

$[(\text{Fe}^{\text{III}}(\text{OH})_2)_3(\text{A}-\alpha\text{-PW}_9\text{O}_{34})_2]^{9-}$ on Cationic Silica Nanoparticles, a New Type of Material and Efficient Heterogeneous Catalyst for Aerobic Oxidations

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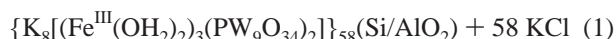
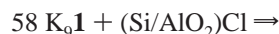
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The development of materials that catalyze selective O_2 /air-based oxidations under mild conditions are of both considerable intellectual interest and potential utility. To date there are very few molecules or materials that catalyze rapid air-based oxidations under mild conditions.¹ We report here the preparation and characterization of a new type of material comprised of anionic metal oxygen clusters (polyoxometalates or “POMs”)² that are electrostatically bound to cationic silica nanoparticles (henceforth “ $(\text{Si}/\text{AlO}_2)^{n+}$ ”).³ The binding of a new sandwich-type POM⁴ of formula, $[(\text{Fe}^{\text{III}}(\text{OH})_2)_3(\text{A}-\alpha\text{-PW}_9\text{O}_{34})_2]^{9-}$ (**1**), to $(\text{Si}/\text{AlO}_2)^{n+}$ forms an active heterogeneous catalyst, for selective O_2 oxidations under mild conditions that is actually more reactive than the same quantity of the same POM catalyst in solution.

The POM, **1**, is prepared by the reaction of $(\text{A}-\text{Na}_8\text{HPW}_9\text{O}_{34})^5$ and $\text{Fe}(\text{NO}_3)_3$ in water, and the K^+ salt readily produces both analytically pure bulk samples and diffraction quality crystals.⁶ The X-ray structure of **1** shows it to be an A-type sandwich POM of approximate D_{3h} symmetry.^{7,8} The charge on **1** was inferred from the number of K^+ counterions determined by both elemental analysis and X-ray crystallography. Bond-valence-sum calculations indicate the three central metals in **1** are ferric ions. It is a trivalent structural analogue of the POMs of formula, $[\text{M}^{\text{III}}_3(\text{A}-\alpha\text{-PW}_9\text{O}_{34})_2]^{12-}$, where $\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{and Zn}^{\text{II}}$, reported by Knoth.^{4b,c} A thermal ellipsoid plot (Figure S1) and all the structural data on the K^+ salt of **1** ($\text{K}_9\mathbf{1}$) ($\text{R1} = 4.19\%$) are given in the Supporting Information.

Whereas the anionic POMs do not bind strongly to conventional negatively charged or neutral silicas (POMs are displaced from most silicas upon simple washing with conventional solvents), they do bind very strongly to cationic $(\text{Si}/\text{AlO}_2)^{n+}$ nanoparticles. Simply stirring aqueous solutions of the POMs with aqueous suspensions of $(\text{Si}/\text{AlO}_2)\text{Cl}$ produces POM-bound nanoparticles.⁹ In the case of **1**, five lines of evidence are consistent with the chemistry and stoichiometry in eq 1 for this process. Namely, there is a loss, on average, of one of the nine cations of the POM ($\text{K}_9\mathbf{1}$) upon binding to the $(\text{Si}/\text{AlO}_2)^{n+}$ nanoparticles, and the POMs form an approximate single layer of $\text{K}_8\mathbf{1}$ monoanions on the surface of each nanoparticle. This translates to an average formula of $\{\text{K}_8[(\text{Fe}^{\text{III}}(\text{OH})_2)_3(\text{PW}_9\text{O}_{34})_2]\}_{58}(\text{Si}/\text{AlO}_2)$ (henceforth $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$) with an average diameter of 17 nm. Figure 1A depicts this association, with **1** shown in combination polyhedral/ball-and-stick notation.



