Supporting Information for

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

Nelya M. Okun, Travis M. Anderson, Craig L. Hill*
Department of Chemistry, Emory University, Atlanta, Georgia 30322

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- S2.** Table of laser light scattering data on **K₈1**/(Si/AlO₂) by a Coulter N4 Plus instrument.
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Figure S1. Thermal Ellipsoid Plot of K₉1.

S2. Laser light scattering data by a Coulter N4 Plus Instrument ^a

K ₈ 1/(Si/AlO ₂) ^b		(Si/AlO ₂)Cl ^c	
Size (nm) ^d	Amount (%)	Size (nm) ^d	Amount (%)
1.0	0.0	1.0	0.0
1.2	0.0	1.2	0.0
1.4	0.0	1.4	0.0
1.6	0.0	1.6	0.0
1.8	0.0	1.8	0.0
2.2	0.0	2.2	0.0
2.5	0.0	2.5	0.0
2.9	0.0	2.9	0.0
3.4	0.0	3.4	0.0
4.0	0.0	4.0	0.0
4.6	0.0	4.6	0.0
5.4	0.0	5.4	0.0
6.3	0.0	6.3	0.0
7.4	0.0	7.4	0.0
8.6	0.0	8.6	0.0
10.0	0.0	10.0	40.5
11.7	0.0	12.1	37.3
13.6	0.0	14.6	17.3
15.8	73.4	17.7	3.7
18.5	21.7	18.5	0.0
21.5	0.0	21.4	0.0
25.1	0.0	25.9	0.0
29.3	0.0	31.3	0.0
34.1	0.0	37.8	0.0
39.8	0.0	45.8	0.2
46.4	0.0	55.4	0.3
54.1	0.0	54.1	0.0
63.1	0.0	66.9	0.3
73.6	0.0	81.0	0.2
85.8	0.0	97.9	0.1
100	4.9	100	0.0

^aGeneral conditions: 25 °C; diluent water; angle 90.0°C; SDP settings: Min = 1.0 nm, Max = 100 nm; Number of Bins = 31; ^b1-modified cationic silica nanoparticles, K₈1/(Si/AlO₂); ^cBindzil CAT[®] (Akzo Nobel); ^dParticle diameter.

S3. Calculation of specific surface area of a (Si/AlO₂)Cl nanoparticle and the number of molecules of 1 associated with each K₈1/(Si/AlO₂) nanoparticle

1. Calculation of specific surface area of a (Si/AlO₂)Cl nanoparticle

Because silica sols consist of discrete spherical particles of amorphous silica, we assume the density of (Si/AlO₂)Cl is ~2.2 g/cm³, which is the density of amorphous, anhydrous, nonporous silica.¹³ Laser light scattering establishes that the average diameter of the initial (Si/AlO₂)Cl particles is 12 nm and that of the product K₈1/(Si/AlO₂) particles is 17 nm. Initial colloidal silica contained 5.24 g of SiO₂ in 100 mL of sol. There are 0.241 mmol of POM in the 100 mL solution.

$$\text{Particle volume } v = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3, \text{ Particle surface area } s = 4\pi\left(\frac{d}{2}\right)^2,$$

$$\text{Density } D = \frac{m(g)}{v(cm^3)}.$$

When particle diameter d is expressed in nm , the specific surface area, A_d , in m^2/g can be calculated from:

$$A_d = \frac{s}{m} = \frac{s}{D \times v} = \frac{6 \times 10^3}{D \times d} = \frac{2720}{d}.$$

[For more information, see reference 10].

Thus, the calculated surface area for initial (Si/AlO₂) particles is 227 m²/g, and for K₈1/(Si/AlO₂) particles is 160 m²/g.

