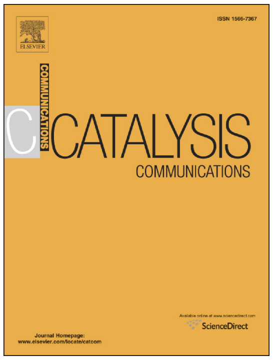

{Mo72Cr30} nanocluster as a novel self-separating catalyst for hydrogen peroxide olefin epoxidation

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{$Mo_{72}Cr_{30}$} nanocluster as a novel self-separating catalyst for hydrogen peroxide olefin epoxidation

Abdolreza Rezaeifard,* Maasoumeh Jafarpour,* Reza Haddad and Fahimeh Feizpour

Catalysis Research Laboratory, Department of Chemistry, Faculty of Science, University of Birjand, Birjand, 97179-414 Iran.

*Corresponding author.

Abstract:

Phase-transfer catalytic epoxidation activity of nanosized {$Mo_{72}Cr_{30}$} Keplerate polyoxometalate in ethanol in the presence of hydrogen peroxide is exploited. The nanocluster acts as a homogeneous catalyst upon treatment with hydrogen peroxide, while it can be easily filtered and reused as a heterogeneous catalyst. The high catalytic activity and durability of catalyst was demonstrated.

Keywords

Keplerate Polyoxometalate; Nanocluster; Phase-transfer catalyst; Epoxidation; {$Mo_{72}Cr_{30}$}; Heterogeneous catalyst

*Corrsponding author, Tel: +98 56 32202516; Fax: +98 56 32202515, E-mail address: rrezaeifard@birjand.ac.ir; rrezaeifard@gmail.com; (A. Rezaeifard); mjafarpour@birjand.ac.ir (M. Jafarpour)

The extensive applications of polyoxometalate (POM) molecular clusters in catalysis, electrochemistry, biomedicine, and magnetism as sensors, surfaces and coatings has offered new opportunities in many different fields.[1,2] The POMs with high solubility in polar solvents are the most commonly used homogenous catalysts, owing to their good catalytic features such as high activity and selectivity. Nevertheless, difficulty in catalyst recycling and contamination by residual catalyst are a number of serious limitations for their industrial applications.[2] POM-based heterogeneous catalysts prepared by various "immobilization" processes or "solidification" with suitable cations, exhibit facile separation and reusability. Nonetheless, the use of heterogeneous catalysts are limited by mass transfer, diffusion, and accessibility of the active sites.[2,3]

The combination of the homogeneous catalysts advantages with heterogeneous ones generates a "Phase-transfer catalyst" (PTC) which is the most adopted strategy to overcome the catalysis limitations and therefore have raised a kind of promising catalyst accommodating environmentally-friendly sustainable development.[4,5] In a phase-transfer catalytic system, homogeneous and heterogeneous states can be switched, achieving homogeneous catalysis of reaction and heterogeneous separation of the catalyst. POM-based PTCs, are mostly organic-inorganic hybrid materials constructed by modification of the cations of POMs with organic compounds such as ionic liquids, quaternary ammonium salts, oligomers and so on. [6,7]

Catalytic olefin oxidation mediated by transition metal complexes is the most elegant and environmentally benign route for the production of epoxides as versatile intermediates in organic synthesis and pharmaceutical products [1, 2]. In this regard, considerable efforts have focused on removing or replacing toxic solvents, reagents, catalysts and additives with safe ones. Moreover, substituting oxidants in particular, Oxone®, NaOCl, iodosylbenzenes, and m-CPBA, with more atom economic oxidants such as O_2 and especially H_2O_2 is a major challenge.[8,9] The epoxidation of various olefins is one typical reaction most widely studied over POM-based

PTCs.[5] Recently, various newly designed POM-based PTCs have been applied in other reactions such as esterification, transesterification, hydroxylation of benzene and oxidation of alcohols,[10,11] expanding the scope of POM-based PTCs.

