

Liquid-phase oxygenation of hydrocarbons with molecular oxygen catalyzed by Fe₂Ni-substituted Keggin-type heteropolyanion

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Abstract

Alkanes such as adamantane, ethylbenzene and cyclohexane, cyclohexene, and aldehydes are selectively oxidized to the corresponding alcohols, ketones, and acids with molecular oxygen alone catalyzed by the Fe_{3-x}Ni_x-substituted Keggin-type heteropolyanion, [PW₉O₃₇{Fe_{3-x}Ni_x(OAc)₃}]^{(9+x)-} (*x* = predominantly 1). The catalytic activities of [PW₉O₃₇{Fe_{3-x}Ni_x(OAc)₃}]^{(9+x)-} for the oxidation of cyclohexane and butyraldehyde were compared with *mono*-transition-metal substituted heteropolytungstates and other compounds having oxo-bridged tri-transition-metal sites. In addition, the effects of acetonitrile as a solvent and the addition of isobutyraldehyde were investigated.

Keywords: Hydrocarbon; Oxidation; Dioxygen; Fe₂Ni-substituted Keggin-type heteropolytungstate

1. Introduction

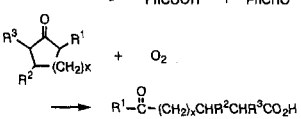
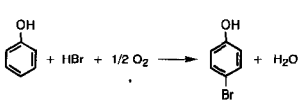
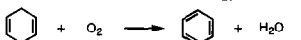
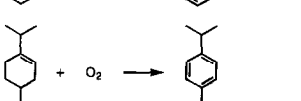
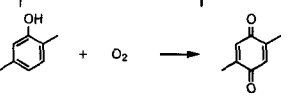
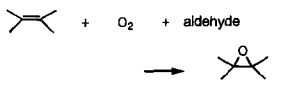
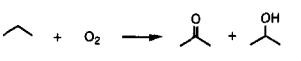
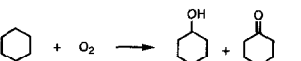
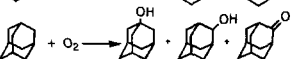
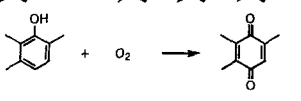
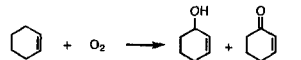
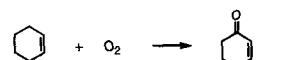
The oxidizing properties or strong acidity of heteropoly compounds induce a lot of studies on the heterogeneous and homogeneous catalysis [1]. The additional attractive and important aspects are oxidatively stability and introduction of various components into heteropolyanions and the counteractions [1].

Typical examples of liquid-phase oxidation with molecular oxygen catalyzed by heteropoly

compounds are listed in Table 1 [1](g) and [2–19]. Introduction of V⁵⁺ or other transition metal ions such as Co²⁺ or Mn²⁺ as addenda atoms usually enhances the catalytic activity, reflecting changes in the reduction potential. PV₂Mo₁₀O₄₀⁵⁻ has usually been used in the acid form. H₅PV₂Mo₁₀O₄₀ catalyzes aerobic oxidative cleavage of cycloalkanes, 1-phenylalkanes, and ketones. For example, the oxidation of 2,4-dimethyl cyclopentanone and 2-methylcyclohexanone gives 5-oxo-3-methylhexanoic acid, and 6-oxoheptanoic acid, respectively, in yields higher than 90% [2,3]. Bromination of arenes with HBr [4], oxidative dehydrogenation of cy-

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Table 1
Liquid-phase oxidation reactions with molecular oxygen catalyzed by heteropoly compounds

