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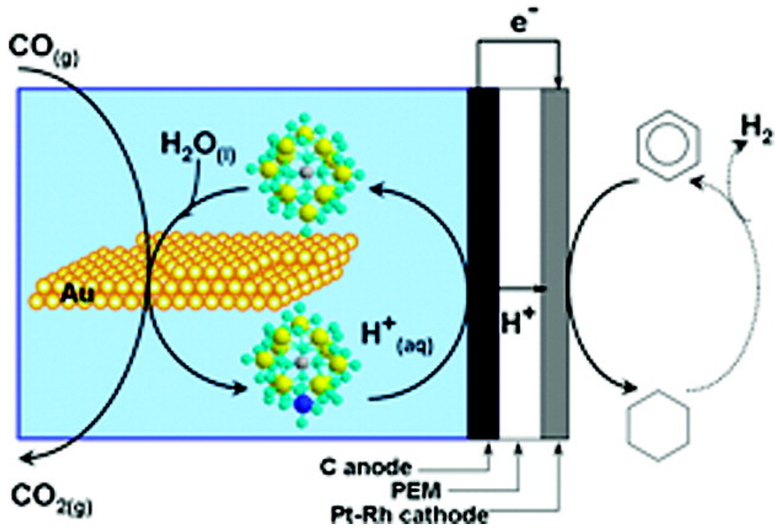

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Hydrogenation of Benzene Using Aqueous Solution of Polyoxometalates Reduced by CO over Gold Catalysts

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Water−gas shift (WGS), $CO + H_2O \rightarrow CO_2 + H_2$, is of importance for the production of fuel-cell-grade H_2 from catalytic reforming of hydrocarbons; however, this reaction has been regarded as a bottleneck in the production of H_2 because of low rates at temperatures near 500 K and the need to vaporize water.[1] Recently, we demonstrated that high rates of CO oxidation with liquid water could be achieved using aqueous polyoxometalate (POM) species, e.g. $H_3PMo_{12}O_{40}$, at room temperature over gold nanoparticles, thus potentially eliminating the difficult WGS step.[2] (Structures of POM species are represented in Figure 1 as an oxidized form having 12 MoO_6 octahedra with yellow Mo^{6+} cations and as a reduced form having one blue Mo^{5+} cation.) This POM-mediated process produces reduced POM species and protons that can be used to power a fuel cell via reoxidation of the reduced POM species.[2] This process using POM species and a gold catalyst can also serve as an efficient system for the preferential oxidation of CO in H_2-rich gas streams for H_2 fuel cells.[3]

In this communication, we show that H_2 gas can be produced by transfer of protons and electrons from an aqueous solution of POM species reduced by CO with water over gold nanoparticles, and we further demonstrate that this reduced solution can be used to hydrogenate unsaturated organic compounds (e.g., benzene to cyclohexane, thereby storing a higher weight density of H_2 in the organic phase than present in the aqueous POM solution) using an electrochemical cell consisting of a carbon anode, a proton-exchange membrane (PEM), and a Pt- or Rh-based cathode.

Figure 1 illustrates the overall scheme for our process using an aqueous POM solution as a reversible oxidizing agent for CO and as an energy carrier (i.e., electron shuttle). First, CO is oxidized to CO_2 by the POM species and liquid water on gold nanoparticles, thus producing two hydrogen atoms that are subsequently oxidized to protons and electrons (represented as eq 1 of Scheme 1). This heterolytic dissociation of water in the liquid phase takes place with a low energy barrier over metal surfaces.[4] The reduced POM is then reoxidized at the carbon anode by transferring electrons to the cathode through an external conductive circuit, and protons diffuse through a proton exchange membrane to the cathode. Gaseous H_2 is produced when inert gas is passed through the cathode chamber via reduction of protons by electrons. Alternatively, if an organic substrate such as benzene is passed through the cathode chamber, then benzene can be hydrogenated to cyclohexane (eq 2), in which case the liquid cyclohexane serves as a hydrogen storage and transport agent, because cyclohexane can be subsequently dehydrogenated to benzene and gaseous H_2 (eq 3) over a Pd membrane, as demonstrated elsewhere.[5] The overall scheme thus corresponds to hydrogen transfer from liquid water via protons and electrons to an organic H-carrier (benzene) upon hydrogenation, finally leading to production of gaseous H_2 by dehydrogenation of cylcohexane (i.e., the dashed arrows in the figure).

