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{Mo₁₃₂} Nanoball as an Efficient and Cost-Effective Catalyst for Sustainable Oxidation of Sulfides and Olefins with Hydrogen Peroxide

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S Supporting Information

ABSTRACT: Atom-efficient and selective oxidation of sulfides to sulfoxides and sulfones in water and epoxidation of olefins in ethanol with hydrogen peroxide catalyzed by Keplerate nanoball polyoxomolybdate {Mo₁₃₂} under heterogeneous conditions are reported. The reaction yield and selectivity was affected crucially by catalyst concentration. A structurally diverse set of sulfides and olefins were transformed into desired oxidation products regardless of the electronic nature of the substituents. In spite of the heterogeneous reaction mixtures throughout the work, no difficulties with reaction progress were noted. Products were isolated easily from green media, and the catalyst could be reused several times without any appreciable decrease in catalytic activity and selectivity. Accelerated reactions under ultrasonic irradiation did not change the selectivity of the oxidation products.

KEYWORDS: Sustainable catalytic oxidations, Keplerate nanoball polyoxomolybdate, Oxidation, Hydrogen peroxide, Water



INTRODUCTION

Selective oxyfunctionalization of organic compounds is a pivotal reaction in many organic syntheses of biologically active molecules such as sulfoxides, sulfones, and epoxides.¹ The long-standing interest in the sulfoxidation of organic sulfides is primarily fueled by its utility in diverse areas of chemistry originating from the constant use of sulfoxides-derived chiral auxiliaries in total synthesis^{2–5} to its use in medicinal chemistry^{6–9} and biology¹⁰ to its application in industrially important desulfurization processes.^{11–14} Moreover, over-oxidation of sulfoxides generates sulfone products that exhibit different biological activities and have been the subject of extensive investigation.^{15–20} Epoxides are also industrially important chemicals that are produced at scales ranging from millions of tons to a few grams per year. They are widely used as intermediates for several perfumery chemicals, plasticizers, and sweeteners.^{21,22}

In the area of oxidative transformations, an important issue is the replacement of stoichiometric procedures using classical toxic waste-producing oxidants with catalytic procedures using environmentally benign oxidants such as molecular oxygen and hydrogen peroxide, where their only “waste” product is water. Furthermore, a major challenge is to accomplish organic processes in nontoxic solvents, particularly in aqueous media.^{23–27} The catalytic oxidation with aqueous H₂O₂ is desirable from the stand points of green sustainable chemistry, and thus, many systems with homogeneous and heterogeneous catalysts have been reported.^{28–32} While acknowledging the

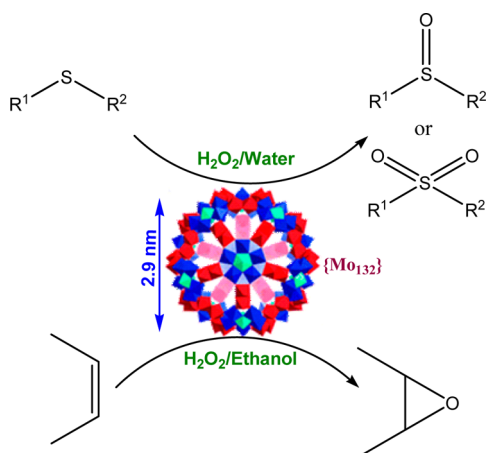
pioneering works, there are some disadvantages: the inability for selective oxidation of a variety of organic compounds, reactivity toward other oxidative functional groups, use of excess H₂O₂ (up to 8.0 equiv) with respect to substrates, lack of reusability of catalyst, use of organic solvents, and harsh reaction conditions.^{28–32} Thus, a practical oxidation method that is capable of selective production of different oxygen-containing compounds, namely, sulfoxides, sulfones, and epoxides, under mild green conditions and that is tolerant of other easily oxidized groups is needed in modern organic synthesis.

Recent progress in the synthesis of nanometer-scale polyoxometalate (POM) molecular clusters, especially polyoxomolybdates and polyoxotungstates with well-defined structures and potential applications in catalysis, electrochemistry, biomedicine, and magnetism as sensors, surfaces, and coatings, has successfully pushed the size of inorganic molecules to the nanometer scale and offered new opportunities in many different fields.^{33–37} Giant polyoxomolybdates, especially spherical ball-like clusters, are nanoscale architectures with more than 500 atoms and the highest Euclidean symmetry.^{38–41} They have gained significant interest as cation carriers, nanosponges, and for various other material science applications in the solid state.^{38,42–44} However, to the

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Scheme 1. Oxidation of Sulfides and Olefins Using H_2O_2 Catalyzed by a $\{\text{Mo}_{132}\}$ Nanoball



best of our knowledge, selective oxidation of thioanisole to the pertinent sulfoxide using H_2O_2 catalyzed by $\{\text{Mo}_{72}\text{Fe}_{30}\}$ cluster that is carried out in methanol is the only actual report on oxidation activity of Keplerate POM.⁴⁵ Just recently, we have discovered catalytic efficiency of the $(\text{NH}_4)_{42}[\text{Mo}_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$ “ $\{\text{Mo}_{132}\}$ ” nanoball in selective epoxidation of aqueous suspension of olefins under mild aerobic conditions.⁴⁶ However, no activity toward sulfides was observed, except for electron-rich allyl sulfides that led to sulfone products.⁴⁶ Now, in continuation of our ongoing research on the development of novel catalytic methods for oxidation of organic compounds in green media,^{47–56} we describe the catalytic activity and selectivity of the easily prepared $\{\text{Mo}_{132}\}$ nanoball, in the heterogeneous oxidation of aqueous suspension of organic sulfides to both sulfoxides and sulfones using 30% H_2O_2 under mechanical stirring (MS) and ultrasonic irradiation (US) conditions (Scheme 1). The heterogeneous epoxidation of different olefins also successfully occurred in ethanol in the presence of the solid nanocatalyst $\{\text{Mo}_{132}\}$. The catalyst was reused in the procedure efficiently many times.

EXPERIMENTAL SECTION

Remarks. Conversion and yields of the products were accomplished by GC-FID on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 μm coating) capillary column using toluene as the internal standard. IR spectra were recorded on a Perkin-Elmer 780 instrument. UV–vis spectra were recorded on a Shimadzu UV-2501pc spectrophotometer. ^1H NMR spectra were recorded with a Bruker Avance DPX FT-NMR 250 and 400 MHz instrument. TEM images were obtained by TEM instrumentation (Philips CM 10). X-ray diffraction (XRD, D8, Advance, Bruker, AXS) and TGA (Shimadzu 50) were employed for characterization of the catalyst.

