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Effects of hydrogen and propylene presence on decomposition of hydrogen peroxide over palladium catalysts

Tao Chen [a], Emila Kertalli [b], T. Alexander Nijhuis [b,c,*], Simon G. Podkolzin [a,*]

[a] Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, United States
[b] Laboratory of Chemical Reactor Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[c] SABIC, STC Geleen, PO Box 5151, 6130 PD Sittard, The Netherlands

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ABSTRACT

Reaction rates for H_2O_2 decomposition in a methanol solution were measured over Pd/SiO_2 catalysts in the presence of gas-phase N_2, H_2 and propylene. The H_2O_2 decomposition rates were higher in the presence of H_2 and lower in the presence of propylene compared to those under N_2, which acted as an inert gas. For interpretation of the experimental results, H_2O_2 decomposition reactions were evaluated with density functional theory calculations on four Pd(111) surfaces: (1) clean, (2) with pre-adsorbed hydrogen, (3) with molecularly pre-adsorbed propylene, and (4) with dissociatively pre-adsorbed propylene. The computational results show that the mechanism of H_2O_2 decomposition can proceed through O—O and O—H bond splitting reactions. The O—O bond splitting reactions are energetically preferable because they are exothermic and have lower activation energies. However, in the absence of H_2, the endothermic O—H bond splitting reactions with higher activation energies are required for the formation of molecular decomposition products: O_2 and H_2O. In contrast, in the presence of H_2, the O—H bond splitting reactions are no longer required, and the H_2O_2 decomposition can proceed only through the facile O—O bond splitting reaction in H_2O_2. The formed surface OH species can readily react with H species from dissociative H_2 adsorption, forming H_2O as the only product. This change in the reaction mechanism from the O—H bond splitting to the O—O bond splitting explains the experimentally observed higher H_2O_2 decomposition rates in the presence of H_2. The lower H_2O_2 decomposition rates in the presence of propylene are due to blocking of Pd surface sites by hydrocarbon species formed on propylene adsorption. Although propylene does not directly participate in H_2O_2 decomposition, it adsorbs on Pd more strongly than H_2O_2 and, therefore, forms surface spectator species that reduce the number of Pd active sites.

1. Introduction

Hydrogen peroxide, H_2O_2, is an important chemical that is widely used as an environmentally-friendly oxidizing agent in numerous household and industrial applications. For example, it is used in the production of disinfectants and laundry detergents as well as for wastewater treatment and for bleaching in the production of paper and textiles. Although the use of H_2O_2 is environmentally-friendly, its current production is based on a multistep anthraquinone process with consecutive hydrogenation and oxidation steps. Since this process requires at least two reactors, large recycle streams and multiple separation units, it is usually economical to operate only large-scale centralized plants. In addition, the concentration of H_2O_2 needs to be increased by distillation prior to its transportation from a production plant in order to reduce the transported volume and then diluted back to smaller concentrations prior to its local use. It is, therefore, desirable to develop an efficient simplified process for small-scale (less than 50,000 tons/year) local on-demand production of H_2O_2 directly from H_2 and O_2 [1–3].

One of the main challenges in the development of an economical process for the direct H_2O_2 synthesis is minimizing the side reactions that lead to wasteful water formation. The challenge is that Pd-based catalysts that are efficient in the direct H_2O_2 synthesis are also effective in catalyzing water formation from two side reactions: (1) directly from H_2 and O_2 and (2) from H_2O_2 decomposition

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* Corresponding authors at: SABIC, STC Geleen, PO Box 5151, 6130 PD Sittard, The Netherlands (T.A. Nijhuis). Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, New Jersey 07030, United States (S.G. Podkolzin).

E-mail addresses: Alexander.Nijhuis@SABIC.com (T.A. Nijhuis), Simon.Podkolzin@Stevens.edu (S.G. Podkolzin).

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in the presence of H_2 [1,4]. The overall result from both reactions is wasteful H_2 burning to water. In order to deconvolute the reaction mechanism of water formation over Pd catalysts, it is useful to analyze separately the H_2O_2 decomposition in the presence of H_2. This reaction is sometimes referred to as H_2O_2 reduction.

Previous studies of H_2O_2 decomposition compared reaction rates in the presence and absence of H_2 over 2 wt.% Pd/SiO_2 in a flow microreactor [5,6], 5 wt.% Pd/Al_2O_3 in a batch reactor [7,8] and 3 wt.% Pd supported on an activated carbon cloth in a batch reactor [9]. These studies showed that the presence of H_2 significantly increased the decomposition rates. This effect was observed with different solvents and stabilizing agents under various experimental conditions. The higher rates in the presence of H_2 were tentatively assigned to an increase in the fraction of metallic Pd atoms. This explanation was proposed based on the observed slow deactivation of a 5 wt.% Pd/C catalyst in consecutive H_2O_2 decomposition reaction runs in a batch reactor at 298 K [10]. The deactivation was attributed to gradual oxidation of the Pd surface by O_2 produced in H_2O_2 decomposition. The argument was that the presence of H_2 makes the Pd surface more metallic and, therefore, makes the catalyst more active. This explanation, however, is inconsistent with the results of H_2O_2 decomposition in the presence of flowing O_2 reported by the same group [7]. The H_2O_2 decomposition rates practically did not change over a 5 wt.% Pd/Al_2O_3 catalyst in a batch reactor at 300 K when the reaction was first conducted under flowing N_2 and then repeated under flowing O_2 [7]. Therefore, the presence of O_2 at the typical reaction conditions was not significant.

