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Keggin phosphomolybdovanadates for catalytic oxidations

John H. Grate

Catalytica Inc., 430 Ferguson Drive, Mountain View, CA 94043, USA

Abstract

This paper describes the practical production of aqueous phosphomolybdovanadates, for use at large scale as well as in the laboratory, and the practical reoxidation of aqueous reduced phosphomolybdovanadates by dioxygen, for use in net catalytic oxidation processes.

Keywords: Phosphomolybdovanadate; Oxidation

1. Introduction

Keggin phosphomolybdovanadates are pragmatically useful, dioxygen-regenerable oxidants for *net* catalytic oxidation processes¹. *Net* catalytic oxidation processes include processes in which the intermediating oxidant (in this case, phosphomolybdovanadate) is alternately stoichiometrically reduced by the substrate and stoichiometrically reoxidized by the terminal oxidant (in this case, dioxygen) as well as formally catalytic processes in which both substrate and terminal oxidant are reacted concurrently with a catalytic amount of the intermediating oxidant.

Process R&D on phosphomolybdovanadate-mediated oxidations at Catalytica in the late 1980s focused on developing practical Wacker-like aqueous palladium-catalyzed oxidations of olefins to carbonyls, in which phosphomolybdovanadates couple the reoxidation of palla-

dium(0) to the reduction of dioxygen (hereafter, simply called oxygen). The rudimentary reaction system was originally developed by Matveev and collaborators in Novosibirsk, who discovered that vanadium(V) in Keggin phosphomolybdovanadates is a oxygen-regenerable oxidant that can provide the same function as copper(II) chlorides in Wacker chemistry [2,3]. The vanadium(V) is reduced to vanadium(IV) by the palladium catalyzed oxidation of the substrate, and is reoxidized by oxygen. Practical shortcomings of the Novosibirsk reaction system were overcome by process R&D at Catalytica. Less abridged accounts of the chemistry and technology have been published elsewhere [4–6].

This paper focuses on two developments at Catalytica that are widely applicable in other phosphomolybdovanadate-mediated net catalytic oxidations. The first is the practical production of phosphomolybdovanadates in aqueous solutions of accurately and precisely predetermined composition, free of other nonessen-

¹ A recent leading reference for polyoxometalates in catalysis is Ref. [1].

tial components. The second is the oxidation of reduced aqueous phosphomolybdovanadates by oxygen at rates suitably rapid for practical net catalytic oxidation processes. These developments are described following some background information on the nature of aqueous phosphomolybdovanadate solutions.

2. Keggin phosphomolybdovanadate solutions [7,8]

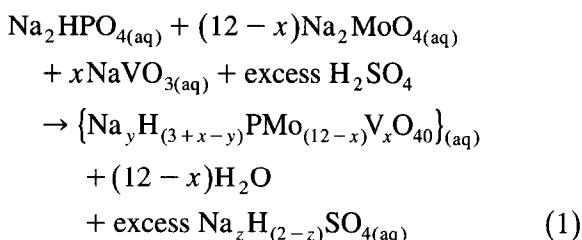
Keggin phosphomolybdovanadates having the general formula $H_y P Mo_{(12-x)} V_x O_{40}^{(3+x-y)-}$ spontaneously assemble in acidic aqueous solutions of the component oxoanion elements in their highest oxidation states: P(V), Mo(VI), and V(V). When the oxoanion elements are present in the Keggin ratio, $[Mo] + [V] = 12[P]$, with $[V]/[P] \geq 1$ and with $[P]$ at decimolar concentrations, the equilibrium formation of the Keggin anions is highly favored. In the oxidized solutions discussed herein, the oxoanion elements are essentially completely incorporated into equilibrium mixtures of Keggin phosphomolybdovanadates varying in vanadium content, x , and, for $x \geq 2$, in isomeric structure (^{31}P - and ^{51}V -NMR) [7,8]. These solutions are, for convenience, designated by the phosphorus concentration (0. X M) and the nominal, macroscopic salt formula in braces; e.g. for sodium salts: 0. X M $\{Na_y H_{(3+x-y)} P Mo_{(12-x)} V_x O_{40}\}$. The mole ratios among Na, P, Mo, and V in solution are specified by x and y . Since P, Mo, and V are predominantly incorporated into Keggin polyanions, x in the nominal formula is essentially the average polyanion composition.