Preparation of the $\{\text{Mo}_{132}\}$ Nanoball. The cluster was prepared according to the literature procedure.⁴¹ $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ (0.8 g, 6.1 mmol) was added to a solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (5.6 g, 4.5 mmol) and $\text{CH}_3\text{COONH}_4$ (12.5 g, 162.2 mmol) in H_2O (250 mL). The solution was then stirred for 10 min (color change to blue green), and 50% CH_3COOH (83.0 mL) was subsequently added. The reaction solution, now green, was stored in an open 500 mL Erlenmeyer flask at 20 $^\circ\text{C}$ without further stirring (fume hood; slow color change to dark brown). After 4 days, the precipitated red-brown crystals of $\{\text{Mo}_{132}\}$ were filtered off over a glass frit (D2), washed with 90% ethanol, ethanol, and diethyl ether, and finally dried in air. Yield: 3.3 g (52% based on molybdate). The Raman (Figure S1, Supporting Information),⁴¹ FT-IR (Figure S2, Supporting Information),⁴¹ UV–vis

spectra (Figure S3, Supporting Information),⁴¹ XRD, (Figure S4, Supporting Information),⁵⁷ and TG analysis (Figure S5, Supporting Information)⁵⁷ confirmed well the structure of prepared $\{\text{Mo}_{132}\}$. TEM images of $\{\text{Mo}_{132}\}$ in ethanol showed ball morphology with the size ranging between 5 and 25 nm (Figure S6, Supporting Information).

General Procedure for Oxidation of Sulfides. To a 1.0 mL aqueous suspension of sulfides (1.0 M) containing 0.1 μmol $\{\text{Mo}_{132}\}$ (1.4 mg) for sulfoxide formation (and 2 μmol , 28.6 mg, for sulfone formation) was added hydrogen peroxide (2.0 mmol 30%, 200 μL), and the reaction mixture was stirred under air at 25 $^\circ\text{C}$ with a magnetic stirrer bar or under US irradiation with a power of 100 W for the required time (Table 2). The reaction progress was monitored by TLC, and the yield of products was determined by GC analysis using toluene as the internal standard. After completion of the reaction ethyl acetate, 3 \times 2 mL was added, and the organic phase was extracted followed by evaporation of solvent. Higher purification of products was achieved by chromatography over silica gel (eluent: n-hexane/ethyl acetate 70:30 for sulfoxides isolation and 90:10 for sulfones isolation). An aqueous solution of $\{\text{Mo}_{132}\}$ was used for the next runs without any purification. Identification of products was made by their ^1H NMR spectra.

General Procedure for Epoxidation of Olefins. A mixture of olefins (1.0 mmol), hydrogen peroxide (2.0 mmol 30%, 200 μL), and $\{\text{Mo}_{132}\}$ (2 μmol , 28.6 mg) in 2.0 mL ethanol was stirred with a magnetic stirrer bar or under US irradiation with a power of 100 W under air at 75 $^\circ\text{C}$ for the required time (Table 3). The reaction progress was monitored by TLC and GC, and the yield of products was determined by GC analysis using toluene as the internal standard. After completion of the reaction, the solid catalyst was isolated by filtration and washed with hot ethanol and used for the next runs. Evaporation of ethanol gave the desired epoxides. Higher purification of products was achieved by chromatography over silica gel (eluent: n-hexane/ethyl acetate 80:20). Identification of products was made by their ^1H NMR spectra.

Note: A UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe that was immersed directly into the reaction mixture was used for sonication.

RESULTS AND DISCUSSION

Catalytic Oxidation of Sulfides. Initially, oxidation of thioanisole was selected as a model reaction, and water was used as a standard “green” solvent. Knowing that molecular oxygen is unable to oxidize the sulfides in the presence of $\{\text{Mo}_{132}\}$,⁴⁶ H_2O_2 was used as oxidant, which did not show any activity in the absence of a catalyst under mild conditions. Our results showed that the reaction yield and selectivity was affected crucially by the catalyst concentration (Figure 1). Methyl phenyl sulfoxide was achieved with excellent yield and selectivity, with 2.0 equiv. of H_2O_2 using 0.01 mol % catalyst within 45 min (procedure A). With catalyst concentration increasing, sulfone selectivity increased significantly and reached its maximum at 0.2 mol %, readily making a new procedure for easy access to the sulfone product with no need for more oxidant and temperature (procedure B). Thus, under mild conditions, both sulfoxide and sulfone products could be secured quantitatively from aqueous media in the desired time (45 min) using a few minutes for the catalyst to demonstrate high atom efficiency of the title nanopolyoxomolybdate (Figure 2). It should be noted that when the catalyst was replaced by MoO_3 , $\text{Na}_2\text{MoO}_4\cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as simple salts of Mo(VI), no oxidation product was observed selectively even at longer reaction times up to 24 h.

The effect of the amount of H_2O_2 used on the conversion and product selectivity was studied at various H_2O_2 /substrate molar ratios in the presence of 0.01 and 0.2 mol % catalyst

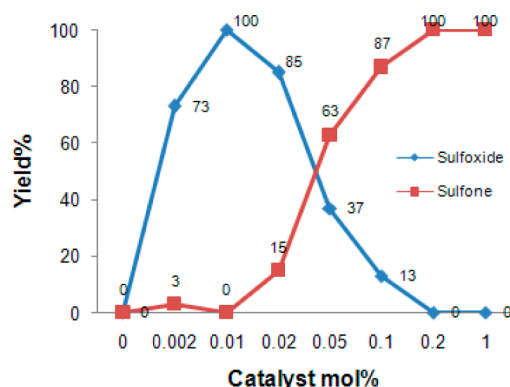


Figure 1. Screening of $\{\text{Mo}_{132}\}$ concentration on the oxidation of thioanisole using H_2O_2 in water. The reactions were run for 45 min under air at 25 °C using 2.0 equiv. of H_2O_2 . Yields determined by GC.

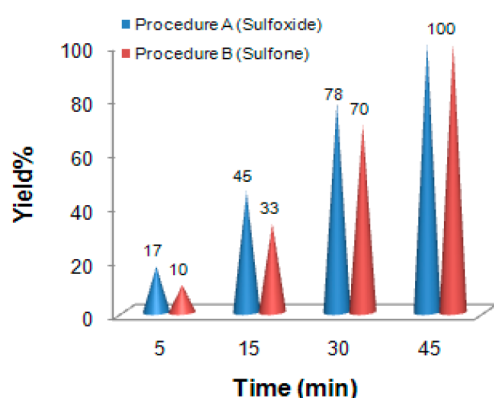


Figure 2. Time course of oxidation products of thioanisole in water at 25 °C using 2.0 equiv. of H_2O_2 under magnetic stirring catalyzed by $\{\text{Mo}_{132}\}$ (0.01 mol %, procedure A; 0.2 mol %, procedure B). Yields determined by GC.