The first line of evidence for this formulation is dynamic laser light scattering (DLS) which shows the average diameter of the initial $(\text{Si}/\text{AlO}_2)\text{Cl}$ particles is 12 nm (surface area $227 \text{ m}^2 \text{ g}^{-1}$), while that of the product $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ particles is 17 nm ($160 \text{ m}^2 \text{ g}^{-1}$) (see Supporting Information) as would be roughly expected if an approximate single layer of $\text{K}_8\mathbf{1}$ monoanions surrounds each polycationic $(\text{Si}/\text{AlO}_2)^{n+}$ particle.¹⁰ Second, the elemental analysis

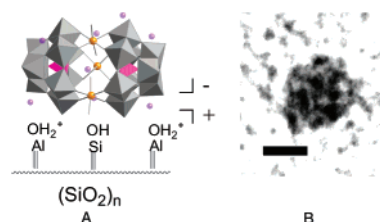


Figure 1. (A) Illustration of the electrostatic association of $\text{K}_8\mathbf{1}$ monoanions with the cationic surfaces of the $(\text{Si}/\text{AlO}_2)^{n+}$ nanoparticles. Compound **1** is shown in combination polyhedral/ball-and-stick notation. The WO_6 and PO_4 polyhedra are shaded gray and pink, respectively, and the Fe atoms and the K^+ cations are shaded orange and translucent purple, respectively. (B) A TEM image of an average-sized ($\sim 17 \text{ nm}$) particle of $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ after catalysis. The sizing bar is 10 nm in length. The dark spots of **1** are more visible on the lighter background of the larger Si/AlO_2 nanoparticle.

is consistent with ~ 58 $\text{K}_8\mathbf{1}$ monoanions per nanoparticle (loss of one K^+ per POM unit).⁹ Third, the relative sizes of **1** from X-ray crystallography and the average $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ particle from DLS are also consistent with an approximate single layer of **1** on the surface of each nanoparticle. Fourth, high-resolution TEM confirms the diameter of the average $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ particle from DLS ($\sim 17 \text{ nm}$). Fifth, the TEM of the $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ particles shows the electrostatically bound electron-dense W-based POMs as dark spots; the reactant $(\text{Si}/\text{AlO}_2)\text{Cl}$ particles show no such spots. The photomicrographs all show some spots the size of individual POMs and larger spots consistent with some POMs that are proximal or on top of one another on a surface that is rough and also one that has a nonuniform distribution of cationic surface sites as per the manufacturer's specifications (Figure 1B).³ Catalysis does not change the appearance of the TEM images.

This new type of material, $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$, is an active catalyst for the aerobic oxygenation of sulfides and the autoxidation of aldehydes (see Supporting Information, part S6), eqs 2 and 3.



Both reactions proceed rapidly using ambient air as the oxidant at 25 or 75 °C for CH_3CHO or THT, respectively. Significantly, an equimolar quantity of **1** alone, either in the same solution ($\text{CH}_3\text{-CN}$) or as a powder, is totally or nearly inactive catalytically. Aerobic sulfide oxidation in the presence of metal complexes rarely if ever proceeds by autoxidation. The marked catalysis of eq 2 (studied most extensively where $\text{R}_2\text{S} = \text{tetrahydrothiophene}$, “THT”) by $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ (Table 1) coupled with the lack of activity of **1** dissolved in the same medium (which, in principle, represents the highest possible total POM “surface area”) argues for some sort of POM activation upon binding to the particles. An induction period in the $\text{THT}-\text{O}_2-\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ system indicates the initial $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ is a precatalyst (see Supporting Information, part S7).¹¹ Typically, the two molecular catalysis parameters, turnover number and turnover frequency, are not used for heterogeneous catalytic processes because the effective concentration of active sites

Table 1. Selective Catalytic Aerobic Oxidation of Tetrahydrothiophene to Tetrahydrothiophene Oxide (THTO) under Ambient Conditions^a

catalyst ^b	POM (mmol) ^c	% conv ^d	% yld ^e	TOF ^f	TOM ^g
(Si/AlO ₂)Cl ^h	0	0	0	0	0
Fe(Si/AlO ₂) ⁱ	0.0008 ^j	1.5	1.5	0	1.8
TBA ₉ Fe ₃ (A-PW ₉ O ₃₄) ₂ (TBA ₉ I) (homogeneous rxn)	0.0045	2.5	2.5	0	2.2
K ₈ I/(Si/AlO ₂) ^k	0.0045	28	28	0.5	60