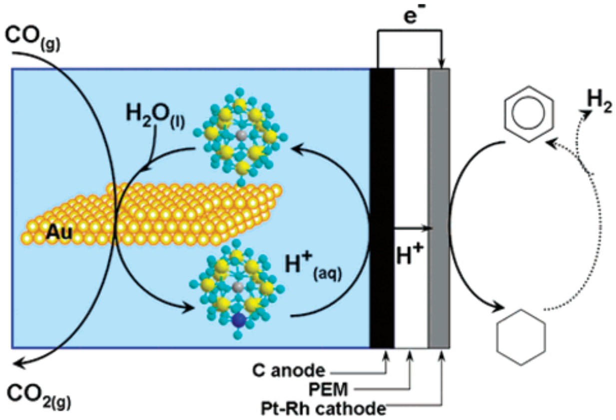

Figure 1. Representative scheme for hydrogen transfer from reduced polyoxometalate (produced from catalytic oxidation of CO with water over a gold catalyst) to benzene using an electrochemical cell consisting of a carbon anode, PEM, and a Pt-based cathode.

Scheme 1. Hydrogen-Transfer Scheme from Liquid Water to Benzene via CO Oxidation Assisted by Reversible Redox of Polyoxometalate Species

$$CO_{(g)} + H_2O_{(l)} + 2(POM)_{(aq)} \rightarrow CO_{2(g)} + 2H^+_{(aq)} + 2e^-(POM)_{(aq)} \quad (1)$$
$$6H^+_{(aq)} + 6e^-(POM)_{(aq)} + C_6H_6 \rightarrow 6(POM)_{(aq)} + C_6H_{12} \quad (2)$$
$$C_6H_{12} \rightarrow C_6H_6 + 3H_{2(g)} \quad (3)$$
$$CO_{(g)} + H_2O_{(l)} \rightarrow CO_{2(g)} + H_{2(g)} \quad \text{Overall}$$

The benzene−cyclohexane system is a potential candidate for H_2 storage in view of the ease of transport of the liquid fuel (e.g., cyclohexane) and the desirable hydrogenation−dehydrogenation properties of this system.[5,6] Moreover, it has been reported that cyclohexane can be used as a direct fuel to generate electrical energy using a PEM fuel cell, providing an alternative for direct methanol fuel cells with good resistance against fuel-crossover, resulting in moderate power densities up to 15 mW cm^{-2}.[7]

Figure 2 shows rates of H_2 evolution from electrolysis of water and from reoxidation of an aqueous solution of reduced POM species. The aqueous POM solution (0.2 M) had been previously reduced with CO and water over a gold catalyst. (See the Supporting Information for detailed procedures.) The extent of reduction of the POM by CO in this work was about five electrons per POM, as calculated by measuring the amount of CO_2 produced. Deionized water or reduced POM solution was delivered to an electrochemical cell consisting of a simple carbon anode, a PEM (Nafion 117, Aldrich), and a Pt- or Rh-based cathode. The anode was a simple carbon cloth (B-1/A, E-Tek) that had been heat-treated at 873 K for 0.5 h to improve its hydrophilic properties. The Pt and Rh cathodes were prepared by pasting 30 mg of the corresponding metal catalyst (Alfa Aesar) onto a carbon paper (B3, E-Tek) that had been wet-proofed by the supplier, i.e., strongly hydrophobic.

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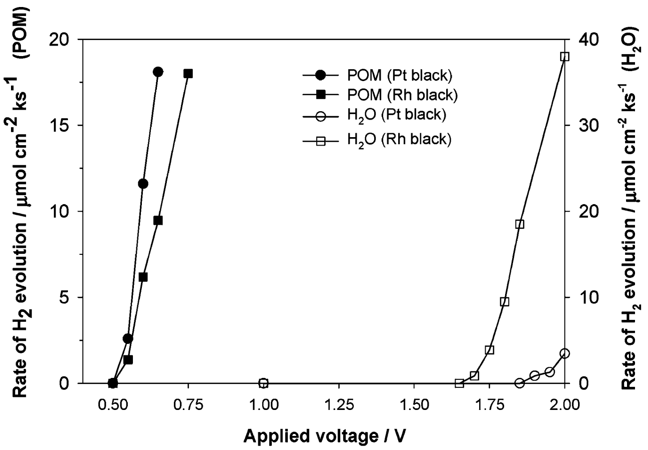

Figure 2. H_2 evolution from pure water or from reduced POM flowing over a carbon anode and N_2 flowing over cathodes with different Pt and Rh catalysts, as noted in parentheses.

