Dibenzothiophene oxidation with hydrogen peroxide: kinetic modeling

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Introduction

Recently, the oxidation-extraction process (O-E) has been investigated as an attractive alternative to obtain diesel fuel with ultralow sulfur content, particularly in the context of the new severe regulations adopted in the world. For example, the Environmental Protection Agency (EPA) has called for the production and use of more environmentally friendly transportation fuels with lower sulfur contents **[1,2]**.
In this work, a kinetic study for the dibenzothiophene oxidation with hydrogen peroxide in a three phase catalytic reactor was performed. The experimental reactions were carried out in a Robinson-Mahoney reactor working at atmospheric pressure and 313 to 343 K temperature range.

Materials and Methods

The reactions (Figure 1) were carried out using a WO_x-Al_2O_3 catayst calcined at 773 K. The catalysts was characterized by nitrogen physical-sorption, Raman spectroscopy, X-ray diffraction and UV-vis spectroscopy before the catalytic reactions. From these results, WO_x-Al_2O_3 catalyst showed tungsten oxides in a tetrahedral coordination, that could be favorable for the dibenzothiophene oxidation **[3,4]**.

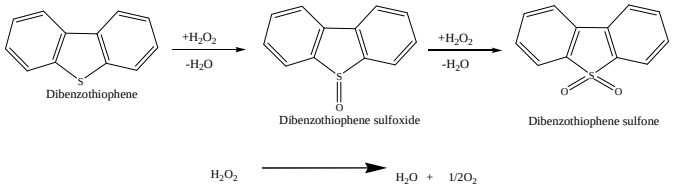

Figure 1. Oxidation of dibenzothiophene with hydrogen peroxide and hydrogen peroxide decomposition reactions

Catalyst mass, particle size and stirring speed were varied to establish an optimal experimental reaction conditions under kinetic regime. Once the optimal conditions were reached a new set of experiments were carried out at different temperatures and initial composition ranges for dibenzothiophene, hydrogen peroxide and dibenzothiophene sulfone.

Results and Discussion

Some kinetic models: Langmuir-Hinshelwood-Hougen-Watson (LHHW), Eley-Rideal (ER), and Mars-van Krevelen (MVK) were examined to select the model that could represent the heterogeneous oxidation reaction of dibenzothiophene. As a result of data analyses, an Eley-Rideal model showed an excellent agreement with experimental data (Table 1). The surface reaction was the rate determining step as it can be confirmed from experimental results (Figure 2).

Table 1. Eley-Rideal kinetic model

Rate determining step	Rate law
Adsorption of DBT: $DBT + X \underset{k_{-DBT}}{\overset{k_{DBT}}{\rightleftharpoons}} DBT{\cdot}X$	$R_1 = k_{DBT} C_{DBT}$
Surface Reaction: $DBT{\cdot}X + H_2O_2 \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} DBTO{\cdot}X + H_2O$	$R_1 = \frac{k_1 K_{DBT} C_{DBT} C_{H2O2}}{1 + K_{DBT} C_{DBT}}$
Desorption of DBTO: $DBTO{\cdot}X \underset{k_{DBTO}}{\overset{k_{-DBTO}}{\rightleftharpoons}} DBTO + X$	$R_1 = k_{-DBTO}$

The Eley-Rideal mechanism postulates that the reaction can occur between adsorbed dibenzothiophene with the hydrogen peroxide in the polar liquid phase. The acid and basic character of catalyst and dibenzothiophene, respectively, in addition with the excess of the hydrogen peroxide in the reaction system, confirmed that this mechanism was consistent with experimental data.

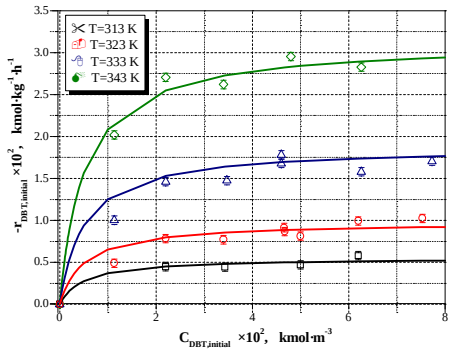

Figure 2. Initial rate for the dibenzothiophene oxidation. The points are the experimental data, solid curves represent the Eley-Rideal kinetic model

The kinetic model parameters were calculated through the minimization of the square of the standard deviation from the experimental and calculated reaction rate values. The Levenberg-Marquardt method was used to minimize the objective function.

The estimated parameters were meaningful since the significance of the overall regression and the individual reaction rate parameters achieve the statistical criteria at 95 % of confidence.

Significance

This work is a step towards understanding the complex catalytic chemistry of the dibenzothiophene oxidation, mechanistic modeling, and kinetic parameter estimation in order to rationalize reactor designs, in the framework of ultraclean fuels production.

References

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