Vanadium-free phosphomolybdates do not appear in these solutions provided $[V]/[P] \geq 1$. Nominal $\{Na_y H_{(4-y)} P Mo_{11} V O_{40}\}$ solutions contain essentially only $PMo_{11}VO_{40}^{4-}$, with insignificant equilibrium disproportionation to $PMo_{10}V_2$ species and vanadium-free phosphomolybdates. Likewise, in solutions with $[V]/[P] > 1$, the equilibrium distributions of $PMo_{(12-x)}V_xO_{40}^{(3+x)-}$ species are limited to species with $x \geq 1$.

3. Preparations of phosphomolybdovanadate solutions

3.1. Acidification of alkaline salt solutions

Conventionally, Keggin phosphomolybdovanadates have been prepared by acidifying aqueous alkaline solutions containing the component element oxoanions. Typically, sulfuric acid is used to acidify a solution of sodium salts of phosphate, molybdate, and vanadate. This results in a solution of sodium phosphomolybdovanadate salts containing sodium sulfate and bisulfate. The following synthesis equation is representative.

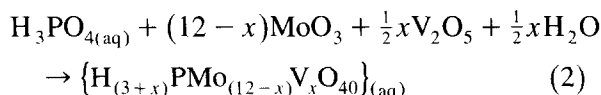


To obtain useful, *acidic* Keggin phosphomolybdovanadate solutions, an excess of sulfuric acid is added over the stoichiometric amount needed to remove oxygens(–II) from the starting component oxoanions ($12-x$ oxygens(–II) in Eq. (1)) as water. Preparation of 0.30 M $\{Na_{4.5}H_{0.5}PMo_{10}V_2O_{40}\}$ by the above equation, results in ~ 0.3 M sulfate salts in solution. As phosphomolybdovanadic acids are strong acids, capable by themselves of providing such acidity in solution, there is no essential requirement for sulfate salts to be included in acidic phosphomolybdovanadate solutions intended for practical purposes. Indeed, sulfate salts proved to undesirably affect our intended applications [6].

While free phosphomolybdovanadic acids can be separated from such salt solutions by still further acidification and extraction as etherates, this is not practical for large scale production and is bothersome even for laboratory use. Moreover, the actual composition of the so-recovered phosphomolybdovanadic acid cannot be unambiguously predetermined and must be assessed analytically.

3.2. Reactive dissolution of the metal oxides

Free phosphomolybdovanadic acids can be prepared in water by dissolving MoO_3 and V_2O_5 with stoichiometric phosphoric acid [9],

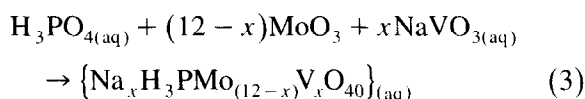


This method introduces only the essential components into solution, but it works well only for very low vanadium contents. Dissolution of V_2O_5 into the polyoxometalate solution is very slow and requires long reaction times at reflux temperature, typically at least one week. Preparation of $\{\text{H}_4\text{PMo}_{11}\text{VO}_{40}\}$ proceeds with essentially complete V_2O_5 incorporation. For desired $\{\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$, stoichiometric V_2O_5 incorporation remains incomplete even after prolonged reflux, and the ultimate composition of the solution must be assessed analytically. (Attempted preparation of 0.30 M $\{\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ yielded a $\{\text{H}_{4.9}\text{PMo}_{10.1}\text{V}_{1.9}\text{O}_{40}\}$ solution after seven days at reflux and filtration from unreacted V_2O_5 . The unreacted V_2O_5 was quantitatively, gravimetrically recovered, and analytically confirmed, to determine the solution composition [10].) Incomplete V_2O_5 incorporation becomes more severe with increasing desired vanadium content, so this method becomes almost useless to prepare compositions with $x \geq 3$. (Attempted preparation of 0.30 M $\{\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}\}$ yielded a $\{\text{H}_{5.4}\text{PMo}_{9.6}\text{V}_{2.4}\text{O}_{40}\}$ after seven days at reflux [10].)

This method was adapted at Catalytica to prepare just slightly neutralized phosphomolybdovanadic acid solutions with $x \geq 2$, with unambiguously predetermined composition. The unreacted V_2O_5 is quantitatively recovered and dissolved in water with a minimal, measured amount of alkali carbonate. The resulting alkali vanadate solution is returned to the phosphomolybdovanadic acid solution. The resulting solution can be reequilibrated at reflux. For examples, the preparations of $\{\text{Na}_{1.2}\text{H}_{4.8}\text{PMo}_9\text{V}_3\text{O}_{40}\}$ and $\{\text{Li}_{1.15}\text{H}_{5.85}\text{PMo}_8\text{V}_4\text{O}_{40}\}$ solutions have been described in detail [10].

