

other oxides seem to induce some amount of tensile stress.

The induced stresses with physical properties which are obtained depending on the type of coated oxides may be of practical importance. The effects of coatings on the magnetic properties play a similar role to those of magnetic field and/or stress annealing on the magnetic properties. Considering that the formation of induced anisotropy in the transverse direction by magnetic field annealing is known to be not easy and the resulting induced anisotropy energy is small in the case of Fe-based amorphous alloy,¹³ the inclination of the hysteresis loop by the sol-gel coating is particularly important. In applications such as choke cores of switching-mode power supply devices, constant permeability over a wide applied field is an important property, which may be achieved by inducing anisotropy in the transverse direction. A rough estimate shows that the energy of induced anisotropy achieved by the present sol-gel coating is about 100 J/m³. A magnetic field annealing of coated ribbons in the transverse direction is expected to increase the induced anisotropy energy further. Work in this direction is under way and will be published elsewhere.

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Catalytic Oxygenation of Alkenes and Alkanes by Oxygen Donors Catalyzed by Cobalt-Substituted Polyoxotungstate

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The cobalt-substituted polyoxotungstate [(CoPW₁₁O₃₉)⁵⁻] has been used as a catalyst in olefin epoxidation and alkane hydroxylation reactions. The epoxidation of olefins by iodobenzene in CH₃CN yielded epoxides predominantly with trace amounts of allylic oxidation products. *cis*-Stilbene was stereoselectively oxidized to *cis*-stilbene oxide with small amounts of *trans*-stilbene oxide and benzaldehyde formation. The epoxidation of carbamazepine (CBZ) by potassium monopersulfate in aqueous solution gave the corresponding CBZ 10,11-oxide product. Other transition metal-substituted polyoxotungstates (M = Mn²⁺, Fe²⁺, Ni²⁺, and Cu²⁺) were inactive in the CBZ epoxidation reaction. The cobalt-substituted polyoxotungstate also catalyzed the oxidation of alkanes with *m*-chloroperbenzoic acid to give the corresponding alcohols and ketones. The presence of CH₂Br₂ in the hydroxylation of cyclohexane afforded the formation of bromocyclohexane, suggesting the participation of cyclohexyl radical. In the ¹⁸O-labeled water experiment, there was no incorporation of ¹⁸O into the cyclohexanol product when the hydroxylation of cyclohexane by MCPBA was carried out in the presence of H₂¹⁸O. Some mechanistic aspects are discussed as well.

Introduction

The controlled and selective oxidation of hydrocarbons un-

der mild conditions has been a tantalizing challenge for chemists to develop new technologies for industrial applications.¹ Often-used catalysts for the oxidation reactions are transition

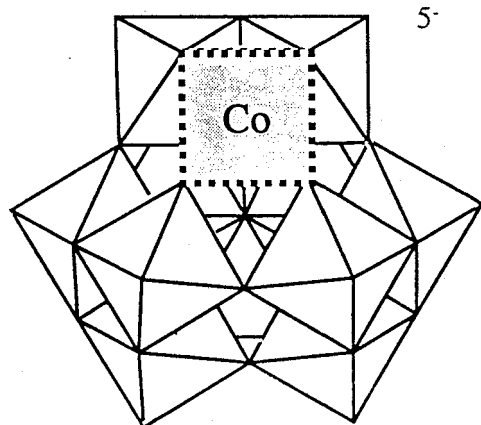


Figure 1. Structure of the cobalt-substituted polyoxotungstate.

metal complexes containing organic ligands such as porphyrins.² The metalloporphyrins show high initial activity under mild conditions and high selectivity; however, a problem often encountered is the irreversible deactivation of the catalytic species by the oxidation of the organic ligand. In order to solve the instability of the porphyrin ligand of the metalloporphyrins with respect to the ligand oxidations, intensive efforts have been put forward to stabilize the catalysts with respect to the oxidative degradation of the porphyrin ligands.³ Another approach to prepare effective catalysts was to synthesize oxidatively stable "inorganic porphyrin" analogues, the so called transition metal-substituted polyoxometalates.⁴

Since Hill *et al.* reported that transition metal-substituted Keggin anions are capable of catalyzing epoxidation of olefins by iodosylbenzene,⁵ various types of polyoxometalates have been studied in the oxidation reactions of organic substrates and a wide variety of oxidants such as iodosylbenzene,^{3(f),5} periodate,⁶ alkyl hydroperoxides,^{3(d),7} hydrogen peroxide,^{3(a),8} and molecular oxygen plus aldehyde⁹ have been utilized in the oxygen transfer reactions. It has been proved that the catalytic systems are remarkably effective and that the polyoxometalates are resistant to oxidative degradation. In this paper, we report the results of the epoxidation of alkenes and hydroxylation of alkanes by cobalt-substituted polyoxotungstate (Figure 1) with various kinds of oxidants such as iodosylbenzene, potassium monopersulfate, and *m*-chloroperbenzoic acid.

