Heterogeneous Catalysis

Preferential Oxidation of CO in H_2 by Aqueous Polyoxometalates over Metal Catalysts**

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Production of H_2 for fuel cells is usually accomplished by a multistep process, which starts with catalytic reforming of hydrocarbons[1] or oxygenated hydrocarbons over metal catalysts[2,3] to produce a mixture of H_2, CO, and CO_2. These reformate gases are subsequently treated by several steps, such as water–gas shift (WGS) ($CO + H_2O \rightarrow CO_2 + H_2$)[4,5] and preferential oxidation of CO in the H_2-rich gas stream (PROX; $CO + 1/2\,O_2 \rightarrow CO_2$),[6,7] for applications involving proton-exchange membrane (PEM) fuel cells, this oxidation of CO is necessary owing to the strong poisoning effects of CO on Pt-based anodes.[8] While these methods for removing CO from H_2 gas stream are well established, they suffer from several limitations. For example, the WGS reaction is slow at the low temperatures (e.g., 500 K) required to achieve favorable thermodynamics for this reaction,[9] and PROX requires the injection of O_2 (or air) into the H_2 gas stream and consumes a fraction of the H_2 as well. Moreover, these processes for CO conversion often involve the use of platinum or platinum-alloy catalysts, which are expensive and compete with fuel-cell electrodes for the limited supply of this precious metal, compared with the abundant holdings of gold in the world.[10]

Recently, we reported the discovery of a room-temperature process for production of electrical energy using a fuel cell containing a carbon anode and operating with an aqueous solution of a polyoxometalate (POM) compound that had been reduced with pure CO over gold-nanotube catalysts.[11] This process for the oxidation and utilization of CO involves the reaction of CO and liquid water with a reducible POM, such as $[H_3PMo_{12}O_{40}]$, which serves as an oxidizing agent for reaction of CO with liquid water and as an energy-storage agent for electrons; the process takes advantage of the high catalytic activities of gold for CO oxidation,[12–14] especially in the presence of liquid water, as shown experimentally using gold-nanotube membrane catalysts[15] and as predicted by density functional theory calculations.[16,17] A representative

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stoichiometric reaction for this process is shown in Equation (1).

$$\mathrm{CO}_{(g)} + \mathrm{H_2O}_{(l)} + [\mathrm{PMo_{12}O_{40}}]^{3-}_{(aq)} \rightarrow \mathrm{CO}_{2(g)} + 2\,\mathrm{H}^{+}_{(aq)} + [\mathrm{PMo_{12}O_{40}}]^{5-}_{(aq)} \quad (1)$$

The aqueous solution of protons and reduced POM formed in this reaction can be delivered to a PEM fuel cell to generate electrical energy by using a carbon anode, thereby regenerating the POM in its initial oxidized state.[11] The POM species thus functions as a redox shuttle, thereby eliminating the need to convert CO with H_2O into gaseous H_2 and CO_2 for the production of electrical energy.

Herein, we demonstrate that this new process for CO oxidation using aqueous POM solutions can be carried out at high rates at room temperature over various metal catalysts, such as nanoparticles of Au, Pt, Pd, and Ir supported on carbon. Importantly, we show that catalysts containing Au nanoparticles are unique because they selectively and rapidly catalyze the oxidation of CO, in H_2-rich gas mixtures containing CO concentrations from 0.1 to 10%, using a reversible POM oxidant, in contrast to the irreversible O_2 oxidant that is employed in the conventional PROX process. Accordingly, our room-temperature process using aqueous POM solutions can be employed effectively for PROX applications without consuming significant amounts of H_2, which is of particular importance in the production and purification of H_2 for the PEM fuel-cell applications.

Rates of CO oxidation by aqueous POM at 298 K are presented in Figure 1 for different supported metal catalysts. All catalysts tested herein showed a monotonic increase of turnover frequency (TOF, s^{-1}) with respect to CO pressure from 3.4 to 15.8 bar, the TOF in this study is defined as the number of CO_2 molecules produced per second normalized by the number of surface metal sites (see caption of Figure 1). All reaction kinetics measurements were made repeatedly, under conditions where the rates were not limited by mass-transport effects, by working at initial conversions of POM lower than 20% (i.e., less than 1 electron transferred per POM) and by decreasing the amount of catalyst and the metal loading until the measured rate per gram of catalyst became independent of the amount of catalyst and the metal loading (i.e., 1 wt%). The values of TOF measured at 3.4 and 15.8 bar of CO pressure are compared over the different metals in Figure 1, showing that the TOF for oxidation of pure CO decreases in the order $Pd > Au > Pt > Ir > Rh > Ru$ at the higher pressure of CO (15.8 bar), with a negligible rate for Ag/C catalyst. The Au/C catalyst showed the highest TOF compared to the other metals at the lower CO pressure of 3.4 bar.