^a General conditions: 0.99 mmol (0.397 M) of THT, catalyst (amount given in column 2), 1 atm of air, 0.875 mmol (0.35 M) trichlorobenzene (internal standard) were stirred in 2.5 mL of acetonitrile at 75 °C for 120 h. ^b No product was observed in the absence of POM, (Si/AlO₂)⁺⁺ or POM/(Si/AlO₂). ^c mmol of total POM present in the catalyst during turnover. ^d % conversion = (moles of THT consumed/moles of initial THT) × 100. ^e % yield = (moles of THTO/moles of initial THT) × 100. ^f Turnover frequency = turnovers/reaction time (120 h). ^g Turnovers = (moles of THTO/moles of POM). ^h Cationic silica (Bindzil CAT)³. ⁱ Fe(III)-coated Bindzil CAT. ^j mmol of Fe₂(SO₄)₃ (no POM present). ^k **1** = [(Fe^{III})₃(A-PW₉O₃₄)₂]⁹⁻ (preparations in Supporting Information).

is not known. We are including them in Table 1 because the collective lines of evidence above make a reasonable case that nearly all the POMs in K₈I/(Si/AlO₂) are accessible to the solvent, and thus their “concentration” can be reasonably approximated. Quantification of the organic reactants (CH₃CHO or THT) and products (CH₃-COOH or sulfoxide, THTO) by gas chromatography and the O₂ consumption by manometry confirm that the stoichiometries are those given in eqs 2 and 3. In a control experiment, a sample of K₈I/(Si/AlO₂) was used as a catalyst, and the mixture was then filtered. The recovered solid was nearly as catalytically active as the initial sample, whereas the filtrate was totally inactive. This indicates that the solid is the actual catalyst and these new catalytic materials are quite stable.

The loss of water molecules is the only change apparent in K₈I/(Si/AlO₂) (as well as K₉I) up to 200 °C on the basis of TGA, DSC, and DRIFT data. The dramatic increase in catalytic activity (Table 1) suggests a significant change in **1** upon binding to (Si/AlO₂)⁺⁺.¹² To probe this change further, IR, ⁵⁷Fe Mössbauer, and EPR studies were conducted. The P–O and W–O stretches in the IR of **1** (1000 and 800 cm⁻¹, respectively) before and after binding are the same within experimental error, but the dominance of the peaks from the abundant (Si/AlO₂)⁺⁺ make further inferences difficult. Scattering of the γ -rays by the heavy tungsten atoms in **1** rendered Mössbauer useless, but EPR shows a high spin ferric signal at $g = 4.30$ that changes slightly and becomes about 15 times as intense when **1** binds to (Si/AlO₂)⁺⁺ (Figure S4). On the basis of this result, a control experiment was conducted: Fe₂(SO₄)₃ was deposited on the (Si/AlO₂)⁺⁺ particles and catalytic activity of this mixture for eq 2 was assessed. It was almost inactive (Table 1), indicating that binding of **1** on the cationic nanoparticles does not likely involve production of solvated or silica-bound Fe(III).

Acknowledgment. We thank F. Menger for use of the DLS apparatus, P. Bergoo and J. Rise of Akzo Nobel for assistance with silica products, K. Hardcastle and W. Neiwert for X-ray crystallography, B. H. Huynh and G. Jameson for EPR, R. P. Apkarian and M. Ritorto (Emory IM&MF) for TEM, and colleagues for discussion.