Reaction	Catalyst	Temp./°C	Ref.
$\text{PhCOCH}_2\text{Ph} + \text{O}_2 \rightarrow \text{PhCOOH} + \text{PhCHO}$	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	60	2
	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	60	2,3
$\text{R}_2\text{S} \rightarrow \text{R}_2\text{SO} \text{ or } \text{R}_2\text{SO}_2$	$\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$	90	4
	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	20	6
	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	70	5,6
	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	25	7
	$\text{H}_5\text{PMo}_{12}\text{V}_2\text{O}_{40}$	60	8
	$\text{PW}_{11}\text{CoO}_{39}^{5-}$ $\text{PMo}_6\text{V}_6\text{O}_{40}^{3-}$	30	9,10
	$\text{H}_7\text{PW}_9\text{Fe}_2\text{NiO}_{37}$	150	11
	$(\text{TBA})_4\text{H}_6\text{PW}_9\text{Fe}_2\text{NiO}_{37}$ TBA, $(n\text{-C}_4\text{H}_9)_4\text{N}$	82	12
	$(\text{TBA})_4\text{H}_6\text{PW}_9\text{Fe}_2\text{NiO}_{37}$ $[\text{WZnRu}_2(\text{OH})(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{11-}$	80-82	12,19
	$\text{Na}_7\text{PMo}_9\text{V}_4\text{O}_{40}$	20	13
	$\text{SiW}_{11}\text{CoO}_{40}^{8-}$	70	14
$\text{SO}_2 + 1/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	$\text{H}_6\text{PMo}_7\text{V}_5\text{O}_{40}$	25	15
$\text{H}_2\text{C}=\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CHO}$	$\text{PdCl}_2 + \text{Na}_x\text{H}_{3-x}\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$ ($x = 2 - 3$)	120	16
	$[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{Na}_3[(1,5\text{-COD})\text{-IrP}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$	38	17
$\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{Cl}$	Pt salt + $\text{Na}_8\text{HPMo}_6\text{V}_6\text{O}_{40}$	120	18

clohexadiene [5,6] and α -terpinene [7], oxidation of 2,4-dimethylphenol [8] and sulfides [15] are other examples. Heteropoly compounds are

used in combination with transition metals in Wacker-type reactions [16].

Recently alkane oxidation in the liquid phase, which does not proceed with the V^{5+} - and mono- Co^{2+} -substituted heteropolyanions, has become possible; pioneering work has been reported by Lyons et al. [11]. However, unclear aspects of this important work include the composition and the structure of the precatalyst. In fact, under all literature conditions, the synthesis of the precatalyst, $\text{PW}_9\text{Fe}_2\text{NiO}_{37}^{7-}$, has failed due to the formation of M–O–M bridged dimer polyanions and mixing of Fe and Ni ions. We have next reported the synthesis of $\text{PW}_9\text{Fe}_2\text{NiO}_{37}^{7-}$ heteropolyanion [12] and the alkane oxidation catalysis. Recently, Neumann et al. reported the adamantane oxidation catalyzed by di-ruthenium-substituted sandwich polyoxometalate [19]. The catalysis of di- or tri-metal-substituted polyoxometalates is interesting to understand the action of iron- or copper-containing biomolecules such as hemerythrin, purple acid phosphatase, hemocyanin, and laccase [20,21].

Another attractive research is the design of transition metal ions in combination with heteropoly compounds or heteropolyanion-supported metals [1](g) and [17,22].

Oxidation of hydrocarbons with molecular oxygen is a rewarding goal because among various oxidants molecular oxygen has the highest % active oxygen and formed no by-product by the utilization [1](f). Therefore, the processes would be available and environmentally friendly. In addition, oxyfunctionalization of alkanes has attracted much attention from the standpoint of energy resources and CH bond activation [23–28].

In this paper we wish to report the aerobically induced catalytic oxygenation of alkanes such as adamantane, ethylbenzene, and cyclohexane, cyclohexene, and aldehydes on $\text{Fe}_{3-x}\text{Ni}_x$ -substituted Keggin-type heteropolyanion, $[\text{PW}_9\text{O}_{37}\{\text{Fe}_{3-x}\text{Ni}_x(\text{OAc})_3\}]^{(9+x)-}$ ($x =$ predominantly 1) without any reductants.

2. Experimental

2.1. Synthesis of $[(n-C_4H_9)_4N]_4H_6[PW_9O_{37}\{Fe_2Ni(OAc)_3\}]$ and reagents

$[(n-C_4H_9)_4N]_4H_6[PW_9O_{37}\{Fe_2Ni(OAc)_3\}]$ (denoted by PW_9-Fe_2Ni) was prepared from iron(III) nitrate, nickel(II) nitrate, and $ANa_9PW_9O_{34}$. IR, NMR, UV, Mössbauer, magnetic susceptibility, and elemental analysis show that the tri-transition-metal-substituted Keggin-type heteropolyanion, $[PW_9O_{37}\{Fe_{3-x}Ni_x\}]^{(9+x)-}$ ($x =$ predominantly 1, denoted by PW_9-Fe_2Ni), was synthesized [12]. The proposed structure is shown in Fig. 1. PW_9-Fe_2Ni was soluble only in acetonitrile among solvents used in this paper. The thermal stability was investigated by the change of IR spectra calcined in air at elevated temperatures. The bands due to $(n-C_4H_9)_4N^+$ and OAc^- almost disappeared at $300^\circ C$ while the bands characteristic of the Keggin structure still remained, suggesting the formation of the acid form of $PW_9O_{37}(Fe_2Ni)$ anion.