High catalytic activity for oxidation of CO by aqueous POM solutions may be related to low binding energy for the adsorption of OH groups on the metal surface (as given in Figure 1 (black bars) by the energy change for the dissociative adsorption of water to give adsorbed OH species and gaseous H_2), combined with sufficiently high binding energies for the adsorption of CO and H-atoms (as given in Figure 1 (light and dark gray bars) by the energy changes for the molecular and dissociative adsorption of CO and H_2, respectively).[18,19] A low value (that is, a positive energy change) of the binding energy for OH species is desirable to ensure that the surface of the metal does not become oxidized and thereby poisoned by the aqueous POM solution. Thus, metals such as Au, Pd, and Pt display high activities because they bind OH species sufficient weakly. A sufficiently high binding energy (that is, a negative energy change) for CO and H-atoms is required for these species to interact with the metal surface during the steps that eventually lead to the formation of protons and electrons. Thus, Ag shows very low catalytic activity because of the very weak interactions of adsorbed CO and H atoms with this metal. Finally, very high (negative) binding energies of CO on the metal surface may be undesirable, since such high values could lead to poisoning of the surface by strongly adsorbed CO at room temperature. Thus, the weaker binding of CO on Au compared to Pt may explain the higher catalytic activity of Au.

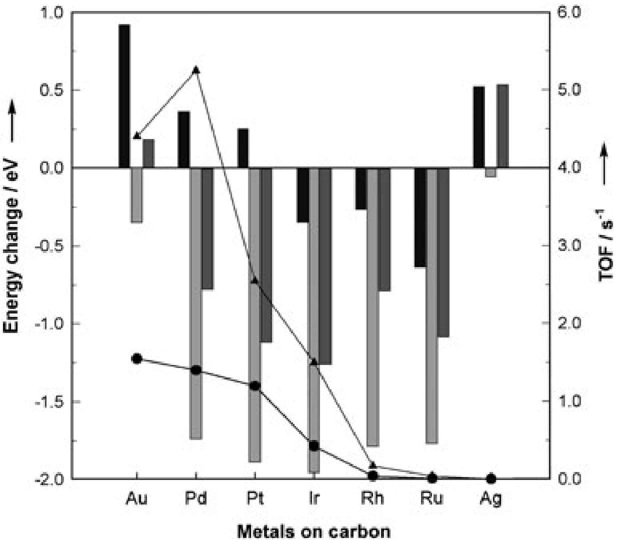

Figure 1. Rate of CO oxidation by aqueous $[H_3PMo_{12}O_{40}]$ (0.05 M) over carbon-supported metal catalysts, (●) TOF at 3.4 bar, (▲) TOF at 15.8 bar, and associated energy changes: (black bar) energy change for dissociative adsorption of water ($H_2O \rightarrow OH_{ads} + 0.5\,H_2$), (light gray bar) energy change for adsorption of CO, (dark gray bar) energy change for dissociative adsorption of H_2 ($H_2 \rightarrow 2\,H_{ads}$). Values for energy changes were determined by DFT calculations for stepped surfaces.[19] To determine the TOF value, the number of surface sites for Au/C was estimated from the TEM-determined metal particle size, for Pd/C, Pt/C, Ir/C, Rh/C, and Ru/C the number of surface sites was measured by CO adsorption at 298 K, and for Ag/C the number of surface sites was determined by O_2 adsorption at 423 K as is established elsewhere.[22] The metal dispersion (the number of surface metal atoms normalized by the total number of metal atoms) is 0.12 for Au/C, 0.39 for Pt/C, 0.23 for Pd/C, 0.13 for Ir/C, 0.18 for Rh/C, 0.55 for Ru/C, and 0.09 for Ag/C.