Furthermore, the reaction kinetics of H_2O_2 decomposition were reported to change over 2 wt.% Pd/SiO_2 at 303–323 K in the presence of H_2 [5,6]. The apparent reaction orders in H_2O_2 at different temperatures were only positive in the absence of H_2 [5]. In contrast, the apparent reaction orders in H_2O_2 changed from being positive, to zero and then to negative with increasing H_2O_2 concentrations in the presence of H_2 under the same reaction conditions [6]. These kinetic differences indicate that the reaction mechanism changes in the presence of H_2.

In this work, reaction rates of H_2O_2 decomposition were systematically compared over oxidized and reduced Pd/SiO_2 catalysts in the absence and presence of H_2. Effects of H_2 presence on elementary reaction steps in H_2O_2 decomposition on Pd were analyzed at the molecular level with density functional theory (DFT) calculations. Our results identify how the reaction mechanism changes in the presence of H_2, explaining the experimental observations.

Due to its environmental friendliness, H_2O_2 is a desirable oxidizing agent for selective oxidation of hydrocarbons in the chemical industry. For example, it is advantageous to use H_2O_2 for selective oxidation of propylene to propylene oxide. Propylene oxide is used in the production of polyurethane plastics and multiple other large-volume commodity chemicals. The current production of propylene oxide is mostly based on either the multistep chlorohydrin process with salty waste streams and chlorinated by-products or another multistep process with an aromatic hydrocarbon by-product [11]. In order to improve the efficiency of propylene oxide production, The Dow Chemical Company and BASF have recently commercialized a new Hydrogen Peroxide – Propylene Oxide (HPPO) process, in which propylene oxide is produced by reacting H_2O_2 with propylene over a TS-1 catalyst in liquid phase [11–13]. In this process, unreacted H_2O_2 in the product stream needs to be decomposed in the presence of hydrocarbons. It is, therefore, useful to determine how the presence of propylene affects H_2O_2 decomposition over metals, such as Pd, that are active in catalyzing H_2O_2 decomposition. For example, effects of the reaction temperature and the solution pH on H_2O_2 decomposition in an HPPO product stream were experimentally evaluated over supported Pt and Pd catalysts with an objective of complete H_2O_2 decomposition [12].

A reverse objective, preventing wasteful H_2O_2 decomposition, is critically important in the development of a single-step process where in situ formation of H_2O_2 or surface OOH species can be combined with their immediate use for selective propylene oxidation in the same reaction mixture. Such a process with H_2, O_2 and propylene as the feed and propylene oxide and H_2O as products is extensively studied as a gas-phase reaction over Au/TiO_2 and Au/TS-1 catalysts [11,14]. For example, our recent study showed that an Au/Ti-SiO_2 catalyst can be used with a membrane, with propylene and O_2 being forced through the catalytic membrane and H_2 reaching the catalyst by counter-diffusion [15]. Alternatively, a membrane reactor can produce H_2O_2 from H_2 and O_2 over Pd/SiO_2 in the first catalytic layer and then immediately utilize the produced H_2O_2 for selective hydrocarbon oxidation over TS-1 in the second catalytic layer [16]. Since such single-step processes in effect combine the direct H_2O_2 synthesis with propylene epoxidation, here it is also useful to determine effects of propylene presence on H_2O_2 decomposition over catalytic metals, including Pd, that are active in catalyzing H_2O_2 formation.

In this work, in addition to the evaluation of H_2 presence effects, reaction rates of H_2O_2 decomposition were systematically compared over oxidized and reduced Pd/SiO_2 catalysts in the absence and presence of propylene. The experimental results were analyzed with DFT calculations by comparing elementary reaction steps in H_2O_2 decomposition on a clean Pd surface and on Pd surfaces with pre-adsorbed hydrogen and propylene.

2. Experimental and computational methods

2.1. Catalyst preparation

2 wt.% Pd/SiO_2 catalysts were prepared using incipient wetness impregnation with palladium acetate (99.9%, Sigma-Aldrich) and Davisil 643 silica (pore size 15 nm, 200–425 mesh, Sigma-Aldrich). Prior to the Pd deposition, the SiO_2 support was dried at 373 K overnight. After the Pd deposition, the samples were first dried in vacuum at 393 K for 12 h and then calcined in air at 573 K for 4 h. After the calcination, the samples were split into two sets. The first set was tested without any additional pretreatment (oxidized Pd/SiO_2). The second set was tested after a reduction pretreatment in 10 mol% H_2/He (99.999%, Linde grade 5.0) at a flow rate of ~20 sccm at 473 K for 2 h (reduced Pd/SiO_2).

The sizes of Pd nanoparticles in the oxidized and reduced samples were analyzed using multiple images obtained with a FEI Tecnai G2 Sphera transmission electron microscope (TEM) at an acceleration voltage of 200 kV. Representative TEM images are shown in Fig. 1. The histograms of particle size distributions for the oxidized and reduced Pd nanoparticles, which are also shown in Fig. 1, demonstrate that, as expected for the conversion of an oxide to the metal, the size of nanoparticles decreased from 2.8 ± 0.6 nm for the oxidized Pd (Fig. 1b) to 2.2 ± 0.6 nm for the reduced Pd (Fig. 1a). Importantly, the particle size distributions indicate that the H_2 treatment did not cause any significant size changes for the Pd nanoparticles, only their reduction.

2.2. Catalyst testing

Rates of H_2O_2 decomposition in a methanol solution were measured using a 100 ml glass autoclave batch reactor immersed in a cooling bath for temperature control. The autoclave had an internal thermocouple, pressure sensor and gas dispersion impeller. The temperature was kept constant at 313 K. The initial total pressure in the reactor was 6 bar. The reactor pressure varied slightly during