The tetra-*n*-butylammonium salts of the transition-metal-substituted heteropolytungstate complexes, $\{PW_{11}(M^{n+})O_{39}\}^{(7-n)-}$ ($M = Co^{2+}$, Cu^{2+} , Fe^{3+} , Ni^{2+} , Mn^{2+} ; denoted by $PW_{11}-M$), $Fe_2NiO(OAc)_6(H_2O)_3$, $Fe_3O(OAc)_6(H_2O)_3$, and $Fe_3O(OAc)_6(H_2O)_3Cl$ were prepared according to the literature [29] and the structures

were confirmed by elemental analysis, IR, and NMR spectra.

All reagents were purchased in their highest commercial purity. Organic substrates were purified before use while inorganic reagents were used without further purification. Infrared spectra were measured as KCl pellets with a Perkin-Elmer Paragon 1000 PC spectrometer.

2.2. Reaction

A typical reaction was performed as follows: The catalyst (11–12 μmol) was introduced into a sealable glass vial (40 cm^3) containing a magnetic stir bar and 2 cm^3 of reactants or solvents and the vial was sealed. Then the glass vial was attached to a vacuum line, cooled to 77 K, and degassed by three freeze–pump–thaw cycles. The vial was allowed to warm to ca. 273 K and 1 atm of O_2 gas was introduced to the system. The reaction vessel was then vigorously stirred. The reaction vessel was removed from the bath every 1–10 h to refill the tube with 1 atm O_2 . The reaction solution was periodically sampled by syringe and analyzed by 1H or ^{13}C NMR and gas chromatography on Unisole F-200 and FFAP columns. Each reaction system was heterogeneous and each carbon balance was more than 90%. The yields based on PW_9-Fe_2Ni count alcohols, ketones, and acids as one.

3. Results and discussion

3.1. Oxidation of alkanes

3.1.1. Oxidation of adamantane

The catalytic oxygenation of adamantane with molecular oxygen was carried out in the presence of PW_9-Fe_2Ni for 48 h at 355 K. The time course is shown in Fig. 2. The products were 1-adamantanol, 2-adamantanol, and 2-adamantanone. 1-adamantanol and 2-adamantanol were first produced and then the formation of 2-adamantanone was observed. The ratio of the amount of 1-adamantanol to those of

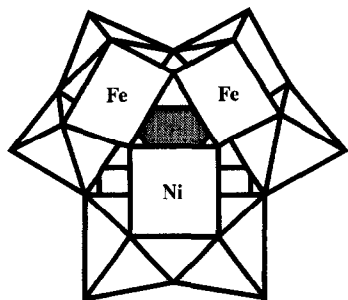


Fig. 1. Polyhedral representation of Fe_2Ni -substituted Keggin-type heteropolytungstate. The internal tetrahedron represents the PO_4^{3-} core and the white octahedra represent WO_6 fragments.

2-adamantanol + 2-adamantanone little changed with time. These facts show that adamantane is directly oxidized into 1-adamantanol and 2-adamantanol and 2-adamantanol is then oxidized into 2-adamantanone. After the reaction the solution was visibly colorless and the UV spectrum of the solution shows no band at 258 nm characteristic of PW_9-Fe_2Ni Keggin anion, showing that PW_9-Fe_2Ni is not dissolved during the reaction.

The conversion and selectivities to 1-adamantanol, 2-adamantanol, and 2-adamantanone were 29, 76, 12, and 12%, respectively, after 48 h (entry 1 in Table 3). Adamantane was found to be catalytically oxidized to give 1-adamantanol (19.1, turnover number (= mol product/mol catalyst used)), 2-adamantanol (3), and 2-adamantanone (2.9).

When one considers that PW_9-Fe_2Ni ($1.1 \text{ m}^2 \text{ g}^{-1}$) was insoluble in cyclohexane, cyclohexene, *n*-decane, ethylbenzene, and benzene, it may be preferable that the turnover number based on PW_9-Fe_2Ni is evaluated per surface polyanion. In this case, the turnover number increased by a factor of ca. 150. However, the turnover number was hereafter calculated for convenience based on the whole PW_9-Fe_2Ni used. PW_9-Fe_2Ni was only soluble in acetonitrile. The turnover number was 25 based on bulk polyanion or 3750 per surface polyanion.

