Fundamental Insights into the Direct Synthesis of H₂O₂ on Pd Catalysts: Active Sites and Mechanism for Decomposition

Anthony Plaut,¹ Ana C. Alba-Rubio,¹ Eric Stangland,¹ James A. Dumesic,¹ and Manos Mavrikakis³*¹

¹Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706 (USA)
²Core Research and Development, The Dow Chemical Company, Midland, MI 48674 (USA)
*manos@engr.wisc.edu

Introduction

The direct synthesis of hydrogen peroxide (H₂O₂) from H₂ and O₂ is an appealing alternative to the existing industrial-scale anthraquinone process, because it has the potential to enable small-scale, integrated production of H₂O₂ [1]. One of the major challenges is identifying catalysts with high selectivity, as complete reduction of O₂ to H₂O₂ is more thermodynamically favorable than partial reduction of O₂ to H₂O₂. Importantly, catalysts must also be inactive for subsequent H₂O₂ decomposition through either its disproportionation or reduction by H₂. Pd-based catalysts are widely studied, and multiple strategies exist to quench decomposition activity including addition of halides/acid to the reaction medium or alloying Pd with other metals, especially Au [2]. In fact, Hutchings et al. demonstrated that by completely “shutting off” the decomposition activity on an Au-Pd catalyst through acid-pre-treatment of the carbon support, >95% selectivity to H₂O₂ was achieved [3]. Clearly, a fundamental understanding of the link between catalyst structure/composition and decomposition activity would greatly benefit the identification of superior catalysts for the direct synthesis of H₂O₂.

Herein we use a combination of density functional theory (DFT) calculations, reaction kinetics experiments, and microkinetic modeling to examine the decomposition of H₂O₂ through disproportionation on a supported Pd catalyst. We present a self-consistent mean-field microkinetic model that well-describes our experimental results, and establishes key insights into the dominant reaction mechanism and nature of the active site on Pd.

Materials and Methods

Periodic, self-consistent DFT calculations (PW91-GGA) were employed to calculate energies of reaction intermediates and activation barriers. Reaction kinetics experiments were conducted on a Pd/SiO₂ catalyst using a 50 mL Parr stirred batch reactor and H₂O as the solvent. Gas analysis for O₂ was performed by gas chromatography using a thermal conductivity detector. H₂O₂ was quantified in the liquid phase by titration with Ce(SO₄)₂. MATLAB was used for numerical integration and parameter fitting in the microkinetic model.

Results and Discussion

DFT calculations of reaction energies and activation barriers on Pd(111) indicate that the most favorable mechanism for H₂O₂ disproportionation proceeds through a series of H-transfer steps between oxygenated surface intermediates — initiated by scission of the O=O bond in an H₂O₂ molecule. This mechanism bypasses the need for recombination of atomic oxygen to close the catalytic cycle, which is a highly activated step on clean Pd(111) but is the only viable channel based on most standard mechanisms in the direct synthesis literature. The H-transfer steps proceed with low activation barriers (<0.20 eV), and are relatively structure insensitive based on calculations on the more open Pd(100) facet.

The proposed mechanism is substantiated through a mean-field microkinetic model, in which all potential elementary steps are considered. The experimental activation barrier, reaction orders with respect to O₂ and H₂O₂, and reaction rates on a supported Pd/SiO₂ catalyst are well-reproduced (Figure I) with minimal adjustments (<0.16 eV) to the DFT-derived parameters on Pd(111). The active Pd(111) surface is predicted to be covered with 0.2-0.4 monolayers of atomic oxygen over the range of reaction conditions studied.

![Figure 1](image)

**Figure 1.** Model-predictions on Pd(111) compared with experimental values on Pd/SiO₂ for H₂O₂ disproportionation: A) Turnover frequencies (TOF); B) Reaction orders with respect to H₂O₂ and O₂, and apparent activation barrier.

Significance

This work helps to identify the favorable mechanism for H₂O₂ decomposition on Pd (in the absence of H₂). It also provides fundamental insights into the nature of the active site responsible for H₂O₂ decomposition on Pd, which is critical to the identification of superior catalysts for direct H₂O₂ synthesis.

References