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Short communication

SHORT COMMUNICATION

Polyoxometalate catalysts in the oxidation of cyclooctane by hydrogen peroxide

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Abstract: A Keggin-type tungstocobaltate, $[\text{Co}(2,2'\text{-bipy})_3]_2\text{H}_2[\text{CoW}_{12}\text{O}_{40}] \cdot 9.5\text{H}_2\text{O}$ ($[\text{Co}]\text{CoW}$) and tetrabutylammonium salt of vanadium-substituted tungstophosphates $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\text{PVW}_{11}\text{O}_{40}]$, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$ (PVW , PV_2W) were used as catalysts for the oxidation of cyclooctane with H_2O_2 as the oxidant in acetonitrile. The activity of $[(n\text{-C}_4\text{H}_9)_4\text{N}_4\text{H}[\text{PCo}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]\cdot 2\text{H}_2\text{O}$ (PCoW) was also compared. The products of the reaction were cyclooctanone, cyclooctanol and cyclooctyl hydroperoxide. The experimental results showed that at an $\text{H}_2\text{O}_2/\text{cyclooctane}$ molar ratio of 3 at 80 °C, $[\text{Co}]\text{CoW}$ yielded a higher conversion and selectivity to cyclooctanone in 9 h. The V-based catalysts were more active than the Co-based tungstophosphate. PV_2W gave rise to high selectivity to cyclooctyl hydroperoxide. Cyclooctane conversion was increased by increasing the reaction time or $\text{H}_2\text{O}_2/\text{cyclooctane}$ molar ratio. In the presence of tungstocobaltate catalyst, 88 % cyclooctane conversion and 82 % selectivity of cyclooctanone were obtained after 12 h using an $\text{H}_2\text{O}_2/\text{cyclooctane}$ molar ratio of 9. This catalyst is stable upon treatment with H_2O_2 . Experiments with radical traps suggested the involvement of a free-radical mechanism.

Keywords: Keggin-type polyoxometalates; cyclooctane; oxidation; hydrogen peroxide; cobalt; vanadium.

INTRODUCTION

The transformation of hydrocarbons into oxygenated derivatives has been extensively investigated because such products are valuable intermediates for industrial organic synthesis. Oxidation of cyclooctane with air was catalyzed by metalloporphyrins and metallophthalocyanines.^{1,2} Cr-MCM-41 materials showed high activity and selectivity for the oxidation of cyclooctane to cyclooctanone,

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using H_2O_2 or *tert*-butyl hydroperoxide.³ A possible way to improve the selectivity is through the selective decomposition of alkyl hydroperoxides formed during the oxidation reactions. Polyoxometalates afford good selectivity towards the formation of alkyl hydroperoxides in the catalytic oxidation of cycloalkanes.⁴

Polyoxometalates are metal–oxygen anionic clusters of early transition metals. They bear many similarities to metal complexes of macrocyclic ligands such as, for example, to metalloporphyrins and related species, because they possess rigid co-ordination sites surrounding a metal centre.⁵ The robust nature of polyoxometalate ligands and their resistance to oxidation lead to their valuable applications in catalysis. Their activities can be controlled by changes in the metal center and the counter cation.⁶ Reports on oxidation using polyoxometalates include $[\text{SiW}_{10}\text{Fe}_2(\text{H}_2\text{O})_2\text{O}_{38}]^{6-}$ and $[\text{M}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$, $\text{M}(\text{II}) = \text{Co}$ or Mn and $[\text{Fe}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{6-}$.^{7,8} A few reports have been published concerning the oxidation of cyclooctane in the presence of polyoxometalates, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_7\text{H}_3[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^9$ and $[\text{XW}_{11}\text{MO}_{39}]^{p-}$, $\text{X} = \text{P}$ or Si and $\text{M} = \text{Fe}$ or Mn , as well as $[\text{XW}_{11}\text{VO}_{40}]^{m-}$.¹⁰ Some vanadium-substituted polyoxometalates have been used as selective oxidation catalysts for a variety of organic reactions,^{11,12} e.g., the oxidation of cyclic and linear alkanes by H_2O_2 over $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\text{PVMo}_{11}\text{O}_{40}]$.¹³ In these catalysts, the presence of a vanadium(V) center in the polyoxometalates is a key factor.