Keplerate-type polyoxometalates as a significant class of inorganic nanocapsules have attracted more and more attention of scientists in the areas of chemistry, physics, biology, and materials. Because they have overwhelming variety of fascinating and unusual properties, which make the supramolecular clusters become good candidates to construct functional materials in the fields of magnetics, optics, electrochemistry and materials science.[12,13] However, remarkably little work has been done with respect to their catalytic performance[14-24] and to the best of our knowledge a partial result on photo-controlled phase-transfer catalysis of azo derivative of $\{Mo_{132}\text{-}SO_4\}$ is the only report on PTC activity of Keplerates.[25]

Following our discovery on catalytic efficiency of $\{Mo_{132}\text{-}OAc\}$ nanoball in aerobic olefin epoxidation [16] as well as oxidation of sulfides and olefins with H_2O_2 [17] a few works on oxidation activity of other Keplerates has been done.[18-21] Catalyst degradation under oxidation conditions is a major concern for using reduced POM such as $\{Mo_{132}\}$ nanocluster. Further investigations, demonstrated that the $\{Mo_{132}\}$ acts as a pre-catalyst.[20] and our finding in Fig. S1 in SI)] It will change to several smaller nuclearity species by treatment with H_2O_2 which could become active species and responsible for the oxidation of substrates.[20]. The residual catalyst (Fig. S1) could be reused efficiently in the oxidation system.[17,20] In addition, solubility of POM catalysts in water suffering its separation from the reaction solution and recycling, impede its use in industrial processes. These results, induce us to search a robust cluster with desired activity under heterogeneous conditions. Mixed metal oxide buckyball $\{Mo_{72}Cr_{30}\}$ Keplerate nanocluster (2.5nm) “$[\{Na(H_2O)_{12}\}\subset\{Mo^{VI}_{72}Cr^{III}_{30}O_{252}(CH_3COO)_{19}(H_2O)_{94}\}]Ca.120H_2O$”[26] is formed either as a water-soluble tiny crystals with a “pale” green colour in very low yield (<1%) at earliest time and also as a “dark” green water-insoluble crystals in desired yield after 5 days.

[26] In this work, for the first time the water-insoluble “dark” green {$Mo_{72}Cr_{30}$} (see Fig. S2-S7 in ESI for full characterization of nanocluster) is introduced as a novel phase transfer catalyst for efficient olefin epoxidation using 30% aqueous hydrogen peroxide as an oxidant in ethanol as a safe solvent.

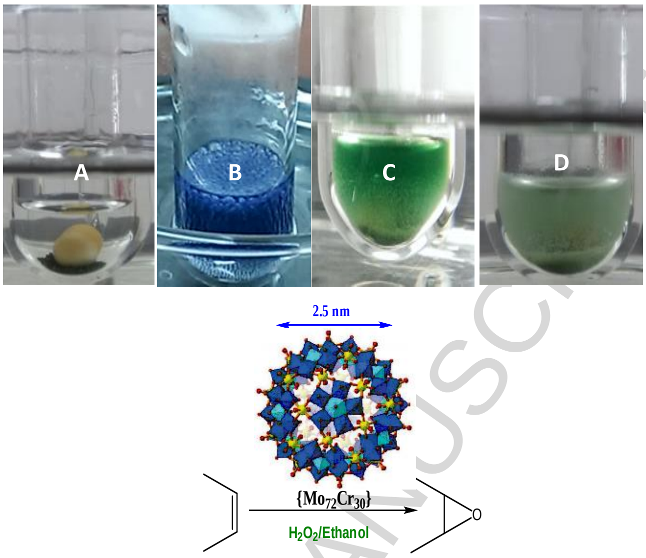


Fig. 1. Epoxidation of olefins using H_2O_2 in ethanol catalyzed by insoluble {$Mo_{72}Cr_{30}$} nanocapsule. (A) Photograph of the catalyst in ethanol at 70 °C before addition of H_2O_2, (B) after addition of H_2O_2, (C) after completion of the reaction, (D) after cooling to room temperature.