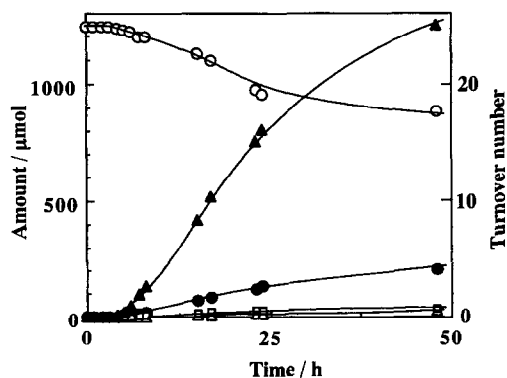


Fig. 2. Time course of oxidation of adamantane on PW_9-Fe_2Ni at 82°C . PW_9-Fe_2Ni , $11 \mu\text{mol}$; solvent, benzene (2 cm^3); adamantane, 1.24 mmol . \circ , conv.; \bullet , 1-adamantanol; \square , 2-adamantanol; \triangle , 2-adamantanone; \blacktriangle , total turnover number.

Table 2

Turnover number of various catalysts for oxidation of adamantane

Catalyst	Reductant	Turnover number	Ref.
PW_9-Fe_2Ni	none	3750 ^a	[12]
$[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$	none	372	[19]
$K[Ru(\text{saloph})Cl_2]^b$	none	13	[30]
$Fe_3O(OAc)_6(py)_3$	Zn	2087	[31]
$[(Fe(HBpz_3)(\text{hfacac}))_2O]^c$	Zn	48	[32]
$Fe(\text{salen})_2O^d$	Zn	2.5	[31]
$[Fe(TPP)_2]O^e$	Zn	1.7	[31]

^a Turnover number per surface polyanion.

^b Saloph: bis(salicylaldehyde-*o*-phenylenediaminato).

^c HBpz₃: hydrotris-pyrazolylborate. Hhfacac: hexafluoroacetylacetonate.

^d Salen: N, N'-etynebis(salicylideneaminato).

^e TPP: tetraphenylporphyrin.

Thus, it was found that the catalytic oxidation of adamantane by molecular oxygen without any reductants is catalyzed by PW_9-Fe_2Ni . In addition, the turnover number of 3750 was the highest level for the dioxygen oxidation of adamantane on μ -oxo di- or tri-iron, $[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$, heteropolyanion, and Ru complexes without any reductants or even with reductants, as compared in Table 2 [19,30–32].

The ratio of tertiary/secondary C–H bond selectivity on a per bond basis was 9.7. The value was in the range 2.6–12 found for other non-porphyrin systems [30,33–37], including $PW_{11}CoO_{39}^{5-}/t$ -butylhydroperoxide (10), $[Fe_2O(C_{10}H_8N_2)_4(OAc)(ClO_4)_3]/t$ -butylhydroperoxide (11), $[Fe_2O(\text{bipy})_4(OH_2)(ClO_4)_4]$ (bipy, 2,2'-bipyridyl/hydrogen peroxide (12), $[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}/$ dioxygen (6.7), μ -oxo di-iron complex/ O_2/Zn (4.7), and $Fe_2O(OAc)_2(\text{bpy})_2Cl_2$ /hydrogen peroxide (3.5) systems. Under free radical conditions, the ratio of tertiary/secondary C–H bond selectivity is normally 3 [19], different from the present value of 9.7, suggesting that the present system does not include free radical formation. However, it was reported that the $PW_{11}CoO_{39}^{5-}/t$ -butylhydroperoxide system further leads to the free radical formation for the

functionalization of alkanes [33] and that methane monooxygenase oxidizes alkanes via radical intermediates [37](a). Further efforts are made to clarify the reaction mechanism in more detail taking into accounts the results of cyclohexane oxidation as described in the next section.

IR spectra of as-prepared and spent $\text{PW}_9\text{-Fe}_2\text{Ni}$ are compared in Fig. 3 to investigate the catalyst stability. The IR spectrum of as-prepared $\text{PW}_9\text{-Fe}_2\text{Ni}$ showed the intense 1054 cm^{-1} , 956 cm^{-1} , 886 cm^{-1} , and the very broad 814 cm^{-1} bands, which are characteristic of Keggin structure and are assigned to $\nu(\text{P-O})$, $\nu(\text{W=O})$, corner-sharing $\nu(\text{W-O-W})$, and edge-sharing $\nu(\text{W-O-W})$, respectively, by analogy to the assignment for $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{PMo}_{12}\text{O}_{40}^{3-}$ Keggin anions [38]. The IR spectrum little changed after the use for the reaction, showing that the Keggin-type structure of $\text{PW}_9\text{-Fe}_2\text{Ni}$ was maintained during the oxidation. In the range of $3500\text{--}1100\text{ cm}^{-1}$, the new peaks were observed at 3235 , ca. 1714 , 1454 , 1239 , 1210 , and 1137 cm^{-1} , which are assignable to adamantane and the oxidation products, 1-

adamantanol, 2-adamantanol, and 2-adamantanone.

