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Direct synthesis of H_2O_2 on Pd and Au_xPd_1 clusters: Understanding the effects of alloying Pd with Au

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ABSTRACT

Direct synthesis ($H_2 + O_2 \rightarrow H_2O_2$) could produce H_2O_2 (an environmentally benign oxidant) more cost-effectively and sustainably than anthraquinone oxidation, enabling broader use of H_2O_2 for industrial oxidations. We examine direct synthesis on Au_xPd_1 clusters to better understand the reasons for the high H_2O_2 selectivities of these materials. Steady-state H_2O_2 and H_2O formation rates were measured as functions of reactant pressure, temperature, and the protic or aprotic nature of the solvent. The analysis of these measurements indicates that H_2O_2 forms by consecutive proton-electron transfer steps on Au_xPd bimetallic catalysts. Among similarly sized Pd and Au_xPd_1 catalysts, increases in the Au:Pd ratio lead to simultaneous but unequal increases in the activation enthalpies ($\Delta H^{\ddagger}$) for both H_2O_2 and H_2O formation, which must result from significant electronic changes to Pd by Au. Detailed comparisons of these changes in $\Delta H^{\ddagger}$ for H_2O_2 and H_2O production to H_2O_2 selectivities provide compelling evidence that these electronic effects are primarily responsible for the high H_2O_2 selectivities commonly reported on AuPd bimetallic catalysts. Additionally, these results lack any clear trends that suggest ensemble effects contribute to the increased preference to form H_2O_2 on AuPd bimetallics within the ranges of compositions typically reported. These findings provide useful information on the significance of electronic effects in these Au_xPd_1 clusters and may guide the design of increasingly selective bimetallic catalysts.

1. Introduction

The direct synthesis of hydrogen peroxide ($H_2 + O_2 \rightarrow H_2O_2$) has the potential to replace the auto-oxidation (AO) of anthraquinones as the dominant method for industrial-scale H_2O_2 production, because direct synthesis avoids the extensive separation steps associated with AO [1,2]. Consequently, direct synthesis could reduce the economic burden of using H_2O_2 (a green oxidant since the primary byproduct is H_2O) for industrial oxidations over less expensive, yet potentially hazardous oxidants such as Cl_2. The direct synthesis reaction could also be used to synthesize H_2O_2 in the same reactor in which it would be used as an oxidant, which would reduce the number of concentration and purification steps typically involved in industrial H_2O_2 formation. The value of coupling H_2O_2 formation with an oxidation process within a single facility has been demonstrated by the success of the hydrogen peroxide – propylene oxide (HPPO) process [3]. However, direct synthesis is currently not used at the industrial-scale primarily due to poor H_2O_2 selectivity over the thermodynamically favored combustion of H_2 to H_2O [2,4,5]. The potential benefits of using direct synthesis over AO are obvious, as such, research efforts have focused on developing deeper understanding of the mechanism of this reaction and the underlying reasons why the addition of specific promoter and the formation of alloys improve H_2O_2 formation rates and selectivities [4–11].

There is significant interest in developing Pd-based bimetallic clusters as alternatives to the use of harmful additives for improving H_2O_2 selectivity. Numerous reaction variables are reported to impact H_2O_2 selectivity (e.g., halide coadsorbates [12–14], solvent identity [11,15], catalyst composition [4,16]), but the reasons for these changes are less than clear. As one example, AuPd nanoparticles supported on carbon provide H_2O_2 selectivities as high as 98%, which are significantly greater than the ~40% H_2O_2 selectivity seen for monometallic Pd under similar conditions [8]. The fundamental manner by which the addition of Au affects this reaction is currently under debate. Density functional theory (DFT) calculations, combined with Bader charge analysis, suggest that increasing the number of adjacent Au atoms to Pd, broadens the density of states near the Fermi level [17], which decreases the amount of e^- back donation into the π^* orbital of the O—O bond in chemisorbed hydroperoxy (OOH^{**}, where ** represents adsorbed species in an η^2 configuration) [9,18]. These changes likely increase barriers for O—O bond rupture and subsequent H_2O formation

