Direct hydrogen peroxide synthesis – kinetic studies assisted by microreactor technology

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Abstract: We have demonstrated that the direct synthesis of hydrogen peroxide synthesis could be successfully implemented using micro-packed bed with intensified safety and efficiency. Here, we demonstrate that the reactor is suitable to study kinetics, which is mandatory to design the process with optimized performance.

Keywords: hydrogen peroxide, direct synthesis, microreactor.

1. Introduction

Much effort has been devoted to realize the direct synthesis of hydrogen peroxide, still it still lacks the opportunity of industrial use due to inherent risk of explosion and insufficient reaction scheme (both reactants are in gas phase and sparse solutes to water). We have demonstrated that the nature of microreactor technology, widening process windows and making the mass transfer efficient, serves a solution to the inherent challenges imposed by the direct process [1-6]. Here we demonstrate that the technology is useful to study the kinetics to optimize the process performance with flexible reaction condition settings..

2. Experimental

We used the glass fabricated microreactors designed by ourselves and manufactured by Tecnisco Ltd. Catalyst was prepared by impregnation over spherically shaped rutile-based TiO_2 support using palladium chloride (denoted as Pd/TiO_2 (I)) or palladium colloid stabilized by poly vinyl pyrrolidone (PVP) (denoted as Pd/TiO_2 (C)). The catalyst was introduced into the microreactor using water suspension to form micro packed bed during the reaction. The reactor was fit in to jigs suitable for the reaction [2-5].

We performed theat an outlet pressure of 0.95 MPaG and the temperature was varied occasionally in order to estimate the activation energy. The reaction solution was prepared by mixing dilute sulfuric acid (0.025 M), phosphoric acid (0.005 M), and sodium bromide (5.1×10^{-4} M) solutions to stabilize the produced hydrogen peroxide. The products were hydrogen peroxide and water; the amont of hydrogen peroxide produced was estimated using permanganate titration while that of water was estimated by the balance between hydrogen consumed and the amount of hydrogen peroxide produced. The hydrogen consumption was monitored using micro GC with MS-5A column.

3. Results and discussion

Table 1 presents the comparison of Pd/TiO_2 (I) and Pd/TiO_2 (C), showing that the latter exhibited higher productivity to hydrogen peroxide. We suppose the difference is due to the surface area of palladium particle supported.

Catal.	$H_2/(H_2+O_2)$	C [%]	S [%]	Y [%]	W [wt%]
Pd/TiO_2 (I)_1wt%	0.2	54	67	36	5.8
_2 wt%	0.2	71	68	49	8.2
_5 wt%	0.2	100-88	0-60	0-53	0-8.2
Pd/TiO2	*0.2*	*42*	*68*	*29*	*4.9**

(C)_1wt%	0.1	66	79	52	8.5
_2 wt%	*0.1*	*37*	*75*	*27*	*4.8**

Table 1. Comparison of catalyst performance between impregnated and nano colloidal precursor. Tot. gas flow rate: 5 sccm ($H_2/(H_2+O_2)$ =0.2) or 10 sccm ($H_2/(H_2+O_2)$ =0.2), liq. flow rate: 0.01 $mLmin^{-1}$. Reaction pressure: 0.95 MPa at the outlet. Performances with* correspond to the reactor with short packed bed (40 mm), otherwise packed bed length was 140 mm.

We studied the conversion –selectivity relationship for both Pd/TiO_2 (I) and Pd/TiO2 (C) catalyst, which showed that hydrogen peroxide is an intermediate product, with water as the final one. Also, our kinetic studies indicated the kinetics based on power-law expression (vide infra) explained the reaction performance (Fig. 1);

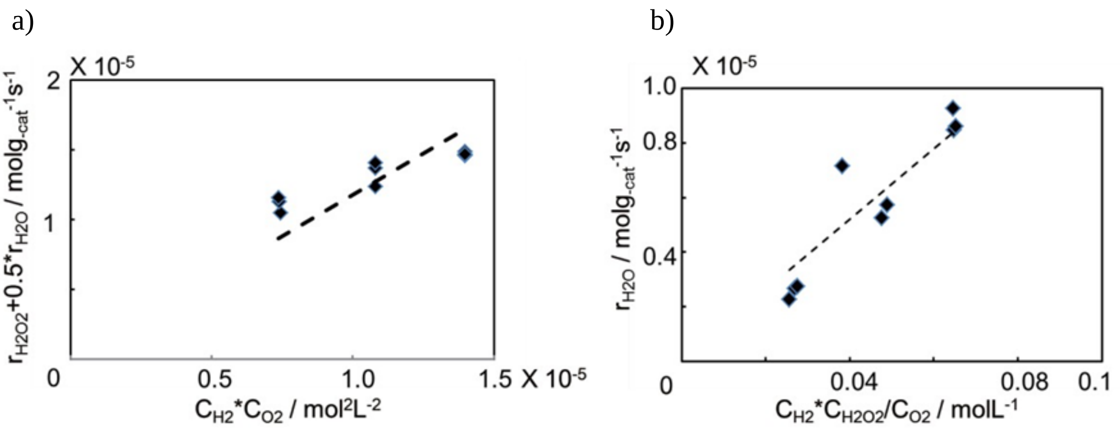

Figure 1. Power law fitting for hydrogen peroxide formation (a, eq. 1) and hydrogenation to form water (b, eq. 2)

Hydrogen peroxide generation ($H_2 + O_2 \rightarrow H_2O_2$)

$$r_{H2O2} + 0.5r_{H2O} = k_f C_{H2}^{sat} * C_{O2}^{sat} \qquad 1)$$

subsequent hydrogen peroxide reduction to water ($H_2O_2 + H_2 \rightarrow 2 H_2O$)

$$r_{H2O} = k_d C_{H2}^{sat} * C_{H2O2}/C_{O2}^{sat} \qquad 2)$$

Where r_{H2O2} and r_{H2O} denote observed hydrogen peroxide production rate and that for water, respectively, and C_{H2}^{sat} and C_{O2}^{sat} denote saturated hydrogen and oxygen formation, respectively. We estimated the activation energy for both rate constant to be 29 $kJmol^{-1}$ for k_f and 39 $kJmol^{-1}$ for k_d, in good agreement with preceding study [7].

4. Conclusions

In the presentation, we will show how the microreactor technology help to obtain kinetics with detailed description of experimental set-ups.

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