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Aerobic Oxidation of Formaldehyde Catalyzed by Polyvanadotungstates

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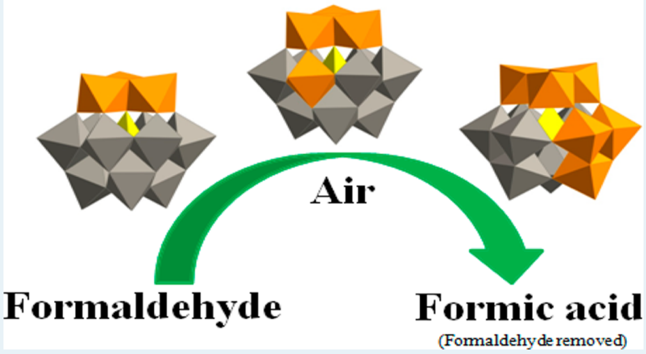
Ⓢ *Supporting Information*



ABSTRACT: Three tetra-*n*-butylammonium (TBA) salts of polyvanadotungstates, $[n\text{-Bu}_4\text{N}]_6[\text{PW}_9\text{V}_3\text{O}_{40}]$ (**PW_9V_3**), $[n\text{-Bu}_4\text{N}]_5\text{H}_2\text{PW}_8\text{V}_4\text{O}_{40}$ (**PW_8V_4**), and $[n\text{-Bu}_4\text{N}]_4\text{H}_5\text{PW}_6\text{V}_6\text{O}_{40}\cdot 20\text{H}_2\text{O}$ (**PW_6V_6**), have been synthesized and shown to be effective catalysts for the aerobic oxidation of formaldehyde to formic acid under ambient conditions. These complexes, characterized by elemental analysis, Fourier transform infrared spectroscopy, UV−vis spectroscopy, and thermogravimetric analysis, exhibit a catalytic activity for this reaction comparable to those of other polyoxometalates. Importantly, they are more effective in the presence of water than the metal oxide-supported Pt and/or Au nanoparticles traditionally used as catalysts for formaldehyde oxidation in the gas phase. The polyvanadotungstate-catalyzed oxidation reactions are first-order in formaldehyde, parabolic-order (slow, fast, and slow again) in catalyst, and zero-order in O_2. Under optimized conditions, a turnover number of ∼57 has been obtained. These catalysts can be recycled and reused without a significant loss of catalytic activity.

KEYWORDS: *polyvanadotungstates, aerobic catalysis, formaldehyde oxidation, water-compatible reaction*

■ INTRODUCTION

Formaldehyde (CH_2O) is a toxic compound that is ubiquitous in human environments. As a consequence, it is of central concern in the context of human health and also high on the list of toxic industrial chemicals (TICs).[1] Long-term exposure to formaldehyde may cause irritation of the mucous membranes of the eyes and is associated with diseases of the nasal and respiratory tract.[2] It was classified as a known carcinogen by the State of California and the World Health Organization in 2004.[3−11] Thus, the removal of formaldehyde is a crucial goal for researchers.

Air-based catalytic organic oxidations have attracted much attention recently, because they utilize only ambient O_2, which is less expensive and more abundant than other oxidants and generates few if any deleterious byproducts.[12−24] Moreover, aerobic organic oxidation reactions are very attractive for decontamination of a wide variety of toxic compounds in human environments, including TICs[20,25−29] and chemical warfare agents (CWAs),[23,30] under mild conditions. Therefore, the aerobic catalytic oxidation of formaldehyde to formic acid, CO, and/or CO_2 under ambient conditions is very attractive from multiple vantages.[28]

Generally, mixtures of metal oxides,[31] precious metals,[32] and supported precious metals[33−36] have been evaluated as catalysts for the oxidation of formaldehyde. Among the metal oxides, MnO_2 has been shown to have a high reactivity for formaldehyde oxidation at moderate conversions.[31,32,37,38] Precious metals such as Au, Ru, Rd, and Pt have been found to be effective catalysts for formaldehyde conversion at moderate temperatures.[39−42] For example, Zhang et al. and Huang et al. reported that Pt nanoparticles supported on TiO_2 are effective catalysts for formaldehyde oxidation at room temperature,[43,44] while catalysts such as Au and Ag supported on TiO_2, CeO_2, Al_2O_3, $MnO_x{-}CeO_2$, and SBA-15 effected formaldehyde oxidation with almost 100% conversion at temperatures of ≥373 K.[45,46] Unfortunately, most of the systems reported so far are based on precious metals that are prohibitively expensive for practical applications and not readily available or involve catalytic oxidations that must be performed at temperatures of ≥400−500 K. However, logistical considerations dictate that many TIC and CWA decontamination and deodorization technologies are far more useful if they can be applied under ambient conditions.