Results and Discussion

Epoxidation of Olefins by Iodosylbenzene Catalyzed by Cobalt-Substituted Polyoxotungstate. Epoxidation of olefins was carried out in CH₃CN solution at room temperature under an inert atmosphere. The results of the olefin epoxidations by [n-C₄H₉]₄N][H(CoPW₁₁O₃₀)] and Co(NO₃)₂ for comparison were listed in Table 1. In all of the reactions, epoxides were yielded predominantly with trace amounts of allylic oxidation products and the cobalt-substituted polyoxotungstate turned out to be a better catalyst than the cobalt salt in the epoxidation of olefins by iodosylbenzene, as previously reported by Hill *et al.*⁵

The reactivity of terminal olefin, *i.e.* 1-octene, judged by the yield of epoxide was inferior to that of internal olefin

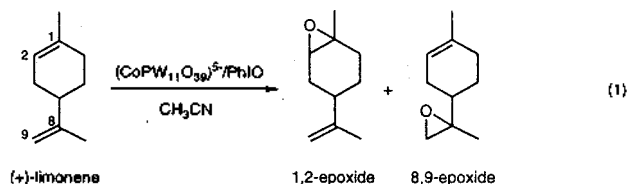
Table 1. Epoxidation of Olefins by Iodosylbenzene Catalyzed by [n-C₄H₉]₄N][H(CoPW₁₁O₃₀)] and Co(NO₃)₂^{a,b}

Substrate	Products	Yield (mM)	
		(CoPW ₁₁ O ₃₀) ⁵⁻	Co(NO ₃) ₂
cyclohexene	cyclohexene oxide	17 ^d	4
cyclooctene	cyclooctene oxide	37	9
1-octene	1,2-epoxyoctane	4	2
(+)-limonene	1,2-limonene oxide	29	7
	8,9-limonene oxide	1.7	1.6
<i>cis</i> -stilbene	<i>cis</i> -stilbene oxide	22	5.1
	<i>trans</i> -stilbene oxide	1.4	1.4
	benzaldehyde	2.5	1.8
<i>trans</i> -stilbene	<i>trans</i> -stilbene oxide	12	4.1
	benzaldehyde	1.6	2.9

^aSee experimental section for detailed experimental procedures.

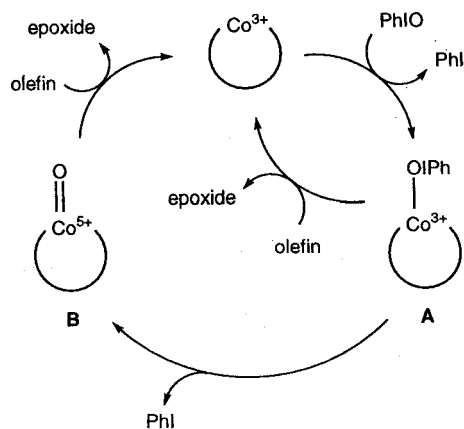
^bEpoxide was not formed in the absence of either the cobalt complex or PhIO. ^cOther oxidants such as H₂O₂ and *tert*-butyl hydroperoxide did not yield cyclohexene oxide. ^dTrace amounts of allylic oxidation products such as cyclohexenol and cyclohexenone were produced.

cyclohexene as was frequently observed in other epoxidation reactions. The regioselectivity of (+)-limonene epoxidation catalyzed by the cobalt complex has been examined in order to study the steric effect versus electronic effect (eq. 1).¹⁰



In the (+)-limonene epoxidation, the major product was the 1,2-epoxide derived from the oxidation of the more electron-rich double bond and the ratio of 1,2-epoxide to 8,9-epoxide products was 17. For comparison, a large preference for the oxidation at the 1,2-position has been observed in the Fe (TTP)Cl-PhIO system, giving a 1,2- to 8,9-oxides ratio of 19.¹¹ Suslick and Cook used sterically hindered metalloporphyrins in order to increase selectivity at the 8,9-position in the epoxidation of (+)-limonene.¹² In the *cis*- and *trans*-stilbene epoxidations, the predominant products were *cis*-stilbene oxide from *cis*-stilbene and *trans*-stilbene oxide from *trans*-stilbene, indicating that the epoxidation reaction is stereospecific. In other cobalt-mediated *cis*-stilbene epoxidation reactions by PhIO, *trans*-stilbene oxide was usually produced as a major product.¹³