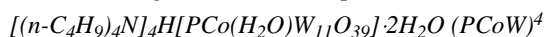
Polyoxometalates can form compounds with a number of organic and complex cations containing N, S, O atoms, e.g., diethylamine and bipyridine.^{14–16} New properties can be obtained from the interplay of the two components, which can be used as effective catalysts. One example is $[\text{H}_5\text{PCo}(4,4'\text{-bipy})\text{Mo}_{11}\text{O}_{39}][\text{H}_3\text{PMo}_{12}\text{O}_{40}] \cdot 3.75(4,4'\text{-bipy}) \cdot 1.5\text{H}_2\text{O}$ for the oxidation of benzaldehyde to benzoic acid using H_2O_2 as the oxidant.¹⁷

In continuation of research on the utilization of polyoxometalates as catalysts for the oxidation of sulfur compounds,¹⁸ cyclohexane and ethylbenzene,¹⁹ polyoxometalates in the oxidation of cyclooctane by H_2O_2 in acetonitrile as solvent were studied. H_2O_2 is regarded as one of the “greenest” oxidants because of its high content of active oxygen species (47 wt. %), high atom efficiency and co-production of only water. The key for the development of efficient H_2O_2 -based oxidation systems is the design of catalysts that can effectively activate H_2O_2 and transfer the active oxygen species to substrates with high efficiencies and selectivities. The results of catalytic activities of the Keggin-type tungstocobaltate, tetrabutylammonium salts of V- and Co-substituted tungstophosphates, the effect of the H_2O_2 /cyclooctane molar ratio and reaction time on cyclooctane conversion and product selectivity are presented herein.

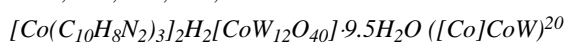
EXPERIMENTAL

All reagents and solvents used in this work were commercially available (Fluka Chemika or Merck) and were used as received. The polyoxometalates were prepared according to

published methods^{4,20,21} with modifications and were identified by elemental analysis using a CHN analyzer (Perkin Elmer PE2400 Series II) and inductively coupled plasma emission ICP spectroscopy (Perkin Elmer Plasma 1000 Emission Spectrometer) and by infrared spectroscopy using a Nicolet FT-IR Impact 410 spectrophotometer. The analytical and spectroscopic data were in agreement with the published values.



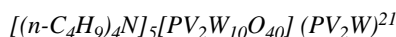
Anal. Calcd. for $C_{64}H_{151}N_4O_{42}PW_{11}Co$: C, 20.44; H, 4.05; Co, 1.57; P, 0.82; W, 53.10; N, 1.49 %; Found: C, 20.20; H, 3.89; Co, 1.54; P, 0.79; W, 53.28; N, 1.38 %. IR (KBr, cm^{-1}): 1060, 963, 886, 810, 760.



Anal. Calcd. for $C_{60}H_{67}N_{12}O_{49.5}W_{12}Co_3$: C, 17.42; H, 1.62; N, 4.06; W, 53.22 %; Found: C, 17.29; H, 1.68; N, 3.93; W, 53.38 %. IR (KBr, cm^{-1}): 935, 870, 760, 457 (from anion) and 1631, 1446, 1168, 1106 (from cation).



Anal. Calcd. for $C_{64}H_{144}N_4O_{40}PVW_{11}$: V, 1.37 %. Found: V, 1.29 %; IR (cm^{-1}): 1095, 1064, 965, 888, 809.



Anal. Calcd for $C_{80}H_{180}N_5O_{40}PV_2W_{10}$: V, 2.84 %; Found: V, 2.76 %. IR (cm^{-1}): 1093, 1064, 962, 888, 808.