3.1.2. Various alkanes

The representative results of $\text{PW}_9\text{-Fe}_2\text{Ni}$ -catalyzed oxidations of various alkanes with molecular oxygen are listed in Table 3. It was confirmed that without catalysts no reactions proceeded in the oxidations of adamantane, cyclohexane, *n*-decane, and ethylbenzene. Alkylated arene, ethylbenzene, was also oxidized at the benzylic position selectively and catalytically (entry 2). The turnover number based on $\text{PW}_9\text{-Fe}_2\text{Ni}$ was 230. The oxygenation of cyclic alkane of cyclohexane was also catalytically oxidized into cyclohexanol and cyclohexanone, but the reaction was slow (entry 3). It was confirmed by iodometric titration and NMR that no hydroperoxide was formed in the blank experiment of cyclohexane, excluding the mechanism that the catalysts promote the decomposition of the hydroperoxide formed by the autoxidation.

Poorly reactive linear alkanes such as propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-decane were very slowly oxidized by molecular oxygen without any additives (entries 4–6). The addition of NaN_3 or the calcination of $\text{PW}_9\text{-Fe}_2\text{Ni}$ at 300°C decreased the activity for the oxidation of propane.

3.1.3. Activity of various catalysts

The turnover number based on $\text{PW}_9\text{-Fe}_2\text{Ni}$ was 5.2 for the oxidation of cyclohexane with molecular oxygen as shown in Table 3. On the other hand, $\text{PW}_{11}\text{-Ni}$ and $\text{PW}_{11}\text{-Fe}$ showed no activity for the oxidation of cyclohexane under the same conditions [12], showing the pronounced synergistic effect and the effectiveness of the multiple active centers for the oxygenation. Neither mononuclear iron complex, $\text{Fe}(\text{acac})_3$ (acac: acetylacetonate) nor iron powder showed catalytic activity under the same conditions [12]. The other binuclear iron species, $\text{Fe}_2\text{NiO}(\text{OAc})_6(\text{H}_2\text{O})_3$, and trinuclear iron species, $\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3$ and

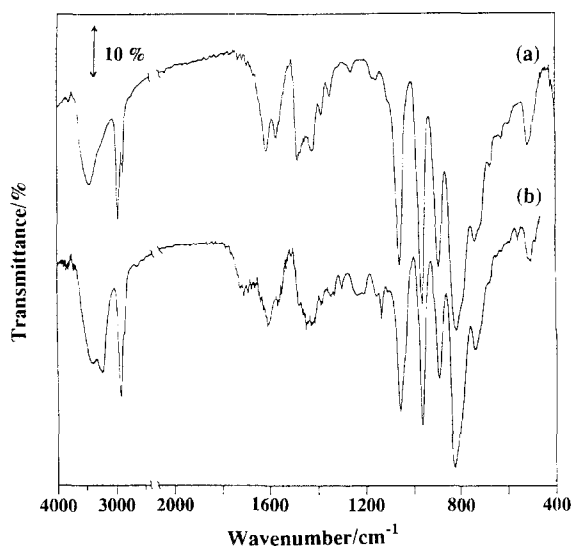


Fig. 3. IR spectra of as-prepared and spent $\text{PW}_9\text{-Fe}_2\text{Ni}$. (a) As-prepared $\text{PW}_9\text{-Fe}_2\text{Ni}$. (b) $\text{PW}_9\text{-Fe}_2\text{Ni}$ used for oxidation of adamantane at 82°C .

Table 3
PW₉-Fe₂Ni-catalyzed oxidation of alkanes by molecular oxygen

Entry	Substrate	Conv. ^a (%)	Turnover number ^b	Turnover number per surface polyanion	Product	Selectivity ^c (%)
1	adamantane ^d	29	25	3750	1-adamantanol	76
					2-adamantanol	12
					2-adamantanone	12
2	ethylbenzene ^e	17	230	34500	acetophenone	73
					1-phenylethanol	26
					benzaldehyde	1
3	cyclohexane ^e	0.36	5.2	780	cyclohexanone	83
					cyclohexanol	17
4	<i>n</i> -decane ^e	0.05	0.43	65	decanones	87 ^f
					decanols	13 ^g
5	<i>n</i> -butane ^h	0.53	1.90	—	acetone	≥ 99
6	propane ⁱ	0.64	2.3	—	acetone	78
					2-propanol	22

^a Based on starting substrates.