Two possible intermediates responsible for the oxygen atom transfer are the high-valent metal oxo complex B and the metal-iodosylbenzene adduct A (see Scheme 1). The high-valent metal oxo complex B has been well accepted as a reactive intermediate in metalloporphyrin systems,^{2(b)} whereas the metal-iodosylbenzene complex A was proposed as an epoxidizing intermediate in Lewis acidic metal-catalyzed epoxidation reactions¹⁴ and in the reactions of metallobleomycin and iodosylbenzene.¹⁵ Since we observed that the



Scheme 1.

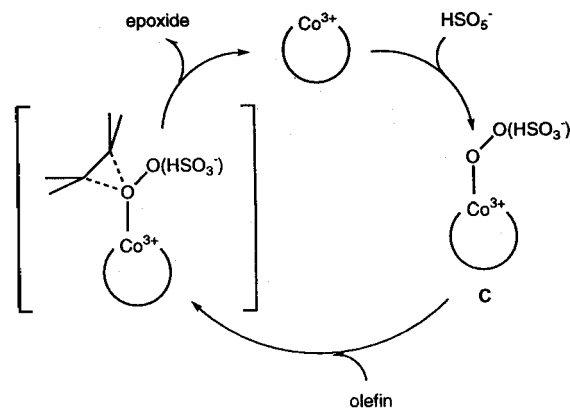
Table 2. Olefin Epoxidation by KHSO_5 Catalyzed by $\text{Na}_5(\text{CoPW}_{11}\text{O}_{30})_4$ ^a

Substrate	Products	Yield (mM)
		0.90
		2.5
		0.1
		0.2

^aSee experimental section for detailed experimental procedures.

oxidation state of the cobalt in the iodosylbenzen reaction was 3+,¹⁶ the cobalt ion in the high-valent cobalt oxo complex **B** should have the oxidation state of 5+. We believe that it is difficult to obtain cobalt in the 5+ oxidation state. Moreover, the cobalt complex reacted with iodosylbenzene was not capable of activating alkanes to give oxygenated products.¹⁷ We therefore suggest that the metal-iodosylbenzene complex **A** is a plausible intermediate for the epoxidation of olefins by iodosylbenzene.

Epoxidation of Olefins by KHSO_5 Catalyzed by Cobalt-Substituted Polyoxotungstate. We have previously shown that cobalt salt, $\text{Co}(\text{NO}_3)_2$, is a competent catalyst for the epoxidation of carbamazepine (CBZ) with KHSO_5 .¹⁸ We therefore tested the cobalt-substituted polyoxotungstate in the CBZ epoxidation by water-soluble oxidant KHSO_5 in aqueous solution. In this reaction, the conversion of CBZ was above 95% with the high yield of CBZ 10,11-oxide product (see Table 2). Formation of CBZ 10,11-oxide was not detected in the absence of either the cobalt complex or KHSO_5 . It is of interest to note that other transition metal-substituted polyoxotungstates ($\text{M}=\text{Mn}^{2+}$, Fe^{2+} , Ni^{2+} , and Cu^{2+}) did not give the oxide product in the CBZ epoxidation reaction. The oxidation of *cis*-stilbene by KHSO_5 , carried out in the solvent mixture of $\text{H}_2\text{O}/\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$, yielded *cis*-stilbene oxide as a major product with the formation of small amounts of *trans*-stilbene oxide and benzaldehyde, as obser-



Scheme 2.

Table 3. Hydroxylation of Alkanes by MCPBA Catalyzed by $[\text{n-C}_4\text{H}_9)_4\text{N}]_4\text{H}(\text{CoPW}_{11}\text{O}_{30})_4$ ^a

Substrate	Products	Yield (mM)
cyclohexane	cyclohexanol	7.2
	cyclohexanone	6.8
cyclohexane ^b	cyclohexanol	3.9
	cyclohexanone	3.6
	bromocyclohexane	1.2
cyclooctane	cyclooctanol	12
	cyclooctanone	10

^aSee experimental section for detailed experimental procedures.^bReaction was carried out in a solvent mixture of CH_3CN (4 mL) and CH_2Br_2 (1 mL).

ved in the *cis*-stilbene epoxidation by PhIO (*vide supra*).

