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Oxygenation of Alkanes by Molecular Oxygen on $[PW_9O_{37}\{Fe_2Ni(OAc)_3\}]^{10-}$ Heteropolyanion

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Adamantane, ethylbenzene, and cyclohexane are catalytically and selectively oxidized to the corresponding alcohols and ketones with molecular oxygen alone on PW_9-Fe_2Ni heteropolyanion.

Recently, the active site of methane monooxygenase has been shown to consist of μ-oxo or μ-hydroxo diiron structure1) and to be active for the oxidation of a variety of alkanes by molecular oxygen under mild conditions.2) Therefore, the oxidation catalysis by oxo-bridged di- or tri-transition metal complexes is living research field to develop new catalytic system and understand the mechanism of the action of iron- or copper-containing biomolecules such as hemerythrin, purple acid phosphatase, hemocyanin, and laccase.3,4) However, efforts to use oxo-bridged di- or tri-iron complexes for the oxidation of hydrocarbons with dioxygen have had only limited success because of the necessity of reductants and the unstableness of the catalysts.2,5)

On the other hand, there are many literatures and patents describing the liquid-phase oxidations of hydrocarbons with various oxygen donors on heteropolyanion due to their oxidizing ability, oxidative resistance, and thermal stability.6) However, little is known of catalysis of di- and tri-transition-metal-ion-substituted Keggin-type heteropolyanion.5e) In this communication we wish to report the aerobically induced high yield catalytic oxygenation of alkanes on $[PW_9O_{37}\{Fe_2Ni(OAc)_3\}]^{10-}$ without any reductants.

$[(n\text{-}C_4H_9)_4N]_4H_6[PW_9O_{37}\{Fe_2Ni(OAc)_3\}]$ (denoted by PW_9-Fe_2Ni) was prepared from iron(III) nitrate, nickel(II) nitrate, and A-$Na_9PW_9O_{34}$. IR, NMR, UV, Mössbauer, magnetic susceptibility, and elemental analysis show that the tri-transition-metal-substituted Keggin-type heteropolyanion, $[PW_9O_{37}\{Fe_{3-x}Ni_x(OAc)_3\}]^{(9+x)-}$ (x=predominantly 1), was synthesized. 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 literatures.7)

The catalytic oxidation was carried out according to Ref. 8. 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 the reactant or the solvent and the vial was sealed. The solvent was not used except for the oxidation of adamantane. 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 placed at 355±1 K ($P_{O_2} \approx 1.3$ atm) and vigorously stirred. The reaction vessel was removed from the bath every 5 - 10 h to refill the tube with 1 atm

Table 1. PW_{11}-Fe_2Ni-Catalyzed oxidation of alkanes by molecular oxygen

Substrate	Total turnover number[a)	Conversion[b) /%	Product	Selectivity[c) /%
Adamantane[d)	25	29	1-Adamantanol	76
			2-Adamantanol	12
			2-Adamantanone	12
Ethylbenzene[e)	230	17	Acetophenone	73
			1-Phenylethanol	26
			Benzaldehyde	1
Cyclohexane[e)	5.2	0.36	Cyclohexanone	83
			Cyclohexanol	17
n-Decane[e)	0.43	0.05	Decanones	87[f)
			Decanols	13[g)

a) Mol products/mol catalyst used. b) Based on starting substrates. c) Percentages of products. Carbon balance for each reaction was more than 95%. d) Benzene (solvent), 2 cm^3; adamantane, 1.24 mmol; reaction temp., 355±1 K; reaction time, 48 h. e) Reaction was carried out without any solvents at 355±1 K (see text). The amounts (2 cm^3) 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. f) 2-One:3-one:(4+5)-ones=36:24:40. g) 2-Ol:3-ol:(4+5)-ols=33:17:50.

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 95%. The yields based on PW_9-Fe_2Ni count alcohols or ketones as one.

