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Solvent-Free Aerobic Oxidation of *n*-Alkane by Iron(III)-Substituted Polyoxotungstates Immobilized on SBA-15

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The tetrairon(III)-substituted polytungstates $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ ($n = 6$, X = As^{III}, Sb^{III}; $n = 4$, X = Se^{IV}, Te^{IV}) were immobilized on (3-aminopropyl)triethoxysilane-modified SBA-15 and showed an excellent catalytic performance for solvent-free aerobic oxidation of long-chain *n*-alkanes using air as the oxidant under ambient conditions through a classical free-radical chain autoxidation mechanism.

Oxidation remains one of the principal paradigms for the activation of alkanes, which are well-known for their low reactivity and are of interest both academically and for applications. Among hydrocarbons, the oxidation of *n*-alkanes has attracted much attention because they are abundant as feedstocks.[1] The "ideal" catalyst would use air as the oxidant under mild conditions, be recyclable, and avoid the wasteful addition of reducing agents and solvents.[2,3] Many challenges are associated with the realization of these goals because of difficulties associated with oxygen and substrate activation and the fact that the solvent plays an important role in the activity of the catalysts for the oxidation of alkanes.[4] To date, only a few catalytic systems have been reported for the liquid-phase oxidation of alkanes using air, but most are in combination with additives such as reducing agents and radical initiators in solvents or under severe conditions (high pressure).[1d,3]

Polyoxometalates (POMs) are metal−oxygen cluster species with a diverse compositional range and an enormous structural variety.[5] Although the class of POMs has been known for about 200 years, the systematic structural design of novel POMs and derivation of known POMs remains a major challenge for synthetic chemists. Transition-metal-substituted POMs have attracted increasing attention in recent years because of their highly tunable nature, coupled with their fascinating properties resulting in potential applications in catalysis, material science, and medicine.[6] Discrete, molecular POMs substituted with transition metals offer the possibility of designing catalytically active sites with tailored redox and acidic properties at the atomic or molecular level. Such POMs can act as effective catalysts for environmentally friendly oxidation reactions under aerobic conditions.[6] Recently, some of us have shown that iron(III)-containing POMs are good homogeneous catalysts for air oxidation of saturated and unsaturated hydrocarbons using conventional and microwave conditions.[7] However, for large-scale processes, it is usually beneficial to use heterogeneous conditions because of advantages in product separation and the ability to recycle the catalysts.[6,8] Further, it has been demonstrated that immobilization of some POM catalysts on silica can lead

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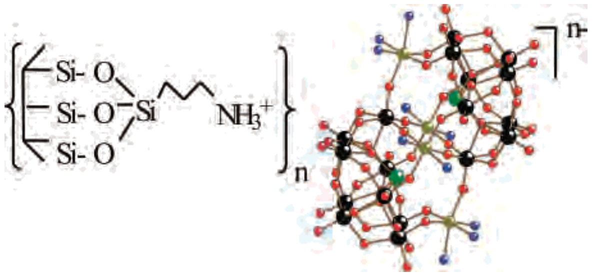

Figure 1. SBA-15−apts−**$Fe_4X_2W_{18}$** ($n = 6$, X = As^{III}, Sb^{III}; $n = 4$, X = Se^{IV}, Te^{IV}).

to improved activities compared to the same POM in solution.[9] Ordered mesoporous materials such as MCM-41[10] and SBA-15[11] have been used as supports for immobilization of several catalysts.[12] In particular, SBA-15 is very interesting because it has a large internal surface area (>800 m^2/g), allowing for the dispersion of a large number of catalytically active sites. Furthermore, the large pores (6−8 nm) facilitate diffusion of substrates and products, while the thick framework walls (3−6 nm) make it thermally and hydrothermally more robust than other supports.[11,13]

To the best of our knowledge, the use of heterogenized POMs for solvent-free aerobic oxidation of long-chain *n*-alkanes has never been reported before. Herein, we report a heterogeneous catalyst system based on the tetrairon(III)-substituted lone pair containing polytungstates $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ ($n = 6$, X = As^{III}, **$Fe_4As_2W_{18}$**; $n = 6$, X = Sb^{III}, **$Fe_4Sb_2W_{18}$**; $n = 4$, X = Se^{IV}, **$Fe_4Se_2W_{18}$**; $n = 4$, X = Te^{IV}, **$Fe_4Te_2W_{18}$**) immobilized with (3-aminopropyl)triethoxysilane (apts)-modified SBA-15 (see Figure 1). The POM catalyst is robust enough to achieve a high catalytic performance for solvent-free aerobic oxidation of *n*-hexadecane using air under ambient conditions through a classical free-radical chain autoxidation mechanism. Moreover, the anchored catalyst can be recycled multiple times without loss of catalytic activity. The four POMs **$Fe_4As_2W_{18}$**, **$Fe_4Sb_2W_{18}$**, **$Fe_4Se_2W_{18}$**, and **$Fe_4Te_2W_{18}$** were synthesized according to the published procedures and isolated as sodium salts ($Na_6[Fe_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 32H_2O$ and $Na_6[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 32H_2O$) or cesium salts ($Cs_4[Fe_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]\cdot 21H_2O$ and $Cs_{3.8}K_{0.2}[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]$), respectively.[14] The identity of the POMs was established by IR. These compounds were then used for immobilization on silica modified with apts.[12d,15,16]