^b Mol products/mol catalyst used.

^c Percentages of products. Carbon balance for each reaction was more than 95%.

^d Benzene (solvent), 2 cm³; adamantane, 1.24 mmol; reaction temp., 82 ± 1°C; reaction time, 48 h; catalyst, 11 μmol.

^e Reaction was carried out without any solvents at 82 ± 1°C. The amounts (2 cm³) of cyclohexane, *n*-decane, and ethylbenzene used were 18.5, 10.3, and 16.3 mmol, respectively. Reaction times for oxygenations of cyclohexane, *n*-decane, and ethylbenzene were 118, 74, and 91 h, respectively. Catalyst, 11–12 μmol.




^f 2-One:3-one:(4 + 5)-ones = 36:24:40.

^g 2-Ol:3-ol:(4 + 5)-ols = 33:17:50.

^h P_{C₄H₁₀}, 2 kg/cm²; P_{O₂}, 9 kg/cm²; solvent, CH₃CN; reaction temp., 50°C; reaction time, 24 h; catalyst, 2 μmol.

ⁱ P_{C₃H₈}, 2 kg/cm²; P_{O₂}, 9 kg/cm²; solvent, CH₃CN; reaction temp., 50°C; reaction time, 77 h; catalyst, 2 μmol.

Table 4
Oxidation of cyclohexane catalyzed by PW-Fe₂Ni in various systems

Entry	Solvent	Oxidant	Additive	Yield / μmol		Turnover number ^a
						
1 ^b	None	O ₂	None	11	52	5.2
2 ^c	CH ₃ CN	O ₂	None	0	0	0
3 ^d	CH ₃ CN	O ₂		3	4	3.5
4 ^e	CH ₃ CN	H ₂ O ₂	None	89	84	87

^a Mol products/mol PW₉-Fe₂Ni.

^b Cyclohexane, 18.5 mmol; catalyst, 12 μmol; reaction time, 118 h; reaction temp., 82°C.

^c Cyclohexane, 200 μmol; catalyst, 2 μmol; reaction time, 12 h; reaction temp., 30°C.

^d Cyclohexane, 200 μmol; isobutyraldehyde, 800 μmol; catalyst, 2 μmol; reaction time, 12 h; reaction temp., 30°C.

^e Cyclohexane, 1.8 mmol; catalyst, 2 μmol; reaction time, 119 h; reaction temp., 50°C; 30% H₂O₂ was used (1.8 mmol).

$\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3\text{Cl}$, showed the activity, which was, however, lower than that of $\text{PW}_9\text{-Fe}_2\text{Ni}$. These facts also indicate the effectiveness of the Fe_2Ni site for the oxidation of cyclohexane. The much higher activity of $\text{PW}_9\text{-Fe}_2\text{Ni}$ than that of $\text{Fe}_2\text{NiO}(\text{OAc})_6(\text{H}_2\text{O})_3$ may be due to the great ligating capability of $\text{PW}_9\text{O}_{34}^{9-}$ heteropolyanion to stabilize the Fe_2Ni trinuclear unit.

The turnover number was increased from 5.2 to 100 when 15 wt% $\text{PW}_9\text{-Fe}_2\text{Ni}$ was supported on SiO_2 and also increased to 440 by the solubilization in 1,2-dichloroethane with the exchange of counteranion [39].

3.1.4. Effects of solvent, aldehyde, and oxidant

Table 4 shows the effects of solvent, aldehyde, and oxidant on the oxidation of cyclohexane. Entries 1 and 2–4 were carried out without solvents and in acetonitrile, respectively. The oxidation in acetonitrile hardly proceeded (entry 2) while the oxidation without solvents gave higher yields of cyclohexanol and cyclohexanone (entry 1).





Murahashi et al. reported that the addition of aldehydes promoted the oxidation of alkanes [40]. Effects of the addition of aldehydes were

investigated in a homogeneous system (entries 2 and 3). The addition of isobutyraldehyde resulted in the increase in the yields. The effectiveness was aldehyde dependent in the order of isobutyraldehyde > crotonaldehyde > propionaldehyde > benzaldehyde. A similar increase in the conversion by the addition of octyl aldehyde was observed for the oxidation of *n*-decane: the conversion increased from 0.05% (entry 4 in Table 3) to 0.8% by the addition of 2.5 mmol octyl aldehyde to the *n*-decane/ $\text{PW}_9\text{-Fe}_2\text{Ni}/\text{O}_2$ system and the selectivities to decanones and decanols became 51 and 49%, respectively.

