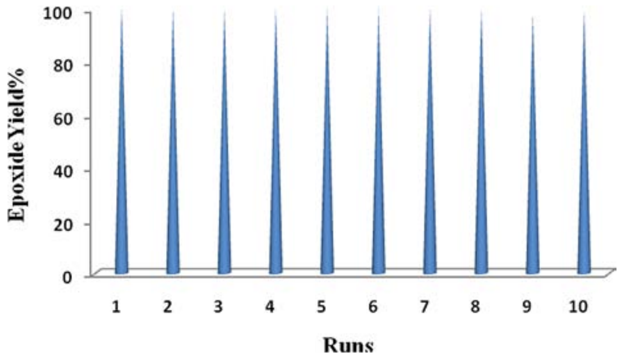


Figure 3. Recycling of the catalytic system for aerobic epoxidation of cyclooctene in water according to the procedure mentioned in Table 1.

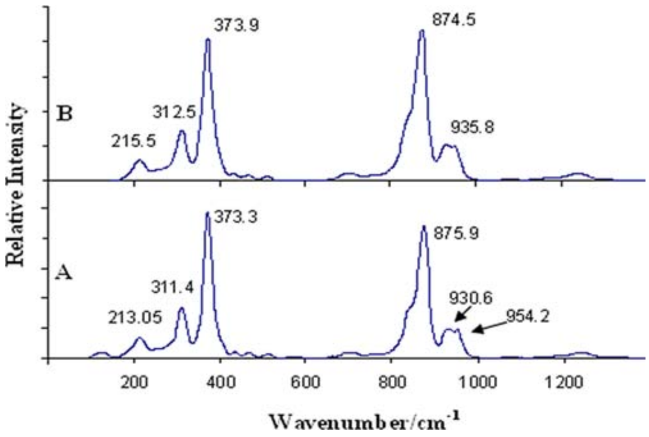


Figure 4. Raman spectra of fresh (A) and used $\{Mo_{132}\}$ after 10 reuses (B) in aerobic epoxidation of cyclooctene in water according to the procedure mentioned in Table 1.

slightly after many recoveries (Figure 4). Also the comparison of UV−vis and IR spectra of the used catalyst with those of a fresh one (Figures S1 and S2 in Supporting Information) illustrated that the structure and morphology of the catalyst remained completely intact. Therefore, the title methodology is environmentally benign because of using molecular oxygen as an oxygen source, water as a reaction media, reusing of an active catalyst with very low catalyst loading, easy isolation of hydrophobic organic products, and finally, no need for reducing agent, radical initiator, toxic reagents, or solvents. These advantages make the method amenable to scalability readily. As an example, a semi-scaled up procedure (20.0 mmol) for epoxidation of cyclooctene in the presence of $\{Mo_{132}\}$ led to isolation of the related epoxide in 93% yield within 2 h.

In conclusion, the catalytic performance of a Keplerate-type, giant-ball nanopolyoxomolybdate $\{Mo_{132}\}$ in the aerobic epoxidation of different olefins that takes place "on water" in the absence of reducing agent or radical initiators was demonstrated. Desired yields and chemo- and stereoselectivity were obtained. These favorable characteristics, plus the easy and safe workup procedure and excellent reusability of the catalyst, are environmentally benign and cost-effective. Thus, our method possesses high generality which makes it suitable for industrial goals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, synthesis, and characterization of the $\{Mo_{132}\}$ and GC trace. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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