2. Calculation of number molecules of 1 associated with each K₈1/(Si/AlO₂) nanoparticle.

Using similar assumptions to those above, the average number of (Si/AlO₂)Cl particles in 100 mL of colloidal silica solution containing C_{SiO_2} g of SiO₂ can be determined from

$$n = \frac{C_{SiO_2}}{1.2 \times 10^{-21} d^3},$$

where d is particle diameter in nm . [This equation was used by H. E. Bergna in U.S. Patent 4,410,405]. The number of molecules of K₉1 in 100 mL solution containing C_1 mmol of K₉1 can be determined from:

$$N = C_1 \times 6.022 \times 10^{20}.$$

Thus, the number of molecules of K₉1 associated with each K₈1/(Si/AlO₂) nanoparticle is

$$\frac{N}{n} = \frac{145 \times 10^{18}}{2.52 \times 10^{18}} \approx 58.$$

S4. Preparation of the TEM and EPR samples

For TEM photographs, dry powders of three materials, Bindzil CAT®, $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ and $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ recovered after 157 turnovers (catalyst was removed by filtration, washed with acetonitrile and dried *in vacuo*) were sonicated in deionized water with a high intensity horn (600 Watt Vibra-Cell model VC-600 from Sonics & Materials, Inc.) at room temperature for 30 min in air. A drop of the suspension was placed on a carbon-coated copper grid (200 mesh) and dried. An estimation of the number of molecules of **1** associated with each $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ nanoparticle was determined from the TEM image.

The mean diameter of the $\text{K}_8\mathbf{1}/(\text{Si}/\text{AlO}_2)$ nanoparticles from the TEM photomicrographs was around 17 nm. All the (Si/AlO_2) hemispheres were partially covered by black spots of **1**. From the X-ray data, the surface area of one molecule of **1** is 1.5 nm^2 . A simple calculation on the particle shown in Figure 1B demonstrates that there are approximately 29 molecules of **1** on the hemispherical surface of this particular particle (or approximately 58 molecules on the entire surface).

For EPR samples 0.2 mmol of **1** and the amount of $\mathbf{1}/(\text{Si}/\text{AlO}_2)$ and $\mathbf{1}/(\text{Si}/\text{AlO}_2)$ recovered after 157 turnovers, that also contain 0.2 mmol of **1** were sonicated with the above mentioned horn in 2 mL of light mineral oil (purchased from Fisher Scientific) for a total of 25 min. After each 30 s of sonication the samples were cooled down to ambient temperature. EPR spectra were recorded at 6 K using a Brüker 200 spectrometer with a microwave frequency of 9.655 GHz and a microwave power of 20 dB.

Figure S4A. EPR spectra of K₉1.

Figure S4B. EPR spectra of K₈1/Si/AlO₂.

Figure S4C. EPR spectra of $K_81/Si/AlO_2$ recovered after 157 turnovers.

S5. Synthesis of $\text{Na}_5\text{2}/(\text{Si}/\text{AlO}_2)$, $\text{Na}_4\text{3}/(\text{Si}/\text{AlO}_2)$, and $\text{Fe}(\text{Si}/\text{AlO}_2)$.

To an aqueous suspension of $(\text{Si}/\text{AlO}_2)\text{Cl}$ (Akzo Nobel Bindzil CAT®; 10 g) was added 0.25 g of $\text{Na}_6\text{V}_{10}\text{O}_{28}$ ($\text{Na}_6\text{2}$) or $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ ($\text{Na}_5\text{3}$) dissolved in 10 mL of deionized water. The mixture was stirred for 3 h at room temperature and then heated to 80 °C until the solvent had evaporated. The resulting solid was dried at 120 °C for 1 h and then washed with three 10-mL portions of acetonitrile, and dried again at 120 °C for 1 h. No POM was lost after the first washing. The formulations, like that for $\text{K}_8\text{1}/(\text{Si}/\text{AlO}_2)$ (see text) are also consistent with the loss, on average, of one cation per bound POM.

Anal. Calcd. for $(\text{Na}_5\text{V}_{10}\text{O}_{28})_{18}(\text{SiO}_2)_{1289}(\text{Al}_2\text{O}_3)_{303}(\text{H}_2\text{O})_{1254}$: V, 6.175. Found: V, 6.0.

Anal. Calc. for $(\text{Na}_4\text{PV}_2\text{Mo}_{10}\text{O}_{40})_{49}(\text{SiO}_2)_{3576}(\text{Al}_2\text{O}_3)_{843}(\text{H}_2\text{O})_{3521}$: Al, 10.76; P, 0.361; V, 1.18. Found: Al, 10.24; P, 0.360; V, 0.810.

