

# Molecular Engineering of Heterogeneous Catalysts: An Efficient Catalyst for the Production of Hydrogen Peroxide

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A goal of chemists for many years has been to control the structure of solid-state compounds to induce desired chemical properties. A porous metal phosphonate compound with chemically active pillaring groups, which allow for the direct production of hydrogen peroxide from hydrogen and oxygen, has been designed. The porous compound,  $Zr_2(PO_4)(O_3PCH_2CH_2\text{-bipyridinium-}CH_2CH_2PO_3)X_3 \cdot 3H_2O$  ( $X = \text{halide}$ ) was prepared by low-temperature hydrothermal reaction. The organic groups of this material act as pillars for the inorganic layers, leading to large pores (ca.  $8 \times 9 \text{ \AA}$ ) in the solid. Platinum and palladium colloids can be incorporated into the structure by ion-exchanging the free halide with a solution of  $K_2MCl_4$  ( $M = Pd$  or  $Pt$ ) followed by hydrogen reduction. In these materials, the Pt and Pd colloids act as microelectrodes for the reduction of viologen by hydrogen, which selectively reduces oxygen to hydrogen peroxide. Treatment of aqueous suspensions of these porous catalysts with  $H_2$  and  $O_2$  gases at atmospheric pressure leads to  $H_2O_2$  solutions with concentrations as high as 0.21 M. Reactions carried out at higher pressures lead to significantly higher concentrations of  $H_2O_2$ . The yield of  $H_2O_2$  based on  $H_2$  consumed was estimated at 40%. © 1996 Academic Press, Inc.

## INTRODUCTION

The controlled synthesis of microporous materials has been an elusive goal for many years. Most microporous solids (e.g., zeolites) are constructed of silicate tetrahedra or mixtures of aluminate, silicate, or phosphate tetrahedra (1). The corner-sharing tetrahedra of these solids can form a variety of arrangements, leading to a large number of unique structures (2). Substitution on the framework can lead to a charged structure, which is balanced by anions or cations in the pores of the material. Most of these porous materials are synthesized under hydrothermal conditions using small organic templates. These organic molecules are typically charged and act as nucleation sites around which the inorganic framework forms. This approach leads to materials whose pore sizes can vary over a wide range. If small

organic molecules are used the pore sizes range from 3 to 13 Å (2), while the use of micelles or vesicles as templates can give materials with pore sizes up to 100 Å, or larger (3). For all of these solids, the pores of the material are filled with the template when they are isolated, giving them no available void space. The inorganic frameworks themselves are typically quite thermally stable, however, so that the truly porous solid can be obtained by burning the template out.

Microporous materials have many important applications. The high charge densities and open structures found in zeolites make them good ion-exchange materials and heterogeneous catalysts (1, 2, 4, 5). Since zeolites are selective with respect to pore size they can function as molecular sieves and shape selective catalysts. The catalytic or ion-exchange sites in these materials are typically acid sites or metal ions of the inorganic framework.

A wealth of selective chemistry has been developed for organic compounds, but the nature of how zeolites are prepared makes it very difficult to combine the selectivity of organic catalysts with the porous and robust nature of the inorganic frameworks of zeolites. The organic groups used in synthesizing zeolites are burned out of the solid to give the porous material. In this paper, we describe a system that allows us to construct robust open frameworks composed of organic and inorganic components, capable of carrying out selective chemical transformations. The synthetic methodology is mild enough to allow active organic molecules to be incorporated into the walls of these porous solids. Herein we have focused on a porous solid with a cationic framework [i.e.,  $Zr_2(PO_4)(O_3PCH_2CH_2\text{-4,4'-bipyridinium-}CH_2CH_2PO_3)X_3 \cdot 3H_2O$  ( $X = \text{halide}$ ), this dialkyl-bipyridinium moiety will also be referred to as viologen]. Ion exchange of the free halide ions for anionic metal complexes (i.e.,  $MCl_4^{2-}$ ,  $M = Pt, Pd$ ), followed by reduction with hydrogen, gives materials with fine metal particles trapped in the pores of the material. The metal particles act as catalysts for the direct reduction of viologen by hydrogen. Reduced viologen is a potent reductant, capable of reducing both organic and inorganic substrates.