The metal loadings of the supported Au, Pd, Pt, and Ir catalysts were determined by inductively coupled plasma (ICP) analysis before and after their use for CO oxidation in aqueous POM solutions. The gold loading of the Au/C catalyst remained unchanged after exposure to reaction conditions, and dissolved gold species were not observed in the aqueous solution within the detection limit of the ICP analysis (≈1 ppm). Moreover transmission electron microscopy (TEM) measurements did not show any changes in average metal particle sizes upon exposure of supported gold catalysts to reaction conditions. We observed 10–20 % loss of the initial catalytic activity after first use, but stable activity was maintained, at levels of at least 50 % of the initial activity, after exposure of the catalyst to 0.05 M POM solution for 3 months. In contrast, Pd was leached from Pd/C into the aqueous solution under the reaction conditions, which led to dissolved species, such as Pd^{2+}, that might serve as a homogeneous catalyst.[20] Slow leaching of metal may take place upon exposure of carbon-supported Pt and Ir catalysts to reaction conditions, ICP analyses detected 10–20 ppm of Pt and 5 ppm of Ir species in 0.05 M POM solutions contacted for 24 h with the Pt/C and Ir/C catalysts, respectively.

Rates of CO versus H_2 oxidation by aqueous POM solution were measured on Au/C, Pt/C, Pd/C, and Ir/C catalysts using pure CO and pure H_2 gases (Figure 2 A), as well as gas mixtures containing 10 % CO in H_2 (Figure 2B) and 1 % CO in H_2 (Figure 2C). The rate of CO oxidation over Au/C was at least 10-times faster than the rate of H_2 oxidation when both gases were passed separately, whereas Pt/C showed a much higher rate of H_2 oxidation than CO oxidation. For a CO:H_2 gas mixture containing 10 % CO (Figure 2B), the rate of CO oxidation was approximately 0.8 s^{-1} on Au/C, and the rate of H_2 oxidation was negligible. The other catalysts also showed an inhibition of the rate of H_2 oxidation by CO when 10 % CO in H_2 was used compared to using pure H_2. When the concentration of CO was decreased to 1 % CO in H_2 (Figure 2C), the Au catalyst maintained its effectiveness for PROX, showing a value for the rate ratio (defined as TOF(CO)/TOF(H_2)) of about 9. In contrast, the other catalysts showed low ratios for the rate of CO versus H_2 oxidation under these conditions.

The rate ratio of 9 for the Au catalyst using the 1 % CO in H_2 gas mixture corresponds to a first-order rate constant of CO oxidation that is 900-times higher than the rate constant for H_2 oxidation at 14.8 bar, assuming that the rates are proportional to the respective reactant pressures. These results indicate that our process for CO oxidation using aqueous POM solutions with gold catalysts can be used to remove CO efficiently from H_2 gas streams even at room temperature without significant consumption of H_2. Indeed, for a lower CO concentration of 0.1 % CO in H_2, the ratio of the rate of CO versus H_2 oxidation was 0.10–0.15 at total pressures of the gas mixture from 14.8 to 49.3 bar, corresponding to a first-order rate constant (see Figure 3B) that is still at least 100 times faster for CO than for H_2 oxidation. The TOF for CO oxidation is not affected by the presence of H_2, and the rate is first order with respect to CO pressure, that is, all the TOF for CO data in Figure 3 A fall on the same line regardless of whether measurements were made using pure CO or using gas mixtures of CO in H_2. In contrast, the TOF for H_2 oxidation is suppressed by the presence of CO, showing a significant decrease of the rate from the case using pure H_2 to when using 99.9 % H_2 (with 0.1 % CO), and the TOF decreases further when using 99 % H_2 (with 1 % CO; Figure 3 A). Note, when the gas mixture containing 90 % H_2 with 10 % CO is employed, there is no measurable rate of H_2 oxidation over the gold catalyst (see Figure 2B).

It is clear from Figure 2 and Figure 3 that Au/C catalyzes the selective oxidation of CO (compared to H_2) by aqueous POM solutions, and the presence of CO inhibits the oxidation of H_2. In contrast, the rate of H_2 oxidation over Pt/C is faster than the rate of CO oxidation, and although the presence of CO inhibits the oxidation of H_2, metals such as Pt, Pd, and Ir are not effective catalysts for selective oxidation of CO, although these metals show high activity for the oxidation of CO without H_2.