(Table 1). The selectivity pattern changed with varying amounts of H_2O_2 in the oxidation of thioanisole. With 2.0 equiv. of H_2O_2 , desired yields and selectivity of sulfoxide (procedure A) and sulfone (procedure B) were achieved. Nevertheless, a further increase in this ratio reduced significantly the conversion and/or selectivity of the reaction products.

Because the structure of POMs is pH dependent,⁵⁸ the oxidation of thioanisole was run at different pH values. When, pH value was adjusted to less than or equal to 8, exactly the same conversions and selectivity were obtained. Nevertheless, a further increase in the pH reduced significantly both the

Table 1. Effect of Varying H_2O_2 Amount on Oxidation of Thioanisole Catalyzed by $\{\text{Mo}_{132}\}$ in Water^a

H_2O_2 (mmol)	procedure A (0.01 mol % catalyst)		procedure B (0.2 mol % catalyst)	
	sulfoxide % ^b	sulfone % ^b	sulfoxide % ^b	sulfone % ^b
1.5	42	0	33	27
2	100	0	0	100
2.5	70	10	0	95
3	48	17	0	67
3.5	30	22	0	35

^aReactions were run under air at 25 °C for 45 min using 1.0 mmol thioanisole. ^bGC yields based on the toluene as the internal standard.

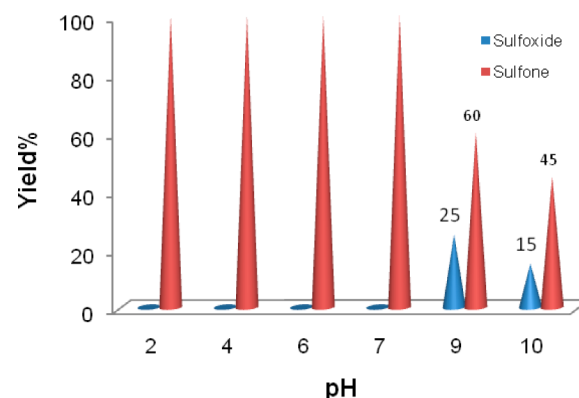


Figure 3. Screening of pH in the aqueous oxidation of thioanisole using 2.0 equiv. of H_2O_2 catalyzed by 0.2 mol % $\{\text{Mo}_{132}\}$ at 25 °C after 45 min according to procedure B. Yields determined by GC.

conversion and selectivity (Figure 3) because the $\{\text{Mo}_{132}\}$ cluster becomes less stable with the consequence that they are broken as established by a UV–vis study.^{46,58}

The use of ultrasound irradiation (US) to accelerate reactions has proven to be a particularly important tool for meeting the green chemistry goals of minimization of waste and reduction of energy requirements.⁵⁹ It was found that the ultrasonic irradiation with a 100 W power accelerated the oxidation of thioanisole to achieve the same conversion and selectivity within 15 min (Figure 4). Improved dispersion of the catalyst as well as organic droplets by sonication can be a good reason for enhancing the reaction rate in the title heterogeneous system. However, thorough mixing of the reactants and the production of hot spots by ultrasonic irradiation should also be taken into account.⁵⁹

Seeking to expand the scope of methodology, different sulfides were subjected to the reaction system in the presence of H_2O_2 under both magnetic stirring and ultrasonic irradiation (Table 2). A structurally diverse set of phenyl alkyl-sulfides, phenyl benzyl-sulfides, dialkyl-sulfides, unsaturated, and hydroxylated alkyl sulfides were transformed into sulfoxides and sulfones regardless of the aggregate state and electronic nature of the substituents. All substrates could be smoothly converted to sulfoxides (procedure A) and sulfones (procedure B) with good to high conversion rates, and excellent selectivities were obtained under mild conditions with both mechanical stirring and ultrasonic irradiation. Sulfoxides could be nearly stoichiometrically produced, and the generation of the corresponding sulfones was well controlled, which makes this process a good alternative for sulfoxide production. Moreover, as mentioned above, the increase in molar ratio of the catalyst/sulfide readily produced a new procedure for easy access to sulfone products with high and excellent yields using the same amount of H_2O_2 (procedure B). The methods possess a novelty regarding chemoselectivity. The $\text{C}=\text{C}$ double bond (entries 4,9) and hydroxyl group (entry 7) that are sensitive to oxidation remained completely intact under the influence of the catalyst, producing the pertinent sulfoxides and sulfones in high yields. In addition, benzyl phenyl sulfide (entry 6) was selectively oxidized to its corresponding sulfoxide and sulfone without formation of any benzylic oxidation byproducts. An additional advantage of this heterogeneous system is that at the end of the reactions, hydrophobic organic sulfoxides and sulfones were isolated easily by adding ethyl acetate as a safe solvent followed by evaporation.

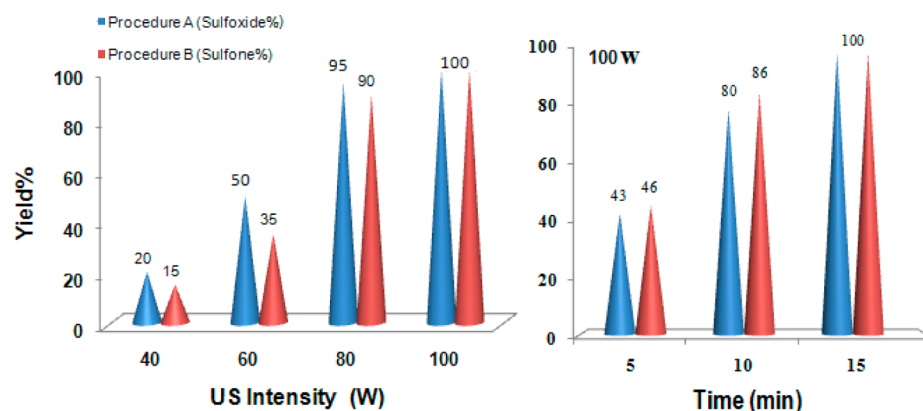


Figure 4. Screening of ultrasonic irradiation intensity (left, after 15 min) and time course of oxidation products under ultrasonic irradiation with a power of 100 W (right) in the oxidation of thioanisole in water at 25 °C using 2.0 equiv. of H₂O₂ catalyzed by {Mo₁₃₂} (0.01 mol %, procedure A; 0.2 mol %, procedure B). Yields determined by GC.

Table 2. Aqueous Oxidation of Sulfides Using H₂O₂ Catalyzed by {Mo₁₃₂}^a

Entry	Sulfide	Sulfoxide Yield% ^{b,c} (procedure A) Time/min (MS)[US]	Sulfone Yield% ^{b,c} (Procedure B) Time/min(MS)[US]
1		92-95 (45)[15]	84-89 (45)[15]
2		89-92 (45)[15]	92-94 (45)[15]
3		83-88 (45)[15]	87-92 (45)[15]
4		93-95 (45)[15]	94 (70)[25]
5		86 (60)[30]	80-85 (60)[20]
6		83-87 (45)[15]	95 (45)[15]
7		91-95 (90)[15]	94 (90)[15]
8		97 ^d (45)[15]	93-95 ^d (45)[15]
9		95 ^d (45) [15]	89-93 ^d (45)[15]

^aReactions were run under air at 25 °C using 2.0 equiv. of H₂O₂ in the presence of {Mo₁₃₂} (0.01 mol %, procedure A; 0.2 mol %, procedure B).