3.3. Catalytica's phosphomolybdovanadate solution preparation [10]

Reactive dissolution of MoO_3 with aqueous dissolved vanadate salt and stoichiometric phosphoric acid directly provides acidic phosphomolybdovanadate partial salt solutions. The following equation is representative



The formation of the phosphomolybdovanadates in solution by this method proceeds without the addition of any other mineral acid, introducing only the essential phosphomolybdovanadate components into the solution. Optionally, the alkali vanadate solution can be first prepared from V_2O_5 in the same pot, which can be conveniently done with stoichiometric alkali carbonate (typically Na_2CO_3).² This provides a rapid, scalable, one-pot synthesis from the metal oxides. With heating at reflux to complete the reactions, the preparation can be completed in a half day in the laboratory.

The preparation proceeds with complete incorporation of the reactants into the phosphomolybdovanadate solution. (Impurities in the starting materials may be removed as insoluble residues.) Accordingly, this method accurately and precisely yields predetermined solution compositions.³

The concentration of the solution can be adjusted either volumetrically or densimetrically. A 0.30 M solution contains ~ 50% phosphomolybdovanadate salt by weight and has a density typically ~ 1.4 kg/L. The precise density of a solution having a specific phosphomolyb-

² V_2O_5 is less costly and usually more pure than commercial NaVO_3 . In our laboratory preparations, some hydrogen peroxide is typically added to the resulting NaVO_3 solution to oxidize the vanadium(IV) usually present in V_2O_5 . The vanadate catalytically decomposes any excess hydrogen peroxide. Details and specific examples of the synthetic method are found elsewhere [6,8,10].

³ The masses of the starting materials and the volume of the resulting solution can be measured more accurately and precisely than the elements can be analyzed in the resulting solution.

dovanate composition and concentration is determined from a small scale preparation of the solution in which its concentration is adjusted volumetrically. For a large scale preparation of the same specific solution, it is then more convenient to adjust the concentration by density, which involves measuring the weight and volume of only a small sample of the large preparation.

This preparation, as exemplified by Eq. (3), provides solutions of $\{\text{Na}_x\text{H}_3\text{PMo}_{(12-x)}\text{V}_x\text{O}_{40}\}$ having $[\text{Na}^+] = [\text{V}]$, from NaVO_3 . (0.30 M $\{\text{Na}_x\text{H}_3\text{PMo}_{(12-x)}\text{V}_x\text{O}_{40}\}$ solutions with $x \leq 4$ have $\text{p}[\text{H}^+] < 1$.) Somewhat lower $[\text{Na}^+]/[\text{V}]$ ratios, and higher acidity, can be obtained using $\text{Na}_6\text{V}_{10}\text{O}_{28}$ as the dissolved vanadate salt. To obtain higher degrees of neutralization and lower acidity, additional base (typically Na_2CO_3) can be added at any time: in the alkali vanadate preparation step, in the phosphomolybdovanadate preparation step, or after storage of the phosphomolybdovanadate solution. Solutions having different degrees of neutralization, or even different macroscopic vanadium contents, x , can be volumetrically blended to obtain intermediate solution compositions. Since the solutions are equilibrium mixtures, their macroscopic compositions can have non-integral values of x and y .

Series of $\{\text{Na}_y\text{H}_{(3+x-y)}\text{PMo}_{(12-x)}\text{V}_x\text{O}_{40}\}$ solutions, with y varied to vary $\text{p}[\text{H}^+]$ ⁴, are readily obtained by using combinations of the free acid preparation (by metal oxides dissolution), Catalytica's salt solution preparation, neutralization, and blending. For example, 0.30 M $\{\text{Na}_y\text{H}_{(5-y)}\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ solutions with y varied over the range 0–4.95 cover the $\text{p}[\text{H}^+]$

range 0–2. Over this entire $\text{p}[\text{H}^+]$ series of nominal $\{\text{Na}_y\text{H}_{(5-y)}\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ solutions, the oxoanion elements are predominantly incorporated into the Keggin polyanions (³¹P- and ⁵¹V-NMR).

