Oxidation of Cyclohexane with Molecular Oxygen Efficiently Catalyzed by Di-Iron(III)-Substituted Silicotungstate, γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$, Including Radical-chain Mechanism

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The tetrabutylammonium salt of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ showed high turnover number of 135-147 for the oxidation of cyclohexane with 1 atm molecular oxygen and the value is of the highest level among silicotungstates with various iron contents and other catalysts reported. Results obtained with radical initiator and scavenger, and the selectivity for oxygenation of adamantane suggest that the reaction involves a radical-chain path.

Catalytic oxidations of hydrocarbons are important both industrially and in organic synthesis.[1-3] Among hydrocarbons, alkanes have attracted much attention because they are abundant as resources and low in reactivities.[4-8] In particular, the selective catalytic oxidation using molecular oxygen is a desirable technology and is an area of continuous research and development.[8,9] Although the oxidation of cyclohexane has been industrialized by using cobalt or manganese acetate catalyst at pressurized molecular oxygen above 373 K,[10] it is mush more desirable that the oxidation is carried out under milder conditions. Several examples of liquid-phase oxidations of cyclohexane with 1 atm molecular oxygen and reducing reagents have been reported: Fe_0/pyridine (Gif system),[11] iron powder/heptanal[12] and $[\{Fe(HBpz_3)(hfacac)\}_2O]$/Zn powder ($HBpz_3$ = hydrotris-1-pyrazolylborate, hfacac = hexafluoroacetylacetone)[13] systems are the examples. On the other hand, Ishii *et al.* reported that $Mn(acac)_2$ and $Co(acac)_2$ showed high conversions of 65 and 45%, respectively, for cyclohexane oxidation in the presence of a radical initiator, *N*-hydroxyphthalimide (abbreviated as NHPI).[14,15]

However, there are only a few examples of oxidations of alkanes without reducing reagents or radical initiators because of the degradation of organic ligands of catalysts. $K[Ru^{III}(saloph)Cl_2]$ (saloph = *bis*(salicyaldehyde-*o*-phenylene diiminato)[16] and $[PW_9O_{37}\{Fe_{3-x}Ni_x(OAc)_3\}]^{(9+x)-}$ (x = predominantly 1)[17] are the examples of catalysts for cyclohexane oxidation. For the achievement of catalytic selective oxidation of alkanes with 1atm molecular oxygen without any additives, the high catalyst turnover numbers are needed and the information on the active structure is important.

In this letter, we compare turnover numbers of iron-substituted silicotungstates and other catalysts reported to be active for cyclohexane oxidation with 1 atm molecular oxygen and find that the value of *di*-iron-substituted silicotungstate, γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$, is of the highest level.

Non-, *mono*-, *di*- and *tri*-iron-substituted silicotungstates, α-$SiW_{12}O_{40}^{4-}$, α-$SiW_{11}\{Fe(OH_2)\}O_{39}^{5-}$, γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ and α-$SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ were synthesized as tetrabutylammonium salts according to literature.[18-21] Cyclohexane was distilled and treated with activated alumina to remove impurities and cyclohexylhydroperoxide. *N*-Hydroxyphthalimide (Tokyo Chemical Industry Co., Ltd.) was commercially obtained and used without the further purification.

The reaction was carried out in a glass vial containing a magnetic stir bar as described previously.[18] The reaction solution was periodically sampled and analyzed by gas chromatography on TC-WAX capillary columns. The oxidation of cyclohexane did not proceed without catalysts under the present conditions.

Figure 1 shows the time course of catalytic oxidation of cyclohexane with 1atm molecular oxygen catalyzed by γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ at 365 K. The main products were cyclohexanol and cyclohexanone and an induction period was observed. The selectivities changed little with time. A small amount of dicyclohexyl, which is formed by the reaction of two cyclohexyl radicals, was observed. Neither acids nor oxoesters were observed. The induction period and the formation of dicyclohexyl suggest that the reaction involves a radical-chain autoxidation mechanism. The conversion was 1.1% after 96h and was increased to 2.4% by increasing the amount of catalyst by a factor of two. The turnover number of γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ reached up to 135-147 after 96 h, of which the value is much higher than 18 and 5 reported for $K[Ru^{III}(saloph)Cl_2]$[16] and $[PW_9O_{37}\{Fe_{3-x}Ni_x(OAc)_3\}]^{(9+x)-}$ (x = predominantly 1),[17] respectively, with 1 atm molecular oxygen. In addition, the value was higher than 130, 121, 90, 11 and 5 reported for $Mn(acac)_2$/NHPI[14] Fe^0/picolinic acid,[1] $Co(acac)_2$/NHPI,[15] iron powder/heptanal,[12] and $[\{Fe(HBpz_3)(hfacac)\}_2O]$/Zn[13] systems, respectively, which work in the presence of reducing reagents or radical initiators.