Figure 4 shows a possible reaction scheme for CO oxidation by an oxidized POM species in aqueous condition on a gold catalyst (the structure of the POM anion is a simplified representation of the Keggin structure[21] in which one PO_4 tetrahedron is surrounded by 12 MoO_6 octahedra). Carbon monoxide and water adsorb, albeit weakly, on the gold surface. In contrast, dissociative adsorption of H_2 on gold is energetically unfavorable compared to the adsorption of CO and is accompanied by a high energy barrier.[18] The results in Figure 2 and Figure 3 indicate that this more favorable adsorption of CO inhibits the activation of H_2 on

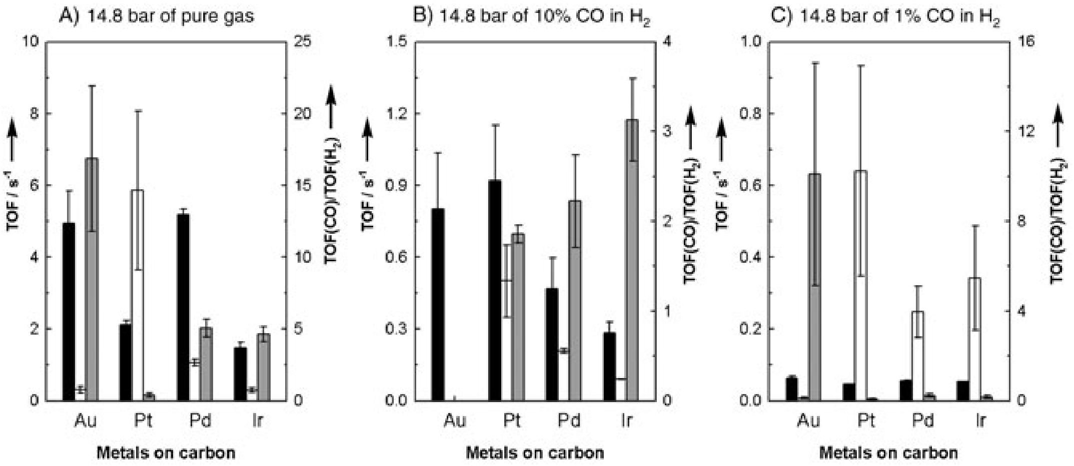

Figure 2. Rates of CO and H_2 oxidation with aqueous [$H_3PMo_{12}O_{40}$] (0.05 M) over carbon-supported metal catalysts in different gas mixtures. (Black bar) CO oxidation, (white bar) H_2 oxidation, (gray bar) ratio of rates for CO versus H_2 oxidation (TOF(CO)/TOF(H_2)).

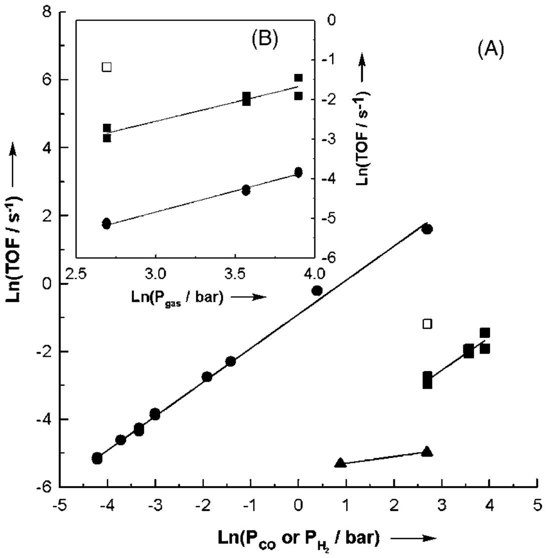

Figure 3. Rates of CO and H_2 oxidation with aqueous $[H_3PMo_{12}O_{40}]$ (0.05 M) over 0.8% Au/C. A) (●) TOF for CO with respect to CO pressure in measurements using pure CO and gas mixtures of CO (10%, 1%, and 0.1%) in H_2, (□) TOF for H_2 using pure H_2, (■) TOF for H_2 with respect to pressure of H_2 in 99.9% H_2 with 0.1% CO and (▲) in 99% H_2 with 1% CO. B) (●) TOF for CO and (■) TOF for H_2 with respect to the total pressure of 0.1% CO:H_2 mixture, (□) TOF of H_2 using pure H_2.