3.4. Preparation of phosphomolybdovanadate solids

Since solutions prepared as above contain only the phosphomolybdovanadate components and counterions in their Keggin polyanion salt proportions, solid phosphomolybdovanadate salts can be recovered by simple evaporation and drying. By evaporating a measured volume of solution having predetermined salt composition and concentration in a tared vessel, the macroscopic equivalent weight and water content of the residual solid can be determined from its mass. The recovered solid is typically pulverized to blend any inhomogeneities in the composition the solids depositing over the course of the evaporation process. A detailed example of the method, for $\{\text{Na}_3\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}\} \cdot 10.8\text{H}_2\text{O}$, can be found elsewhere [10].

The yield of the solid phosphomolybdovanadate salt from this method is quantitative, all the way from the starting materials used to prepare the phosphomolybdovanadate salt in solution. The solid's bulk composition is precisely known from simple volumetric (aqueous solution) and gravimetric (solid product) measurements.

4. Oxidation of reduced aqueous phosphomolybdovanadates by oxygen

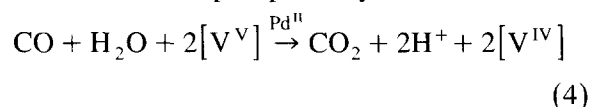
4.1. Experimental method

Oxidations of reduced aqueous phosphomolybdovanadates by oxygen were conducted in 300 mL stirred-tank reactor systems whose design and operation are presented in more detail elsewhere [4]. The reactors were each equipped with a hollow shaft stirring impeller, having a hole in the shaft high in the reactor for gas inlet and another at its six-blade flat disk

⁴ Acidity is reported on the concentration scale, $\text{p}[\text{H}^+] = -\log[\text{H}^+]$, not on the activity scale, $\text{pH} = -\log(a_{\text{H}^+})$. $\text{p}[\text{H}^+]$ measurements were calibrated using solutions of $\text{A}_y\text{H}_{(4-y)}\text{PMo}_{11}\text{VO}_{40}$ with the same P concentration and A^+ counterion as the solution to be measured. $\text{PMo}_{11}\text{VO}_{40}^{4-}$ is completely unprotonated even in concentrated solutions of its free acid, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ [7,8]. Accordingly, solutions of $\text{A}_y\text{H}_{(4-y)}\text{PMo}_{11}\text{VO}_{40}$, have $[\text{H}^+] = (4-y)[\text{P}]$. Details of the $\text{p}[\text{H}^+]$ measurement method can be found elsewhere [6,10].

turbine, and one or more vertical baffles. Centrifugal vacuum at the spinning turbine pulls gas down the hollow shaft for efficient dispersion of the gas through the liquid. The capability to provide highly efficient gas–liquid mixing is essential for obtaining reaction rates suitably rapid for practical net catalytic oxidation processes.

Reduced phosphomolybdovanadate solutions were generated in the reactor by palladium catalyzed reduction of the oxidized phosphomolybdovanadates by carbon monoxide. As reported by the Novosibirsk group, palladium catalyzes the oxidation of carbon monoxide by vanadium(V) in phosphomolybdovanadates⁵,



100 mL of oxidized phosphomolybdovanadate solution, containing 0.10 mM dissolved palladium(II), was reacted at 120°C under 150–250 psi initial carbon monoxide pressure, with efficient gas–liquid mixing, for at least 10 min. After the reaction, the solution was cooled to room temperature and the excess carbon monoxide and co-product carbon dioxide were vented from the reactor and purged from the solution by several fill–mix–vent cycles with nitrogen. When so-reacted with excess carbon monoxide, the vanadium(V) in the phosphomolybdovanadate solution is quantitatively reduced to vanadium(IV), as evidenced by the stoichiometry of oxygen consumption on reoxidation to vanadium(V) (see below).

⁵ Although the equation as written suggests the acidity of the solution may increase with vanadium(V) reduction, it does not. Phosphomolybdovanadate solutions are typically less acidic after vanadium(V) reduction, at least once fully equilibrated. For example, 0.30 {Na₃H₃PMo₃V₃O₄₀} has p[H⁺] = 0.45, but after its full reduction and equilibration, the solution has p[H⁺] > 2. Evidently, after vanadium(V) is reduced to vanadium(IV), the polyoxoanion species undergo reequilibrations that consume hydrogen ions. Dissociation of V^{IV}O₂⁺ and reconstitution of Keggin ions having lower vanadium content, which are hydrogen ion consuming processes (see Eq. (7)), have been confirmed by equilibrium analysis [7]. See also the discussion immediately preceding and following Eq. (7) in this paper.