The solid catalyst is dissolved easily upon treatment with hydrogen peroxide in ethanol which produces a deep “blue” solution exhibiting high activity and excellent selectivity in the oxidation of different olefins. Nonetheless, it is filtrated easily at the end of reaction as a “dark” green solid. (Fig. 1). The nanocluster maintains its icosahedral structure as well as its activity after recycling.

The catalytic activity of {$Mo_{72}Cr_{30}$} was examined in the oxidation of cyclooctene as a model olefin under different conditions knowing that H_2O_2 has not ability to trigger the reaction under catalyst-free condition (Table S1 in ESI). The results for screening of different solvents (entries 1-9), using different amounts of oxidant (entries 5, 10-12) or catalyst (Table S1, entries 5, 13-15) at various temperatures (Table S1, entries 5, 17-20) are given in Table S1. The “dark” green {$Mo_{72}Cr_{30}$} which is insoluble in all solvents examined at 70 °C, dissolved rapidly in ethanol at

70 °C after treatment with hydrogen peroxide (and to a lesser extent in other solvents). A homogeneous "blue" solution (Fig. 1B) with characteristic absorption band at 590 nm assigned to peroxide-Cr charge-transfer [27,28] was appeared (Fig. S8). The Raman spectra of "blue" solution (Fig. S9) showed new vibrations at 530 and 1195 cm^{-1} rationalized to Cr-OO and O-O stretching of a superoxo species [29-31] or a Cr-peroxo species [28] attached to numerous strong electron deficient Mo(VI) centers. More evidences should be gathered to elucidate the actual active species involved in the reaction mechanism.

After completion of the reaction, the catalyst self-precipitated from the reaction medium (Fig. 1C, D) making it amenable to recyclability by filtration. For other solvents little amounts of "green" solids were precipitated at room temperature, requiring a high speed centrifuge for catalyst separation. Thus, ethanol is the best offer for the reaction media, based on the high catalytic efficiency and self-separation of catalyst. Next, the temperature effect on the catalytic efficiency was screened. The best catalytic performance was observed at 70 °C leading to full conversion of cyclooctene within 45 min and 96% cyclooctene oxide was achieved, while, no diol by-product was detected in the reaction. (Table S1, entry 5, Table 1, entry 1). At this temperature the decomposition of hydrogen peroxide after formation of "blue" solution in the presence of {$Mo_{72}Cr_{30}$} in ethanol proceeded slowly (<10% per hour, Fig. S10). However, based on the results presented in Table S1 (entry 12) a molar equiv. amount of H_2O_2 was not enough and the use of at least 1.5 equiv. of oxidant is necessary to the complete conversion of cyclooctene (Table S1, entry 5, 11). The screening of catalyst amount (Table S1, entries 5, 13-15) demonstrated that the reaction required 0.4 mol% of {$Mo_{72}Cr_{30}$} to proceed with high performance after 45 min (27 and 65% cyclooctene oxide yields at 15 and 30 min, respectively). It is worth mentioning that, performing the reaction using lesser amount of catalyst (0.1 mol%) gave 70% cyclooctene conversion after 1 h illustrating a turnover frequency of 700 for title catalyst. Moreover, the durability of {$Mo_{72}Cr_{30}$} nanocluster was established by a TON of 15750 resulted from 63%

conversion during 24 h under controlled conditions (0.004 mol% catalyst, 60 °C) (see infra). When the catalyst was replaced by $CrCl_3.6H_2O$ (12 mol%) and $NaMoO_4.2H_2O$ (29 mol%) with the same metal concentration as is in $\{Mo_{72}Cr_{30}\}$, no oxidation products were observed under the same conditions during 12 h. Nevertheless, the use of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (4 mol%) as catalyst gave 28, 50 and 69% cyclooctene oxide after, 1, 4 and 12 h respectively. Further, the addition of $CrCl_3.6H_2O$ to the above mentioned Mo salts did not promote the catalytic activity.

