

DIRECT SYNTHESIS OF HYDROGEN PEROXIDE – REMARKS ON MECHANISM, RATE EQUATIONS AND BATCH/SEMIBATCH REACTOR MODELING

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Summary

The direct synthesis of hydrogen peroxide was tested in a batch reactor over a commercial Pd/SiO₂ catalysts obtaining good selectivity towards H₂O₂ formation (50%). A detailed kinetic model for the H₂O₂ formation was implemented taking into account the vapour-liquid equilibrium and adsorption effects in the catalyst surface. The experimental data obtained in the batch reactor was confronted with the proposed model obtaining a high degree of explanation.

Keywords

H₂O₂, kinetic modeling, Pd, direct synthesis.

Introduction

Today, hydrogen peroxide is produced by an indirect process in which an alkyl anthraquinone is sequentially hydrogenated with a catalyst and oxidized. In this way hydrogen and oxygen are kept separated during the manufacturing process. A process where the direct reaction of H₂ + O₂ → H₂O₂ takes place could be preferred if control of the sequential hydrogenation can be achieved, but none of the current available processes has solved the productivity vs. safety dilemma.

Despite an extensive body of research on the direct synthesis process, there are limited studies where the kinetic rate expressions on the full reaction network are described and verified. Few attempts to obtain rate equations describing the kinetics of the direct synthesis reaction have been made by Voloshin and coworkers¹, Melada and collaborators² and Inoue et al.³ and further development is still needed.

Our goal is to determine the kinetics of the direct synthesis of H₂O₂ in a batch reactor at high pressure, taking into account vapour-liquid equilibrium between gas and liquid phases and adsorption effects in the catalyst surface.

Experimental

The kinetic experiments were performed in a Parr stainless steel batch reactor with a volume of 600 ml and a maximum working pressure of 200 bar with a commercial 2 wt.% Pd/SiO₂ catalyst (Evonik). Mixing was carried out

with a Heidolph RZR 2021 rotor operating at 1000 rpm.

During each experiment, the reactor was charged with 0.1 g of catalyst. The autoclave was initially filled with a 25 mol.% O₂/CO₂ mixture until reaching the desired working pressure. The addition of 400 ml of the reaction solvent (methanol) was successively done. Pure hydrogen was sequentially added, keeping the total pressure constant. The reaction temperature was kept constant at 0 °C by using ethylene glycol as a coolant.

The concentration of the reactants (H₂ and O₂), as well as the total pressure of the system were systematically varied as follows: i) keeping the total pressure of the system at 20 bar and the partial pressure of hydrogen p_{H₂}=0.5 bar, the O₂ partial pressure was varied between 3 and 8 bar; ii) keeping the total pressure of the system at 20 bar and the partial pressure of O₂ at 5 bar, the H₂ partial pressure was varied between 0 and 4 bar; and iii) keeping the partial pressures of H₂ and O₂ constants (0.5 and 5 bar, respectively), the total pressure of the system was varied between 10 and 30 bar.

After the introduction of all the gases, sampling was done with a time interval of 15 minutes during the first hour. After 1 h, samples were taken every 30 minutes until reaching a reaction time of 4 h. The H₂O₂ production was determined by iodometric titration. The production of water was quantified by volumetric Karl-Fischer method.

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Mathematical Modeling

The following assumptions were applied in the modeling of the batch and semibatch-wise operated stirred tank reactor: the reactor vessel was isothermal and completely backmixed, since the temperature was controlled and high stirring rates were applied. The system operated in the kinetic regime, since the reactions are slow compared with mass transfer rates. This was confirmed with experiments carried out with different stirring speeds and amounts of catalyst. The effect of internal diffusion was evaluated with a reaction-diffusion model for solid catalyst particles. Isobaric conditions prevailed in the semibatch experiments, since the gas addition was controlled in such a way that the total pressure was kept constant.

The fact that interfacial mass transfer is rapid, allowed us to add the transient balance equations for the components in the (semi)batch reactor. Thus the concentrations of volatile components in gas and liquid phases can be related by the phase-equilibrium ratio (K_i), the value of which was obtained from gas solubility data and from equations of state. The mass balance for an arbitrary component (i) in the liquid phase can thus be written as:

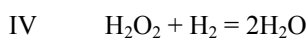
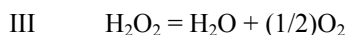
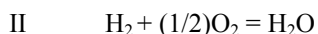
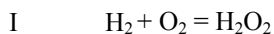
$$dc_{L,i}/dt = (\alpha K_i + 1)^{-1} (\rho_B r_i + x_{0G,i} \beta)$$

where α is the gas-to-liquid volume ratio in the reactor, ρ_B is the catalyst bulk density (mass of catalyst-to-liquid volume), $x_{0G,i}$ is the mole fraction of the component in the gas feed and β is a correction factor originating from the enrichment of inert gases in the reactor,

$$\beta = -[K_{H_2} r_{H_2} / (\alpha K_{H_2} + 1) + K_{O_2} r_{O_2} / (\alpha K_{O_2} + 1)] \rho_B / \sum K_j x_{0j} (\alpha K_j + 1)^{-1}$$

where the sum in the denominator comprises all gaseous components in the system. The generation rates of the components were obtained from the overall stoichiometry.

In calculating the overall stoichiometry, the following reactions were taken into account: formation of hydrogen peroxide from hydrogen and oxygen (I), formation of water from hydrogen and oxygen (II), decomposition of hydrogen peroxide to water and oxygen (III) as well as hydrogenation of hydrogen peroxide to water (IV). The overall reactions are summarized below;



Several surface reactions mechanisms can be sketched down, which result in the four overall reactions displayed above. We started from the following hypotheses, taking into account previous knowledge about palladium catalysts. The adsorption of hydrogen and oxygen were assumed to be rapid and of dissociative character, surface hydroxyls are formed from adsorbed hydrogen and

oxygen, adsorption and desorption of hydrogen peroxide and water are rapid steps compared to the surface reaction steps, i.e. reactions between two surface hydroxyls and reactions between surface hydroxyls and hydrogen. These assumptions lead to a set of rate equations describing the overall reactions (I-IV). For instance, for the formation of hydrogen peroxide we obtained the rate expression

$$r_1 = k'_1 (c_{H_2} c_{O_2} - c_{H_2O_2} / K'_1) / D^2$$

where D is the adsorption term incorporating the adsorption constants and concentrations of the components in the system. Analogous rate expressions were obtained for reactions II-IV. In addition, rival kinetic models based on slightly different assumptions concerning the rate determining steps and surface intermediates were derived and tested.

The rate model was coupled to the reactor model and the parameters (rate and adsorption parameters along with their temperature dependencies) were estimated with nonlinear regression analysis. The reactor model was solved with a backward difference algorithm during the parameter estimation procedure. In general, the fit of the model to the experimental was reasonable and the approach turned out to be fruitful for the description of direct synthesis of hydrogen peroxide on Pd catalysts in batch and semibatch reactors.

References

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