Reactions of so-reduced phosphomolybdovanadate solutions with oxygen were conducted in fed-batch mode under constant pressure, with regulated, on-demand feed of oxygen from a reservoir of known volume at higher pressure. To set up the reaction, the solution under 1 atm nitrogen was heated to the intended reaction temperature and the autogenous pressure at this temperature was noted. With gentle stirring-sufficient to keep the solution thermally mixed but insufficient for significant gas–liquid mixing-oxygen was regulated into the reactor to a total pressure equal to the autogenous pressure plus the intended oxygen partial pressure. (Without significant gas–liquid mixing, no detectable reaction occurs.) With the regulated gas feed system set to deliver oxygen from the reservoir on demand, the reaction was initiated by increasing the stirring impeller speed to provide dispersion of the gas through the liquid. The increase in stirring speed occurred instantly relative to the time scale of the ensuing reaction. Reactions were allowed to proceed until oxygen uptake ceased.

Thermocouples and pressure transducers monitored the temperatures and pressures in the reactor and the reservoir. A magnetic-sensing tachometer monitored the stirring shaft revolution rate. These transducers were interfaced to a microcomputer system for continuous data acquisition. The moles of oxygen reacted was measured as the moles fed from the reservoir, calculated from the volume, pressure, and temperature data using the ideal gas equation. Reaction rates reported herein are the initial volumetric reaction rates, in (millimole oxygen/liter solution)/second, abbreviated mmol/L · s.

Multiple cycles of carbon monoxide and oxygen reactions could be conducted with a single batch of phosphomolybdovanadate solution in the reactor.

4.2. Typical fed-batch reaction profile

Fig. 1 shows the oxygen reacted versus time for a reaction at 36 psi partial pressure with 100

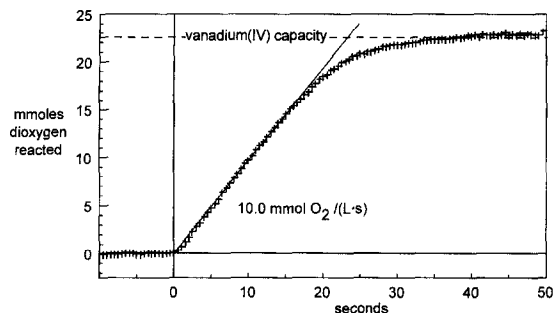
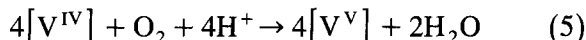


Fig. 1. Oxygen reacted versus time for reaction at constant 36 psi partial pressure with 100 mL of reduced 0.30 M $\{\text{Na}_3\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}\}$ at 110°C. Data points are at every half second. Zero on the time axis is when efficient gas–liquid mixing started. The slope of the superimposed line, calculated by linear regression, corresponds to the indicated initial reaction rate.

ml of reduced 0.30 M $\{\text{Na}_3\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}\}$ at 110°C. As soon as the stirring speed is increased to provide efficient gas–liquid mixing (zero on the time axis), the reaction begins. It proceeds to react an amount of oxygen corresponding to all the vanadium in the solution being initially present as vanadium(IV), according to the stoichiometry of the following equation⁶.



This stoichiometry implies that any intermediates of oxygen reduction to water react with the vanadium(IV) more rapidly than the oxygen is reacting with it.

The reaction of Fig. 1 was conducted under constant oxygen partial pressure. The reaction rate is nearly constant to high conversion of the initial vanadium(IV). Linear regression gives the slope 1.00 mmol/s, for a volumetric rate of 10.0 mmol/L · s.

Complete oxidation of the initial 0.9 N vanadium(IV) in the reaction of Fig. 1 is essentially complete in 30 s. At higher oxygen partial pressures and with better gas–liquid mixing,

⁶ Although the equation as written suggests the acidity of the solution may decrease with vanadium(IV) oxidation, it does not. Phosphomolybdovanadate solutions are typically more acidic after vanadium(IV) oxidation, at least when comparing fully equilibrated solutions. See the discussion in the preceding footnote.