^bIsolated yield ranges of magnetic stirring (MS) and ultrasonic stirring (US). ^cSelectivity of products were >99% based on GC and ¹H NMR analyses. ^dGC yields were based on the toluene as internal standard.

Catalytic Epoxidation of Olefins. Promising results obtained from epoxidation activity of the {Mo₁₃₂} nanoball under mild aerobic conditions⁴⁶ induce us to evaluate its catalytic potential toward hydrogen peroxide. Cyclooctene, indene, and 1-octene were chosen as model olefins. No activity was observed for olefins in aqueous solution containing 2.0 equiv. of H₂O₂ and a 0.2 mol % {Mo₁₃₂} nanoball at ambient temperature even at long period of time. With increasing temperature up to 75 °C, cyclooctene converted 67% after 3 h; nevertheless, minor progresses in the oxidation of 1-octene (8%) and indene (12%) were observed. When, ethanol was added to the aqueous media at 25 °C, the reactions were triggered. For example, oxidation of indene in the water/ethanol mixture (1:1) produced 12%, 22%, 47%, and 66% of

indene oxide after 1.5, 2, 6, and 8 h, respectively. The conversion rate was enhanced with rising temperature up to 75 °C producing 28% and 43% yields of 1-octene oxide and indene oxide, respectively, after 3 h in the same media. Full conversion of title olefins was observed at the same time in neat ethanol making a heterogeneous system with a solid catalyst (Figure 5). Using this heterogeneous catalytic system, cyclooctene oxidation took only 30 min. The screening of the catalyst and oxidant amounts was also investigated. It was observed that the reaction required 0.2 mol % {Mo₁₃₂} to proceed with high performance. For example, 60% and 98% cyclooctene oxide were obtained using 0.1 and 0.2 mol % catalyst, respectively, after 30 min according to GC analysis (Figure S7, Supporting Information). Moreover, as illustrated in Figure 6, to complete

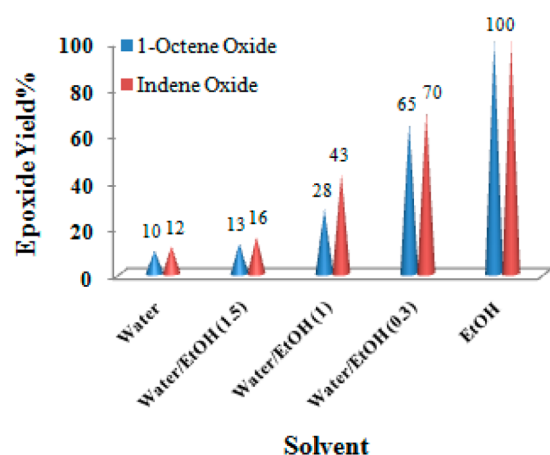


Figure 5. Effect of ethanol on the epoxidation of indene and 1-octene using 2.0 equiv. of 30% H_2O_2 catalyzed by 0.2 mol % $\{\text{Mo}_{132}\}$ at 75 °C after 3 h. Yields determined by GC.

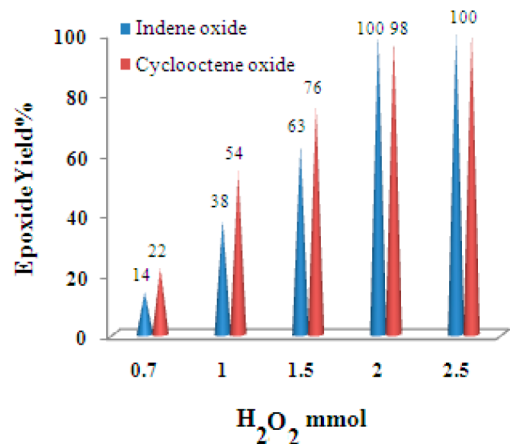


Figure 6. Screening of H_2O_2 amounts on the epoxidation of indene (1.0 mmol, after 3 h) and cyclooctene (1.0 mmol, after 30 min) using 30% H_2O_2 catalyzed by 0.2 mol % $\{\text{Mo}_{132}\}$ at 75 °C. Yields determined by GC.

the reaction at desired times, 2.0 equiv. of 30% H_2O_2 is adequate.

The influence of ultrasonic irradiation on the oxidation of indene was also investigated (Figure 7). With a sonication

power of 100 W, indene was consumed completely in less than 60 min, albeit with the same selectivity as demonstrated in sulfide oxidation.

Under optimized conditions, different olefins were subjected to oxidation procedures under both magnetic stirring and ultrasonic irradiation (Table 3). Cyclooctene, cyclohexenes, norbornene, and indene oxidized in desired times and pertinent epoxides were isolated in 89–95% yields after a simple filtration and evaporation. No allylic oxidation occurred in the oxidation of cyclohexenes. Moreover, the catalyst was able to oxidize electron-deficient 2-cyclohexene-1-one to the related epoxide in high yield (entry 14). The procedure presented excellent chemoselectivity. The hydroxyl group, which is sensitive to oxidation, remained completely intact under the influence of the catalyst producing the pertinent epoxides in desired yields (entries 11–13). To confirm our claim, a competitive reaction between cyclooctene and benzyl alcohol was run. After 2h, cyclooctene oxide was obtained quantitatively as the only product.

The stereoselectivity of the method was also noteworthy. Norbornene oxide formed exclusively as an *exo*-isomer. Moreover, epoxidation of *cis*- and *trans*-olefins proceeded with absolute stereospecificity (entries 8, 15, 16). However, 1-octen-3-ol (entry 12) gave an equal yield of diastereoisomers of *erythro*- and *threo*-1,2-epoxy-3-octanol (50:50 ratio).⁴⁶ The reaction also proceeded smoothly with 1-octene (entry 10), a less reactive terminal olefin, and 92% of the corresponding epoxide was secured as the only product. It should be noted that hindered olefins such as 1-phenyl cyclohexene and *trans*- β -methyl styrene as well as stilbenes (entries 4, 8, 15, 16) displayed poor reactivity, demonstrating the steric hindrance around the active site of catalyst. In addition, *cis*-stilbene reacted faster than that of the corresponding *trans*-olefin as observed under aerobic conditions.⁴⁶ The reactions also proceeded well under Ar atmosphere. Moreover, by the presence of radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol (BHT), no noticeable change in the conversion and selectivity of oxygenation of cyclooctene was observed. For example, cyclooctene oxide appeared in 92% yield (GC) as the sole product within 30 min using 0.2 mol % catalyst in the presence of greater than 5 equiv. of BHT. These results rule out a radical pathway for the present system to a high extent, although some contribution of free radicals could exist.