The nature of the active species formed in the reaction of the cobalt-substituted polyoxotungstate and KHSO_5 is not clear at this moment. However, as Meunier *et al.* suggested that $(\text{O})\text{Mn}^{\text{V}}\text{-HSO}_4$ complex is able to abstract hydrogen atom from unactivated C-H bond,¹⁹ we propose that the cobalt(III)- HSO_5 complex **C** in Scheme 2 is a possible intermediate responsible for the olefin epoxidations. In recent years, several groups have shown that metal-OOR complexes are able to transfer their oxygen atoms to olefins prior to the O-O bond cleavage (see Scheme 2).²⁰ More detailed mechanistic studies are under investigation in this laboratory.

Hydroxylation of Alkanes with MCPBA. The results for the hydroxylation of alkanes by MCPBA catalyzed by the cobalt-substituted polyoxotungstate were given in Table 3. In the reactions, equal amounts of alcohols and ketones were produced. We suggest that the ketones formed resulted from the further oxidation of alcohols produced in the reactions, on the basis of the observation that the oxidation of cyclooctanol under the conditions of catalytic reactions yielded a good amount of cyclohexanone.²¹ This suggestion was further confirmed by the hydroxylation of cyclooctane with increasing amount of MCPBA added. As shown in Figure 2, the formation of cyclooctanol dominated at the beginning of the reaction. As more MCPBA was added to the reaction solution, the total amount of cyclooctanol product did not change, but cyclooctanone gradually formed and it became

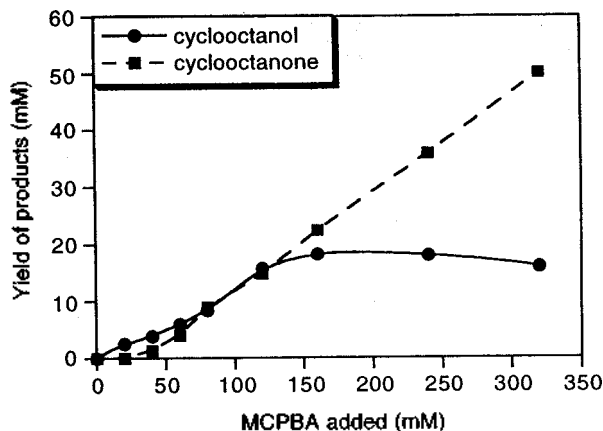


Figure 2. Hydroxylation of cyclooctane by varying amounts of MCPBA added. Reaction conditions were as follows: Appropriate amounts of MCPBA were added to the reaction solution containing cobalt-substituted polyoxotungstate (2 mM) and cyclooctane (0.5 M) in CH_3CN (5 mL), and then the reaction solution was stirred for 40 min.

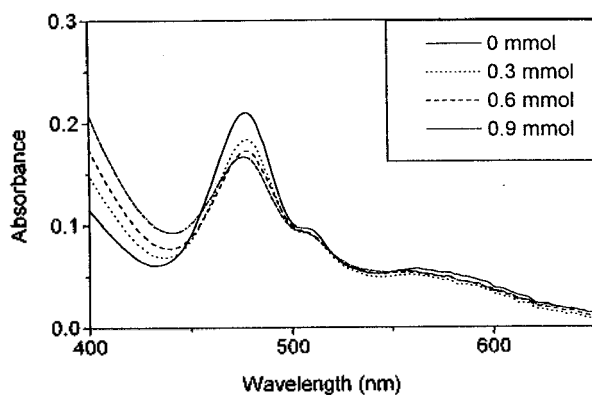
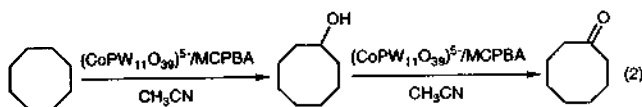


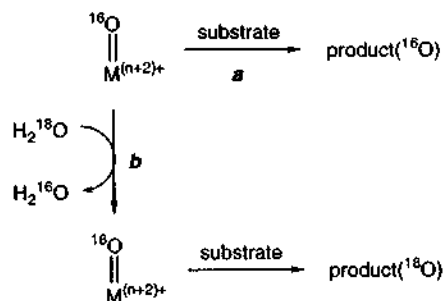
Figure 3. UV-vis spectra of the cobalt polyoxotungstate taken during the hydroxylation of cyclooctane by MCPBA.