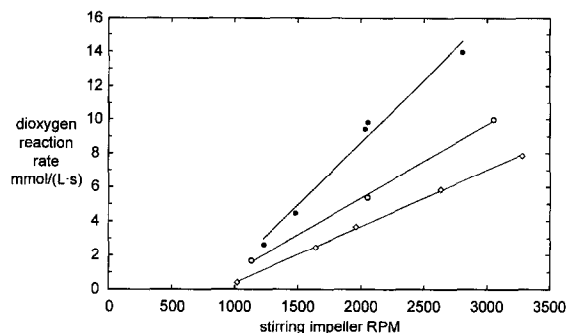


Fig. 2. Oxygen reaction rate versus stirring impeller speed for reduced phosphomolybdovanadate solutions in three different reactors. The solutions contained palladium(II) catalyst for reducing the phosphomolybdovanadates with carbon monoxide. In each series, a batch of solution was alternately reacted with carbon monoxide and oxygen to obtain the data at different stirring impeller speeds: ●, ○ 0.30 M reduced $\{\text{Na}_3\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}\}$, 36 psi O_2 , 110°C; ◇ 0.30 M reduced $\{\text{Li}_4\text{HPMo}_{10}\text{V}_2\text{O}_{40}\}$, 27 psi O_2 , 120°C.

even faster reaction rates have been obtained, and complete reoxidation of all of the vanadium in such solutions has been accomplished within 10 s (see rate data points in Fig. 2 and Fig. 3). Prior to these studies, the kinetic reactivity of reduced aqueous phosphomolybdovanadates for such rapid oxidations by oxygen had not been reported. The discovery of this reactivity for suitably rapid reoxidation is highly advantageous, and in some cases essential, for practical

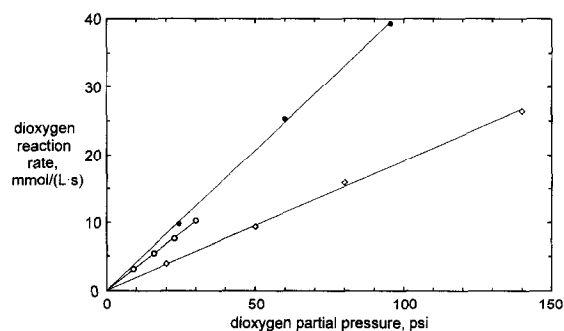


Fig. 3. Oxygen reaction rate versus oxygen partial pressure for reduced phosphomolybdovanadate solutions under different gas–liquid mixing conditions. The solutions contained palladium(II) catalyst for reducing the phosphomolybdovanadates with carbon monoxide. In each series, a batch of solution was alternately reacted with carbon monoxide and oxygen at the different pressures: ●, ○ 0.30 M reduced $\{\text{Na}_3\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}\}$, 110°C; ◇ 0.30 M reduced $\{\text{Li}_4\text{HPMo}_{10}\text{V}_2\text{O}_{40}\}$, 120°C.

applications of aqueous phosphomolybdovanadates in net catalytic oxidation processes using oxygen.

4.3. Appraising diffusion limitations

Possible diffusion limitations in these rapid oxygen reactions were assessed by measuring reaction rates for nominally identical reactions conducted with different stirring impeller speeds. Fig. 2 shows series of data from three stirred-tank reactor systems. In all three series, the rates increased linearly with stirring impeller speed, up to the highest stirring speeds available. (The different slopes manifest different mixing capabilities — like different baffling — in the different reactors.) The vanadium(IV) in these solutions is so reactive towards oxygen that its reaction rate is diffusion limited in all these reactions. Indeed, with our preferred phosphomolybdovanadate solutions (0.30 M reduced $\{\text{Na}_y\text{H}_{(3+x-y)}\text{PMo}_{(12-x)}\text{V}_x\text{O}_{40}\}$, $x = 2-3$, with y such that $\text{p}[\text{H}^+] \geq 0.2$ when oxidized) at reaction temperatures $> 100^\circ\text{C}$, we have never exposed, in any reactor, *initial* oxygen reaction rates limited by chemical kinetics. Only once most of the initial vanadium(IV) is oxidized — as in the reaction of Fig. 1 at $\geq 80\%$ conversion, having ≤ 0.2 N vanadium(IV) remaining — do chemical kinetics begin to be manifested for the oxidation of the remaining, diminishing vanadium(IV).

