Product distribution analysis of the hydrogen peroxide direct synthesis in an isothermal batch reactor

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ABSTRACT

The direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen on a supported palladium catalyst was studied at 258–297 K in a laboratory-scale batch reactor. The catalyst was in the form of finely dispersed slurry in methanol/CO_2 to suppress the internal and external mass transfer resistances. Experiments carried out under kinetic control revealed that hydrogen peroxide was successfully formed on the catalyst surface, but it was hydrogenated as the reaction time was prolonged. The mass balances of the components were considered in detail and a reaction mechanism was proposed, based on the competitive adsorption of hydrogen and oxygen on the palladium surface. The surface reactions leading to the formation of hydrogen peroxide and water were assumed to be rate determining, and the rate equations describing direct synthesis, water formation as well as peroxide hydrogenation and decomposition were derived. A special kind of product distribution analysis was used to interpret the kinetic phenomena and to make the estimation of the kinetic parameters very robust. The parameters were estimated by nonlinear regression analysis and the model gave a good fit to the experimental data. The usefulness of the product distribution analysis was clearly demonstrated.

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1. Introduction

The currently applied industrial process for the production of hydrogen peroxide, the anthraquinone process, is based on successive hydrogenation and oxidation of quinonic components. Despite the high yield of hydrogen peroxide per cycle, the process major disadvantages are the side reactions, requiring regeneration of both the working solution and the hydrogenation catalyst, and the several steps necessary for the purification and concentration of the peroxide [1]. For both these reasons, the cost of the hydrogen peroxide is nowadays relatively high, limiting the industrial large scale use of H_2O_2. Moreover, the current process has high capital and operation costs, and is suitable for real large-scale operation only. In future, the interest towards on-site production of chemicals in a smaller scale is predicted to increase. This would require a simpler process for the synthesis of hydrogen peroxide.

It has been a long time the dream of chemists and chemical engineers to develop a new process, based on the direct synthesis of hydrogen peroxide from its primary molecular constituents, molecular hydrogen and oxygen. The pioneering work was carried out by Pospelova et al. [2] in early 1960s. A lot of catalyst development work has taken place during the recent decade, the most promising heterogeneous catalysts for the direct synthesis being Pd and Pd–Au catalysts [3].

Catalyst development alone does not bring us to a success in the development of a hydrogen peroxide process based on the direct synthesis. Early attempts to apply direct synthesis failed because of low reaction rates and selectivities – the catalyst enhances water formation and hydrogen peroxide decomposition, too. Thus, the study of direct synthesis should also be combined to studies of the optimal reaction conditions. For instance, very recently our research group has carried out an optimization study to maximize H_2O_2 productivity in a trickle bed reactor [4]. The introduction of methanol as solvent and the presence of carbon dioxide in the reaction environment have implied real breakthroughs in the process development. In this way, the solubilities of the reacting gases can be essentially improved and the reaction rate is enhanced.

In spite of the huge interest on the direct synthesis, only few detailed kinetic studies are available in open literature [5,6].

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Notation

A	interfacial area
A'	frequency factor
c	concentration
c_*	concentration of a surface species
D	denominator in rate expression
E_a	activation energy
K	equilibrium constant
k	reaction rate constant
k'	merged rate constant, product of rate constant, adsorption equilibrium constant and total concentration of active sites
N	flux
n	amount of substance
n^{exp}	number of experimental data (Eqs. (44) and (48))
R	gas constant
r	reaction rate
r_i	component (i) generation rate
T	temperature
t	time
V	volume
α	gas-to-liquid volume ratio
β	parameter in product distribution analysis
ν	stoichiometric number
ω	parameter in product distribution analysis

Subscripts and superscripts

G	gas
i, j	component indices
L	liquid
P	reaction route
TOT	total amount
0	initial property