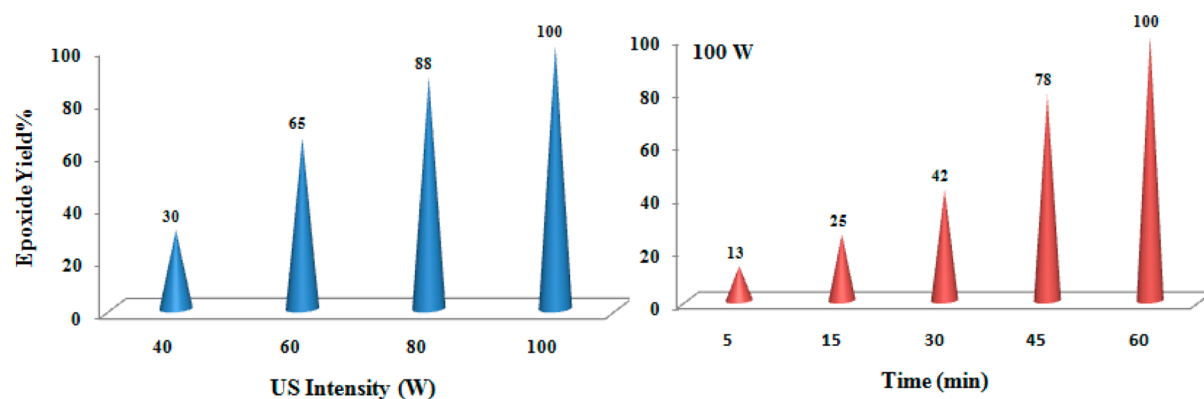


































Figure 7. Screening of ultrasonic irradiation intensity (left, after 60 min) and time course of epoxide formation under ultrasonic irradiation with a power of 100 W (right) in the epoxidation of indene in ethanol at 75 °C using 2.0 equiv. of H_2O_2 catalyzed by 0.2 mol % $\{\text{Mo}_{132}\}$. Yields determined by GC.

Table 3. Olefin Oxidation with 30% H₂O₂ in Ethanol Catalyzed by {Mo₁₃₂}^a

Entry	Substrate	Product	Yield% ^{b,c}	Time/min, MS (US)
1			90-94	30 (15)
2			89-93	150 (45)
3			83-88	150 (45)
4			40-43	150 (45)
5			92	90 (30)
6			93	30 (15)
7			85-91	60 (30)
8			39-47	150 (30)
9			89-93	120 (60)
10			90-93	120 (90)
11			89-92	150 (60)
12			<i>erythro</i> 39-53 ^d <i>threo</i> 38-48 ^d	150 (30)
13			90-94	150 (90)
14			80-83	150 (90)
15			50-52	5h (3h)
16			11-27	5h (3h)

^aReactions were run under air at 75 °C using 2.0 equiv. of 30% H₂O₂ in the presence of {Mo₁₃₂} (0.2 mol %). ^bIsolated yield ranges of magnetic stirring (MS) and ultrasonic stirring (US). ^cSelectivity of products were >98% based on GC and ¹H NMR (entries 5, 12, 15, and 16) analysis, except for entry 12, which gave a mixture of diastereoisomers. ^d¹H NMR yields.

Contrary to other olefins, a terminal C=C bond conjugated with phenyl rings solely gave the related carbonyl compounds, indicating that the epoxide ring-opening reactions occurred at high temperature, which supply high energy to break the C=C bond.^{60,61} It should be noted that ultrasonic irradiation that reduced the reaction times to even less than half in some cases did not change the selectivity of olefin oxidation.

Catalyst Activity. The good to high yields of oxidation products obtained by this catalytic system for both sulfide and olefin oxidation indicates the high catalytic efficiency of the title nanocatalyst. More evidence for such an activity was obtained by determining of the turnover numbers of {Mo₁₃₂} in aqueous media. The turnover numbers of 4500 and 2500 per hour (TOF) were achieved for thioanisole and diphenyl sulfide, respectively, using a 25,000:50,000:1 molar ratio for sulfide/H₂O₂/catalyst under agitation with magnetic stirring. After 24 h, these numbers increased to 16,500 and 10,500, respectively. Thioanisole and aqueous H₂O₂ form two separable phases at 25

°C, but the reaction took place surprisingly well. This can be rationalized in terms of the reaction conditions as a heterogeneous suspension of organic droplets in water (“on water”).^{62–68} However, the excellent dispersity of the {Mo₁₃₂}-type cluster in an aqueous solution, particularly under US irradiation, generating discrete single-molecular clusters should be taken into account for such an activity.⁶⁹ The additional advantage of the reported nanocatalyst relates to a simple and safe procedure for its preparation. The possibility to use water as a standard “green” solvent for preparation of a catalyst as well as a reaction medium is a salient feature especially due to the very low solubility of organic compounds in water providing easy separation of products. After isolation of hydrophobic organic sulfoxides and sulfones by ethyl acetate at the end of the reactions, an aqueous solution of the catalyst was reused directly for the next round of reactions without further purification. In other procedures, the solid catalyst in the epoxidation reactions in ethanol could also be isolated

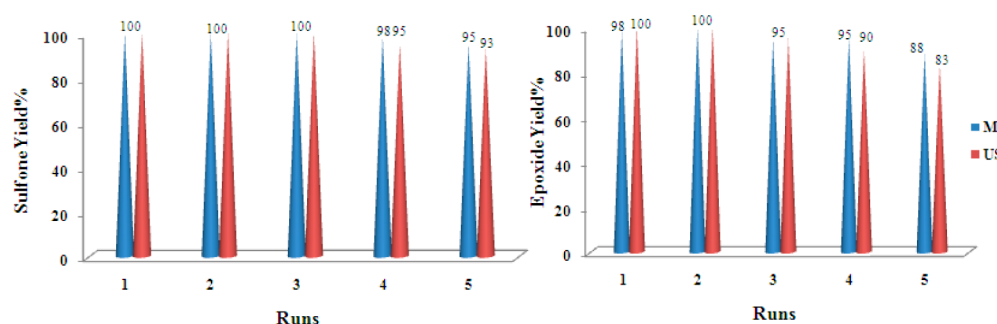


Figure 8. Recycling of the catalytic system for thioanisole (left) and cyclooctene (right) oxidation using 2.0 equiv. of H_2O_2 and 0.2 mol % $\{\text{Mo}_{132}\}$ under magnetic stirring (MS) and ultrasonic stirring (US) according to the procedures mentioned in Tables 2 and 3. Yields determined by GC.

easily by simple filtration and reused in the next runs after washing with ethanol and ethyl acetate. The nanocatalyst could be reused at least five times without any significant loss of initial catalytic activity (Figure 8). After the fifth run, the yield of methyl phenyl sulfone (procedure B, Table 2) and cyclooctene oxide (Table 3) were 93–95% and 83–88%, respectively, under both magnetic stirring and ultrasonic irradiation at the same times. Further works on different Keplerates using various oxidation systems are currently under investigation in our laboratory.

