Solvent Molecules Act as Co-Catalysts and Co-Reactants during the Direct Synthesis of H_2O_2 in Aqueous Solutions

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Abstract: The direct synthesis of H_2O_2 proceeds on metal nanoparticles by pathways that utilize solvent molecules (e.g., H_2O, CH_3OH, and C_2H_5OH) as both co-catalysts and co-reactants, in the case of alcohols. Comparisons of rates in protic and aprotic solvents, isotopically-labelled solvents, and the simultaneous production of alcohol oxidation products suggest that proton-electron and proton-hydride transfer steps reduce O_2 to H_2O_2 at the solid-liquid interface. These results show that the choice of solvent used for this reaction influences H_2O_2 formation rates and selectivities by introducing new reaction mechanisms and not only by changing rates of mass transport, as often proposed.

Keywords: oxygen reduction, proton-electron transfer, catalytic transfer hydrogenation,

1. Introduction

Direct synthesis of H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) could enable on-site, and even *in situ*, H_2O_2 production, which motivates searches for highly selective catalysts and process conditions. H_2O_2 formation rates and selectivities depend sensitively on the addition of other transition metal atoms (e.g., Au, Zn, Sn) or the adsorption of halides to Pd nanoparticles. Moreover, the apparent kinetics for the formation of H_2O_2 and H_2O as well as the selectivities to H_2O_2 differ significantly between systems operating within alcohol (or aqueous alcohol solutions) solvents or within pure water. The reasons for these changes are not completely understood and are difficult to explain in the absence of a molecularly detailed mechanism for this deceptively complex reaction.

2. Experimental

Pd and Pd-alloy nanoparticles were synthesized by strong electrostatic adsorption or colloidal methods, and characterized by transmission electron microscopy, CO chemisorption, and X-ray diffraction. Steady-state H_2O_2 and H_2O formation rates and selectivities (at differential conversions) were measured at 268-323 K, 10-400 kPa H_2 and 10-400 kPa O_2, within aqueous and alcoholic solvents. Kinetic isotope effects on formation rates due to substituting the solvents (e.g., CH_3OH, CH_3OD, and CD_3OH) and the reactants (H_2, D_2) were determined in semi-batch reactors with online mass spectrometry. In all cases, H_2O_2 concentrations were determined by colorimetric titration using neocuproine-$CuSO_4$ or $TiOSO_4$ solutions and UV-vis absorption measurements. The Madon-Boudart criterion was used to show that rate measurements were not influenced by intrapellet mass transfer restrictions.

3. Results and discussion

H_2O_2 and H_2O formation rate measurements on Pd, PdAu, and PdZn nanoparticles increase with the pressure of H_2 and remain independent of O_2 pressures over a wide range of conditions in pure methanol and aqueous mixtures of methanol. These pressure dependencies indicate that reactive surface intermediates derived from H_2 and O_2 do not compete for active sites, which is not consistent with standard Langmuirian reaction mechanisms. In addition, initial H_2O_2 formation rates in protic solvents (water, methanol, or aqueous alcohol mixtures) are at least 10^3 larger than those measured in aprotic liquids such as propylene carbonate, dimethylsulfoxide, and acetonitrile. These observations indicate that chemisorbed oxygen (O_2*) species react in steps mediated by protic solvents, namely proton-electron transfer processes. Comparisons of rates between isotopically labelled methanol solvents show large primary kinetic isotope effects ($k_H/k_D > 7$) when the hydroxyl group of methanol is deuterated, whereas, a significant inverse kinetic isotope effect is evident when the methyl group is deuterated. Formaldehyde accumulates in the solvent phase at formation rates similar to those for H_2O_2. Post-reaction H-NMR of the methanol solvent reveals significant extent of H/D-atom scrambling between the reactant hydrogen and the solvent methanol, which demonstrates that the dehydrogenation of methanol is a rapid and reversible process in comparison to the H_2O_2 formation. These observations within methanol solvents are consistent only with a mechanism in which a proton-hydride pair transfers from chemisorbed methanol of adjacent O_2* species to form H_2O_2 and CH_2O. Alcohols therefore serve both as co-catalysts but also as co-reactants for kinetically relevant steps for H_2O_2 formation.

In parallel, O-O bonds within chemisorbed intermediates cleave to form H_2O with rates that are greater in water than in alcohol solvents. In pure water (i.e., without alcohol co-solvents), H_2O_2 forms via distinct steps that exhibit strong primary kinetic isotope effects when rates are compared between H_2 and D_2 reactants, which suggests that surface H*-atoms may be involved in these reactions. Strongly bound decomposition products of alcohol solvent (e.g., CO*, CH_2O*) appear to decrease H_2O formation rates by reducing the coverage of H*-atoms and the availability of unoccupied sites required for O-O bond dissociation transition states.

4. Conclusions

The direct synthesis of H_2O_2 proceeds at measurable rates only in protic solvents, because protic molecules provide low energy for proton-electron transfer processes that selectively reduce O_2 to H_2O_2. Moreover, this chemistry occurs with greater apparent rates and H_2O_2 selectivities in alcohol solvents than in water, because alcohols may directly transfer proton-hydride pairs to O_2* at higher rates while also producing strongly bound residues that competitively adsorb and reduce the coverage of unoccupied sites necessary for O-O bond dissociation and subsequent formation of H_2O. This mechanistic insight provides valuable guidance for the design of complete catalytic systems (i.e., both catalyst, solvent, and promoters) for the formation of H_2O_2.

References

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