the major product. This result indicates that alcohols formed was converted to the corresponding ketones in the oxidation reaction (eq. 2). It has been suggested in other hydroxylation reactions that alkanes were directly oxidized to ketones.²²

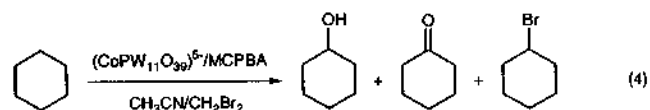
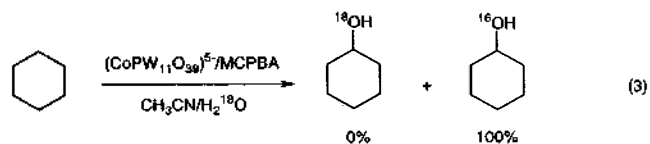


The stability of the cobalt complex was investigated by following UV-vis spectrum of the reaction mixture during the catalytic reactions (see Figure 3). The complex was found to be unchanged at the end of the reaction and the catalytic activity of the cobalt complex appeared not to be diminished by multiple turnovers. These observations indicate that the cobalt-containing polyoxotungstate is stable under the reaction conditions and capable of sustaining high turnover numbers.

In order to understand the nature of the intermediate and the reaction mechanism for the cobalt-substituted polyoxotungstate-catalyzed hydroxylation of alkanes by MCPBA, we

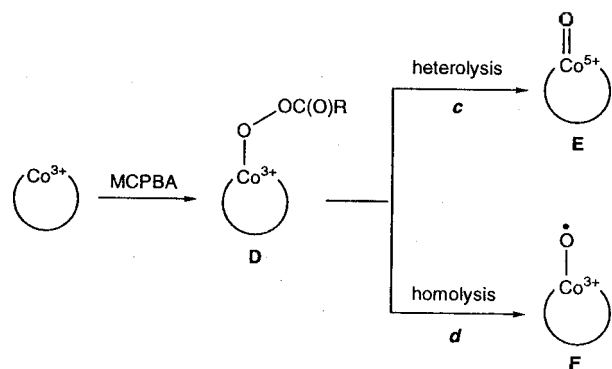


Scheme 3.



attempted two mechanistic studies which have been often used in metal-catalyzed oxidation reactions. One is the isotopically labeled water, H_2^{18}O , experiment which has been used as an indirect evidence for the intermediacy of high-valent metal oxo complexes in catalytic oxygenation reactions of organic substrates.²³ When the hydroxylation of cyclohexane by MCPBA catalyzed by the cobalt-substituted polyoxotungstate was conducted in the presence of H_2^{18}O , we obtained result that there was no ^{18}O incorporation into the cyclohexanol product (eq. 3). Although the incorporation of ^{16}O from H_2^{16}O into the oxygenated products has often been considered as sufficient evidence for the intermediacy of high-valent metal oxo species in catalytic oxygenation reactions,²³ the absence of ^{16}O in the cyclohexanol product formed does not imply that high-valent cobalt oxo species can be ruled out as a potent oxidizing agent since recent studies showed that the oxygen exchange between high-valent metal oxo complex and water (pathway *b* in Scheme 3) is slow relative to the rate of substrate oxidation (pathway *a* in Scheme 3) in some cases.^{3(c),23(a),24}

Another mechanistic study that we carried out is the hydroxylation of cyclohexane performed in the presence of halogenated solvent. The presence of CH_2Br_2 (10% of solvent by volume) in the oxidation of cyclohexane afforded the formation of both oxygenated and brominated products (eq. 3 and see Table 3). The halogen transfer reaction has been observed in metalloporphyrin- and non-porphyrin metal complex-catalyzed oxidations of alkanes,²⁵ in which high-valent metal oxo intermediates formed abstract hydrogen atom from alkane C-H bond to generate alkyl radical, $\text{R}\cdot$. Then, the solvent CH_2Br_2 intercepts the relatively long-lived alkyl radical, resulted in the formation of bromocyclohexane. Therefore, the observation that brominated product was formed suggests the involvement of cyclohexyl radical in the cobalt-substituted polyoxotungstate-catalyzed hydroxylation reaction. This result implies that the intermediate responsible for the C-H bond activation is a cobalt oxo complex. The



proposed structures of the intermediate species are E and F shown in Scheme 4. The intermediate E is formed via the heterolytic cleavage of the O-O bond of the cobalt-MCPBA complex D (pathway c in Scheme 4), whereas the homolytic O-O bond cleavage (pathway d in Scheme 4) produces F. As discussed earlier, it might be difficult to obtain the cobalt ion in the oxidation state of 5+. We therefore suggest that the complex F is a more plausible intermediate for the abstraction of hydrogen atom from the C-H bond,²⁶ which resulted in giving the oxygenated and halogenated products.