Oxidation reactions

The reactions were realized in a Parr reactor. Cyclooctane 1 ml (7.6 mmol) and catalyst (11.5 μ mol) were added in 10 ml acetonitrile followed by 30 % H_2O_2 (in different H_2O_2 /cyclooctane ratios). The reactions were usually performed under air. When a reaction was performed in an inert atmosphere, N_2 was bubbled through the reaction mixture before the addition of H_2O_2 and a rubber balloon with N_2 was maintained at the top of the condenser during the reaction. After stirring at the required reaction temperature for the required time, 25 % H_2SO_4 was added to the reaction mixture and the reaction products were extracted with diethyl ether. The organic layer was neutralized with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4 . The products were analyzed by gas chromatography using a Shimadzu model CG-17A instrument equipped with a flame ionization detector and OV-1701 0.50 μ m capillary column (30 m, 0.25 mm). *n*-Octane was used as an internal standard. The chromatographic conditions for cyclooctane were initial temperature: 80 $^{\circ}C$ (2 min), a temperature ramp at 20 $^{\circ}C$ min^{-1} to the final temperature of 220 $^{\circ}C$ (1 min); injector temperature: 250 $^{\circ}C$ and detector temperature: 250 $^{\circ}C$. Cyclooctanone and cyclooctanol were identified unambiguously by comparison with authentic standards. The percentage of each compound in the reaction mixture was estimated directly from the corresponding chromatographic peak areas. Blank experiments were also conducted in the absence of catalyst or oxidant. At the end of the oxidation reaction, cyclooctyl hydroperoxide was determined by treating the final reaction solution with an excess of PPh_3 before the GC analysis. PPh_3 reduces the cyclooctyl hydroperoxide quantitatively to the corresponding cyclooctanol, giving triphenylphosphine oxide. The amount of cyclooctyl hydroperoxide was determined by comparing the concentrations of the cyclooctanone and of the cyclooctanol, measured before and after the treatment of the sample with PPh_3 .²² A few experiments were performed in the presence of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol). To test stability of the [Co]CoW catalyst in the presence

of H₂O₂, infrared and UV spectra were recorded using a Nicolet FT-IR Impact 410 spectrophotometer and a Shimadzu UV-250 spectrometer, respectively.

RESULTS AND DISCUSSION

Oxidation of cyclooctane

The oxidation of cyclooctane over polyoxometalates catalysts were performed in acetonitrile solvent using H₂O₂ as the oxidant. All the catalysts were soluble in hot acetonitrile. The results are summarized in Table I. No oxidized products were detected in the absence of catalyst (entry 1) or H₂O₂ (entry 2). For all the catalyzed reactions, cyclooctanone and cyclooctanol were detected as the oxidized products together with cyclooctyl hydroperoxide. The performances of the different catalysts in the oxidation of cyclooctane with H₂O₂ as oxidant were compared under the same reaction conditions: cyclooctane 1 ml (7.6 mmol), catalyst 11.5 μmol, H₂O₂/cyclooctane molar ratio = 3, CH₃CN 10 ml at 80 °C for 9 h. It was found that [Co]CoW showed the highest activity (50 % conversion) with cyclohexanone as the main product (80 % selectivity) while PCoW showed the lowest activity (34 % conversion and 58% selectivity to cyclooctanone). PV₂W showed a slightly higher activity than PVW (42 and 39 % in entries 7 and 6, respectively) with a similar product selectivity. This activity order is in agreement with the result reported in a previous study using these vanadium catalysts for the oxidation of sulfur compounds¹⁸ and also in the oxidation of aldehydes over H₄PVMo₁₁O₄₀ and H₅PV₂Mo₁₀O₄₀ with H₂O₂.²³ When the oxidation over the [Co]CoW and PV₂W catalysts was performed in the presence of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol), no oxidized products were found (entries 5 and 8).

TABLE I. Oxidation of cyclooctane by H₂O₂ using various catalysts; reaction conditions: cyclooctane, 1 ml (7.6 mmol), catalyst, 11.5 μmol, H₂O₂/cyclooctane molar ratio, 3, CH₃CN, 10 ml, temperature 80 °C, time 9 h

Entry	Catalyst	Conversion ^a , %	Selectivity ^b , %		
			CyONE	CyOH	CyOOH
1	No catalyst	0	0	0	0
2	No H ₂ O ₂	0	0	0	0
3	PCoW	34	58	42	0
4	[Co]CoW	50	80	19	1
5	[Co]CoW ^c	0	0	0	0
6	PVW	39	65	20	15
7	PV ₂ W	42	63	17	20
8	PV ₂ W ^c	0	0	0	0

