High turnover number of $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$ for oxygenation of cyclohexane with 1 atm molecular oxygen†

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An all-inorganic oxo-bridged dimanganese-containing silicotungstate, $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$, showed the highest turnover number of 789 among various metal-substituted silicotungstates for the oxygenation of cyclohexane with 1 atm molecular oxygen; this is the highest level when compared with other catalysts reported so far.

Catalytic oxygenation of alkanes has attracted much attention. The utilization of molecular oxygen for catalytic oxygenation is a rewarding goal because among oxidants molecular oxygen has the highest content of active oxygen and forms no by-products.[1–7] Reducing reagents or radical initiators have been added for in an attempt to facilitate reaction lowering the reaction temperature and resulting in the suppression of overoxidation of oxygenated products.[8–13] However, there are only a few examples of ideal homogeneous oxygenation systems for alkanes with molecular oxygen in the absence of reducing reagents or radical initiators because of catalyst deactivation and difficulty of C–H bond/oxygen activation.[1–24] The oxidation of cyclohexane has been industrialized by using a cobalt catalyst with pressurized molecular oxygen above 423 K, low conversions, however, are a drawback in suppressing overoxidation of the products.[5,25,26] It is clearly desirable if oxygenation can be carried out with higher turnover numbers under milder conditions. Fe(DPA) (DPA = 2,6-dicarboxylatopyridine), $K[Ru^{III}(saloph)Cl_2]$ [saloph = *N*,*N′*-*o*-phenylenebis(salicylideneaminato)] $PW_9O_{37}\{Fe_{3-x}Ni_x(OAc)_3\}^{(9+x)-}$ (x) = predominantly 1) and $\gamma\text{-}SiW_{10}\{Fe^{III}(OH_2)\}_2O_{38}^{6-}$ are examples of catalysts for cyclohexane oxygenation with 1 atm molecular oxygen.[14–16,20]‡ Cobalt-containing aluminophosphate and $[Co(NCMe)_4](PF_6)_2$ have also been reported to be active for oxygenation of cyclohexane with pressurized molecular oxygen.[21–24] However, the turnover numbers are low at < 180.

Little is known of the structures of the active manganese centers for the oxygenation of cyclohexane with molecular oxygen. Here, we report that the oxo-bridged dimanganese-containing silicotungstate, $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$, can efficiently catalyze the oxygenation of cyclohexane with 1 atm molecular oxygen.

Cyclohexane was distilled and treated with activated alumina to remove impurities and cyclohexyl hydroperoxide. The other reagents were commercially obtained and used as received. The reaction was carried out in a glass vial containing a magnetic stir bar as described previously.[27] The reaction solution was periodically sampled and analyzed by gas chromatography on TC-WAX capillary columns. The oxidation of cyclohexane did not proceed without catalyst under the present conditions.

Cyclohexanol and cyclohexanone were mainly formed after an induction period for the catalytic oxygenation of cyclohexane with 1 atm molecular oxygen catalyzed by $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$ at 365 K. Only small amounts of dicyclohexyl and cyclohexyl hydroperoxide were observed and neither acids, oxoesters nor carbon oxides were observed. The selectivities changed little with time. The conversion was 6.4%, and the turnover number of $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$ reached 789 after 96 h, much higher than values reported for the oxygenation of cyclohexane catalyzed by Fe(DPA)/O_2(1 atm),[14] $K[Ru(saloph)Cl_2]/O_2$ (1 atm),[15] $\gamma\text{-}SiW_{10}\{Fe^{III}(OH_2)\}_2O_{38}^{6-}/O_2$ (1 atm),[20] $[Co(NCMe)_4](PF_6)_2/O_2$ (3 atm)[21] or cobalt-containing aluminophosphate/O_2 (15 atm).[23] In addition, the value was higher than those of 130, 90, 5 and 3 reported for $Mn(acac)_2$/NHPI (NHPI = *N*-hydroxyphthalimide),[11] $Co(acac)_2$/NHPI,[13] $[\{Fe(HBpz_3)(hfacac)\}_2O]$-/Zn ($HBpz_3$ = hydrotris(1-pyrazolyl)borate, hfacac = 1,1,-1,5,5,5-hexafluoroacetylacetone)[28] and $[R_fMn(R_fTACN)]^{2+}$/TBHP (R_fTACN = tris-*N*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,-11,11-heptadecafluoroundecyl)-1,4,7-triazacylononane; R_f = C_8F_{17})[12] systems, respectively, which work in the presence of reducing reagents or radical initiators with 1 atm molecular oxygen.