In summary, we have shown in this study that cobalt-substituted polyoxotungstate is an effective catalyst for the epoxidation of olefins by oxygen atom donors such as iodosylbenzene and potassium monopersulfate. We also obtained results that the cobalt-substituted Keggin compound is capable of catalyzing the hydroxylation of unactivated hydrocarbons by MCPBA. The cobalt complex is found to be very stable in the aforementioned oxidation reactions and capable of giving high catalytic turnover numbers.

Experimental Section

Materials. The reagents purchased from Aldrich Chemical Co. were the highest purity commercially available and used without further purification unless otherwise indicated. H_2^{18}O (95% ^{18}O enrichment) was obtained from Aldrich Chemical Co. CBZ 10,11-oxide was prepared by a literature method^{22(b)} and used as an authentic sample for the determination of product yields. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate with aqueous NaOH and kept at 0 °C.²⁷

The polyoxotungstate $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ was prepared by a literature method.²⁸ The transition metal-substituted polyoxotungstates were prepared from the reaction of corresponding metal salt and $\text{Na}_7\text{PW}_{11}\text{O}_{39}$. Alkylammonium salts of the transition metal-substituted polyoxotungstates were prepared by the treatment of aqueous $[\text{MPW}_{11}\text{O}_{39}]^{5-}$ with tetra-*n*-butylammonium bromide.⁵ The purification of the prepared compounds were judged by elemental analyses.

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 5890 spectrophotometer. Product analyses were performed on either a Donam Systems DS6200 gas chromatograph equipped with an HP-1 capillary column or Orom Vintage 2000 high performance liquid chromatography

equipped with a variable wavelength detector. ^{18}O analyses for H_2^{18}O experiment were performed on a Hewlett Packard 5890 II gas chromatograph coupled with Hewlett Packard Model 5988 mass selective detector. ESR spectra were obtained on Bruker ESP-300 spectrometer.

Epoxidation of Olefins with Iodosylbenzene. All reactions were carried out in a Vacuum Atmospheres glove box or an inert atmosphere. In a typical experiment, iodosylbenzene (80 mM) was added to a reaction solution containing metal catalyst (2 mM), olefin (0.4 M for cyclohexene, cyclooctene, 1-octene, and (+)-limonene and 0.2 M for *cis*- and *trans*-stilbene), and an appropriate amount of an inert internal standard in 5 mL of CH_3CN . The reaction solution was stirred for 2 h at room temperature and then filtered through a 0.45- μm filter. The products were analyzed by GC or HPLC.

Epoxidation of Olefins with Potassium Monopersulfate. In a typical experiment, KHSO_5 (10 mM) was added to a reaction solution containing a catalyst (0.1 mM) and olefin (CBZ=1 mM, introduced as a 10 mM solution in methanol, and *cis*-stilbene=10 mM) in 5 mL of solvent (solvent=water for CBZ epoxidation and solvent=a mixture of 50% H_2O , 40% CH_3CN , 10% CH_3OH for *cis*-stilbene oxidation). The reaction mixture was stirred for 1 h at room temperature and analyzed by HPLC.

Hydroxylation of Alkanes by MCPBA Catalyzed by Cobalt-Substituted Polyoxotungstate. All reactions were carried out in a Vacuum Atmospheres glove box or an inert atmosphere. MCPBA (80 mM) was added to a reaction solution containing $[\text{n-C}_4\text{H}_9)_4\text{N}]_4\text{H}(\text{CoPW}_{11}\text{O}_{39})$ (2 mM), alkane (0.5 M), and an appropriate amount of an internal standard in 5 mL of CH_3CN . The reaction solution was stirred for 2 h at room temperature and analyzed by GC.

Isotopically labeled water experiment has been carried out CH_3CN (5 mL) solution containing cobalt-substituted polyoxotungstate (2 mM), cyclohexane (0.5 M) and H_2^{18}O (100 μL , 95% ^{18}O enrichment). After MCPBA (80 mM) was added to the mixture, the reaction solution was stirred for 1 h at room temperature. ^{16}O and ^{18}O compositions in cyclohexanol were determined by the relative abundances of mass peaks at $m/z=57$ for ^{16}O and $m/z=59$ for ^{18}O .

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