We have examined the porous viologen-containing materials described above as catalysts for the direct production

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of hydrogen peroxide from hydrogen and oxygen gases. Presently, hydrogen peroxide is commercially produced by the AO process (6), developed in the late 1940s and early 1950s (7). In this homogeneous process, the first step involves the hydrogenation of 2-alkyl-9,10-anthraquinone to the corresponding hydroquinone. Oxidation of the hydroquinone with oxygen yields hydrogen peroxide. Hydrogen peroxide is then extracted with water from the working solution. The aqueous peroxide solution is always contaminated with organic solvent and has to be purified, which is costly for a homogeneous process. For hydrogen peroxide to be used in many industrial applications all traces of organic solvent must be removed (6). For environmental reasons it would be beneficial to remove organic solvents from the process completely. For these reasons an efficient heterogeneous catalyst for producing hydrogen peroxide that would function in an all-aqueous system is highly desirable. Heterogeneous catalysts for the direct production of hydrogen peroxide from hydrogen and oxygen have been reported (8). These catalysts consist of group VIII metal particles on inert supports. While these materials show good activity, they require high pressures of hydrogen and oxygen to prepare useful concentrations of hydrogen peroxide. The system presented here is a heterogeneous catalyst that uses an organic catalyst (viologen) as the source of reducing potential to generate  $\text{H}_2\text{O}_2$  from  $\text{O}_2$ . The catalyst also reduces hydrogen peroxide to water in the presence of hydrogen, but at a much slower rate, leading to very efficient hydrogen peroxide production. Direct comparison of the catalyst reported here with a supported metal catalyst shows that our materials are significantly more active at low pressures.

## RESULTS AND DISCUSSION

Metal phosphate and phosphonate compounds have been examined by several groups as robust materials for the organization of organic molecules in the solid state (9). Compounds prepared with tetravalent metals are highly insoluble, requiring mineralizing agents for the growth of even microcrystalline materials. The most common formula for these materials is  $\text{M}(\text{O}_3\text{P-R})_2$  ( $\text{M}$  = tetravalent metal ion,  $\text{R}$  = OH, H alkyl, aryl), which tend to crystallize in layered structures. In these materials, the R groups project into the interlamellar space. Unlike most solid-state reactions, metal phosphates and phosphonates are made at low temperatures from aqueous solutions (9–11). This allows for well-ordered materials to be synthesized, well below the temperatures that would lead to decomposition of the organic group.

If a mixture of phosphoric and phosphonic acids is used during synthetic preparation, mixed metal phosphonates can be obtained (9, 11, 12). Bisphosphonic acids have been used in mixed phosphonates, i.e.,  $\text{Zr}(\text{O}_3\text{P-OH})_{2x}(\text{O}_3\text{P-R}'\text{-PO}_3)_{1-x}$  ( $x = 0-1$ ), and generally act as bridging or pillar-

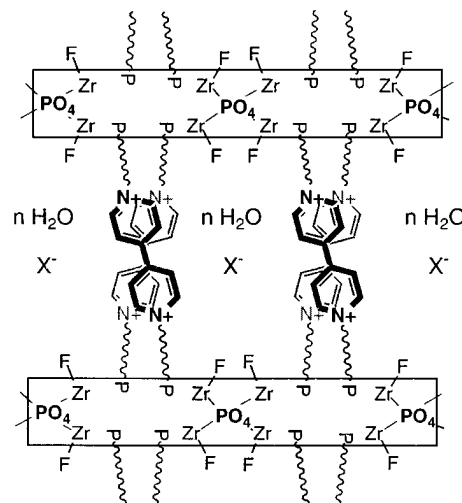


FIG. 1. Schematic representation of  $\text{Zr}_2(\text{PO}_4)_2\text{PVX}_3$ . Viologen groups shown in bold are in the foreground.

ing groups between adjacent inorganic layers. We have recently found that cationic pillaring groups can be used to prepare porous structures. The pillars in this compound consist of alkyl bisphosphonic acids with dicationic 4,4'-bipyridinium (viologen) groups incorporated into the alkyl chain, i.e.,  $\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2$  viologen  $\text{CH}_2\text{CH}_2\text{PO}_3\text{H}_2\text{X}_2$  ( $\text{X}$  = halide), abbreviated **PV**. The electrostatic repulsion of adjacent viologen groups prevents them from forming a dense segregated phase or collapsing (13).