Next, we test the catalyst activity and stability after self-precipitation. Oxidation reaction was carried out with the regenerated catalyst under the optimized conditions. Our founding showed no change in selectivity, and only a 4 percentage decrease in conversion was observed after 5 cycles, probably resulting from minor loss of catalyst during filtration and washing (Fig. S11). The leaching of Mo and Cr from catalyst was ruled out by AAS analysis of filtrates. The analysis of the product mixtures after centrifuge of hot solution (Fig. 1C) or filtration at room temperature (Fig. 1D) showed no Mo or Cr within the limit of detection (<1 ppm). Moreover, the solid-free filtrate was then subjected to fresh oxidant and stirred under standard reaction conditions. The catalyst-free reaction produced <5% cyclooctene oxide after 12 h which is consistent with preliminary control experiments (Table S1, entry 16).

Fig. 2 shows the FT-IR spectra of fresh catalyst (Fig. 2a and Fig. S2), after treatment with H_2O_2 (Fig. 2b and Fig. S12), and the recycled catalyst (Fig. 2c and Fig. S13). No vibrational changes were observed after recycling, indicating good stability of the catalyst (see also Fig. S14 for FT-IR spectra of catalyst after second recycling). There were also no noticeable changes in the UV-Vis (Fig. S15), XRD pattern (Fig. S4, S16) as well as magnetic hysteresis curves (Fig. S7 and S17) of $\{Mo_{72}Cr_{30}\}$, which further reveals that the reaction had no effect on the structure and properties of catalyst. These results suggest that contrary to $\{Mo_{132}\}$, [17,20 and Fig. S1] $\{Mo_{72}Cr_{30}\}$ rather than the products of its destruction acts as an active catalyst in the oxidation process.

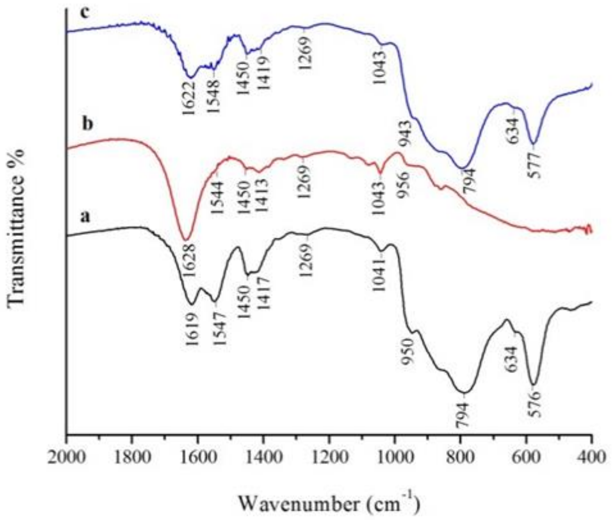
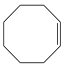
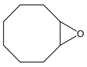
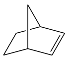
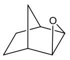
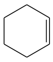
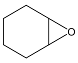
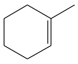
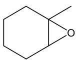
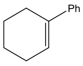
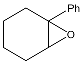
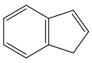
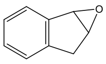
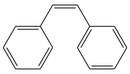
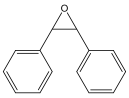
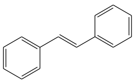
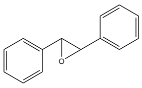
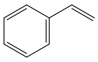
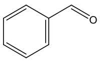
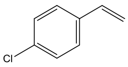
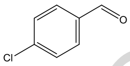
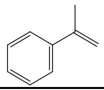
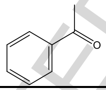


Fig. 2. FT-IR spectra of fresh catalyst (a), after the reaction with H_2O_2 (b), and the recycled catalyst (c).