Abbreviations

H	hydrogen
O	oxygen
P	hydrogen peroxide
W	water

Deguchi et al. [7] were the only one taking into account the adsorption of the promoters in the kinetic study. Therefore, we constructed a special batch reactor system to determine the very precise kinetics of hydrogen peroxide synthesis and decomposition. The reaction rates and product distribution were measured at different temperatures and partial pressures of hydrogen and oxygen to reveal the kinetic phenomena [8]. The goal of this work is to improve our previous kinetic analysis [8] and obtain a more rapid and reliable estimation of the kinetic parameters, neglecting mass transfer limitations and negligible reactions. The time dependence of the concentrations was also eliminated with the aid of product distribution analysis. In particular, the product distribution analysis was applied in order to improve the reliability of the parameter estimation in this multicomponent system of composite reactions.
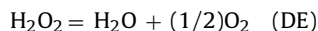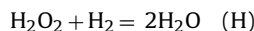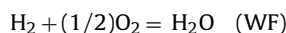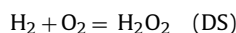
2. Experimental

The batch reactor was a 600 ml unbaffled autoclave (Büchi) equipped with a self-sucking six-blade impeller. Typically, 0.15 of a commercial 5 wt% Pd/C catalyst was loaded in the reactor vessel. Methanol expanded with carbon dioxide was used as solvent in all experiments. Carbon dioxide and oxygen were introduced to the vessel, after which 400 ml of methanol was injected and

hydrogen was fed as a limiting reactant (total pressure in the range 14–20 bar, depending on temperature). The stirring rate was adjusted to 1000 rpm to ensure the operation in the kinetic regime. Samples were withdrawn from the liquid phase; the water and hydrogen peroxide concentrations in the samples were determined by Karl Fischer and iodometric titrations, respectively. Isothermal experiments were carried out at 258, 268, 273, 283 and 297 K. Note that, though the presence of CO_2 can theoretically lead to an acidic environment, it is assumed acid-free in the actual experimental condition, where methanol was used as solvent and the measured concentration of H_2O was always very low. The details of the experimental equipment and procedures are described in the previous publications of our group [9,10].

3. Reaction mechanism and rate equations

The following overall reactions, confirmed by Biasi et al. [11] and Gemo et al. [8], are considered in connection of hydrogen peroxide formation and decomposition: the reactions between hydrogen and oxygen yielding hydrogen peroxide and water as well as spontaneous decomposition and hydrogenation of hydrogen peroxide. The overall reactions are summarized below:

$$H_2 + O_2 = H_2O_2 \quad \text{(DS)}$$

$$H_2 + (1/2)O_2 = H_2O \quad \text{(WF)}$$

$$H_2O_2 + H_2 = 2H_2O \quad \text{(H)}$$

$$H_2O_2 = H_2O + (1/2)O_2 \quad \text{(DE)}$$

All these reactions are highly exothermic and thermodynamically favourable, as discussed for instance by Biasi et al. [12] and Gemo et al. [8]. The experiments of Gemo et al. [8], carried out in a laboratory-scale batch reactor, revealed that the hydrogenation reaction (H) clearly dominates over the decomposition reaction (DE) in the conditions studied.

The rate equations for reactions (DS to DE) should in principle be based on the knowledge of the true reaction mechanism: if the mechanism is precisely known, the appropriate rate equations can be derived based on the elementary steps on the solid catalyst surface.

Several surface mechanisms on palladium can give the overall process described by equations (DS to DE). Voloshin et al. [5] screened some mechanisms to describe kinetic data obtained from microstructured reactors and concluded that a Langmuir–Hinshelwood-type mechanism with the surface reaction steps as rate determining ones gave the best agreement with experimental data. Some mechanistic studies have given information about the reaction mechanism. For instance, Dissanyake and Lunsford [13] proposed that the O—O bond does not dissociate during the H_2O_2 synthesis process and Sivadinarayana et al. [14] confirmed the species HO_2- on a gold catalyst surface. However, it is clear that water formation requires the rupture of the O—O bond on the catalyst surface. Oxygen is known to adsorb both dissociatively and non-dissociatively on Pd surfaces. Concerning the state of the active site on the Pd surface, no general agreement exists. Both Pd^0 and PdO have been proposed as active oxidations states for the direct synthesis [15–18]. Very many support materials, such as carbon, alumina, silica, ceria and titania have been screened, and the catalyst performances have been compared [11]. In a recent study, Rossi et al. [19] have shown that Pd single crystals exhibit a considerable activity in the direct synthesis of H_2O_2. The recent development is summarized, for instance, by Samanta [20] and Centi et al. [3].