The second class of catalysts developed for the aerobic oxidation of formaldehyde under ambient conditions (using air at room temperature) consists of polyoxometalates (POMs), and in particular POMs with 3d metals substituted at surface positions.[28,29,47,48] POMs make up a family of metal oxide clusters with versatile applications in medicine, magnetism, electrochemistry, and catalysis.[49−54] In particular, organic oxidations catalyzed by POMs have received much attention because the acid−base and redox properties of POMs are

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highly tunable.[51,55] In addition, POMs are thermally, oxidatively, and hydrolytically stable under oxidative conditions.[51,56] In 2004, Kholdeeva, Hill, and their co-workers reported that supported Keggin-type Co-containing POMs, $[n\text{-Bu}_4\text{N}]_4\text{HPW}_{11}\text{CoO}_{39}$ and $[n\text{-Bu}_4\text{N}]_5\text{PW}_{11}\text{CoO}_{39}$, were effective catalysts for the aerobic oxidation of aldehydes (including formaldehyde) under ambient conditions.[47] In 2005, they further investigated the catalytic activity of the Keggin-type Ce-containing POM ($\text{NaH}_3[\text{SiW}_{11}\text{Ce}^{\text{IV}}\text{O}_{39}]$) for the aerobic oxidation of formaldehyde.[28] The Ce-containing POM was shown to be a selective and effective catalyst for the production of formic acid with a CH_2O conversion of ~20% under mild conditions. Vanadium-substituted heteropolyanions, $\text{PMo}_{12-n}\text{V}_n\text{O}_{40}{}^{(3+n)-}$ ($\mathbf{PMo_{12-n}V_n}$) and $\text{PW}_{12-n}\text{V}_n\text{O}_{40}{}^{(3+n)-}$ ($\mathbf{PW_{12-n}V_n}$) ($n = 1-6$),[57−61] have been reported to catalyze the aerobic oxidation of many organic compounds, including ketones and aldehydes (some of which are TICs) under ambient conditions.[53,58,60,62−72] However, formaldehyde oxidation under ambient conditions catalyzed by polyvanadotungstates has not been described.

We report here that the TBA salts of polyvanadotungstates, $[n\text{-Bu}_4\text{N}]_6[\text{PW}_9\text{V}_3\text{O}_{40}]$ ($\mathbf{PW_9V_3}$), $[n\text{-Bu}_4\text{N}]_5\text{H}_2\text{PW}_8\text{V}_4\text{O}_{40}$ ($\mathbf{PW_8V_4}$), and $[n\text{-Bu}_4\text{N}]_4\text{H}_5\text{PW}_6\text{V}_6\text{O}_{40}\cdot 20\text{H}_2\text{O}$ ($\mathbf{PW_6V_6}$) POMs, are efficient catalysts for the aerobic oxidation of formaldehyde to formic acid under ambient conditions (using only air at room temperature). Comparison of four POMs ($[n\text{-Bu}_4\text{N}]_5[\text{W}_3\text{V}_3\text{O}_{19}]$, $[n\text{-Bu}_4\text{N}]_3\text{H}_3\text{V}_{10}\text{O}_{28}$, $[n\text{-Bu}_4\text{N}]_7\text{SiW}_9\text{V}_3\text{O}_{40}$, and $[n\text{-Bu}_4\text{N}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$), each with extensive and reversible redox chemistry, confirms that the catalytic activity is derived from the polyanion properties [structure, V(V/VI) potential, etc.]. Importantly, these formaldehyde removal reactions are less inhibited by water than these same oxidations catalyzed by supported noble metals. Under optimized conditions, a turnover number (TON) of ~57 is obtained with $\mathbf{PW_6V_6}$.

■ EXPERIMENTAL SECTION

General Methods and Materials. All chemical reagents used were from commercially available sources and were used without further purification unless otherwise noted. The formaldehyde solutions were prepared by diluting 35% aqueous formalin with acetonitrile (Fluka), *N,N*-dimethylacetamide, *N,N*-dimethylformamide, or tetrahydrofuran as needed for each catalytic entry. Infrared spectra (2% sample in KBr pellet) were recorded on a Nicolet TM 6700 Fourier transform infrared (FT-IR) spectrometer. UV−vis spectra were recorded with an Agilent 8453 spectrophotometer equipped with a diode array detector using a 1.0 cm optical path length quartz cuvette with acetonitrile as the solvent. The thermogravimetric data were collected on an STA 6000 thermal analyzer. Elemental analyses (V and W) were conducted by Galbraith Laboratories (Knoxville, TN). ^{1}H and ^{31}P nuclear magnetic resonance (NMR) spectra were acquired on a Varian INOVA 400 spectrometer using deuterated chloroform (δ 7.24) and H_3PO_4 (δ 0) as external standards. Gas chromatography (GC) analysis of the liquid phase was performed on a Hewlett-Packard 6890 instrument with a 5% phenyl methyl silicone capillary column (while the formic acid was independently detected with an Agilent J&W DB-FFAP column), a flame ionization detector, a Hewlett-Packard 3390A series integrator, and N_2 as the carrier gas. The gas phase was analyzed using an Agilent 7890 gas chromatograph with a 5 Å molecular sieve column and argon carrier gas.

Preparation of Catalysts. *Synthesis of* $[n\text{-Bu}_4\text{N}]_6[\alpha\text{-1,2,3-PW}_9\text{V}_3\text{O}_{40}]$ ($\mathbf{PW_9V_3}$). The TBA salt of the vanadium-substituted Keggin-type POM was prepared by a modified literature method.[73] In a typical preparation, 8.2 g of sodium acetate (100 mmol) in 6 mL of acetic acid was added to 100 mL of distilled water until a pH of approximately 5.0 was reached. To this solution were added sodium metavanadate (3.05 g, 25 mmol) and $\text{Na}_9[\text{A-PW}_9\text{O}_{34}]$ (20 g, 8.2 mmol). The solution was stirred for 24 h and filtered. Subsequently, TBABr (15 g, 48 mmol) in 20 mL of distilled water was added to the solution to produce a light orange product (17.7 g, 54% yield based on vanadium) whose purity was confirmed by FT-IR spectroscopy: FT-IR (2000−500 cm^{-1}, KBr) 1482 (m), 1462 (sh), 1380 (w), 1152 (w), 1087 (s), 1053 (w), 1029 (sh), 994 (w), 949 (s), 879 (s), 792 (s), 732 (sh), 598 (w), 510 (w) cm^{-1}. The number of TBA cations was determined by thermogravimetric analysis (TGA). Elemental analysis (calcd/found): W, 42.3/44.1; V, 3.9/4.2.