The possibility of gas phase diffusion limitations was checked by comparing oxygen reaction rates with and without added nitrogen pressure, simulating air. (Oxygen was fed to maintain constant oxygen partial pressure.) The rate was unchanged by the added pressure of inert gas, confirming the absence of gas phase diffusion limitations.

Accordingly, the oxygen reaction is gas-liquid diffusion rate limited, occurring in the liquid film at the gas-liquid interface and limited by the rate of oxygen diffusion into it. The kinetic equation for reactions in this fast reaction regime has the form of Eq. (6), where k_L is

the mass transfer rate constant, a is the gas-liquid interfacial area, and P is the partial pressure.

$$-d(\text{O}_2)/dt = k_L a P_{\text{O}_2} \quad (6)$$

Higher stirring impeller speeds generate more interfacial area, a , for gas-liquid diffusion. The far slower rates of oxygen reaction with reduced phosphomolybdovanadate solutions in all prior reports indicate that the gas-liquid mixing provided was relatively inefficient.

4.4. Kinetic dependence on oxygen pressure

In according with Eq. (6), the oxygen reaction rate is first order dependent on the oxygen pressure. Fig. 3 shows three series of reaction rates versus oxygen partial pressures. Within each series the reactions were conducted with fixed gas-liquid mixing conditions (same reactor, same impeller stirring speed), but among the series the gas-liquid mixing conditions differed. While rates limited by chemical kinetics could also exhibit a first order dependence on oxygen pressure, the different slopes obtained under different mixing conditions again evidence that these rates are gas-liquid diffusion limited.

4.5. Providing the chemical reactivity for rapid, diffusion limited oxygen reactions

Having such rapid, diffusion limited oxygen reactions available for our applications, the chemical kinetics of the reaction of reduced phosphomolybdovanadates with oxygen under conditions where they might be exposed (at lower temperature or lower concentration, for example) were not fully characterized at Catalytica. Certain requirements of the composition of the phosphomolybdovanadate solutions to provide the reactivity for such rapid reactions were evaluated.

One inquiry was whether the palladium catalyst provided in the solution to couple the reduction of the phosphomolybdovanadates to the

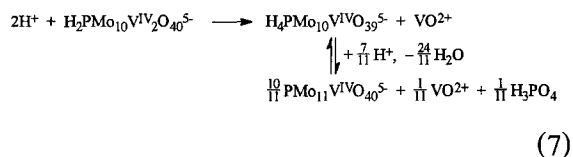
oxidation of carbon monoxide and other substrates might also provide an essential catalyst enabling the rapid reaction of reoxidation of the reduced phosphomolybdovanadates by oxygen. To test this possibility, palladium-free 0.30 M $\{\text{Li}_4\text{HPMo}_{10}\text{V}_2\text{O}_{40}\}$ was reduced with hydrazine hydrate (at $\text{N}_2\text{H}_4:\text{V} = 1:4$) in a sealed reactor at 120°C . Dinitrogen evolution from hydrazine oxidation was monitored by pressure increase to constant pressure. Subsequent reaction of this solution with oxygen (120°C) proceeded at the same rapid, gas–liquid diffusion limited rate as the reaction of another 0.30 M $\{\text{Li}_4\text{HPMo}_{10}\text{V}_2\text{O}_{40}\}$ solution containing a palladium catalyst, reduced with carbon monoxide, and reacted with oxygen under the same pressure, temperature and mixing conditions. Evidently, vanadium(IV) in the reduced phosphomolybdovanadate solution reacts directly with oxygen with a chemical kinetic reactivity exceeding the diffusion limitations in our reactors.

The Novosibirsk group had reported that the oxygen reaction rate with reduced phosphomolybdovanadate solutions is appreciably diminished at $\text{pH} < 1$, referring to the pH of the solutions as prepared, oxidized [3]. This requires that increased acidity, below pH 1 (when oxidized), would so decrease the reactivity of the vanadium(IV) in the solution that the chemical kinetics of its reaction become rate limiting. Yet, we recorded oxygen reaction rates with reduced phosphomolybdovanadate solutions having $\text{p}[\text{H}^+] < 1$ (when oxidized) that were more than an order of magnitude faster than the fastest rates reported by the Novosibirsk group and were still rate limited by gas–liquid diffusion. (The 0.30 M $\text{Na}_3\text{H}_3\text{PMo}_9\text{V}_3\text{O}_{40}$ solution used in the reactions of Figs. 1–3 has $\text{p}[\text{H}^+] = 0.45$ when oxidized.)