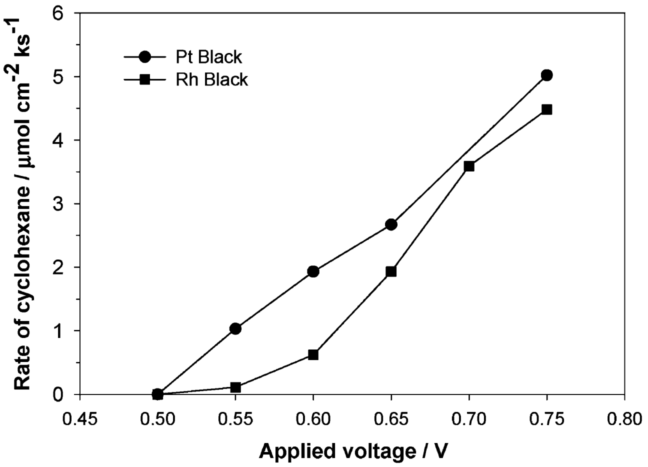

Figure 3. Rate of benzene hydrogenation from reduced POM at cathodes containing Pt and Rh catalysts.

The electrolysis of pure water takes place at applied voltages higher than 1.23 V, in agreement with other studies[6] indicating that voltages higher than 1.4−1.5 V are required to produce gaseous H_2 using an electrochemical cell consisting of a membrane−electrode assembly in which Pt−Rh was chemically deposited on both sides of the PEM membrane. When a simple carbon cloth was used at the anode side, voltages higher than 1.7 V were required because of the higher activation overpotential for water electrolysis in the absence of precious metal catalyst at the anode (Figure 2, open symbols). Importantly, gaseous H_2 is produced from the reduced POM solution (filled symbols) at voltages that are lower by at least 1.15 V compared to the case of pure water in our electrochemical cell, i.e., showing H_2 evolution at voltages as low as 0.55 V. This rate of H_2 evolution was measured at 5 min after the voltage was applied. The decrease in the voltage required to produce H_2 from the reduced POM solution as compared to water electrolysis can be related to the low reduction potentials for $H_3PMo_{12}O_{40}$, as measured in different electrolyte solutions.[8,9] According to the reported reduction potentials for $H_3PMo_{12}O_{40}$, and the fact that the extent of reduction was about five electrons per POM, the expected shift between water electrolysis and reoxidation of the POM should be within the range of 0.95−1.4 V, and the observed shift by 1.15 V in Figure 2 is within this predicted range.

Figure 3 demonstrates the feasibility of using an aqueous solution of reduced POM species for the electrochemical hydrogenation of benzene. The rate of cyclohexane production increases with applied voltage, similar to the curves in Figure 2 for the rate of hydrogen production. In fact, the rates of hydrogen production are not very sensitive to the presence of benzene in the cathode chamber, although the rates of hydrogen transfer are slightly enhanced at higher voltages in the presence of benzene (see Figure S1 in the Supporting Information). A fraction of the hydrogenation of benzene appears to take place via a non-Faradaic reaction (i.e., catalytic reaction with H_2), since approximately 40−80% of the rates for benzene hydrogenation shown in Figure 3 were achieved by flowing gaseous H_2 through the cathode chamber at zero applied voltage (see Figures S2 and S3 in the Supporting Information). This result suggests that an improved electrocatalyst for the cathode is required to achieve selective hydrogenation of benzene compared to H_2 generation. We have not observed any intermediates such as cyclohexadiene or cyclohexene in the gas phase, because these intermediates are not likely to desorb from the metal surface. First-principle calculations also predict that cyclohexene and cyclohexadiene are not formed in the dominant reaction path for benzene hydrogenation.[10]

The above demonstrations show that at applied voltages near 0.55 V, gas-phase H_2 can be produced or benzene can be hydrogenated electrochemically to cyclohexane from aqueous solutions of reduced POM species by electrons and protons present in liquid water, which are produced during CO oxidation by water and POM species over gold catalysts. The hydrogenation of benzene is a promising model system as a hydrogen-storage agent and hydrogen carrier because the hydrogenated product, cyclohexane, contains a high content of hydrogen (7.1 wt % H_2). Liquid cyclohexane is easy to transport, and H_2 can be readily extracted at the location where it is to be used.[5] The storage density of this system corresponds to 54.9 g of H_2 per liter of cyclohexane. Further study is needed to improve the electrode and membrane assemblies to alleviate over-potentials by facilitating mass transport and minimizing the use of such expensive metals as Pt and Rh.

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Supporting Information Available: Experimental details for procedures and supplementary results are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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