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and perhaps also those for H_2O_2 formation (i.e., electronic effects) [5]. On the other hand infrared spectroscopy of CO and kinetic measurements show that adding Au to Pd clusters reduces the prevalence of groups of multiple, contiguous Pd atoms on the catalyst surface [19–21], which in turn changes the distribution of active sites (i.e., ensemble effects) among those that preferentially form H_2O_2 (e.g., monomers of Pd) and those that largely produce H_2O (e.g., groupings of multiple Pd atoms) [17]. Either ensemble or electronic effects may cause increasing surface molar ratios of Au to Pd to yield greater H_2O_2 selectivities, which is consistent with prior batch reactor studies of silica-supported AuPd clusters [22]. Recently, we presented experimental evidence that suggested monometallic Pd clusters facilitate proton-electron transfer (PET) steps that reduce O_2 to form H_2O_2 during direct synthesis and which was inconsistent with the direct hydrogenation of O_2 with surface H-atoms [9]. These PET pathways were not considered in previous computational investigations of direct synthesis nor the corresponding predictions for how the addition of Au influences the elementary steps for H_2O_2 formation (assumed to involve direct hydrogenation of O_2) in comparison to those for H_2O formation (O—O bond dissociation) over AuPd bimetallic catalysts.

In this study, we show that Au_xPd_1 (where x is the bulk averaged atomic ratio of Au to Pd) cluster catalysts give greater selectivities for H_2O_2 than do monometallic Pd catalysts, because the presence of Au increases barriers for the kinetically relevant steps that form H_2O more than for those steps that create H_2O_2. These conclusions are supported by steady-state H_2O_2 and H_2O formation rates measured as functions of H_2 and O_2 pressure and temperature on both Pd and Au_xPd_1 catalysts. Formation rates of H_2O_2 and H_2O depend on H_2 and O_2 pressures in the same manner on Pd and Au_xPd_1, as shown by comparable fits of the same rate expressions to rates of H_2O_2 formation and H_2O formation by both primary and secondary pathways for Pd and Au_xPd_1 catalysts. Additionally, we found that H_2O_2 formation rates on both Pd and Au_xPd_1 were at least orders of magnitude higher in a protic solvent than in an aprotic solvent, in which H_2O_2 formation rates were immeasurable. These observations suggest that PET is a necessary step in the direct synthesis reaction and that H_2O_2 and H_2O likely form by the same mechanisms on Au_xPd_1 and Pd. Consequently, differences in H_2O_2 selectivity must arise from changes in the geometric or electronic structure of the active sites. Activation enthalpies ($\Delta H^‡$) for both H_2O_2 and H_2O formation increase with the Au composition of the clusters, and the difference between H_2O_2 and H_2O enthalpies on a given catalyst ($\Delta\Delta H^‡$) becomes larger with increasing ratio of Au to Pd (an increase in $\Delta\Delta H^‡$ values of 8 kJ mol^{-1} between Pd and Au_7Pd_1). Comparisons of $\Delta\Delta H^‡/T$ to measured ratios of the rates for H_2O_2 formation to those for H_2O formation for each catalyst demonstrate that electronic effects are primarily responsible for the greater H_2O_2 selectivities on catalysts with large Au:Pd ratios and result from changes in the grouping of Pd atoms on the surface. These findings show that the alloying of Au with Pd increases H_2O_2 selectivities primarily by modifying the electronic structure of the active sites and not by changing the ratios of unique sites that form either H_2O_2 or H_2O or by changing the mechanism of these reactions.