We have recently determined the crystal structure of one of these porous materials (14). The compound has a formula unit of  $\text{Zr}(\text{PO}_4)_2\text{PVX}_3 \cdot 3\text{H}_2\text{O}$ . A schematic drawing of the structure is shown in Fig. 1, and a ball-and-stick representation viewed down the  $c$  axis is shown in Fig. 2. The water molecules and halides that fill the pores of the material have been removed in Fig. 2 for clarity. Under our synthetic conditions the halide ions of the material are principally fluoride, so the compound is referred to as a trifluoride, even though we have not measured the exact ratio of fluoride to the other halides present. The Zr atoms are octahedrally coordinated by two oxygen atoms from the phosphate groups, three oxygen atoms from the viologen phosphonate groups (in a facial geometry), and an F atom pointing into the organic layer. The viologen phosphonate molecules bridge the inorganic lamellae and form a criss-cross stack, which minimizes the electrostatic repulsions of adjacent viologen groups. The closest viologen–viologen contact across the pore (along  $b$ ) is approximately 8 Å, with a layer-to-layer distance of 13.5 Å giving rise to fairly large pores. The cavities are occupied by three water molecules and one halide ion per formula unit. An alternate way of listing the compound, which emphasizes the difference between the different types of halide in the structure, is  $[(\text{ZrF})_2(\text{PO}_4)_2\text{PV}]^+ \text{F}^- \cdot 3\text{H}_2\text{O}$ .

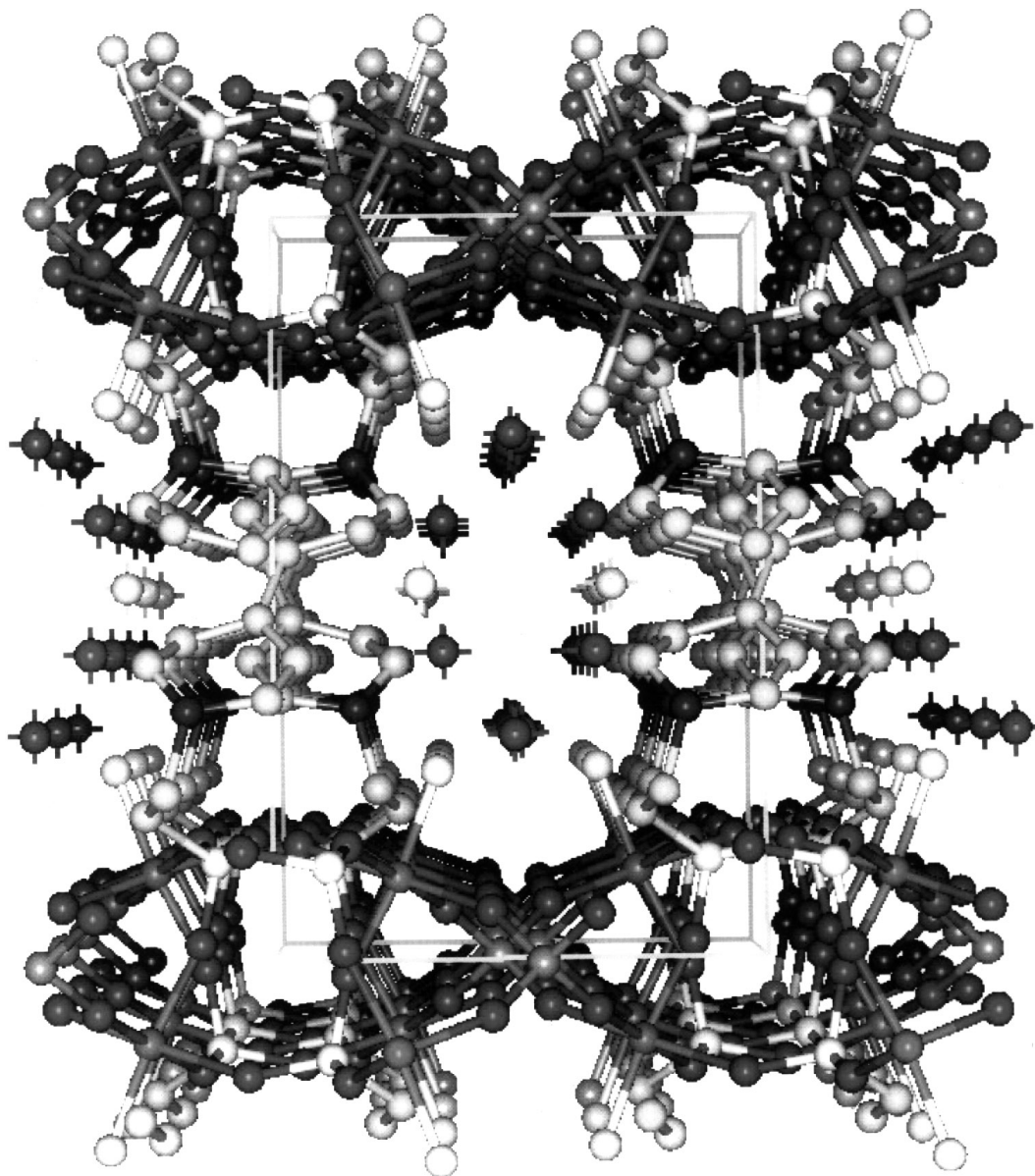
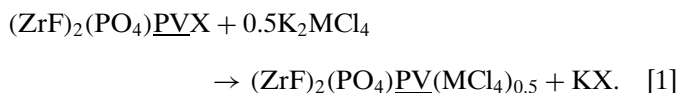