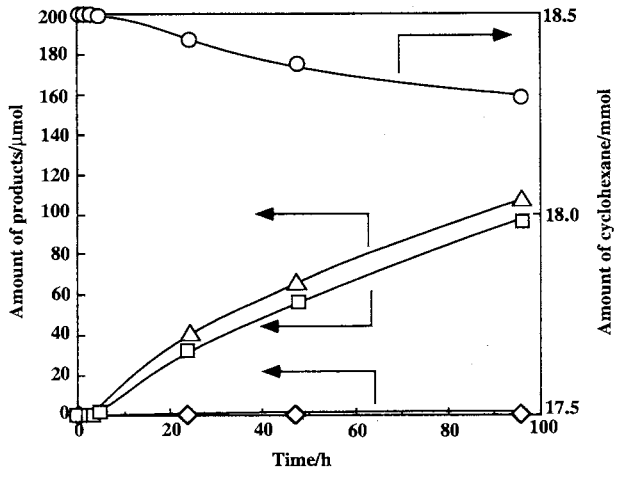

Figure 1. Time course of oxidation of cyclohexane with molecular oxygen catalyzed by γ-$SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ at 356 K.
○, cyclohexane; □, cyclohexanone; △, cyclohexanol; ◇, dicyclohexyl.

Table 1. Oxidation of cyclohexane with molecular oxygen catalyzed by iron-substituted silicotungstates at 356 K[a]

catalysts	turnover number[b]	conversion/%[c]	selectivity/%		
			cyclohexanol	cyclohexanone	dicyclohexyl
$[\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$	135	1.1	53	47	trace
$[\alpha\text{-}SiW_9\{Fe(OH_2)\}_3O_{37}]^{7-}$	39	0.3	47	53	trace
$[\alpha\text{-}SiW_{11}\{Fe(OH_2)\}O_{39}]^{5-}$	0	0.0	-	-	-
$[\alpha\text{-}SiW_{12}O_{40}]^{4-c}$	0	0.0	-	-	-

[a]Reaction conditions: catalyst, 1.5 μmol; solvent, 1,2-$C_2H_4Cl_2$ (1.5 mL)/acetonitrile (0.1 mL); cyclohexane, 18.5 mmol; *P(O2)*, 1 atm; reaction time, 96 h. [b]Moles of products/moles of catalysts used. [c]Moles of products/moles of cyclohexane used.

Table 1 compares turnover numbers for cyclohexane oxidation with molecular oxygen catalyzed by iron-substituted silicotungstates. The turnover numbers for iron-substituted silicotungstates decreased in the order of $\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$ > $\alpha\text{-}SiW_9\{Fe(OH_2)\}_3O_{37}^{7-}$ > $\alpha\text{-}SiW_{11}\{Fe(OH_2)\}O_{39}^{5-} \approx \alpha\text{-}SiW_{12}O_{40}^{4-} \approx 0$. In addition, among *tri*-transition metal-substituted silicotungstates, $\alpha\text{-}SiW_9\{M^{n+}(OH_2)\}_3O_{37}^{(16-3n)-}$ (M = Fe^{3+}, Ni^{2+}, Cu^{2+}), the order of turnover numbers was Fe > Ni > Cu. These facts show that the *di*-iron site is effective for the oxygenation of cyclohexane with molecular oxygen.

Adamantane was also oxidized with 1atm molecular oxygen catalyzed by $\gamma\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}^{6-}$. The conversion reached up to 3.9% after 118 h at 365 K. The main products were 1-adamantanol, 2-adamantanol and 2-adamantanone with the % selectivities of 79 : 11 : 10, respectively. The selectivities changed little with time. The ratio of tertiary/secondary C-H bond selectivity per bond was 9. Under free radical conditions, the order of the reactivity is 3° > 2° and the ratio of tertiary/secondary C-H bond selectivity is typically in the range of 3 - 20,[22,23] while under non-radical conditions such as Gif system, the selectivity is 1.0.[24] The value of 9 observed for the present system is within those for free radical conditions. The addition of alkyl-radical scavenger of *p-tert*-butylcatechol resulted in no reactions. These facts suggest that the reaction proceeds via radical-chain mechanism. Radical initiator, NHPI, greatly increased the conversion from 1% to 75%, supporting the idea. The conversion of 75% are higher than $Mn(acac)_2$+NHPI and $Co(acac)_2$+NHPI systems, which are reported to be the effective radical autoxidation system.[14,15]

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