2. Methods and materials characterization

2.1. Synthesis of supported Au, Pd, and Au_xPd_1 catalysts

2.1.1. Synthesis of supported Au and Au_xPd_1 catalysts for steady-state rate measurements

Au and Au_xPd_1 clusters were formed in solution using a colloidal technique [23], followed by deposition of the colloidal solution onto silica and a subsequent reductive treatment. Briefly, the Au precursor ($HAuCl_4{\cdot}3H_2O$, Sigma-Aldrich, ≥99.9%) was added to deionized (DI) water (173–431 cm^3, 17.8 MΩ) to obtain a solution with a Au concentration of 0.44 mM, which was then heated to 333 K while stirring at 150 rpm. In a separate container, an aqueous reductant solution containing 1.7 mM trisodium citrate dihydrate ($Na_2C_6H_5O_7{\cdot}2H_2O$, Sigma-Aldrich, ≥99%), 0.37 mM tannic acid ($C_{76}H_{52}O_{46}$, Sigma-Aldrich, ≥99.99%), and 1.6 mM potassium carbonate (K_2CO_3, Sigma-Aldrich, ≥99.995%) was also heated to 333 K while stirring at 150 rpm. A quantity of the reductant solution (25% of the volume of the Au solution) was then added to the Au solution, and the mixture was stirred at 150 rpm for 2 min before being removed from the water bath and allowed to cool to ambient temperature over 12 h. The stable colloidal Au particles formed were separated from the supernatant and concentrated by centrifugation ($4.1{\cdot}10^4$ rpm, $2.0{\cdot}10^7$ m s^{-2}; Beckman, XL-70) for 1 h. The supernatant was decanted and the concentrated Au precipitate was re-dispersed by adding DI H_2O to achieve a volume of 18 cm^3.

Au_xPd_1 clusters were synthesized by adding 1 cm^3 of a solution of K_2PdCl_4 (19–76 mM, Sigma-Aldrich, 99.99%) to the Au colloid solution after centrifugation but prior to re-dispersion in DI H_2O. H_2 was then bubbled (>100 cm^3 min^{-1}) through the solution using a dispersion tube for 1 min to promote the electroless deposition of metallic Pd onto the Au colloids. All gases used were 99.999% pure and supplied by Airgas unless otherwise stated. For all compositions (Au, Au_1Pd_1, Au_7Pd_1, and $Au_{12}Pd_1$), the re-dispersed metal colloidal dispersion was dripped onto 15g of silica (Sigma-Aldrich, Davisil 646, 35–60 mesh) until the point of saturation. The wet silica was then allowed to dry at ambient conditions for 1 h. These solids were heated to 573 K at 5 K min^{-1} and then held at 573 K for 4 h in a flowing H_2/He mixture (40 kPa H_2, 61 kPa He, 100 cm^3 min^{-1}) with the intent to remove organic residues and fully reduce the Au and Au_xPd_1. Subsequently, the catalysts were cooled to ambient temperature and passivated by exposure to dilute O_2 (4 kPa O_2, 97 kPa He, 500 cm^3 min^{-1}) for 0.5 h.

2.1.2. Synthesis of supported Pd catalysts for steady-state rate measurements

Pure Pd catalysts were synthesized by strong electrostatic adsorption (SEA) of a Pd precursor onto silica, as previously described [9,24]. Briefly, SEA of Pd was performed by adding 15 g of silica to a basic aqueous solution (pH ≥ 11; 14.5 M NH_4OH, Macron, 28–30 wt%) followed by 17.4 mg of $Pd(NH_3)_4Cl_2$ (Sigma-Aldrich, ≥99.99%) for the 7 nm Pd and 18.8 mg of $Pd(NO_3)_2{\cdot}2H_2O$ (Sigma-Aldrich, ~40% Pd basis) for the 0.6 nm Pd. The resulting mixture was stirred by hand every 0.5 h over the course of 3 h to allow the $Pd(NH_3)_4^{2+}$ or Pd^{2+} species to electrostatically adsorb onto the negatively charged silica surface. The solids were recovered, rinsed with 500 cm^3 of DI water, dried by vacuum filtration, and subsequently reduced by heating to 573 K at 5 K min^{-1} and holding the sample at 573 K for 4 h (40 kPa H_2, 61 kPa He, 100 cm^3 min^{-1}). The mean diameter of the 7 nm Pd clusters was increased from ~1 nm to 7 nm (Table 1) by heating the reduced Pd-SiO_2 sample at 5 K min^{-1} in flowing dry air (100 cm^3 min^{-1}) to 973 K and holding for 4 h. This treatment was followed by a subsequent reductive treatment at 573 K for 4 h (40 kPa H_2, 61 kPa He, 100 cm^3 min^{-1}). All Pd, Au, and Au_xPd_1 catalysts were stored in glass vials with reflective coverings within evacuated desiccators to minimize exposure to ambient light and moisture.

2.1.3. Synthesis of supported Pd, Au, and Au_xPd_1 catalysts for infrared spectroscopy

Due to their low metal loadings, the samples that were implemented for kinetic studies gave poor signal to noise ratios in Fourier transform infrared (FTIR) spectroscopic measurements of