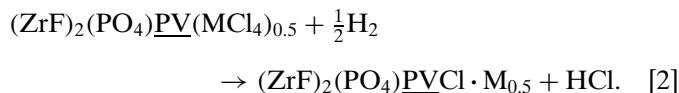
FIG. 2. Structure of  $Zr_2(PO_4)PVF_3$  viewed along the  $c$  axis (shown in perspective). The intrapore water molecules and halide atoms have been left out for clarity.

The double positive charge on the viologen groups in  $Zr_2(PO_4)PVX_3$  gives the compounds a high positive charge density, which is counterbalanced with halide ions (12, 13). The halide ions of these porous solids can be exchanged for a number of other anions, by treating the solid with an aqueous solution of the desired anion. In addition to other halides or pseudohalides, the chloride ions can be exchanged for anionic metal complexes, such as  $MX_4^{2-}$  ( $M = Pt, Pd; X = Cl, Br$ ), as shown in the equation



If a mixture of Pt and Pd salts is used, the Pt: Pd ratio found in the bulk solid is similar to that in the solution (as shown by ICP analysis of the dissolved solids and solutions). On ion exchange with Pt and Pd salts the materials change from white to brown-orange. The ion exchange of the metal species for the halide ions is not complete after a single exchange. Treatment of an exchanged solid with a fresh solution of the metal salt results in significantly higher levels of metal incorporation. The Zr: (Pt + Pd) ratio was typically 15: 1 for a sample that had only been ion exchanged once, compared with 4: 1 for theoretical complete exchange. Exchanging for 3 days with a fresh solution each day leads to a Zr: (Pt + Pd) ratio of 5: 1. If these exchanged solids are

treated with hydrogen gas, the metal salts are reduced to colloidal metal particles:



These reduced materials are abbreviated  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{M}$  ( $\text{M} = \text{Pt}$  or  $\text{Pd}$ ) for materials exchanged with only a single metal and  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt,Pd}$  for materials exchanged with both  $\text{PtCl}_4^{2-}$  and  $\text{PdCl}_4^{2-}$  simultaneously. SEM and TEM studies of the reduced solids do not show any sign of metal particles on the surfaces of the  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}}$  microcrystals of  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt}$  or  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt,Pd}$ , suggesting that the Pt and Pd metal is within the pores of the solid.

In addition to providing the necessary interlayer repulsion to give an open lattice, the viologen groups were chosen for their potential catalytic properties. Viologens have been studied extensively as electron acceptors in photochemical electron transfer systems (15). The reduced form of viologen is a potent reductant, capable of selectively reducing organic and inorganic substrates (16). We have found that the viologen groups of porous solids are readily photoreduced (12, 17). To extract the photochemically generated reducing equivalents from the system, colloidal platinum particles were incorporated into the materials (14, 18). The metal particles in these materials act as microelectrodes, with the electrochemical potential determined by the reduced viologen molecule (19).

If  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{M}$  ( $\text{M} = \text{Pt}$  or  $\text{Pd}$ ) or  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt,Pd}$  is treated with hydrogen gas the viologen groups of the solid are rapidly reduced and the solid takes on a blue or purple color. Exposure of this colored material to air bleaches the solid immediately. The product of this bleaching reaction is hydrogen peroxide. The rate of oxygen reduction by reduced viologen is very high ( $k = 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (20). If streams of hydrogen and oxygen gas are passed through an aqueous suspension of these porous catalysts at atmospheric pressure, hydrogen peroxide is observed within the first few minutes and reaches a steady-state concentration within a few hours (Table 1).