The oxygenation of cyclohexane with 1 atm molecular oxygen proceeded catalytically even at 305 K,§ whilst no oxygenation was observed for $\gamma\text{-}SiW_{10}\{Fe^{III}(OH_2)\}_2O_{38}^{6-}$ at the same temperature. It has been reported that the commercial catalyst, $Co(oct)_2$ (oct = 2-ethylhexyl octanoate), was inactive at 348 K with 3 atm molecular oxygen.[21] All these results demonstrate that $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-}$ can catalyze the selective oxygenation of cyclohexane with high turnover number and under mild conditions.

Table 1 compares turnover numbers for cyclohexane oxygenation with molecular oxygen catalyzed by manganese-substituted silicotungstates. The turnover numbers for manganese-substituted silicotungstates decreased in the order $\gamma\text{-}SiW_{10}\{Mn^{III}(OH_2)\}_2O_{38}^{6-} > \alpha\text{-}SiW_{11}\{Mn^{III}(OH_2)\}O_{39}^{5-} > \alpha\text{-}SiW_9\{Mn^{III}(OH_2)\}_3O_{37}^{7-} \approx \alpha\text{-}SiW_{12}O_{40}^{4-} \approx 0$. No oxygenation proceeded for $\gamma\text{-}SiW_{10}\{Mn^{II}(OH_2)\}_2O_{38}^{8-}$ in which the oxidation state of manganese is +2. In addition, among *mono*-transition metal-substituted silicotungstates, $\alpha\text{-}SiW_{11}\{M^{n+}(OH_2)\}O_{39}^{(8-3n)-}$ (M = Mn^{3+}, Fe^{3+}, Cu^{2+}), the order of turnover numbers was $Mn^{3+} > Fe^{3+} > Cu^{2+}$. These facts show that manganese is an effective element for catalysis and that a dimanganese site with the oxidation state of +3 is the most effective for the oxygenation of cyclohexane with molecular oxygen.

Small amounts of dicyclohexyl, which is formed by the reaction of two cyclohexyl radicals, and cyclohexyl hydroperoxide were observed. The addition of an alkyl-radical scavenger, *p*-*tert*-butylcatechol, led to complete inhibition. These facts suggest that the reaction includes a radical-chain mechanism. Further mechanistic work is in progress.

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

			Selectivity (%)			
Catalyst	Turnover number[b]	Conversion[c] (%)	Cyclohexanol	Cyclohexanone	Cyclohexyl hydroperoxide	Dicyclohexyl
$[\alpha]\text{-SiW}_{12}O_{40}]^{4-}$	0	0.0	—	—	—	—
$[\alpha\text{-SiW}_{11}\{Mn^{III}(OH_2)\}O_{39}]^{5-}$	295	2.4	57	41	2	Trace
$[\gamma\text{-SiW}_{10}\{Mn^{III}(OH_2)\}_2O_{38}]^{6-}$	789	6.4	51	48	1	Trace
$[\gamma\text{-SiW}_{10}\{Mn^{II}(OH_2)\}_2O_{38}]^{8-}$	0	0.0	—	—	—	—
$[\alpha\text{-SiW}_9\{Mn^{III}(OH_2)\}_3O_{37}]^{7-}$	0	0.0	—	—	—	—
$[\gamma\text{-SiW}_{10}\{Fe^{III}(OH_2)\}_2O_{38}]^{6-}$ [d]	135	1.1	53	47	—	Trace
$[\gamma\text{-SiW}_{10}\{Cu^{II}(OH_2)\}_2O_{38}]^{8-}$	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; $P(O_2)$, 1 atm; reaction time, 96 h. [b] Mol of products/mol of catalysts used. [c] Mol of products/mol of cyclohexane used. [d] Cited from ref. 20.

Notes and references

‡ The turnover numbers for Fe(DPA), K[Ru^{III}(saloph)Cl_2], $PW_9O_{37}\{Fe_{3-x}Ni_x(OAc)_3\}^{(9+x)-}$ and $\gamma\text{-SiW}_{10}\{Fe^{III}(OH_2)\}_2O_{38}{}^{6-}$, cobalt-containing aluminophosphate and $[Co(NCMe)_4](PF_6)_2$ catalysts were 0.2 (reaction temperature, 295 K), 18 (298–318 K), 5 (356 K), 135 (356 K), 167 (403 K) and 180 (348 K), respectively.

§ The selectivity to cyclohexanone and turnover number for $\gamma\text{-SiW}_{10}\{Mn^{III}(OH_2)\}_2O_{38}{}^{6-}$ catalyst were 100% and 3, respectively, after 96 h.

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