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Kinetics of hydrogen peroxide synthesis by direct combination of H_2 and O_2 in a microreactor

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Abstract

Hydrogen peroxide is an industrially important oxidant with a growing number of applications in the chemical and textile industries, and in environmental remediation. Production of H_2O_2 by the direct combination of H_2 and O_2 is much less energy-intensive than the currently used anthraquinone autoxidation method, but it has not been implemented commercially because of the explosive nature of H_2 and O_2 mixtures. In this work, hydrogen peroxide was safely produced by direct combination of hydrogen and oxygen in a microreactor in the explosive regime. Concentrations as high as 1.3 wt% H_2O_2 were achieved. Optimum ranges of the temperature and pressure for H_2O_2 production were determined, and the reaction was shown to be free of mass transfer limitations at the conditions of kinetic experiments. A plan for obtaining the overall kinetics of direct H_2O_2 formation is described, which involves the determination of rate expressions of H_2O_2 synthesis, and of consequent decomposition of H_2O_2. A mechanism for the H_2O_2 synthesis reaction is proposed on the basis of past research and kinetic data. A rate expression is derived based on the proposed mechanism, and kinetic data were used to calculate the kinetic constants. This is the first step toward the determination of complete kinetics of direct H_2O_2 formation.

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1. Introduction

1.1. Overview

Hydrogen peroxide is an industrially important chemical with a large number of applications. It is widely used as an environmentally friendly oxidant for soil remediation and in the paper and textile industries, where it replaces chlorine bleaches. Global demand for hydrogen peroxide has been growing for the last two decades due to rising environmental concerns [1]. Since the middle of the twentieth century, the large majority of commercial hydrogen peroxide was produced by the anthraquinone autoxidation (AO) method [1]. The AO process has several important drawbacks. Hydrogen peroxide must be produced in large amounts and at high concentrations of about 70% [2] in order for the process to be profitable, which requires an energy-intensive distillation step for increasing the H_2O_2 concentration. The high concentrations are required for minimizing the liquid volume that needs to be transported to the end-users, thus decreasing the transportation expenses. Since many end-users require concentrations as low as 0.5–10 wt% [3], dilution by the end-user adds an additional expense.

A direct combination (DC) of hydrogen and oxygen in the presence of a catalyst and a solvent seems to be the simplest method of producing hydrogen peroxide. The potential commercial importance of this process attracted a large number of inventors since the first DC patent of Henkel and Weber [4]. Even though a large number of patents were issued for different variations of this process over the years [5–14], the DC method has not reached the commercialization stage yet due to a number of technical challenges. First, hydrogen and oxygen form a flammable mixture over a wide range of concentrations (5–96% H_2 in O_2). Thus, in most patents the preferred operating gas composition is below the explosive limit, and at high pressures on the order of several thousand psi, which are required in order to increase the concentration of dissolved hydrogen in the liquid solvent. Second, the catalytic

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Nomenclature

a_{gl}	gas–liquid interfacial area per unit volume of reactor (m^2/m^3)
C_A	concentration of species A in liquid (mol/cm^3)
$C_{A,sat}$	saturated concentration of species A in liquid (mol/cm^3)
$D_{eff,A}$	overall effective molecular diffusivity of species A in the gas–liquid mixture ($=D_A = D_{A,G}x_G + D_{A,L}x_L$) ($cm^2/s$)
$D_{eff,A,G}$	effective molecular diffusivity of species A in the gas phase (cm^2/s)
$D_{eff,A,L}$	effective molecular diffusivity of species A in the liquid phase (cm^2/s)
E_a	activation energy (kJ/mol)
F	volumetric flow rate of reactants or products (m^3/s)
ΔH	enthalpy of reaction (kJ/mol)
P_A	partial pressure of species A in the gas phase (psia)
r_a	intrinsic reaction rate with respect to species a (g/g cat/h)
R	ideal gas constant (kJ/mol K)
R_A	observed reaction rate with respect to species A (g/g Pd/h)
R_p	average radius of catalyst particles (m)
T_w	reactor wall temperature (K)
W	catalyst mass (g)
x_G	volumetric gas fraction
x_L	volumetric liquid fraction

Greek letters

λ_e	effective thermal conductivity of porous catalyst (W/m K)
ρ_p	density of catalyst particles (g/m^3)

reaction of hydrogen and oxygen involves several reaction pathways, most of which result in the production of water. A catalyst that maximizes the selectivity for H_2O_2 is critical for the viability of this process.