If the colloidal metal particles in the material are Pt, the steady-state concentration of  $\text{H}_2\text{O}_2$  is quite low ( $<5 \text{ mM}$ ). The likely reason for this is that platinum metal is an excellent catalyst for the reduction of hydrogen peroxide to water. Thus, the metal particles that are leading to formation of the reduced viologen may be reducing the peroxide in a destructive side reaction. It has recently been reported that mixed Pd/Pt colloidal particles on inert supports give respectable yields of hydrogen peroxide from hydrogen and oxygen gases (8). When an aqueous suspension of the supported Pd/Pt catalyst is treated with 2000 psi of hydrogen and oxygen, a 12.6% hydrogen peroxide solution is generated. When a sample of  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt,Pd}$  is treated with  $\text{H}_2$  and  $\text{O}_2$  gases, the level of hydrogen per-

TABLE 1  
Hydrogen Peroxide Production by  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt,Pd}$  Compounds

Pt <sup>a</sup> (mol%)	After 1 h		[H <sub>2</sub> O <sub>2</sub> ] <sub>final</sub> (mM)
	[H <sub>2</sub> O <sub>2</sub> ] (mM)	Turnover <sup>b</sup>	
No Pt or Pd	0	0	0
0	22	19	80
0.2	16	13	210
7	51	42	144
9	10	8	73
44	10	8	29
100	0	0	<5
2	—	—	139 <sup>c</sup>
2	—	—	335 <sup>d</sup>

<sup>a</sup> 100 × Pt/(Pt + Pd).

<sup>b</sup> Turnover = 2 × moles of H<sub>2</sub>O<sub>2</sub>/moles of viologen.

<sup>c</sup> Reaction carried out at 15 psi of H<sub>2</sub>, 100 psi of O<sub>2</sub>, and 60 psi of N<sub>2</sub> in a thick-walled glass vessel as described in the text.

<sup>d</sup> The reaction vessel was vented and charged with a fresh H<sub>2</sub>/O<sub>2</sub> mixture three times.

oxide produced increases dramatically relative to the materials with only platinum. Table 1 shows typical results for the catalytic production of hydrogen peroxide from these materials. In all of these experiments, the rate of hydrogen peroxide formation is high initially and gradually drops off as a steady-state concentration is reached. At atmospheric pressure, the steady-state concentration is reached in 6–10 h. A mixture of platinum and palladium is essential for the most active catalyst. While  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pd}$  does catalyze the production of H<sub>2</sub>O<sub>2</sub>, the best peroxide production was obtained using a catalyst whose colloidal particles are less than 10 mol% Pt. Pt content higher than 15–20% led to a significant decrease in hydrogen peroxide concentration. For comparison to our catalyst, a sample of the silica-supported Pt/Pd catalyst with an optimal ratio of Pt : Pd as given in Ref. (8) (i.e., 32 wt% Pt) was treated with a H<sub>2</sub>/O<sub>2</sub> mixture at atmospheric pressure, in a manner identical to  $\text{Zr}_2(\text{PO}_4)\underline{\text{PV}} \cdot \text{Pt,Pd}$ , and gave a low steady-state concentration of H<sub>2</sub>O<sub>2</sub> (0.07 M). The fact that significantly less hydrogen peroxide is generated suggests that the peroxide formation is going on at the viologen groups and not at the colloid particles.

After approximately 20 h the catalyst begins to degrade, due to oxidation of the colloidal particles. ICP analysis of the used catalyst and peroxide solution indicate that the Pd partly dissolves, leading to a higher weight percentage of Pt in the solid. For example, chemical analysis of a spent catalyst showed an increase in Pt from 8 to 17 mol%. A sample richer in Pt will give lower steady-state values for the hydrogen peroxide since the metal colloid itself will act to reduce H<sub>2</sub>O<sub>2</sub> to water.

The concentration of  $O_2(g)$  in a saturated aqueous solution at atmospheric pressure (0.25 mM) (21) can be used as an upper limit to the oxygen concentration in our catalytic system. The concentration of hydrogen peroxide produced in our system is roughly 1000 times greater than that of the upper limit for the dissolved oxygen present in the system. This shows that the catalysts are very effective at selectively reducing oxygen to hydrogen peroxide. The amount of peroxide produced is limited by the concentration of oxygen gas in solution. If the flow rate of oxygen is reduced, the steady-state concentration of  $H_2O_2$  decreases. If the oxygen flow to the system is interrupted completely, the concentration of  $H_2O_2$  quickly drops to zero, as the catalysts are also respectable catalysts for the reduction of  $H_2O_2$  to water. The selectivity seen in formation of hydrogen peroxide is most likely due to the significant difference in the rates of reduction of oxygen and hydrogen peroxide by reduced viologen.

