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Authors: Lech Nowicki, Dorota Siuta, Mariusz Godala

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Determination of the chemical reaction kinetics using isothermal reaction calorimetry supported by measurements of the gas production rate. A case study on the decomposition of formic acid in the heterogeneous Fenton reaction.

Lech Nowicki^{a*}, Dorota Siuta^a, Mariusz Godala^b

^aLodz University of Technology, Faculty of Process and Environmental Engineering, Wolczanska 213, 90-924 Lodz, Poland

^bBureau for Chemical Substances, Dowborczyków 30/34, 90-019 Lodz, Poland

*Corresponding author Tel.: +48 426313781, E-mail address: lech.nowicki@p.lodz.pl

Highlights

- A new method for the identification of the reaction kinetic model is proposed.
- The method can be applied to chemical reactions that produce gaseous products.
- Decomposition of H₂O₂ and oxidation of HCOOH catalysed by goethite is showed as a case study.
- Usefulness of aL-H type of rate law for H₂O₂ decomposition is confirmed.

Abstract

One of the most important steps in studying chemical reaction kinetics is to determine a rate law for the reaction. In this paper, a method for the identification of the reaction kinetic model using isothermal calorimetric data and additional measurement of the rate of pressure change in a constant volume of a calorimetric vessel is described. This method can be applied to fairly fast chemical reactions (i.e. those that can be completed within about 2 hours) that produce gaseous products. The decomposition of formic acid in the heterogeneous Fenton process is employed as a case study to demonstrate the use of the developed method for the kinetic analysis of a complex reaction system. It was found that the rate of decomposition of hydrogen peroxide can be described by the Langmuir-Hinshelwood type of equation in the form $r = kC_P/(1+K_PC_P)$ (where C_P is a molar concentration of H₂O₂) both in the case of the decomposition of the aqueous hydrogen peroxide solution as well as during the oxidation of formic acid. A simple, purely empirical rate equation for the decomposition of formic acid was also proposed.

Keywords: Hydrogen peroxide; Formic acid; Fenton reaction; Heterogeneous catalysis; Reaction kinetics

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