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 ratio of the amount of 1-adamantanol to those of 2-adamantanol + 2-adamantanone little changed with time. 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). After the reaction the solution was visibly colorless and it was confirmed by UV and IR that the Keggin-type structure of PW_9-Fe_2Ni was maintained during the oxidation. The total turnover number was 25 based on bulk polyanion or 3750 per surface polyanion.[9) 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 total turnover number of 3750 was the highest level for the dioxygen oxidation of adamantane on μ-oxo di- or tri-iron and Ru complexes without any reductants or even with reductants.[5,10)

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 - 10 found for other non-porphyrin systems,[2a,5a,6,11) including $PW_{11}CoO_{39}^{5-}$/t-butyl hydroperoxide (10) and μ-oxo diiron complex/O_2/Zn (4.7) systems, of which the former further leads to the free radical formation for the functionalization of alkanes. It has also been reported that methane monooxygenase oxidizes alkanes via radical intermediates.[2a)

Table 2. Oxygenation of cyclohexane by molecular oxygen[a)]

Catalyst	Total turnover number[b)]	Conversion[c)] $/10^{-2}\%$	Product/μmol	
			Cyclohexanone	Cyclohexanol
PW_9-Fe_2Ni	1.9	12.2	18.1	4.6
$Fe_2NiO(OAc)_6(H_2O)_3$	0.4	2.3	3.4	0.9
$Fe_3O(OAc)_6(H_2O)_3$	1.1	7.2	7.9	5.4
$Fe_3O(OAc)_6(H_2O)_3Cl$	0.1	0.3	0.5	0.1
PW_{11}-Fe	0.0	0.0	0.0	0.0
PW_{11}-Ni	0.0	0.0	0.0	0.0

a) Catalyst, 12 μmol; cyclohexane, 2.0 cm^3 (18.5 mmol); reaction temp., 355±1 K; reaction time, 43 - 45 h. c) See note (a) of Table 1. c) Based on starting substrates.

The representative results of PW_9-Fe_2Ni-catalyzed oxidations of various alkanes with molecular oxygen are listed in Table 1. Alkylated arene, ethylbenzene, was also oxidized at the benzylic position selectively and catalytically. The total turnover number based on PW_9-Fe_2Ni was 230. The oxygenations of cyclohexane and *n*-decane were very slow: The total turnover numbers based on PW_9-Fe_2Ni were 5.2 and 0.43, respectively. The total turnover number to the oxygenated compounds of cyclohexane was increased up to 100 when 15 wt% PW_9-Fe_2Ni was supported on SiO_2. Without catalysts no reactions proceeded in the oxidations of adamantane, cyclohexane, *n*-decane, and ethylbenzene. Poorly reactive linear alkanes such as *n*-pentane, *n*-hexane, and *n*-heptane were hardly oxidized by molecular oxygen without any additives.

The activities of various catalysts are compared by using cyclohexane oxygenation in Table 2. PW_9-Fe_2Ni was the most active for the reaction among the neat catalysts tested. In contrast, no catalytic activity was observed for mono-transition-metal-substituted polyanions, PW_{11}-M (M = Co, Mn, Fe, Cu, Ni). Neither mononuclear iron complex, $Fe(acac)_3$ (acac, acetylacetonate) nor iron powder showed catalytic activity under the same conditions. The other binuclear iron species, $Fe_2NiO(OAc)_6(H_2O)_3$, and trinuclear iron species, $Fe_3O(OAc)_6(H_2O)_3$ and $Fe_3O(OAc)_6(H_2O)_3Cl$, showed the activity, which was, however, lower than PW_9-Fe_2Ni. These facts indicate the effectiveness of the di- or tri-iron sites for the present reaction. The much higher activity of PW_9-Fe_2Ni than that of $Fe_2NiO(OAc)_6(H_2O)_3$ may be due to the great ligating capability of $PW_9O_{34}{}^{9-}$ heteropolyanion to stabilize the Fe_2Ni trinuclear unit.

In summary, a novel catalytic oxygenation of adamantane, ethylbenzene, and cyclohexane with molecular oxygen and without any reductants on PW_9-Fe_2Ni heteropolyanion was found. 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. Further efforts would be devoted to clarify the mechanism.

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