CONCLUSION

In this work, we used the easily prepared $\{\text{Mo}_{132}\}$ nanoball as an efficient nanocatalyst for environmentally friendly oxidation of various sulfides into both sulfoxides and sulfones at 25 °C in water and olefins to epoxides at 75 °C in ethanol using 30% H_2O_2 . The transformation worked well with both the liquid and solid sulfides in spite of a heterogeneous reaction mixture, and no difficulties with stirring were noted. Sulfides containing C=C, benzylic C–H, and C–OH bonds were selectively oxidized into their sulfoxides and sulfones. The epoxidation procedure also presented excellent chemoselectivity. The hydroxyl group remained completely intact under the influence of the catalyst producing the pertinent epoxides in desired yields. Notable stereoselectivity was observed for oxidation of norbornene as well as *cis*- and *trans*-olefins. No surfactants, additives, toxic reagents, or solvents and byproduct were involved, and no laborious purifications were necessary in most cases. In addition to the above-mentioned advantageous, the use of eco-friendly oxidant and solvents as well as easy and safe workup procedures and reusability of the catalyst are cost-effective, environmentally benign, and possess high generality, which makes title methodologies suitable for industrial goals.

ASSOCIATED CONTENT

Supporting Information

Raman, FT-IR, UV–vis spectra, XRD, TGA, and TEM images of prepared $\{\text{Mo}_{132}\}$; GC trace for cyclooctene oxide analysis; and ^1H NMR spectra of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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ABBREVIATIONS

$\{\text{Mo}_{132}\}$, $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$

REFERENCES

- (1) Backvall, J. E. *Modern Oxidation Methods*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2010.
- (2) Garcia Ruano, J. L.; Fernandez-Ibanez, M. A.; Fernandez-Salas, J. A.; Maestro, M. C.; arquez-Lopez, P. M.; Rodriguez-Fernandez, M. M. Remote stereocontrol mediated by a sulfinyl group: Synthesis of allylic alcohols via chemoselective and diastereoselective reduction of γ -methylene δ -ketosulfoxides. *J. Org. Chem.* **2009**, *74*, 1200–1204.
- (3) Fernandez de la Pradilla, R.; Castellanos, A.; Osante, I.; Colomer, I.; Sanchez, M. I. Highly diastereoselective Katsuki–Jacobsen oxidation–epoxidation of α -silyloxy sulfinyl dienes: Synthetic applications. *J. Org. Chem.* **2009**, *74*, 170–181.
- (4) Fernandez de la Pradilla, R.; Lwoff, N.; del Aguila, M. A.; Tortosa, M.; Viso, A. [2,3]-Sigmatropic rearrangements of 3-sulfinyl dihydropyrans: Application to the syntheses of the cores of *ent*-dysiherbaine and deoxymalayamicin A. *J. Org. Chem.* **2008**, *73*, 8929–8941.
- (5) Pellissier, H. Use of chiral sulfoxides in asymmetric synthesis. *Tetrahedron* **2006**, *62*, 5559–5601.
- (6) Legros, J.; Dehliand, J. R.; Bolm, C. Applications of catalytic asymmetric sulfide oxidations to the syntheses of biologically active sulfoxides. *Adv. Synth. Catal.* **2005**, *347*, 19–31.
- (7) Shin, J. M.; Choand, Y. M.; Sachs, G. Chemistry of covalent inhibition of the gastric (H^+ , K^+)-ATPase by proton pump inhibitors. *J. Am. Chem. Soc.* **2004**, *126*, 7800–7811.
- (8) Cotton, H.; Elebring, T.; Larsson, M.; Li, L.; Sorenson, H.; Unge, S. V. Asymmetric synthesis of esomeprazole. *Tetrahedron: Asymmetry* **2000**, *11*, 3819–3825.
- (9) Padmanabhan, S.; Lavinand, R. C.; Durrant, G. J. Asymmetric synthesis of a neuroprotective and orally active *N*-methyl-D-aspartate receptor ion-channel blocker, CNS 5788. *Tetrahedron: Asymmetry* **2000**, *11*, 3455–3457.
- (10) Bently, R. Role of sulfur chirality in the chemical processes of biology. *Chem. Soc. Rev.* **2005**, *34*, 609–624.
- (11) Li, C.; Jiang, Z.; Gao, J.; Yang, Y.; Wang, S.; Tian, F.; Sun, F.; Sun, X.; Ying, P.; Han, C. Ultra-deep desulfurization of diesel: Oxidation with a recoverable catalyst assembled in emulsion. *Chem.—Eur. J.* **2004**, *10*, 2277–2280.
- (12) Figueras, F.; Palomeque, J.; Lorient, S.; Feche, C.; Essayem, N.; Gelbard, G. Influence of the coordination on the catalytic properties of supported W catalysts. *J. Catal.* **2004**, *226*, 25–31.