Synthesis of $[n\text{-Bu}_4\text{N}]_5\text{H}_2\text{PW}_8\text{V}_4\text{O}_{40}$ ($\mathbf{PW_8V_4}$). The TBA salt of the vanadium-substituted Keggin-type POM was prepared by metathesis of $(\text{NH}_4)_6\text{HPW}_8\text{V}_4\text{O}_{40}\cdot 9\text{H}_2\text{O}$[74] with TBABr in distilled water. Typically, 0.483 g of TBABr (15 mmol) was added to an aqueous solution of $(\text{NH}_4)_6\text{HPW}_8\text{V}_4\text{O}_{40}\cdot 9\text{H}_2\text{O}$ (0.197 g, 0.1 mmol). The precipitate was centrifuged and washed with distilled water to remove excess TBABr. The product was recrystallized three times from acetonitrile [yield of 0.214 g, 60% yield based on vanadium in $(\text{NH}_4)_6\text{HPW}_8\text{V}_4\text{O}_{40}\cdot 9\text{H}_2\text{O}$]. Its purity was confirmed by FT-IR spectroscopy: IR (2000−500 cm^{-1}, KBr) 1482 (m), 1380 (w), 1154 (w), 1100 (sh), 1078 (m), 1052 (sh), 950 (s), 882 (s), 789 (s), 595 (w), 509 (w) cm^{-1}. The number of TBA cations was determined by TGA. Elemental analysis (calcd/found): W, 41.5/40.2; V, 5.7/5.9.

Synthesis of $[n\text{-Bu}_4\text{N}]_4\text{H}_5\text{PW}_6\text{V}_6\text{O}_{40}\cdot 20\text{H}_2\text{O}$ ($\mathbf{PW_6V_6}$). The TBA salt of the vanadium-substituted Keggin-type POM was prepared by a method similar to that used for $\mathbf{PW_8V_4}$ except that 0.228 g of $(\text{NH}_4)_5\text{H}_4\text{PW}_6\text{V}_6\text{O}_{40}\cdot 6\text{H}_2\text{O}$[74] was used [yield of 0.167 g, 49% yield based on vanadium in $(\text{NH}_4)_5\text{H}_4\text{PW}_6\text{V}_6\text{O}_{40}\cdot 6\text{H}_2\text{O}$]. Its purity was confirmed by FT-IR spectroscopy: IR (2000−500 cm^{-1}, KBr) 1481 (s), 1379 (m), 1152 (w), 1074 (m), 1030 (sh), 949 (s), 886 (s), 798 (s), 594 (s), 509 (s) cm^{-1}. The number of TBA cations was determined by TGA. Elemental analysis (calcd/found): W, 32.0/31.4; V, 8.9/8.6.

Preparation of $\mathbf{[\textit{n}\text{-}Bu_4N]_5[W_3V_3O_{19}]}$**,** $\mathbf{[\textit{n}\text{-}Bu_4N]_3H_3V_{10}O_{28}}$**,** $\mathbf{[\textit{n}\text{-}Bu_4N]_7SiW_9V_3O_{40}}$**,** $\mathbf{[\textit{n}\text{-}Bu_4N]_9P_2W_{15}V_3O_{62}}$**,** $\mathbf{[\textit{n}\text{-}Bu_4N]_5PW_{11}CoO_{39}}$**, and** $\mathbf{[\textit{n}\text{-}Bu_4N]_4[SiW_{11}Ce^{IV}O_{39}]}$**.** $[n\text{-Bu}_4\text{N}]_5[\text{W}_3\text{V}_3\text{O}_{19}]$ and $[n\text{-Bu}_4\text{N}]_4[\text{SiW}_{11}\text{Ce}^{\text{IV}}\text{O}_{39}]$ were prepared by metathesis of $(\text{NH}_4)_2\text{Na}_3[\text{W}_3\text{V}_3\text{O}_{19}]\cdot 20\text{H}_2\text{O}$ and $\text{NaH}_3[\text{SiW}_{11}\text{Ce}^{\text{IV}}\text{O}_{39}]$ with TBABr in distilled water.[28,75] $[n\text{-Bu}_4\text{N}]_3\text{H}_3\text{V}_{10}\text{O}_{28}$, $[n\text{-Bu}_4\text{N}]_7\text{SiW}_9\text{V}_3\text{O}_{40}$, $[n\text{-Bu}_4\text{N}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$, and $[n\text{-Bu}_4\text{N}]_5\text{PW}_{11}\text{CoO}_{39}$ were prepared following literature methods.[47,76,77]

Preparation of an Internal Standard Acetone DNP-Hydrazone Solution. To a solution of 150 mg of 2,4-dinitrophenylhydrazine (97%, 0.74 mmol) in 95 mL of anhydrous acetonitrile was added 5 mL of acetic acid, followed by addition of 50 μL of an aqueous solution of acetone (0.01 M). The formed product by reacting acetone with 2,4-dinitrophenylhydrazine, denoted as acetone DNP-Hydrazone, was stirred vigorously for at least 3 days before being used as an internal standard solution.