In addition, when cyclohexane was oxygenated by hydrogen peroxide, the turnover number greatly increased to 87 (entry 4). The value was much higher than 5 (entry 1) and 7.4, reported for the oxidation of cyclohexane with *t*-butylhydroperoxide on mono-iron-substituted $\text{PW}_{12}\text{O}_{40}^{3-}$ [33]. The main product was cyclohexanone for the oxidation without solvents (entry 1) while about equimolar amounts of cyclohexanone and cyclohexanol were formed for the oxidation with hydrogen peroxide and molecular oxygen + isobutyraldehyde.

Next, the reaction was carried out at higher

Table 5
Oxidation of cyclohexene catalyzed by $\text{PW-Fe}_2\text{Ni}$ in various systems

Entry	Solvent	Oxidant	Additive	Yield / μmol			Turnover number ^a
							
1 ^b	None	O_2	None	0	trace	1856	186
2 ^c	CH_3CN	O_2	None	0	0.1	0.6	0.07
3 ^d	CH_3CN	O_2		146	5	14	660
4 ^e	CH_3CN	H_2O_2	None	7	trace	19	2.6

^a Mol products/mol $\text{PW}_9\text{-Fe}_2\text{Ni}$.

^b Cyclohexene, 18.5 mmol; catalyst, 10 μmol ; reaction time, 48 h; reaction temp., 82°C.

^c Cyclohexene, 1000 μmol ; catalyst, 10 μmol ; reaction time, 14 h; reaction temp., 30°C.

^d Cyclohexene, 250 μmol ; catalyst, 0.25 μmol ; reaction time, 12 h; reaction temp., 30°C.

^e Cyclohexene, 250 μmol ; catalyst, 10 μmol ; reaction time, 12 h; reaction temp., 30°C; 30% H_2O_2 was used (3 mmol).

pressures and temperatures to increase the yields. When the oxidation of cyclohexane was catalyzed by PW_9-Fe_2Ni without solvents at $130^\circ C$ and P_{O_2} of 15 atm for 7 h, the turnover number was 42, higher than that shown in entry 1. The yields of cyclohexanol, cyclohexanone, and benzene were 74, 93, and $333 \mu mol$, respectively, and the main product was benzene.

3.2. Oxidation of cyclohexene

Table 5 shows the effects of solvent, aldehyde, and oxidant on the oxidation of cyclohexene. The O_2 + aldehyde system has been reported to be effective for the epoxidation of alkenes [41,42]. Therefore, the oxidation of cyclohexene by O_2 was carried out in the presence of isobutyraldehyde. Entries 1 and 2–4 were carried out with and without an acetonitrile solvent, respectively. The oxidation without solvents (entry 1) proceeded much faster than that in acetonitrile (entry 2). When aldehydes were added to the homogeneous oxidation systems, turnovers and selectivities were changed. The turnovers changed in the order of isobutyraldehyde \gg benzaldehyde > propionaldehyde > crotonaldehyde with relative ratios of 1.0:0.16:0.10:0, respectively. It was reported that

Table 6
Oxidation of aldehydes by molecular oxygen catalyzed by PW_9-Fe_2Ni at $30^\circ C$ in acetonitrile

Entry	Substrate	Product	Yield ^a (%)
1 ^b	acetaldehyde	acetic acid	86
2 ^c	propionaldehyde	propionic acid	92
3 ^d	butyraldehyde	butyric acid	95
4 ^e	isobutyraldehyde	isobutyric acid	≥ 98
5 ^f	octyl aldehyde	octanoic acid	≥ 98

Acetonitrile, 3 cm^3 ; P_{O_2} , 1 atm.

^a Based on starting substrates.

^b Acetaldehyde, 1.0 mmol; reaction time, 53 h; catalyst, $10 \mu mol$.

^c Propionaldehyde, $200 \mu mol$; reaction time, 19 h; catalyst, $2 \mu mol$.

^d Butyraldehyde, 2.0 mmol; reaction time, 2 h; catalyst, $20 \mu mol$.

^e Isobutyraldehyde, $200 \mu mol$; reaction time, 19 h; catalyst, $2 \mu mol$.

^f Octyl aldehyde, 1 mmol; reaction time, 19 h; catalyst, $20 \mu mol$.