^aBased on gas chromatographic peak areas; ^bexpressed as percentages of total products formed. CyONE = cyclooctanone, CyOH = cyclooctanol, CyOOH = cyclooctyl hydroperoxide; ^cin the presence of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol, 3 equivalents

Vanadium substituted tungstophosphates catalysts

The catalytic activity of PV_2W was further studied by varying the reaction condition. The results are given in Table II. Increasing the H_2O_2 /cyclooctane molar ratio resulted in an increasing conversion of cyclooctane. At a molar ratio H_2O_2 /cyclooctane of 9, an 84 % conversion was obtained with selectivities to cyclooctanone:cyclooctanol:cyclooctyl hydroperoxide of 24:7:69. When the reaction time was increased from 9 h to 12 h, the conversion increased to 89 % and the selectivity to cyclooctyl hydroperoxide was further increased (cyclooctanone:cyclooctanol:cyclooctyl hydroperoxide = 23:2:75). At longer times, 18 h, the conversion remained constant. A decomposition of cyclooctyl hydroperoxide produced additional amount of cyclooctanone (entry 5). Under the same reaction condition, the activity of the PVW catalyst was lower (entry 2 vs. 6). The activity of the PVW catalyst was previously reported by Balula *et al.* (entries 7–9).⁹ They also observed that the activity of $[(n-C_4H_9)_4N]_4[PVW_{11}O_{40}]$ was higher than that of $[(n-C_4H_9)_4N]_3[PW_{12}O_{40}]$. When W(VI) in a polyoxometalate was substituted by V(V), the substitution resulted in the generation of a more reactive oxygen associated to the W–O–V species.²⁴ In this work, the tetrabutylammonium salt dissolved well in acetonitrile. Compared to the sodium salt catalyst: $Na_5PV_2Mo_{10}O_{40}$, it was reported to yield 10 % conversion with a 70 % selectivity to cyclooctanone (reaction conditions: cyclooctane 0.8 mmol, catalyst 2.8 μ mol, H_2O_2 1 ml, in 1,2-dichloroethane at refluxing temperature).²⁵

TABLE II. Oxidation of cyclooctane over the PV_2W and PVW catalysts; reaction conditions: cyclooctane, 1 ml (7.6 mmol), catalyst, 11.5 μ mol, CH_3CN , 10 ml, temperature 80 °C

Entry	Catalyst	H_2O_2 /cyclooctane mole ratio	Time, h	Conversion, %	Selectivity, %		
					CyONE	CyOH	CyOOH
1	PV_2W	3	9	42	63	17	20
2		6	9	66	43	12	45
3		9	9	84	24	7	69
4		9	12	89	23	2	75
5		9	18	89	29	2	69
6	PVW	6	9	60	33	10	57
7	PVW ^a	2	9	26	46	13	41
8		9.8	9	87	23	0	77
9		9.8	12	94	23	0	77

^aCyclooctane, 1 mmol, catalyst, 1.5 μ mol, CH_3CN , 1.5 ml, temperature 80 °C⁹

The [Co]CoW catalyst

The oxidation of cyclooctane over the [Co]CoW catalyst was performed by varying the H_2O_2 /cyclooctane molar ratio and the reaction time. The reactions were also performed in the absence of air (under a N_2 atmosphere) or oxidant, and at room temperature. The results are shown in Table III.

When the reaction was conducted under an atmosphere of nitrogen, a similar result to that in air was obtained (compare entry 2 with entry 1). Therefore, the possibility of auto-oxidation may be excluded. In addition, an experiment performed under open air without H₂O₂ (entry 3) did not afford any noticeable amount of product, indicating that oxygen plays no role in this oxidation reaction under the employed experimental conditions. In entry 4, using an H₂O₂/cyclooctane molar ratio of 3 and a reaction time of 12 h, the conversion of cyclooctane was increased to 71 % and the product selectivity cyclooctanone:cyclooctanol:cyclooctyl hydroperoxide was 70:14:16. In entry 5, a higher conversion (77 %) was obtained by increasing the molar ratio to 6, cyclooctyl hydroperoxide decomposed to form more cyclohexanol and cyclohexanone (cyclooctanone:cyclooctanol:cyclooctyl hydroperoxide was 76:20:4). The reaction time could be shortened by increasing the H₂O₂/cyclooctane molar ratio to 9 (entry 6). No cyclooctyl hydroperoxide was detected. The maximum conversion (88 %) was obtained after 12 h reaction time (entry 7) giving 82 % cyclooctanone and remained unchanged after that (entry 8). There was no reaction at room temperature (entry 9).