Catalytic Aerobic Oxidative Removal of Formaldehyde. Typical reactions were conducted in 15 mL glass vessels under ambient conditions (room temperature, 1 atm). The catalytic formaldehyde oxidations were conducted separately in solutions of acetonitrile (CH_3CN) and H_2O [20/1 (v/v)], *N*,*N*-dimethylacetamide (DMA) and H_2O [20/1 (v/v)], *N*,*N*-dimethylformamide (DMF) and H_2O [20/1 (v/v)], and tetrahydrofuran (THF) and H_2O [20/1 (v/v)]. The water in the reaction solutions was supplied by the aqueous formaldehyde (Formalin) solution. Typically, 0.004 mmol of catalyst and 2 mL of solvent containing 0.52 mol of formaldehyde per liter were mixed and stirred vigorously. The unreacted formaldehyde was quantified by stoichiometric conversion to the corresponding 2,4-dinitrophenylhydrazone (DNP-Hydrazone) derivative using the acetone DNP-Hydrazone as internal standard by gas chromatography (GC). Typically, 10 μL of the reaction solution was added to 1 mL of the internal standard solution (which contains excess DNPH) and the mixture stirred vigorously for 30 min. Aliquots were withdrawn from the Schlenk tube, and the unreacted formaldehyde was quantified by gas chromatography. The formic acid was independently analyzed by GC using decane as an internal standard. The postreaction solutions were dried under vacuum, and the residue was weighed and the catalyst recycled. The products in the reaction using $\mathbf{PW_9V_3}$ as a catalyst in a DMA/H_2O [20/1 (v/v)] solvent system were also analyzed via ^1H NMR spectroscopy by diluting a 400 μL aliquot of the reaction solution after 144 h with 400 μL of deuterated chloroform.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Catalysts. The vanadium-substituted Keggin-type heteropolyanions $\mathbf{PMo_{12-n}V_n}$ and $\mathbf{PW_{12-n}V_n}$ (n = 1−6) have been synthesized previously by our group[78−81] and other groups.[57,59] They are composed of a central PO_4 tetrahedron surrounded by 12 randomly distributed WO_6 and VO_6 metal−oxygen octahedra.[82] In this work, we prepared the TBA salt of $\mathbf{PW_9V_3}$ by precipitation of the heteropolyanion using an excess of TBABr. The TBA salts of $\mathbf{PW_8V_4}$ and $\mathbf{PW_6V_6}$ were prepared by metathesis of $(NH_4)_6HPW_8V_4O_{40}·9H_2O$ and $(NH_4)_5H_4PW_6V_6O_{40}·6H_2O$ with TBABr in distilled water. TGAs confirm the number of TBA counterions in $\mathbf{PW_9V_3}$, $\mathbf{PW_8V_4}$, and $\mathbf{PW_6V_6}$ (six, five, and four, respectively) and that the first two POMs are anhydrous (no feature for the loss of hydration water molecules) and the last POM is hydrophilic [feature showing 12% weight loss of hydration water molecules (Figure S1 of the Supporting Information)].

Figure 1 shows the polyhedral structures of the three polyvanadotungstates studied in this work with three, four, and six vanadium centers. The compositions of vanadium and tungsten in each compound were determined by elemental analysis. The VO_6 octahedra in each compound are statistically distributed between many positions, especially for compounds synthesized using a one-pot method (e.g., $\mathbf{PW_8V_4}$ and $\mathbf{PW_6V_6}$ in this work). In other words, there are many heteropolyanion positional isomers, which were identified some time ago for the polyvanadomolybdates.[58,83] These positional isomers cocrystallize, leading to disorder in the solid state and general structural complexity. The ^{31}P NMR spectra of $\mathbf{PW_9V_3}$ and $\mathbf{PW_8V_4}$ show major peaks at −44.5 and −41.9 ppm, respectively, confirming the purity of these two compounds (Figure S2 of the Supporting Information). However, the ^{31}P NMR spectrum of $\mathbf{PW_6V_6}$ shows numerous signals indicating that multiple positional isomers and different polyvanadotungstates with varying V-to-W ratios (Figure S2 of the Supporting Information) exist. The formula of $[n\text{-}Bu_4N]_4H_5PW_6V_6O_{40}·20H_2O$ was based on elemental analysis as well as TGA. It is common to have multiple positional and compositional isomers in multi-vanadium-containing POMs.[58,83]

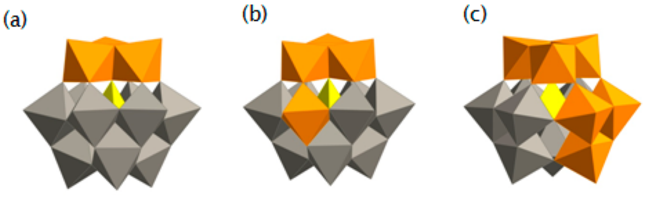

Figure 1. Representative polyhedral representations of the vanadium-substituted Keggin-type polyvanadotungstates of (a) $\mathbf{PW_9V_3}$, (b) $\mathbf{PW_8V_4}$, and (c) $\mathbf{PW_6V_6}$ based on X-ray crystal structures of the parent Keggin POMs. Code: orange octahedra, VO_6; yellow tetrahedra, PO_4; gray octahedra, WO_6.