Major disadvantages of either the AO process or of the patented DC methods can be overcome by producing hydrogen peroxide in a microreactor. The DC reaction can be carried out safely with a high hydrogen concentration (in the regime that would be explosive in a large-scale reactor) because the width of microreactor channels is smaller than the quenching distance of hydrogen and oxygen radicals. In other words, much higher temperatures and pressures are required to start an explosion in a microchannel than in a macrochannel [15,16]. This makes the DC reaction intrinsically safe in a microreactor for all H_2/O_2 ratios and all process conditions that might be used for H_2O_2 production. The ability to use safely high hydrogen concentrations makes it unnecessary to use very high pressures to achieve significant reaction rates, thus avoiding the need for expensive high-pressure equipment. The DC process is not restrained by the requirements of high quantity and high concentration of the present AO process. Also, the distillation step of the AO process is eliminated, which leads to significant energy savings. Portability of the microreactors opens the possibility of installing microreactor plants at the end-users' sites, leading to greatly decreased transportation costs.

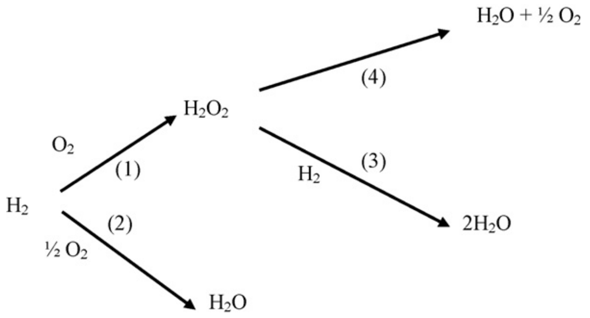
In this study, we describe the production of H_2O_2 in a microreactor by the direct combination process. Optimum operating conditions were found that enable us to obtain 1.3 wt% H_2O_2 using a catalyst prepared in-house. The H_2O_2 synthesis step was studied in a differential microreactor with the suppression of other reactions and kinetics of this reaction were obtained.

1.2. Reaction pathways involved in the DC process

Reactions that take place in parallel and in series in the synthesis of H_2O_2 by the DC process are shown in Scheme 1. H_2O_2 synthesis, the desired reaction, is numbered as reaction (1). Reaction (2) is direct formation of water, which is in parallel with reaction (1). Reaction (3) is decomposition of H_2O_2 by reduction, and reaction (4) is H_2O_2 decomposition by disproportionation. Both reaction (3) and reaction (4) are in series with reaction (1).

The main products of DC process are hydrogen peroxide and water. The optimum catalyst and operating conditions are such that will improve the yield of H_2O_2 by favoring reaction (1), while suppressing reactions (2)–(4) as much as possible.

A growing number of researchers who studied the DC process focused on determining the reaction mechanisms, and on clarifying the relative importance of the multiple reactions. The earliest work on direct formation of H_2O_2 in scientific literature was done by the group of Pospelova [18–20], who described the essential properties of this system and proposed a mechanism for H_2O_2 synthesis that involved dissociative adsorption of H_2 on an active site consisting of two palladium atoms, non-dissociative adsorption of O_2 on the same site, and a surface reaction between H_2 and O_2 to form H_2O_2 through a HO_2^- intermediate. The same group also found that certain halide salts and acids can act as promoters for H_2O_2 formation. The fact that O–O bond does not dissociate during H_2O_2 formation was experimentally confirmed by Dissanyake and Lunsford [21] and the presence of HO_2^- on catalyst surface during the reaction was discovered by Sivadinarayana et al. [22].



Scheme 1. Reactions involved in the formation of hydrogen peroxide [17].

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