- (13) Palomeque, J.; Clacens, J.-M.; Figueras, F. Oxidation of dibenzothiophene by hydrogen peroxide catalyzed by solid bases. *J. Catal.* **2002**, *211*, 103–108.
- (14) Hulea, V.; Fajula, F.; Bousquet, J. Mild oxidation with H_2O_2 over Ti-containing molecular sieves—A very efficient method for removing aromatic sulfur compounds from fuels. *J. Catal.* **2001**, *198*, 179–186.
- (15) Nielsen, M.; Jacobsen, C. B.; Holub, N.; Paixão, M. W.; Jørgensen, K. A. Asymmetric organocatalysis with sulfones. *Angew. Chem., Int. Ed.* **2010**, *49*, 2668–2679.
- (16) Alba, A.-N. R.; Companyó, X.; Rios, R. Sulfones: New reagents in organocatalysis. *Chem. Soc. Rev.* **2010**, *39*, 2018–2033.
- (17) Shyshkina, O. O.; Popov, K. S.; Gordivska, O. O.; Tkachuk, T. M.; Kovalenko, N. V.; Volovenko, T. A.; Volovenko, Yu. M. Synthesis and chemical properties of cyclic β -keto sulfones. *Chem. Heterocycl. Compd.* **2011**, *47*, 923–945.
- (18) Ettari, R.; Bonaccorso, C.; Micale, N.; Heindl, C.; Schirmeister, T.; Calabrò, M. L.; Zappalà, M. Development of novel peptidomimetics containing a vinyl sulfone moiety as proteasome inhibitors. *Chem. Med. Chem.* **2011**, *6*, 1228–1237.
- (19) Newton, A. S.; Glória, P. M. C.; Gonçalves, L. M. D.; dos, J.; Santos, V. A.; Moreira, R.; Guedes, R. C.; Santos, M. M. Synthesis and evaluation of vinyl sulfones as caspase-3 inhibitors. A structure–activity study. *Eur. J. Med. Chem.* **2010**, *45*, 3858–3863.
- (20) Harrak, Y.; Casula, G.; Basset, J.; Rosell, G.; Plescia, S.; Raffa, D.; Cusimano, M. G.; Pouplana, R.; Pujol, M. D. Synthesis, anti-inflammatory activity, and in vitro antitumor effect of a novel class of cyclooxygenase inhibitors: 4-(Aryloyl)phenyl methyl sulfones. *J. Med. Chem.* **2010**, *53*, 6560–6571.
- (21) Yudin, A. K. *Aziridines and Epoxides in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2006.
- (22) Sienel, G.; Rieth, R.; Rowbottom, K. T. *Ullmann's Encyclopedia of Organic Chemicals*; Wiley-VCH: Weinheim, Germany, 1999.
- (23) Dixneuf, P.; Cadierno, V. *Metal-Catalyzed Reactions in Water*; Wiley-VCH, Weinheim, Germany, 2013.
- (24) Ballini, R. *Eco-Friendly Synthesis of Fine Chemicals*, RSC Publishing: London, 2009.
- (25) Lindstrom, U. M. *Organic Reactions in Water: Principles, Strategies and Applications*; Wiley-VCH: Weinheim, Germany, 2007.
- (26) Sheldon, R.; Arends, A.; Hanefeld, I. U. *Green Chemistry and Catalysis*; Wiley-VCH: Weinheim, Germany, 2007.
- (27) Mikami, K. *Green Reaction Media in Organic Synthesis*; Blackwell: Oxford, U.K., 2005.
- (28) Amini, M.; Haghdoost, M. M. Oxido-peroxido molybdenum(VI) complexes in catalytic and stoichiometric oxidations. *Coord. Chem. Rev.* **2013**, *257*, 1093–1121.
- (29) Mizuno, N.; Kamata, K. Metal-catalyzed asymmetric sulfoxidation, epoxidation and hydroxylation by hydrogen peroxide. *Coord. Chem. Rev.* **2013**, *257*, 3030–3050.
- (30) Evgenii, P.; Talsi, K.; Bryliakov, P. Chemo- and stereoselective CH oxidations and epoxidations/cis-dihydroxylations with H_2O_2 , catalyzed by non-heme iron and manganese complexes. *Coord. Chem. Rev.* **2012**, *256*, 1418–1434.
- (31) Faveri, G. D.; Ilyashenko, G.; Watkinson, M. Recent advances in catalytic asymmetric epoxidation using the environmentally benign oxidant hydrogen peroxide and its derivatives. *Chem. Soc. Rev.* **2011**, *40*, 1722–1760.
- (32) Noritaka, M.; Keigo, K. Catalytic oxidation of hydrocarbons with hydrogen peroxide by vanadium-based polyoxometalates. *Coord. Chem. Rev.* **2011**, *255*, 2358–2370.
- (33) Winter, R. S.; Yan, J.; Busche, C.; Mathieson, J. S.; Prescimone, A.; Brechin, E. k.; Long, D.-L.; Cronin, L. Nanoscale control of polyoxometalate assembly: A $\{Mn_8W_4\}$ cluster within a $\{W_{36}Si_4Mn_{10}\}$ cluster showing a new type of isomerism. *Chem.—Eur. J.* **2013**, *19*, 2976–2981.
- (34) Borrás-Almenar, J. J.; Coronado, E.; Müller, A.; Pope, M. T. *Polyoxometalate Molecular Science: From Biology to Nanotechnology*; Kluwer: Dordrecht, 2003.
- (35) Müller, A.; Henry, M. Nanocapsule Water-based Chemistry. *C. R. Chim.* **2003**, *6*, 1201–1208.
- (36) Casañ-Pastor, N.; Gómez-Romero, P. Polyoxometalates: From inorganic chemistry to materials science. *Front. Biosci.* **2004**, *9*, 1759–1770.
- (37) Lehn, J. M. *Supramolecular Chemistry*; Wiley-VCH, Weinheim, Germany, 1995.
- (38) Long, D.-L.; Tsunashima, R.; Cronin, L. Polyoxometalates: Building blocks for functional nanoscale systems. *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758.
- (39) Müller, A.; Das, S. K.; Krickemeyer, E.; Kuhlmann, C. *Inorganic Syntheses*; Wiley: New York, 2004, 34.
- (40) Müller, A.; Kögerler, P.; Dress, A. W. M. Giant metal-oxide-based spheres and their topology: From pentagonal building blocks to keplerates and unusual spin systems. *Coord. Chem. Rev.* **2001**, *222*, 193–218.
- (41) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtman, M.; Peters, F. Organizational forms of matter: An inorganic super fullerene and keplerate based on molybdenum oxide. *Angew. Chem., Int. Ed.* **1998**, *37*, 3359–3363.
- (42) Zhang, L.; Xiong, T.; Zhou, Y.; Zhang, L. En route to nanodevices of polyoxometalate: Incorporating the giant nanoporous molybdenum-oxide based wheels and balls into nanotubular arrays. *Chem. Asian J.* **2010**, *5*, 1984–1987.
- (43) Mishra, P. P.; Pigga, J.; Liu, T. Membranes based on “Keplerate”-type polyoxometalates: Slow, passive cation transportation and creation of water microenvironment. *J. Am. Chem. Soc.* **2008**, *130*, 1548–1549.
- (44) Kurth, D. G.; Lehmann, P.; Volkmer, D.; Müller, A.; Schwahn, D. Biologically inspired polyoxometalate-surfactant composite materials. Investigations on the structures of discrete, surfactant-encapsulated clusters, monolayers, and Langmuir–Blodgett films of $(DO-D A)_{(40)}(N H_4)_{(2)}[(H_2 O)_{(n)}]_{subset}$ of $Mo_{132}O_{372}(CH_3CO_2)_{(30)}(H_2O)_{(72)}$. *Dalton Trans.* **2000**, 3989–3998.
- (45) Izarova, N. V.; Kholdeeva, O. A.; Sokolov, M. N.; Fedina, V. P. Catalytic properties of the macromolecular polyoxomolybdate cluster in selective oxidation of sulfides. *Russ. Chem. Bull., Int. Ed.* **2009**, *58*, 134–137.
- (46) Rezaeifard, A.; Haddad, R.; Jafarpour, M.; Hakimi, M. Catalytic epoxidation activity of Keplerate polyoxomolybdate nanoball toward aqueous suspension of olefins under mild aerobic conditions. *J. Am. Chem. Soc.* **2013**, *135*, 10036–10039.
- (47) Rezaeifard, A.; Farshid, P.; Jafarpour, M.; Kardan Moghaddam, G. Silica-coated magnetite nanoparticles stabilized simple Mn-tetraphenylporphyrin for aqueous phase catalytic oxidations with tert-butyl hydroperoxide. *RSC Adv.* **2014**, *4*, 9189–9196.
- (48) Rezaeifard, A.; Jafarpour, M. Catalytic efficiency of Fe-porphyrins supported on multi-walled carbon nanotube in heterogeneous oxidation of hydrocarbons and sulfides in water. *Catal. Sci. Technol.* **2014**, DOI: 10.1039/C3CY00554B.
- (49) Jafarpour, M.; Ghahramaninezhad, M.; Rezaeifard, A. Catalytic activity and selectivity of reusable α - MoO_3 nanobelts toward oxidation of olefins and sulfides using economical peroxides. *RSC Adv.* **2014**, *4*, 1601–1608.
- (50) Rezaeifard, A.; Soltani, V.; Jafarpour, M. Nanoaggregates of simple Mn porphyrin complexes as catalysts for the selective oxidation of hydrocarbons. *Eur. J. Inorg. Chem.* **2013**, 2657–2664.
- (51) Rezaeifard, A.; Jafarpour, M.; Naeimi, A.; Salimi, M. Efficient and highly selective aqueous oxidation of alcohols and sulfides catalyzed by reusable hydrophobic copper (II) phthalocyanine. *Inorg. Chem. Commun.* **2012**, *15*, 230–234.
- (52) Rezaeifard, A.; Jafarpour, M.; Naeimi, A.; Mohammadi, K. Highly selective aqueous heterogeneous oxygenation of hydrocarbons catalyzed by recyclable hydrophobic copper (II) phthalocyanine nanoparticles. *J. Mol. Catal. A* **2012**, *357*, 141–147.
- (53) Rezaeifard, A.; Jafarpour, M.; Farshid, P.; Naeimi, A. Nanomagnet-supported partially brominated manganese–porphyrin as a promising catalyst for the selective heterogeneous oxidation of