The FT-IR spectra of $\mathbf{PW_9V_3}$, $\mathbf{PW_8V_4}$, and $\mathbf{PW_6V_6}$ are very similar and display a fingerprint region that is characteristic of substituted Keggin-type POMs (Figure 2). The bands around 1080, 980, 890, 800, and 590 cm^{-1} are related to asymmetric vibrations of P−O_a, W=O_t, W−O_b−W, and W−O_c−W and the bending mode of O_a−P−O_a, respectively. When the tungsten is substituted with vanadium, the band for the P−O_a asymmetric stretch (around 1080 cm^{-1}) splits because of the decrease in the degree of structural symmetry. The shift and the split of the P−O_a band, as shown in the spectra, reflect the substitution of tungsten with vanadium.[82,84] Moreover, the peak around 1100 cm^{-1} in the spectra of $\mathbf{PW_9V_3}$ exhibits a splitting that is greater than the splitting of the corresponding peaks of $\mathbf{PW_8V_4}$ and $\mathbf{PW_6V_6}$, indicating a lower level of local symmetry and greater deviation from idealized T_d symmetry for the former than the latter.

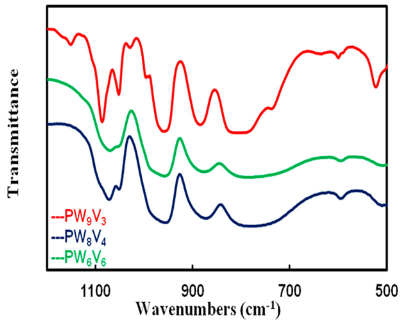

Figure 2. FT-IR spectra of $\mathbf{PW_9V_3}$ (red), $\mathbf{PW_8V_4}$ (blue), and $\mathbf{PW_6V_6}$ (green).

The normalized UV−vis absorption spectra of $\mathbf{PW_9V_3}$, $\mathbf{PW_8V_4}$, and $\mathbf{PW_6V_6}$ in anhydrous acetonitrile are presented in Figure 3. The ligand-to-metal charge-transfer (LMCT) band around 350−450 nm is attributed to the V(V) center. The corresponding oxo-to-W(VI) band should appear between 250 and 300 nm (not shown). The new 350−450 nm band indicates substitution of W(VI) with V(V). The intensity of this band increases with increasing numbers of vanadium centers in each polyvanadotungstate. Thus, the color intensity decreases in the following order: $\mathbf{PW_6V_6}$ (most intense) > $\mathbf{PW_8V_4}$ > $\mathbf{PW_9V_3}$ (least intense).

Catalytic Aerobic Oxidative Removal of Formaldehyde. The TBA salts of $\mathbf{PW_9V_3}$, $\mathbf{PW_8V_4}$, and $\mathbf{PW_6V_6}$ were assessed for their catalytic activity in the aerobic oxidation of

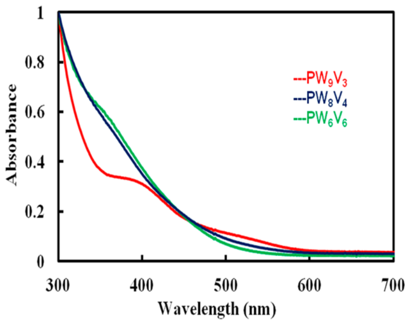

Figure 3. Normalized UV−vis absorption spectra of **PW_9V_3** (red), **PW_8V_4** (blue), and **PW_6V_6** (green) at 0.5 mM in 100% acetonitrile.

formaldehyde to formic acid (eq 1) under ambient conditions (the O_2 in air at room temperature). Initial studies show that a catalytic amount of $(NH_4)_6HPW_8V_4O_{40}\cdot 9H_2O$ added to an aqueous solution of formaldehyde results in oxidation to formic acid; no formaldehyde oxidation products are found in independent control experiments without catalyst. No CO or CO_2 is detected by GC.

$$CH_2O + \frac{1}{2}O_2 \rightarrow HCOOH \tag{1}$$

However, the hydration equilibrium constant [K_{eq} (eq 2)] for formaldehyde is quite large (~10^4 at 20 °C),[85] indicating that formaldehyde exists primarily in hydrated forms (dihydroxymethane and polymers thereof). This in turn makes it far harder to oxidize. We therefore decided to investigate the effect of different solvents on the reaction conversion by conducting the reaction at room temperature in the presence of 0.52 M formaldehyde and 4.0 mM catalyst.

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2 \tag{2}$$

The experimental results (Table 1) show that the extent of reaction conversion for the aerobic oxidation of formaldehyde using **PW_8V_4** increases with solvent system in the following order: $THF/H_2O < CH_3CN/H_2O < DMF/H_2O < DMA/H_2O$. The order of solvent polarity is parallel: THF < CH_3CN < DMF < DMA.[86] In the polar solvent systems of CH_3CN, DMF, and DMA, the activity of **PW_8V_4** is higher than that of $(NH_4)_6HPW_8V_4O_{40}\cdot 9H_2O$ in an aqueous solution. This likely derives in part from the fact that the extent of formaldehyde hydration in the polar solvent systems of CH_3CN, DMF, and DMA is lower than that in a 100% aqueous solution.[87] The THF/H_2O mixed solvent system exhibits an aerobic formaldehyde oxidation activity similar to that of pure water with a TON of ~19. The DMA/H_2O solvent system was used for subsequent experiments because it was the most effective, and DMA, unlike DMF, is not prone to decomposition. The effect of solvent on the reaction (conversion, rates, and selectivity) is not easily interpreted for these complex oxidations and was not further addressed in this initial study. These **PW_8V_4**-catalyzed air-based formaldehyde oxidations were studied as a function of formaldehyde and catalyst concentration (Table S1 of the Supporting Information) in a DMA/H_2O [20/1 (v/v)] solvent system. The optimal solvent system and concentrations (substrate and **PW_8V_4** catalyst) afford a TON of ~47 (entry 4 in Table S1 of the Supporting Information).