In addition to the experiments carried out at atmospheric pressure, the production of hydrogen peroxide was examined at pressures up to 175 psi. In these experiments, a slurry of the catalyst was loaded into a thick-walled glass tube and the tube charged with the  $H_2/O_2$  gas mixture. After 20–24 h the vessel was vented and the gas above the solution examined by gas chromatography. During the course of the reaction all of the hydrogen is consumed. From the volume of the glass vessel, the initial pressure of hydrogen, and the final concentration of  $H_2O_2$ , a 40% yield of  $H_2O_2$  (based on hydrogen) was determined. In this closed system the oxygen pressure was usually 100 psi, leading to higher concentrations of dissolved oxygen than in our previous experiments at atmospheric pressure. The increase in oxygen concentration leads to a large increase in the concentration of hydrogen peroxide produced, as expected.

## CONCLUSION

The design of efficient new heterogeneous catalysts requires the control of both the structure and chemical reactivity of the new material. By using porous metal phosphonates we are able to control both of these properties of the new material. The catalyst described herein is active toward reduction by hydrogen gas and subsequent electron transfer to oxygen to give hydrogen peroxide. At atmospheric pressure, between 0.15 and 0.2 M  $H_2O_2$  was produced, whereas 0.3–0.4 M  $H_2O_2$  was produced in the higher-pressure experiment. Increasing the pressure to 2000 psi, as is typically done for heterogeneous catalysts (8), should increase the concentration of  $H_2O_2$  dramatically.

We are currently examining the use of these porous reduced viologen materials for the reduction of organic substrates. By changing the size of the bisphosphonic acid pillars in these porous materials it may be possible to control the pore sizes on these materials, leading to shape or size selective reduction catalysts. The approach described here

for the construction of heterogeneous catalysts can be extended to many different organic compounds, which will lead to active solid catalysts for a wide range of different reactions.

## EXPERIMENTAL

*Synthesis of materials.* Porous zirconium phosphate/viologen phosphonate was prepared by the methods in Ref. (9). The ion-exchange reactions were accomplished by preparing a solution consisting of  $K_2PtCl_4$  and  $Na_2PdCl_4$  in 100 ml of water [e.g., 0.015 g of  $K_2PtCl_4$  and 0.217 g  $Na_2PdCl_4$ , corresponding to a Pt content (Pt/(Pt + Pd)) of 4.6%] and heating a suspension of 100 mg of the zirconium compound in this solution at 60°C for 12 h. The solution was protected from exposure to light, to limit the degradation of the salts to metal colloids in solution. Repeating the exchange with a fresh solution for an additional 12 h increases the Pt : Pd content of the sample. The solids change from white to orange on exchange. The Pt/Pd mole percentage in the isolated material varied from run to run and was determined for each solid sample by ICP analysis of the dissolved solids; these numbers are listed in Table 1 for several catalysts. While the mole fraction in the solid varied from run to run, the obtained material is typically close to the mole percentage of the reacting solution.

The reduction to metal colloids was achieved by bubbling  $H_2$  gas into a stirred suspension of the material for 1 h at 60°C. The suspension had a deep dark blue color caused by the reduction of viologen. Exposure to air leads to a gray solid.

*Catalytic production of hydrogen peroxide.* In a typical experiment, 25 mg of catalyst and 10 ml of 0.1 N HCl were added to a 50-ml canonical flask. The system was sealed with a rubber septum and hydrogen and oxygen gas was bubbled through the aqueous suspension. The oxygen stream was saturated with water vapor which slowed the solvent loss inside the reaction vessel. The peroxide concentration was measured by removing a known amount of solution, typically 0.200 ml, and diluting to 5 ml with a  $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ /sulfuric acid solution. This reagent reacts with hydrogen peroxide quantitatively to form an orange complex whose absorbance was measured at 410 nm. The hydrogen peroxide concentration was back-calculated from a Beer's law plot which was obtained by a redox titration of standardized  $KMnO_4$  with  $H_2O_2$  solutions.

In our experimental setup, control of the hydrogen and oxygen flow rates is very important in the production of hydrogen peroxide. When the oxygen flow rate is 75 ml/min and the hydrogen flow rate is varied from 5 to 75 ml/min, the best peroxide concentration is obtained when the  $H_2$  and  $O_2$  rates are both at 75 ml/min. Higher flow rates increased peroxide formation initially but the same steady state was reached.

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