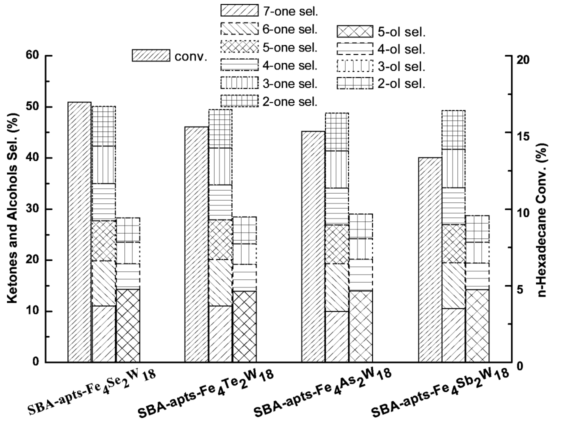

Figure 2. Oxidation of *n*-hexadecane in air catalyzed by **$Fe_4X_2W_{18}$** immobilized on SBA-15. Reaction conditions: 10 mg of catalyst, 5 mL (3.875 g) of *n*-hexadecane, air-flow rate 30 mL/min, temperature 150 °C, and reaction time 6 h.

In order to evaluate the catalytic efficiency of the immobilized POM catalysts, the solvent-free aerobic oxidation of *n*-hexadecane was examined using SBA-15−apts−**$Fe_4X_2W_{18}$** (see Figure 2). Typically, air oxidation of *n*-hexadecane was carried out with a two-neck, round-bottom flask containing 5 mL of fresh substrate and 10 mg of catalyst and then heated to 150 °C with stirring at a constant air flow and without solvent. After the reaction, the solution was allowed to cool to ambient temperature and samples were taken for gas chromatography−mass spectrometry (GC−MS) and GC analysis with a flame ionization detector, using a Varian GC 3900 instrument, HP-FFAP column, and helium as the carrier gas. The loss of substrate during analysis was <5% for all experiments performed. The conversion of *n*-hexadecane is the highest for SBA-15−apts−**$Fe_4Se_2W_{18}$**, whereas selectivities to C_{16} ketones (ca. 50%) and C_{16}

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(15) Briefly, 1 g of mesoporous silica SBA-15 was heated to 130 °C for 5 h in vacuum to remove the adsorbed water. Then, under a nitrogen atmosphere, 30 mL of a 1 wt % solution of apts in anhydrous toluene was added to the silica. After refluxing for 5 h, the solids were filtered and washed with toluene to remove unanchored apts. The solids were collected and dried for the condensation process to obtain the amino group modified silica. To immobilize **$Fe_4X_2W_{18}$** thereon, 0.5 g of the modified silica was mixed with 100 mL of water, and HCl (2 M) was added to adjust the pH to about 2. Then, 0.1 g of a POM was added, and the mixture was stirred for 8 h. The solids were filtered and washed with water and then dried. The same modification and immobilization procedure was applied to SiO_2 and MCM-41. The final loadings were determined by elemental analysis.

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Table 1. Catalytic Activity of $\mathbf{Fe_4Se_2W_{18}}$ Immobilized on Silica for *n*-Hexadecane Oxidation with Air[a]

catalyst	POM loading (wt %)[b]	surface area (m^2/g)	pore volume (cm^3/g)	pore size (nm)	convn (%)[c]	ketone selectivity (%)[d]	TOF (h^{-1})[e]
$\mathbf{Fe_4Se_2W_{18}}$	100	<10			3.0	51.2	17
SBA−apts−$\mathbf{Fe_4Se_2W_{18}}$	4−6	334	0.48	5.8	18.0	50.6	2043
MCM−apts−$\mathbf{Fe_4Se_2W_{18}}$	4−6	568	0.55	2.0	15.6	49.5	1770
SiO_2−apts−$\mathbf{Fe_4Se_2W_{18}}$	4−6	87	0.13	9.8	13.0	50.6	1475

[a] Reaction conditions: 10 mg of catalyst, 5 mL (3.875 g) of *n*-hexadecane, air-flow rate 30 mL/min, temperature 150 °C, reaction time 6 h. [b] POM loading detemined by ICP. [c] *n*-C_{16} convn (%) = (reacted *n*-hexadecane/introduced *n*-hexadecane) × 100. [d] Selectivity of ketones (%) = (produced ketone/reacted *n*-hexadecane) × 100. [e] TOF = moles of *n*-hexadecane converted per mole of POM per hour.