Table III. Oxidation of cyclooctane over the [Co]CoW catalyst; reaction conditions: cyclooctane, 1 ml (7.6 mmol), catalyst, 11.5 μmol, CH₃CN, 10 ml, temperature 80 °C

Entry	H ₂ O ₂ /cyclooctane mole ratio	Time, h	Conversion, %	Selectivity, %		
				CyONE	CyOH	CyOOH
1	3	9	50	80	19	1
2 ^a	3	9	49	78	22	0
3 ^b	3	9	0	0	0	0
4	3	12	71	70	14	16
5	6	12	77	76	20	4
6	9	9	79	80	20	0
7	9	12	88	82	18	0
8	9	15	88	83	17	0
9 ^c	9	12	0	–	–	–

^aUnder an N₂ atmosphere; ^bwithout H₂O₂; ^cexperiment performed at room temperature

The high activity of the [Co]CoW catalyst might result from many factors: solubility, redox property or cation. [Co]CoW consists of two discrete [Co(2,2'-bipy)₃]²⁺ held weakly with a [CoW₁₂O₄₀]⁶⁻. It was dissolved in hot CH₃CN. The metal active centers are W(VI) and Co(II). An electrochemical study of a related anion, [CoMo₁₂O₄₀]⁶⁻ showed a one-electron redox Co(III)/Co(II) couple and reversible redox processes ascribed to Mo centers. This was ascribed to the distribution of the charge on Co²⁺ over the whole polyoxometalate cluster.²⁶ In addition, it was reported that in the presence of an oxidant, the [CoW₁₂O₄₀]⁶⁻ could be oxidized to give [CoW₁₂O₄₀]⁵⁻, which is a very strong oxidizing agent.^{27,28}

[Co(2,2'-bipy)₃]²⁺ might contribute to the activity, similar to [Cu(bipy)₃]²⁺, which catalyzed the oxidation of cyclohexane by H₂O₂.²⁹ In addition, this same

tungstocobaltate with $[\text{Co}(\text{phen})_2]^{2+}$ as a cation was reported to show that the electrochemical behavior of Co(II) differ from those of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{HCoW}_{12}\text{O}_{40}]$. This arose from the different coordinated environments of the Co atoms.³⁰

It is known that Keggin polyoxometalates degrade in the presence of excess H_2O_2 to form peroxo species $\{(\text{PO}_4)[\text{MO}(\text{O}_2)_2]_4\}^{3-}$ or $[\text{M}_2\text{O}_3(\text{O}_2)_4]^{2-}$ (M = W or Mo), which are the catalytically active intermediate in the oxidation of organic compounds by H_2O_2 .³¹ Santos *et al.* reported that $(\text{THA})_2[\text{W}_2\text{O}_3(\text{O}_2)_4]$ (THA = tetrahexylammonium) catalyzed the oxidation of cyclooctane with 83 % conversion and 59:12:29 selectivity to cyclooctanone:cyclooctanol:cyclooctyl hydroperoxide at 80 °C in 12 h. A stoichiometric amount of catalyst was used (catalyst/cyclooctane molar ratio = 1.5:1). They reported that in solution, the $[\text{W}_2\text{O}_3(\text{O}_2)_4]^{2-}$ complex may be involved in a dissociative process, peroxide occupying the empty sites of the W coordination sphere that result from the breakage of the oxygen bridges in solution.³²

In order to check the stability of $[\text{Co}]\text{CoW}$ upon reaction with H_2O_2 , FTIR and UV spectra were taken of the H_2O_2 -treated sample. In the FTIR spectrum of the H_2O_2 -treated sample, bands attributed to the Keggin anion were almost preserved, although the band shapes were more or less deformed. The UV spectrum of the H_2O_2 -treated sample in CH_3CN exhibited two absorption peaks at 196 and 300 nm ascribed to the charge-transition absorption of O–W. These results indicate that $[\text{Co}]\text{CoW}$ was stable.