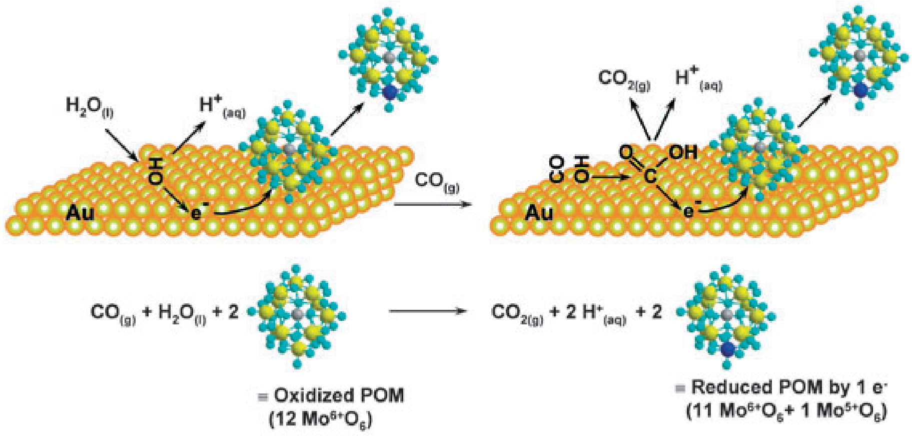

Figure 4. Reaction schematic for oxidation of CO using aqueous polyoxometalate ($[H_3PMo_{12}O_{40}]$) solutions over gold catalysts. The POM reduced by 1 electron is represented by showing 1 Mo atom in the distinct blue color of the reduced compound, the other Mo centers are yellow, O turquoise, P gray. See text for details.

the gold surface for reaction with the POM species when the CO is present in concentrations higher than about 0.1%. The adsorbed water molecule dissociates heterolytically in the presence of liquid water,[16,17] forming a hydroxy group adsorbed on the metal surface and hydrogen atom that is subsequently oxidized by transfer of an electron into the metal and formation of a proton stabilized in liquid water. The electron is then transported through the metal to the reducible POM species present on the metal. The adsorbed hydroxy species interacts with adsorbed CO to form an intermediate surface species, such as adsorbed COOH, which dissociates eventually to produce CO_2, which results in the formation of a proton in liquid water and transfer of an electron to the gold surface, this electron is subsequently transported to a reducible POM species.

Experimental Section

In a typical experiment, a batch reactor loaded with 20 cm^3 of 0.05 M POM ($[H_3PMo_{12}O_{40}]$, purchased from Aldrich) solution and catalyst was purged three times with CO and then filled with CO at specific pressures. The reactor was a stainless steel vessel (approximately 350 cm^3 volume), in which the POM solution and catalyst were placed in a glass liner with a magnetic stirrer. For the oxidation of CO in H_2, the reactor was purged three times with N_2 and then filled with a CO:H_2 mixture. Gas-phase products were analyzed at specific times by releasing pressure to an online gas chromatograph equipped with a thermal conductivity detector. The rate of H_2 oxidation was measured by monitoring the color change of the POM solution using a UV/Vis spectrometer operating at 500 nm.

CO and mixtures of CO:H_2 were supplied from AGA. Carbon-supported gold catalyst (Au/C) was supplied from the World Gold Council (Type D, Lot No. 4D), which was characterized by the supplier as 0.8 wt% Au with an average Au particle diameter of 10.5 nm. Catalysts consisting of 1 wt% Pt/C and 1 wt% Pd/C were purchased from Aldrich and 1 wt% Ir/C was purchased from Alfa. A catalyst containing 1 wt% Rh on carbon (Vulcan carbon) was prepared using a solution reduction method of $RhCl_3$ by $NaBH_4$, followed by rinsing with deionized water and drying in a vacuum desiccator. Preparations of 1 wt% Ru and Ag on carbon were carried out by impregnation of $RuCl_3$ and $AgNO_3$, followed by reduction at 623 K with flowing H_2. All catalysts were characterized by ICP to determine the actual metal loadings on the catalysts.

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