Table 1. Aerobic Oxidation of Formaldehyde Catalyzed by PW_8V_4 in Different Solutions[a]

solvent	CH_2O conversion (%)[b]	HCOOH yield (%)[c]	TON[d]
H_2O	15	14	21
DMA/H_2O [20/1 (v/v)]	35	32	47
CH_3CN/H_2O [20/1 (v/v)]	30	28	43
THF/H_2O [20/1 (v/v)]	14	14	19
DMF/H_2O [20/1 (v/v)]	32	31	46

[a] Reaction conditions: concentration of formaldehyde of 0.52 M, concentration of catalyst of 4.0 mM, 1 atm of air, 2 mL of solvent, room temperature, 144 h reaction time. [b] CH_2O conversion (%) = moles of CH_2O consumed per mole of initial CH_2O. [c] GC yield based on initial CH_2O. [d] TON = moles of CH_2O consumed per mole of catalyst.

Two different aspects of the kinetics of aerobic formaldehyde oxidation by **PW_8V_4**, **PW_6V_6**, and **PW_9V_3** in a DMA/H_2O [20/1 (v/v)] solvent system are shown in Figure 4. All of the catalysts are quite active relative to the control (no activity). Of particular interest are the aerobic formaldehyde oxidations catalyzed by **PW_8V_4** and **PW_6V_6**; these are faster than those catalyzed by **PW_9V_3**, indicating that the number of V(V/VI) redox sites and the number of counterions are significant factors in catalytic activity.[29] Some POM-catalyzed oxidation reactions are known to be cocatalyzed by acid. Some more highly protonated POMs are more reactive than less protonated ones despite the fact that higher levels of POM protonation parallel the number of V(V)-for-W(VI) substitutions. The number of these metal substitutions increases the polyanion charge, which lowers the POM V(VI/V) potential. This, in turn, lowers the overall organic substrate oxidation rate if POM oxidation of the substrate is the rate-limiting step in the mechanism.[52]

It has been fairly well established that some of the organic oxidations catalyzed by the analogous polyvanadomolybdate systems, **$PMo_{12-n}V_n$**, proceed via the general two-step mechanism (eqs 3 and 4).[51,55,58,88] It was found that **PMo_{12}** (with $n = 0$) is not a highly reactive catalyst for the aerobic oxidation of aldehydes under ambient conditions. The reversible V(V/IV) redox couple is involved in the efficient oxidation of organic compounds catalyzed by vanadium-substituted Keggin-type heteropolyanions.[51,55,89]

$$\begin{aligned}&\mathbf{PMo_{12-\mathit{n}}V_\mathit{n}} + (\text{organic substrate}) + mH^+\\&\quad\rightarrow H_m(\mathbf{PMo_{12-\mathit{n}}V_\mathit{n}}) + (\text{organic substrate})_{ox}\end{aligned} \tag{3}$$

$$H_m(\mathbf{PMo_{12-\mathit{n}}V_\mathit{n}}) + \frac{1}{4}mO_2 \rightarrow \mathbf{PMo_{12-\mathit{n}}V_\mathit{n}} + \frac{1}{2}mH_2O \tag{4}$$

However, several lines of evidence are consistent with a radical chain mechanism[90−92] for aerobic formaldehyde oxidation catalyzed by **PW_9V_3**. First, the initial rate of the reaction is pseudo-first-order in formaldehyde and parabolic-order in catalyst; i.e., the rate increases, reaches a maximum, and then decreases with an increasing catalyst concentration (Figure 5a,b). Similar parabolic catalyst concentration dependencies are a well-documented and studied feature of metal-catalyzed autoxidation reactions.[93] Second, the rate is essentially independent of oxygen pressure (Figure S3 of the Supporting Information). Third, the reaction is retarded by addition of small quantities of the radical scavenger 4-*tert*-butylcatechol (1.0 μmol) or formic acid (0.6 mmol) (Figure S4 of the Supporting Information).[94,95] Similar phenomena were

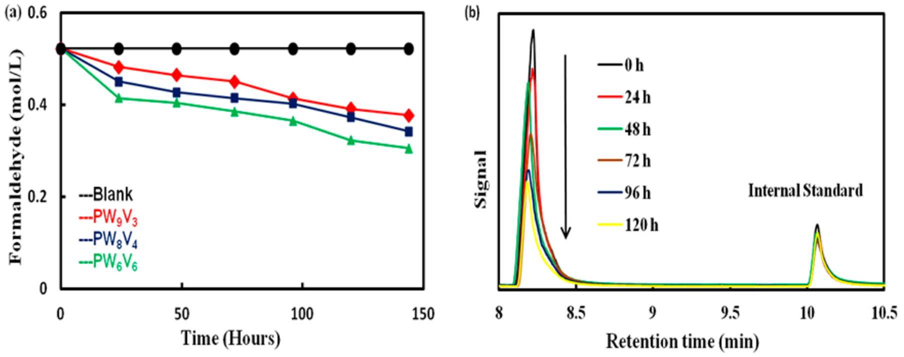

Figure 4. (a) Time profile of formaldehyde consumption catalyzed by $\mathbf{PW_9V_3}$ (red diamonds), $\mathbf{PW_8V_4}$ (blue squares), $\mathbf{PW_6V_6}$ (green triangles), and blank (black circles) in a DMA/H_2O [20/1 (v/v)] solvent system. (b) Formaldehyde DNP-Hydrazone peaks as detected by GC at various time points over 120 h using $\mathbf{PW_9V_3}$ as the catalyst in a DMA/H_2O [20/1 (v/v)] solvent system.