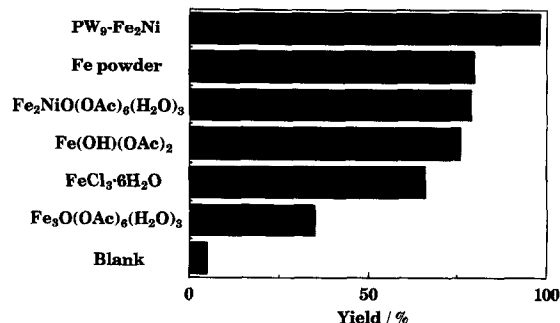


Fig. 4. Oxidation of butyraldehyde catalyzed by various compounds in acetonitrile at $30^\circ C$. Catalyst, $20 \mu mol$; reaction time, 2 h; butyraldehyde, 2 mmol; P_{O_2} , 1 atm.

the higher the turnover the more easily the aldehyde is oxidized [9]. The example of the addition of isobutyraldehyde was shown in entry 3. When isobutyraldehyde was added in the reaction system, the turnover was increased to more than 9400 times greater than that without isobutyraldehyde and the cyclohexene oxide was produced with 89% selectivity. The selectivity was higher than those ($\leq 30\%$) in the oxidations with hydrogen peroxide on PW_9-Fe_2Ni (entry 4), $H_{3+n}XM_{12}O_{40}$ ($n = 0-2$; $X = P, Si, C, B$; $M = Mo, W$) [43], or $[(n-C_4H_9)_4N]_5Na_3[(1,5-COD)Ir \cdot PW_{15}Nb_3O_{62}]$ [22]. However, the yield of cyclohexene oxide of 58% was still lower than those reported in isobutyraldehyde/ O_2 / $PW_{11}CoO_{39}^{5-}$ [9] and isobutyraldehyde/ O_2 / $(1,5-COD)Ir \cdot PW_{15}Nb_3O_{62}^{8-}$ [42] systems. Further addition of isobutyraldehyde gave identical rates and yields, suggesting that PW_9-Fe_2Ni might be stable under the conditions employed.

3.3. Oxidation of aldehydes

The oxidations of various aldehydes are shown in Table 6. The yields of acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, and octyl aldehyde were 86, 92, 95, ≥ 98 , and $\geq 98\%$, respectively, and the latter two were quantitatively oxidized into corresponding acids by molecular oxygen (entries 4 and 5).

The catalytic activity of PW_9-Fe_2Ni is compared with other Fe-containing compounds in Fig. 4. The activity decreased as follows: $PW_9-Fe_2Ni > Fe \text{ powder} \approx Fe_2NiO(OAc)_6(H_2O)_3 \approx Fe(OH)(OAc)_2 > FeCl_3 \cdot 6H_2O > Fe_3O(OAc)_6 \cdot (H_2O)_3$ with relative oxygenation activities of 1:0.81:0.80:0.78:0.66:0.35, respectively. A similar order was observed for the oxidation of other aldehydes. It is noted that PW_9-Fe_2Ni was the most active for the oxidation of various aldehydes among the various Fe-containing catalysts.

In addition, the catalytic activity of PW_9-Fe_2Ni is compared with mono-transition-metal-substituted heteropolytungstates, $PW_{11}-Fe$ and $PW_{11}-Ni$. The major product is cyclohexene oxide for each catalyst. The activity decreased as follows: $PW_9-Fe_2Ni > PW_{11}-Fe \geq PW_{11}-Ni$ with relative oxygenation activities of 1:0.23:0.19, respectively. This result indicates the effectiveness of the Fe_2Ni site for the oxidation of cyclohexene with molecular oxygen.

4. Conclusion

To summarize, the above results demonstrate: (1) the example of aerobically induced catalytic oxygenation of alkanes, alkene, and aldehydes by molecular oxygen on a species having oxo-bridged mono- or tri-transition-metal site; (2) that the preferred catalyst for the oxidation of cyclohexane, cyclohexene, and butyraldehyde is the Fe_2Ni -substituted Keggin-type heteropolyanion, PW_9-Fe_2Ni ; (3) that the presence of the oxidation-resistant basic oxide ligand, $PW_9O_{34}^{9-}$, enhances the catalytic activity; (4) that the turnover number for the oxidation of adamantane in the preferred $PW_9-Fe_2Ni + O_2$ system was higher than those of catalysts reported to be active; (5) that butyraldehyde and octyl aldehyde were catalytically and quantitatively oxidized into corresponding acids on PW_9-Fe_2Ni ; (6) that the addition of aldehydes promoted not only the epoxidation of cyclohexene but also the oxygenation of poorly reactive alkanes such as cyclohexane and *n*-decane.

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