hydrocarbons and sulfides in water. *Eur. J. Inorg. Chem.* **2012**, 5515–5524.

(54) Rezaeifard, A.; Jafarpour, M.; Naeimi, A.; Haddad, R. Aqueous heterogeneous oxygenation of hydrocarbons and sulfides catalyzed by recoverable magnetite nanoparticles coated with copper(II) phthalocyanine. *Green Chem.* **2012**, *14*, 3386–3394.

(55) Rezaeifard, A.; Jafarpour, M.; Naeimi, A.; Kaafi, S. A novel strategy for clean and selective oxygenation of hydrocarbons with *n*-Bu₄NHSO₅ in neat water catalyzed by recyclable water-insoluble iron (III) tetraphenylporphyrins. *Catal. Commun.* **2011**, *12*, 761–765.

(56) Rezaeifard, A.; Jafarpour, M.; Naeimi, A. A practical innovative method for highly selective oxidation of alcohols in neat water using water-insoluble iron and manganese porphyrins as reusable heterogeneous catalysts. *Catal. Commun.* **2011**, *16*, 240–244.

(57) Ostroushko, A. A.; Tonkushina, M. O.; Safronov, A. P.; Men'shikov, S. Yu.; Korotaev, V. Yu. Thermal behavior of polyoxometalate Mo₁₃₂. *Russ. J. Inorg. Chem.* **2009**, *54*, 172–179.

(58) Liu, T.; Imber, B.; Diemann, E.; Liu, G.; Cokleski, K.; Li, H.; Chen, Z.; Muller, A. Deprotonations and charges of well-defined {Mo₇₂Fe₃₀} nanoacids simply stepwise tuned by pH allow control/variation of related self-assembly processes. *J. Am. Chem. Soc.* **2006**, *128*, 15914–15920.

(59) Chen, D.; Sharma, S. K.; Modhoo, A., Eds.; *Handbook on Applications of Ultrasound: Sonochemistry for Sustainability*; CRC Press: Boca Raton, FL, 2012.

(60) Tyagi, B.; Sharma, U.; Jasra, R. V. Epoxidation of styrene with molecular oxygen over binary layered double hydroxide catalysts. *Appl. Catal., A* **2011**, *408*, 171–177.

(61) Meng, X.; Lin, K.; Sun, J.; Yang, M.; Jiang, D.; Xiao, F.-S. Catalytic epoxidation of styrene over copper hydroxyphosphate Cu₂(OH)PO₄. *Catal. Lett.* **2001**, *71*, 241–244.

(62) El-Batta, A.; Jiang, C.; Zhao, W.; Anness, R.; Cooksy, A. L.; Bergdahl, M. Wittig reactions in water media employing stabilized ylides with aldehydes. Synthesis of α,β -unsaturated esters from mixing aldehydes, α -bromoesters, and Ph₃P in aqueous NaHCO₃. *J. Org. Chem.* **2007**, *72*, 5244–5259.

(63) Gonzalez-Cruz, D.; Tejedo, D.; de Armas, P.; Garcia-Tellado, F. Dual reactivity pattern of allenolates “on water”: The chemical basis for efficient allenolate-driven organocatalytic systems. *Chem.—Eur. J.* **2007**, *13*, 4823–4832.

(64) Price, B. K.; Tour, J. M. Functionalization of single-walled carbon nanotubes “on water”. *J. Am. Chem. Soc.* **2006**, *128*, 12899–12904.

(65) (a) Narayan, S.; Muldoon, J.; Finn, M. G.; Fokin, V. V.; Kolb, H. C.; Sharpless, K. B. “On water”: Unique reactivity of organic compounds in aqueous suspension. *Angew. Chem.* **2005**, *117*, 3339–3343; (b) *Angew. Chem., Int. Ed.* **2005**, *44*, 3275–3279.

(66) Pirrung, M. C.; Sarma, K. D. Multicomponent reactions are accelerated in water. *J. Am. Chem. Soc.* **2004**, *126*, 444–445.

(67) Lubineau, A. Water-promoted organic reactions: Aldol reaction under neutral conditions. *J. Org. Chem.* **1986**, *51*, 2142–2144.

(68) Rideout, D. C.; Breslow, R. Hydrophobic acceleration of Diels–Alder reactions. *J. Am. Chem. Soc.* **1980**, *102*, 7816–7817.

(69) Roy, S.; Planken, K. L.; Kim, R.; Mandele, D. v. d.; Kegel, W. K. Direct evidence on the existence of [Mo₁₃₂] Keplerate-type species in aqueous solution. *Inorg. Chem.* **2007**, *46*, 8469–8471.