To an aqueous suspension of $(\text{Si}/\text{AlO}_2)\text{Cl}$ (Akzo Nobel Bindzil CAT®; 10 g) was added 0.021 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ dissolved in 10 mL of deionized water. The mixture was stirred for 3 h at room temperature and then heated to 80 °C until the solvent had evaporated. The resulting solid was dried at 120 °C for 1 h and then washed with three 10-mL portions of acetonitrile, and dried again at 120 °C for 1 h.

S6. Acetaldehyde Data.

The catalytic activity of three POMs, **1**, $\text{Na}_6\text{V}_{10}\text{O}_{28}$ (**Na₆2**) and $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (**Na₅3**), both as powders and electrostatically bound to Akzo Nobel Bindzil CAT® particles, for the aerobic oxidation of acetaldehyde along with control experiments are given in Table S6. Quantification of the acetaldehyde reactant and acetic acid product by gas chromatography and the O_2 consumption by manometry confirm that the stoichiometry is that in eq 3 in the text. Conventional radical-chain oxidation (autoxidation) is by far the most common mechanism for aerobic aldehyde oxidations in solution, and POM-catalyzed aldehyde oxidations by **3** are documented to proceed by this mechanism. We demonstrated that eq 3 in the text, in the presence of $\text{K}_8\text{1}/(\text{Si}/\text{AlO}_2)$, exhibited an incubation period (Figure S6) and the rate of this process was retarded 85% in the presence of 1.5 equivalents of the radical scavenger 2,6-di-*t*-butyl-4-methyl phenol (BHT) per equivalent of **1** (0.0014 mol of BHT per mol of acetaldehyde). Both findings are fully consistent with a radical-chain mechanism. Table S6 shows that the POMs electrostatically bound to the cationic surfaces of the $(\text{Si}/\text{AlO}_2)^{n+}$ nanoparticles are effective heterogeneous catalysts for the aerobic oxidation of acetaldehyde using the ambient environment (air at room temperature). Whereas immobilization of soluble catalysts ("heterogenization") generally results in substantially lower turnover rates, quite the opposite is true here (for both sulfide and aldehyde oxidations).

Figure S6. Kinetics curves for the air based oxidation of acetaldehyde catalyzed by $\text{K}_8\text{1}/(\text{Si}/\text{AlO}_2)$. Conditions: 25 °C; 1 atm air; $[\text{CH}_3\text{CHO}] = 0.159$ M in hexane with trifluoroethanol (0.68 mmol) as the internal standard. **A:** kinetics of CH_3CHO oxidation; **B:** kinetics of CH_3COOH formation; **C:** kinetics of CH_3CHO oxidation (●) and CH_3COOH formation (▲).

Table S6. Aerobic Oxidation of Acetaldehyde in Hexane by Various Systems^a.

Catalyst ^b	POM (mmol) ^c	% conv ^d	% yld ^e	TOF ^f (h ⁻¹)	TON ^g
(Si/AlO ₂)Cl ^h	0	0	0	0	0
Fe(Si/AlO ₂) ⁱ	0.0008 ^j	2.9	2.8	0.5	19.6
Na ₆ V ₁₀ O ₂₈ (Na ₆ 2)	0.120	0	0	0	0
Na ₅ PV ₂ Mo ₁₀ O ₄₀ (Na ₅ 3)	0.180	55	42	0	1.3
K ₉ Fe ₃ (A-PW ₉ O ₃₄) ₂ (K ₉ 1)	0.570	2	2	0	0
Na ₅ 2 /(Si/AlO ₂) ^k	0.0017	14	14	1	40
Na ₄ 3 /(Si/AlO ₂) ^k	0.0019	11	10	0.8	33
K ₈ 1 /(Si/AlO ₂) ^k	0.0006	14	14	3	131

^aGeneral conditions: 0.56 mmol (0.160 M) of CH₃CHO, catalyst (amount given in column 2), 1 atm of air, 0.68 mmol (0.194 M) trifluoroethanol (internal standard) were stirred in 3.5 mL of hexane at 25 °C for 40 h.; ^bno product was observed in the absence of POM, (Si/AlO₂)ⁿ⁺ or POM/(Si/AlO₂); ^cmmol of total POM present in the catalyst during turnover; ^d% conversion = (moles of CH₃CHO consumed/moles of initial CH₃CHO) × 100; ^e% yield = (moles of CH₃COOH/moles of initial CH₃CHO) × 100; ^fturnover frequency = turnovers/reaction time (40 h); ^gturnovers = (moles of CH₃COOH/moles of POM); ^hcationic silica (Bindzil CAT®); ⁱFe(III)-coated Bindzil CAT®; ^jmmol of Fe₂(SO₄)₃ (no POM present); ^k**1** = [(Fe^{III})₃(A-PW₉O₃₄)₂]⁹⁻, **2** = V₁₀O₂₈⁶⁻, **3** = PV₂Mo₁₀O₄₀⁵⁻.