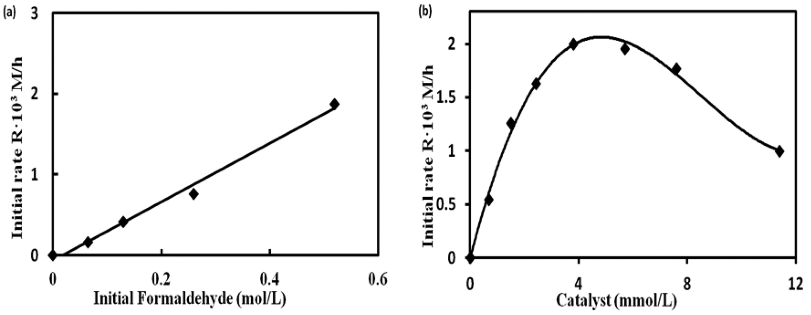

Figure 5. (a) Initial rate of formaldehyde oxidation as a function of the initial reactant concentration (3.8 mM $\mathbf{PW_9V_3}$). (b) Initial rate of formaldehyde oxidation as a function of the initial catalyst ($\mathbf{PW_9V_3}$) concentration (0.52 M CH_2O).

also identified for aerobic formaldehyde oxidation catalyzed by $NaH_3[SiW_{11}Ce^{IV}O_{39}]$.[28]

These observations not only indicate that oxygen is not involved in the rate-limiting step but also argue against the well-established two-step mechanism; they are more consistent with radical chain autoxidation. The processes in eqs 5−10 are likely based on the experimental results described above and literature studies.[28,93] These processes include the aldehyde autoxidation steps (eqs 5−7) and the Haber−Weiss aqueous phase hydroperoxide decomposition processes (eqs 8 and 9) together with the Baeyer−Villiger oxidation of formaldehyde by treatment with peroxy acid (eq 10). These processes taking place simultaneously give rise to complex dependences on catalyst/initiator concentration.

$$\text{initiation: } RCHO + V^{V} \rightarrow RCO^{\bullet} + V^{IV} + H^{+} \tag{5}$$

$$\text{propagation: } RCO^{\bullet} + O_2 \rightarrow RCO_3^{\bullet} \tag{6}$$

$$RCO_3^{\bullet} + RCHO \rightarrow RCO_3H + RCO^{\bullet} \tag{7}$$

$$\text{Haber−Weiss process: } RCO_3H + V^{V} \rightarrow RCO_3^{\bullet} + V^{IV} + H^{+} \tag{8}$$

$$RCO_3H + V^{IV} \rightarrow RCO_2^{-} + V^{V} + OH^{\bullet} \tag{9}$$

$$\text{Baeyer−Villiger process: } RCO_3H + RCHO \rightarrow 2RCOOH \tag{10}$$

Comparison of Supported Noble Metal and POM Catalysts for Aerobic Formaldehyde Oxidation. Six POMs, each with extensive and reversible redox chemistry, were also prepared and evaluated as catalysts for the aerobic oxidation of formaldehyde under ambient conditions (Table 2). These POMs include $[n\text{-}Bu_4N]_5[W_3V_3O_{19}]$; $[n\text{-}Bu_4N]_3H_3V_{10}O_{28}$, a POM with little documented ability to catalyze aerobic organic oxidations;[96−98] $[n\text{-}Bu_4N]_7SiW_9V_3O_{40}$, a Keggin-type trivanadium-containing POM with silicon as the heteroatom; $[n\text{-}Bu_4N]_9P_2W_{15}V_3O_{62}$, a Wells−Dawson POM with three incorporated vanadium centers; $[n\text{-}Bu_4N]_5PW_{11}CoO_{39}$, a Keggin-type Co-containing POM with phosphorus as the heteroatom; and $[n\text{-}Bu_4N]_4[SiW_{11}Ce^{IV}O_{39}]$, a Keggin-type Ce-containing POM. Four of the V-containing

Table 2. Aerobic Oxidation of Formaldehyde Catalyzed by Different POMs[a]

entry	catalyst	CH_2O conversion (%)[b]	HCOOH yield (%)[c]	TON[d]
1	$\mathbf{PW_9V_3}$	28	26	38
2	$\mathbf{PW_8V_4}$	35	32	47
3	$\mathbf{PW_6V_6}$	42	41	57
4	$[n\text{-}Bu_4N]_5[W_3V_3O_{19}]$	0	–	–
5	$[n\text{-}Bu_4N]_3H_3V_{10}O_{28}$	0	–	–
6	$[n\text{-}Bu_4N]_7SiW_9V_3O_{40}$	0	–	–
7	$[n\text{-}Bu_4N]_9P_2W_{15}V_3O_{62}$	0	–	–
8	$[n\text{-}Bu_4N]_5PW_{11}CoO_{39}$	24	23	32
9	$[n\text{-}Bu_4N]_4[SiW_{11}Ce^{IV}O_{39}]$	39	39	53

[a] Reaction conditions: concentration of formaldehyde of 0.52 M, concentration of catalyst of 3.8 mM, 1 atm of air, 2 mL of solvent, ambient temperature, 144 h reaction time. [b] CH_2O conversion (%) = moles of CH_2O consumed per mole of initial CH_2O. [c] GC yield based on initial CH_2O. [d] TON = moles of formaldehyde consumed per mole of catalyst.

complexes are effectively inactive. This finding also indicates that the polyanion properties [structure, V(V/VI) potential, etc.] dictate reactivity in the radical chain aerobic oxidation of formaldehyde. The polyvanadotungstates exhibit an activity comparable to that of the well-documented Keggin-type Co-containing and Ce-containing POMs in a DMA/H_2O [20/1 (v/v)] solvent system.