Proposed mechanism

As shown in Table I, the oxidation reaction over the $[\text{Co}]\text{CoW}$ and PV_2W catalysts in the presence of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol) yielded no oxidized products, suggesting the involvement of a free-radical mechanism. This is similar to the previously proposed mechanism for the $[\text{PVM}_{11}\text{O}_{40}]^{4-}$ (M = Mo or W) and $[\text{PMW}_{11}\text{O}_{39}]^{4-}$ (M = Fe or Mn).^{10,13} Thus for PV_2W , H_2O_2 was coordinated to V(V), followed by the formation of V(IV) and peroxy radicals. Hydroxyl radicals were formed upon interaction of a V(IV) species with H_2O_2 .

In the case of the $[\text{Co}]\text{CoW}$, it is thought that the same mechanism could be applied. The activation of H_2O_2 may occur simultaneously at W and Co.¹⁰ The difference in product selectivity of these two catalysts, lower selectivity to cyclooctyl hydroperoxide for the $[\text{Co}]\text{CoW}$ might be due to Co(II) compared to V(VI). The generation of molecular oxygen, *in situ* from H_2O_2 , may not be as extensive as proposed for PV_2W .

CONCLUSIONS

The $[\text{Co}(2,2'\text{-bipy})_3]_2\text{H}_2[\text{CoW}_{12}\text{O}_{40}] \cdot 9.5\text{H}_2\text{O}$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$ were shown to be efficient catalysts for the selective oxidation of cyclooctane

using the environmental friendly oxidant, H_2O_2 . The vanadium-substituted tungstophosphate gave high selectivity to cyclooctyl hydroperoxide. With the Keggin-type tungstocobaltate, oxidation of cyclooctane could be obtained with high selectivity to cyclooctanone (82 %) with a conversion of 88% at 80 °C in 12 h. The oxidation catalyzed by these catalysts appeared to be a radical process.

ИЗВОД

ПОЛИОКСОМЕТАЛАТИ КАО КАТАЛИЗАТОРИ ОКСИДАЦИЈЕ ЦИКЛООКТАНА
ПОМОЋУ ВОДНИК-ПЕРОКСИДА

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Keggin-тип волфрам-кобалтата, $[Co(2,2-bipy)_3]_2H_2[CoW_{12}O_{40}] \cdot 9,5H_2O$ ($[Co]CoW$) и тетрабутиламонијум соли ванадијумом супституисаних волфрамфосфата, $[(n-C_4H_9)_4N]_4[PVW_{11}O_{40}]$, $[(n-C_4H_9)_4N]_5[PV_2W_{10}O_{40}]$ (PVW , PV_2W) су употребљени као катализатори за оксидацију циклооктана помоћу H_2O_2 у ацетонитрилу као растварачу. Поред тога, одређена је каталитичка активност за $[(n-C_4H_9)_4N]_4H[PCo(H_2O)W_{11}O_{39}] \cdot 2H_2O$ ($PCoW$) и добијени резултати у овом случају су поређени са претходним. Нађено је да су производи у овим реакцијама циклооктанон, циклооктанол и циклооктил-хидропероксид. Добијени експериментални резултати су показали да $[Co]CoW$, када је вредност молског односа H_2O_2 /циклооктан = 3 и на температури од 80 °C за време од 9 h, даје високу конверзију и селективност у циклооктанон као производ реакције. Катализатори који садрже ванадијум су показали већу активност у односу на катализаторе који садрже кобалт-волфрам-фосфате. Катализатор типа PV_2W даје високу селективност у циклооктил-хидропероксид. Конверзија циклооктана се повећавала са повећањем реакционог времена, или молског односа за систем H_2O_2 /циклооктан. У присуству волфрамо-кобалтата као катализатора за време од 12 сати и при молском односу H_2O_2 /циклооктан = 9, конверзија циклооктана је износила 88 %, док је селективност била 82 %. Поред тога, овај катализатор је показао велику стабилност након третмана са H_2O_2 .

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