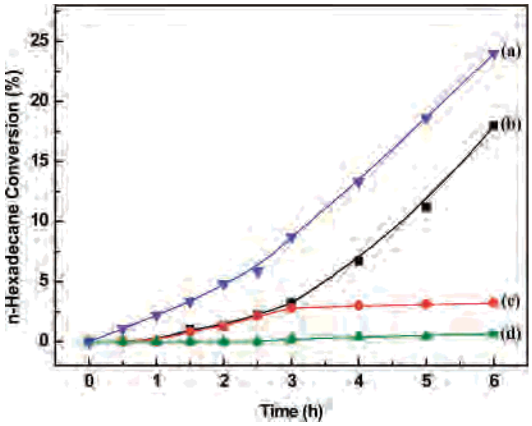

Figure 3. Comparative kinetic plots for the oxidation of *n*-hexadecane using SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$ catalysts: (a) addition of a radical initiator (7.5% TBHP); (b) SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$, (c) solid catalyst was filtered hot after 3 h; (d) addition of radical scavenger 3,5-*tert*-butyl-4-hydroxytoluene.

alcohols (ca. 28%) were similar for all SBA-15−apts−$\mathbf{Fe_4X_2W_{18}}$ catalysts, which is not unexpected because of the isostructural nature of the four POMs.[7,14] Simultaneous combustion of hydrocarbon took place as evidenced by the formation of lower carbon chain (mainly C_6−C_{13}) carboxylic acids (ca. 12%). The other trace compounds of the product mixture were found to be aldehydes, paraffins, and ketones with less than 10 carbon atoms.

We have discovered that SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$ is an exceptionally good catalyst (see Figure 2 and Table 1) for solvent-free aerobic oxidation of *n*-hexadecane. Its catalytic activity is also superior to that of MCM-41−apts−$\mathbf{Fe_4Se_2W_{18}}$ and SiO_2−apts−$\mathbf{Fe_4Se_2W_{18}}$, respectively. This is not unexpected because amorphous silica has limitations due to nonuniform pore size and small surface area. Although MCM-41 has a very large surface area (∼1000 m^2/g) and a uniform pore size (∼2−4 nm), POMs prefer to fill larger pores.[17] The higher catalytic activity of SBA−apts−$\mathbf{Fe_4Se_2W_{18}}$ might therefore be due to the large and regular mesopores, allowing for easy access and discharge of reactants/products/oxidant.[12d,18] Heterogeneous catalysts often suffer extensive leaching of the active metal species during the reaction accompanied by a loss of catalytic activity. However, the SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$ catalyst maintained its high catalytic activity even after four cycles of catalyst reuse. Moreover, hot-filtered-solution experiments (see Figure 3) indicated that there was no contribution from leached, homogeneous, catalytically active POM species.[19]

In line with earlier observations for alkane oxidation, the oxidation of *n*-hexadecane was found to proceed via a free-radical autoxidation mechanism. This is evidenced by (i) an induction period of ca. 2 h seen in *n*-hexadecane conversion versus time plots, (ii) the fact that this induction period is greatly diminished by prior addition of traces of free-radical initiators such as *tert*-butyl hydroperoxide (TBHP), which greatly increases both the rate and degree of conversion of *n*-hexadecane while still retaining a high preference for the three desired products, (iii) the observation that the addition of small quantities of a free-radical scavenger (3,5-*tert*-butyl-4-hydroxytoluene) essentially terminates the reaction and profoundly affects the product distribution, and (iv) for the oxidation of cyclohexane (for which the peroxide is easier to analyze than for *n*-alkanes), the presence of cyclohexyl hydroperoxide (ROOH) during the initial stages of the reaction (subsequent decomposition to ketones and alcohols) has been detected under conditions identical with those of $\mathbf{Fe_4X_2W_{18}}$.[7,20]

In conclusion, the four tetrairon(III)-substituted polytungstates $\mathbf{Fe_4As_2W_{18}}$, $\mathbf{Fe_4Sb_2W_{18}}$, $\mathbf{Fe_4Se_2W_{18}}$, and $\mathbf{Fe_4Te_2W_{18}}$ have been immobilized on apts-modified SBA-15. The resulting SBA-15−apts−$\mathbf{Fe_4X_2W_{18}}$ materials are efficient heterogeneous catalysts for long-chain *n*-alkane oxidation using air as the oxidant in a solvent-free system through a classical free-radical chain autoxidation mechanism. The catalyst was also shown to be readily recyclable by filtration without any loss of activity.

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Supporting Information Available: Figure S1 showing IR spectra of SBA-15−apts, the catalyst SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$, the catalyst SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$ after reaction, and $\mathbf{Fe_4Se_2W_{18}}$ and Figure S2 showing DRIFT spectra of SBA-15−apts, the catalyst SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$, and the catalyst SBA-15−apts−$\mathbf{Fe_4Se_2W_{18}}$ after reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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