Supporting Information Available: CIF file for K₉I, DLS, TEM, EPR, and catalytic data for CH₃CHO and THT oxidations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Synthesis of K₉[(Fe(OH)₂)₃(A- α -PW₉O₃₄)₂·20H₂O (K₉I):** Solid A-Na₉-PW₉O₃₄·7H₂O (10 g, ca. 3.7 mmol) and Fe(NO₃)₃·9H₂O (3.2 g, 8 mmol) were added simultaneously to 80 mL of deionized water. The mixture was stirred for 15 min at 50 °C to form a clear yellow solution to which KCl (11 g) was added. The resulting precipitate (ca. 8 g) was separated by filtration and redissolved in a minimal amount of 50 °C water, and the solution was filtered to remove any insoluble material. The filtrate was cooled to 5 °C overnight to afford 6 g of yellow-orange crystals (yield 60%). Diffuse-reflectance-Fourier transform-infrared (5% sample in KBr, 1200–400 cm⁻¹): 1080 (s), 1058 (s, sh), 953 (s), 881 (m), 799 (s), 752 (s, sh), 595 (w), and 517 (w). Anal. Calcd for H₄₆Fe₃K₉O₉₉P₂W₁₈: H, 0.85; Fe, 3.08; K, 6.47; P, 1.14; W, 60.82. Found: H, 0.88; Fe, 3.13; K, 6.53; P, 1.17; W, 59.09. Magnetic susceptibility: $\mu_{\text{eff}} = 6.1 \mu_{\text{B}}/\text{mol}$ at 296K. MW: 5441.
- Crystal data for K₉[(Fe(OH)₂)₃(A- α -PW₉O₃₄)₂·20H₂O (K₉I): Orthorhombic space group *Fdd2*, dark yellow efflorescent crystal, with $a = 40.376(4)$, $b = 27.904(2)$, and $c = 31.186(2)$ Å, and $Z = 16$. The data were collected on a Bruker D8 SMART APEX CCD sealed-tube diffractometer with Mo K α (0.71073 Å) radiation (temperature = 100(2) K). At final convergence, $R_1 = 4.19\%$ and $GOF = 1.117$ based on 31,831 reflections with $F_o > 2\sigma F_o$.
- Each of the three Fe atoms in the central unit exhibit a MO₆ coordination polyhedron; each has two oxygens from each trivacant Keggin subunit, one exterior oxygen atom, and one interior oxygen atom. The latter two oxygens are most likely water molecules, although the hydrogen atoms could not be located. There is crowding of the interior water molecules, and the O–O distances between these oxygen atoms (ranging from 1.97 to 2.07 Å) are consistent with strong internal hydrogen bonding (which consequently leads to buckling and lowering of the symmetry to C_s).
- Synthesis of POM-modified cationic silica nanoparticles, K₈I/(Si/AlO₂):** To an aqueous suspension of (Si/AlO₂)Cl (Akzo Nobel Bindzil CAT; 10.0 g) was added 0.25 g of K₉I dissolved in 10 mL water. This mixture was stirred for 3 h at 25 °C and then at 80 °C until the solvent had evaporated. The resulting powder was dried at 120 °C for 1 h, washed with three 10-mL portions of CH₃CN (with no loss of POM after the first wash), and dried again at 120 °C for 1 h. The average number of (Si/AlO₂)⁺⁺ particles was calculated from the (Si/AlO₂)⁺⁺ content in the sol and the average particle diameter. Anal. Calcd for “K₈I/(Si/AlO₂)”, i.e., (K₈I)₅₈-(SiO₂)₁₅₅₇₀(Al₂O₃)₄₃₁₅(H₂O)₂₃₀₉₅: Al, 11.23; Fe, 0.454; K, 0.954; P, 0.168; Si, 21.00. Found: Al, 11.57; Fe, 0.475; K, 0.865; P, 0.175; Si, 21.34.
- The specific surface area was calculated from the diameters, taking the density of silica as 2.2 g/cm³ (Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979; p 346.).
- The reaction is first order in THT and K₈I/(Si/AlO₂) and zero order in O₂. The reaction shows a 20 h induction period. See Supporting Information, part S7.
- The surface charge of (Si/AlO₂)⁺⁺ and K₈I/(Si/AlO₂) was recently determined on a Muetek particle charge detector PCD02. The results were consistent with a reduction in charge (i.e., the surface charge is now less positive) upon addition of K₉I.

JA0267223