Some precious metals, e.g., Au, Ru, Pd, and Pt, in large-surface area formulations are known to be very effective catalysts for the gas phase aerobic oxidation of formaldehyde at moderate temperatures.[39,40] As noted above, Pt nanoparticles supported on TiO_2 have been shown to be an effective catalyst for formaldehyde oxidation at room temperature.[33,43] Importantly, most of these noble metal-catalyzed formaldehyde oxidations to date are gas phase reactions. However, water is ubiquitous in human environments, and thus, formaldehyde exists nearly exclusively in its hydrated form [$CH_2(OH)_2$]. Therefore, in this work, metal oxide-supported Au and Pt nanoparticles (Au/TiO_2, reduced Pt/TiO_2) with 1 wt % loading (Figure S6 of the Supporting Information) were prepared by the literature methods[33,44] and assessed for their ability to catalyze aerobic oxidation of formaldehyde in the presence of water.

The catalytic activities of **PW_9V_3**, **PW_8V_4**, **PW_6V_6**, and the supported noble metal catalysts in the presence of water at 40 °C are shown in Figure 6. In a DMA/H_2O [20/1 (v/v)] solvent system with ~4 vol % water, the reduced Pt/TiO_2 shows the highest activity with a formaldehyde conversion of 61%, a finding consistent with the results of Huang et al. and other groups.[99] The Au/TiO_2 also catalyzes formaldehyde oxidation with a conversion of 34%. Critically, however, with an increase in the water concentration (volume percent), the activity of the supported noble metal catalysts decreases precipitously. In aqueous solutions (100 vol % water), the activities of the supported noble metal catalysts for aerobic formaldehyde oxidation are markedly lower than those of **PW_9V_3**, **PW_8V_4**, and **PW_6V_6**. These results indicate that the polyvanadotungstates are water-compatible active catalysts for oxidative removal of formaldehyde.

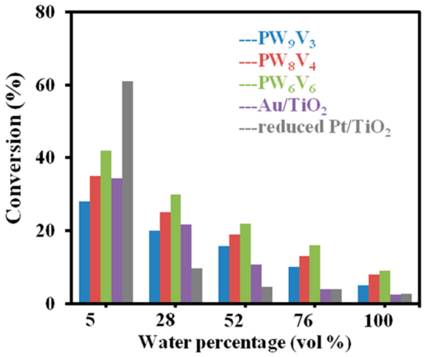

Figure 6. Oxidative removal of formaldehyde catalyzed by **PW_9V_3**, **PW_8V_4**, **PW_6V_6**, reduced Pt/TiO_2, and Au/TiO_2 in the presence of water. [CH_2O] = 0.52 M, [catalyst] = 3.8 mM, 1 atm of air, 2 mL of solvent, 40 °C, 144 h reaction time.

Stability and Reusability of the Catalyst. From a practical point of view, stability and reusability issues should be taken into account when using catalysts for organic reactions. A quite stable catalyst that can be recovered and reused several times and does not become easily deactivated is highly attractive. The stability and reusability of the TBA salts of the polyvanadotungstates were investigated for aerobic formaldehyde oxidation in three successive runs. The postreaction solutions in each run were completely dried under vacuum and weighed, and the catalyst was recycled. The recovered catalysts were reused in subsequent reactions under conditions identical to those in the first run. Two lines of evidence indicate that the vanadium-substituted POMs are quite stable under turnover conditions. (1) The recycled POMs catalyze aerobic oxidation of formaldehyde for at least three cycles without a significant loss of activity. (2) The FT-IR spectra of **PW_9V_3**, **PW_8V_4**, and **PW_6V_6** after the catalytic reactions retain all the characteristic peaks of the spectra of the substituted Keggin-type POMs (Figure S7 of the Supporting Information). These results indicate that TBA salts of the polyvanadotungstates exhibit excellent stability and reusability for the aerobic oxidation of formaldehyde.

■ CONCLUSIONS

This study reveals that the tetra-*n*-butylammonium (TBA) salts of polyvanadotungstates, [n-$Bu_4N]_6[PW_9V_3O_{40}]$ (**PW_9V_3**), [n-$Bu_4N]_6HPW_8V_4O_{40}\cdot 9H_2O$ (**PW_8V_4**), and [n-$Bu_4N]_5H_4PW_6V_6O_{40}\cdot 6H_2O$ (**PW_6V_6**), can work as robust catalysts for the aerobic oxidation of formaldehyde under ambient conditions. This is of note because formaldehyde is both a major TIC and a general health concern in human environments. The catalysts work best in the DMA/water mixed solvent system of [20/1 (v/v)]. Optimization of the reaction conditions led to a system that affords 57 turnovers. A kinetic study of a representative reaction (**PW_9V_3** catalyst, 0.52 M aqueous formaldehyde reagent, and 1.0 atm of air) establishes that the reaction is first-order in formaldehyde substrate, parabolic-order in catalyst, and zero-order in O_2, findings that are all consistent with a radical chain mechanism. Comparison with other related POMs and metal oxide-supported Pt/Au catalysts indicates that the TBA salts of polyvanadotungstates show promise as water-compatible catalysts (can be made and used in water) for oxidative removal of formaldehyde under ambient, high-humidity conditions. Systematic optimization and mechanistic studies are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TGAs of polyvanadotungstates, X-ray diffraction patterns of supported Pt/Au nanoparticles, and FT-IR spectra of polyvanadotungstates after catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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