Under optimized conditions, different olefins subjected to the oxidation procedure under catalytic influence of $\{Mo_{72}Cr_{30}\}$ (Table 1). Cyclohexene and norbornene were also oxidized completely within 45 min and pertinent epoxides were isolated in high yields (Table 1, entries 2,3) and no allylic oxidation by-product was observed. Hindered olefins such as 1-substituted cyclohexenes (Table 1, entries 4 and 5) displayed less reactivity than that of non-substituted molecule. Moreover, indene (Table 1, entry 6) required longer reaction time for its oxidation. An interesting aspect of title methodology that needs to be highlighted is absolute stereospecificity in the oxidation of cis- and trans-stilbenes as well as norbornene.

Despite the desired epoxide selectivity obtained in the oxidation of the above mentioned olefins, terminal C=C bond conjugated with phenyl rings gave mainly the related carbonyl compounds (Table 1, entries 10-12). Ring-opening reactions occurred at high temperature which supply high energy to break the C=C bond.[32]

Table 1. Hydrogen peroxide olefin oxidation catalyzed by $\{Mo_{72}Cr_{30}\}$ nanocluster in ethanol[a]

Entry	Olefin	Product	Yield%[b]	Time/min
1			96	45
2			91	45
3			97	45
4			75	60
5			36	120
6			80	90
8			94	180
9			69	180
10			88	45
11			85	45
12			72	45

[a]The reactions were run under air at 70 °C using 1.5 equiv. H_2O_2 in the presence of $\{Mo_{72}Cr_{30}\}$(0.4 mol%).[b] The products were identified by comparison with authentic samples. The selectivity of products were >99% except for entry 10 and 11 which were 93% and 95% (5-7% styrene oxides). Yields and selectivity were determined by GC-FID except for entries 2, 8 and 9 which did by ^1H NMR analysis.

In conclusion, $\{Mo_{72}Cr_{30}\}$ nanocluster was used successfully as a phase-transfer catalyst for olefin epoxidation with hydrogen peroxide in ethanol. The polyoxometalate acts as a homogeneous catalyst while it can be easily filtered and reused like a heterogeneous catalyst. The reactions proceeded with high selectivity for production of epoxides or carbonyl compounds. The use of ethanol as a safe solvent, H_2O_2 as an eco-friendly oxidant in combination with $\{Mo_{72}Cr_{30}\}$ as an easily recyclable catalyst offer a novel sustainable oxidation protocol. The spectral data revealed that the catalyst preserved its integrity make it appropriate for industrial application.

Acknowledgement

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Supporting Information

The procedure for the synthesis of catalyst and epoxidation of olefins, characterization of as-prepared and reused catalyst including FT-IR, Raman, UV-Vis, XRD, TGA, EDS, magnetic hysteresis curves and recycling results “This material is available free of charge via the Internet at http://....”

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Note: The synthesis procedure of {$Mo_{72}Cr_{30}$} is very tricky and two green solids may be produced under controlled conditions. After mixing $CrCl_3.6H_2O$ with sodium molybdate in 35% water/acetic acid mixture, the solution is acidified using HCl. Then the solution needs to be heated under reflux and left to cool at room temperature. After that we need to keep watching the solution if there areany small “pale” green crystals grow! (having a similar IR spectrum to the final product). The amount is very tiny (<1%) and need to FILTER THEM RIGHT AWAY. The “pale” green crystals are soluble in water. Nevertheless, if the solutions kept for a longer time (5 or more days), those “pale” green crystals grow gradually and the resulting “dark” green crystals (in desired yield) will not be soluble in water, ethanol, ethyl acetate, dichloroethane, chloroform and dichloromethane. It is only solved slightly in methanol under sonication at higher temperature (>40 ^oC) (see supporting information for complete characterization of as-prepared “dark” green {$Mo_{72}Cr_{30}$}).

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Research Highlight

- Phase-transfer catalytic activity of $\{Mo_{72}Cr_{30}\}$ Keplerate polyoxometalate
- The high catalytic activity and selectivity as well as durability of catalyst
- Acting as a homogeneous catalyst and reusing like a heterogeneous one