S7. Kinetics curves for the air-based oxidation of THT.

Figure S7A. Kinetics of aerobic THT oxidation catalyzed by the Si/AlO₂ (open squares), the soluble tetra-*n*-butylammonium salt of [(Fe^{III}(OH₂)₂)₃(A- α -PW₉O₃₄)₂]⁹⁻ (TBA1) (triangles), and the insoluble **1**/(Si/AlO₂) systems (first use (open circles), second use (diamonds), third use (filled circles)). Conditions in all reactions: 8.4 mg (0.015 mmol) of **1** in 2.5 mL of acetonitrile; [THT] = 0.40 M, 75 °C; 1 atm of air (see Experimental section for details). The incubation period of 20 h (0.72 x 10⁵ s) was taken into account in fitting the data to the integrated first-order (exponential) rate law. Data points 6-14 yield a first-order rate constant, $k_{obs} = 2.67 \times 10^{-7} \text{ s}^{-1}$ ($R^2 = 0.999$). Data points 15-19 yield a first-order rate constant, $k_{obs} = 1.6 \times 10^{-7} \text{ s}^{-1}$ ($R^2 = 0.999$).

Figure S7B Kinetic van't Hoff plot for THTO formation as a function of $[(\text{Fe}^{\text{III}}(\text{OH}_2)_2)_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{9-}$ (**1**) (mmol). Conditions for all 8 reactions: $[\text{THT}] = 0.45 \text{ M}$; 75°C ; 1 atm of air; 120 h. The slope is 1.007 with $R^2 = 0.992$ indicating the reaction is first order in **1**.

Figure S7C. Kinetic van't Hoff plot for THTO formation as a function of [THT]. Conditions: 0.180 g of **1**/(Si/AlO₂), where **1** = [(Fe^{III}(OH₂)₂)₃(A- α -PW₉O₃₄)₂]⁹⁻ (if **1** was completely soluble, this would generate a 1.85 $\times 10^{-3}$ M solution); 75 °C; 1 atm of air; 120 h. The slope of the line is 1.005 with $R^2 = 0.998$ and therefore the reaction is first order in THT.

Table S7. Oxygen Dependence Data

THT oxidation dependence of [O ₂] ^a				
[THT] ₀ (M)	POM (M)	[O ₂] (vol.%)	THTO (M)	% conv.
0.270	0.0046	0	0	0
0.270	0.0046	9.26	0.0700	25.92
0.270	0.0046	15.0	0.0703	26.04
0.270	0.0046	20.95	0.0700	26.00
0.270	0.0046	100.0	0.0718	26.59

^a Conditions: 75 C; 1 atm air; reaction conducted in acetonitrile; adsorbed THT and THTO desorbed with DMSO.

S8. DRIFT data for K₉1 (dashed line) and K₈1/(Si/AlO₂) (solid line).

S9. TGA-DSC for K₉1 and K₈1/(Si/AlO₂).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data for K₉1 and K₈1/(Si/AlO₂) were performed on ISI TGA 1000 and DSC 550 instruments, respectively. Samples were heated from 323 K to 600 K at a rate of 20 K/min. The sample of K₉1 shows a weight loss between 323 K and 540 K corresponding to the loss of twenty waters of hydration. This is consistent with the data from the X-ray crystallographic analysis. Differential scanning calorimetry data show a single endothermic peak below 600 K. This is also consistent with the loss of lattice water molecules. TGA-DSC were also used to establish the stability of K₈1/(Si/AlO₂) between 323 K to 600 K. The results show a continuous, step-wise loss of solvent water molecules with no detectable decomposition processes occurring over the range of this study.