The possible influence of acidity on the oxygen reaction was evaluated by comparing reactions of reduced 0.30 M $\{\text{Li}_y\text{H}_{(5-y)}\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ solutions, varying y to vary $\text{p}[\text{H}^+]$. The pressure (30 psi oxygen), temperature (120°C), and mixing conditions were

kept constant among the reactions. In all cases, the *initial* reaction rate of the *fully reduced* solution (meaning all the vanadium as vanadium(IV)) was at the gas–liquid diffusion limit. The solutions having $y \geq 2$ ($\text{p}[\text{H}^+] \geq 0.15$ when oxidized) exhibited the constant, diffusion limited rate to $\geq 80\%$ vanadium(IV) conversion. In the more acidic solutions, however, chemical kinetics became exposed at lower vanadium(IV) conversions. The solution with $y = 0$, 0.30 M $\{\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ ($\text{p}[\text{H}^+] = -0.07$ when oxidized) exhibited the constant, diffusion limited rate up to only $\sim 50\%$ vanadium(IV) conversion, after which the rate decelerated as the vanadium(IV) was further converted. The solution with $y = 1$ exhibited intermediate behavior. The position of such transitions between diffusion limited rates and chemical kinetics limited rates can also depend on the reaction temperature and the gas–liquid mixing efficiency provided, which were held constant over these experiments.

The decreased reactivity of a fraction of the vanadium(IV) in the most acidic reduced solutions is attributed to the equilibrium dissociation of vanadium(IV) from reduced phosphomolybdovanadates as vanadyl dication, VO^{2+} . For example, on reducing both vanadium(V) in $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ species, the resulting $\text{H}_2\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ species dissociate VO^{2+} , and in part reconstitute as reduced Keggin polyanions with one vanadium; Eq. (7) [7]. As shown here, such VO^{2+} dissociation is favored by increasing acidity.



^{51}V - and ^{31}P -NMR examination of a freshly oxidized solution from fully reduced 0.30 M $\{\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ showed substantial redistribution of the Keggin species into predominantly $\text{PMo}_{11}\text{VO}_{40}^{4-}$. The original equilibrium distribu-

tion, containing predominantly $\text{PMo}_{10}\text{V}_2$ species, recovered with time after oxidation. Freshly oxidized solutions from fully reduced 0.30 M $\{\text{Li}_y\text{H}_{(5-y)}\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$ showed, in order of increasing y , increased preservation of their original, oxidized equilibrium distributions.

According to this rationale, dissociated VO^{2+} is oxidized sluggishly compared to vanadium(IV) in phosphomolybdovanadates. Vanadium(IV) in phosphomolybdovanadates reacts with oxygen rapidly, after which vanadium(IV) remaining as VO^{2+} continues to be oxidized at a slower rate. Even so, VO^{2+} may be oxidized more rapidly in these reactions than if reacting with oxygen in the absence of phosphomolybdovanadates. VO^{2+} may be oxidized by intermediate species of oxygen reduction, such as peroxy species, generated during the reaction of vanadium(IV)-phosphomolybdovanadates with oxygen. This would provide oxidation of some VO^{2+} at the same rapid rate as the vanadium(IV)-phosphomolybdovanadates, but only until the vanadium(IV) initially present in phosphomolybdovanadates is essentially all oxidized. The oxidized phosphomolybdovanadates might still catalyze the oxidation of remaining vanadyl dication by electron exchange.

In addition to increasing acidity, VO^{2+} dissociation from reduced phosphomolybdovanadates is also favored by: increasing vanadium content, x , in the phosphomolybdovanadate composition, $\{\text{PMo}_{(12-x)}\text{V}_x\}$; increasing fraction of the total vanadium present as vanadium(IV); and decreasing concentration of the phosphomolybdovanadates (favoring dissociative equilibria). The appreciably diminished oxygen reaction rates, apparently limited by chemical kinetics, obtained by the Novosibirsk group from solutions having $\text{pH} < 1$ (when oxidized) may have reflected the relatively high vanadium content of their preferred composition, $\{\text{PMo}_6\text{V}_6\}$.

From a pragmatic viewpoint, the important result is that certain reduced phosphomolybdovanadate solutions have sufficient chemical

reactivity for very rapid oxidation by oxygen, enabling the practical utilization of aqueous phosphomolybdovanadate oxidants in net catalytic oxidation processes using oxygen.

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