

GLYCEROL OXIDATION IN AQUEOUS PHASE BY USING SILVER-BASED CATALYSTS: KINETIC ANALYSIS AND MODELLING

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Abstract

The present work describes a kinetic model proposed for the glycerol oxidation in aqueous phase, by using a silver-based catalyst (Ag/CeO₂). A Langmuir-Hinshelwood model was proposed, with an activity term to quantify the catalyst deactivation. The proposed model predicted well the experimental results in a wide range of temperatures and reactant concentrations. As expected, the kinetic parameters revealed that the catalyst was more selective towards C-C cleavage products. Moreover, the zeroth order deactivation constant was significant and confirmed the catalyst deactivation by leaching.

Keywords

Heterogeneous catalysis, Chemical kinetics, Computational methods.

Introduction

During the past decade, the use of biofuels as an alternative energy source to fossil fuels has been established. Among biofuels, the production of biodiesel, based on transesterification of vegetable oils or waste fats, leads to glycerol (GLY) as an inevitable by-product: over 100 kg of GLY are produced per tonne of biodiesel (Gil et al., 2011). There are many GLY transformation pathways, and, among them, the catalytic oxidation in the liquid phase has gained a great interest. The use of Ag in this reaction has been seldom studied. This metal has been proven to be selective to glycolic acid (Skrzyńska et al., 2015), which is used in food, cosmetic and textile industries.

The aim of this work is to develop kinetic models of the GLY oxidation in the liquid phase by using different Ag-based catalysts. So far, a kinetic model has been developed, by using the experimental results obtained with a Ag/CeO₂ catalyst.

Kinetic model

The kinetic model was performed by considering the effect of the reaction temperature (40-100 °C), GLY initial concentration (0.1-0.5 mol/L) and NaOH/GLY ratio (0-4 mol/mol).

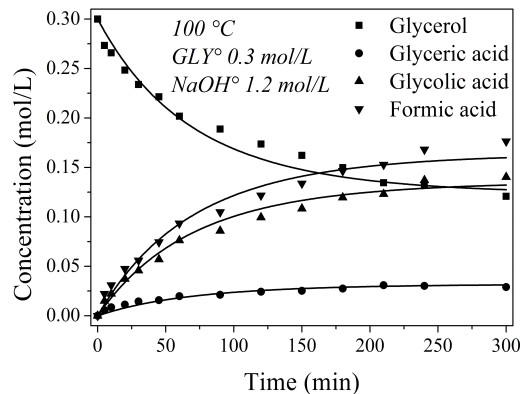


Figure 1. Experimental and calculated C-t profile

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The reaction pathways have been proposed on the basis of the experimental results. This way, Figure 1 revealed that glyceric, glycolic and formic acid were primary products of GLY. Figure 2 shows the proposed reaction pathways.

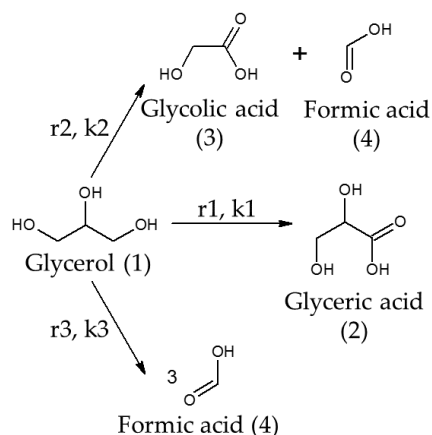


Figure 2. Proposed reaction pathways of GLY oxidation

A Langmuir-Hinshelwood model was proposed, by assuming the surface reaction as the rate determining step, competitive adsorption, first order reaction of GLY and NaOH and a carbon balance close to 100%. Moreover, deactivation kinetics was included. Parameter fitting was carried out by using Matlab. The general reaction rate equation can be written as follows:

$$r_i = \frac{k_i \cdot K_1 \cdot K_{OH} \cdot C_1 \cdot C_{OH}}{(1 + K_1 \cdot C_1 + K_{OH} \cdot C_{OH})^2} \cdot a \quad (1)$$

$$\frac{da}{dt} = -k_d \cdot a \quad (2)$$

The rate and adsorption constants are given by the orthogonalised Arrhenius and Van't Hoff equations. Table 1 listed the final parameter estimation of the model, as well as the relative standard deviations and the coefficient of determination.

Table 1. Estimates of the kinetic parameters and coefficient of determination

	k (60°C) (mol/L·min)	%Std. Dev.	Ea (kJ/mol)	%Std. Dev.
r1	$6.84 \cdot 10^{-4}$	2.7	46	7.3
r2	0.0036	4.0	40	3.6
r3	$2.67 \cdot 10^{-4}$	2.5	39	10.3
Deactivation	0.0041	1.2	27	8.4
	K (60°C) (L/mol)	%Std. Dev.	ΔH (kJ/mol)	%Std. Dev.
GLY	7.77	3.1	-26	5.8
OH	4.63	2.9	-28	18.8
Model r²			0.9965	

Discussion

The results listed in Table 1 suggests that the proposed kinetic model was statistically significant. Moreover, Figure 1 shows an example of how good the prediction of the experimental results was.

Results revealed that the Ag/CeO₂ catalyst favoured the C-C cleavage of GLY to glycolic and formic acid. Reaction r2 was 10 times faster than the other ones at 60 °C, whereas the activation energies of reactions 2 and 3 were slightly lower than that of r1 (oxidation without C-C cleavage).

The estimated activation energies of this work were lower than those obtained by unsupported Au nanoparticles (60-70 kJ/mol) (Díaz et al., 2015) or by Pt-based catalysts (70 kJ/mol) (Hu et al., 2011). However, the Ag/CeO₂ seems to be less stable in the reaction media. Ag particles could be prone to suffer leaching, which would explained the zeroth order dependence of the activity coefficient.

Conclusions and future work

A Langmuir-Hinshelwood model has been proposed for the GLY oxidation by using a Ag/CeO₂ catalyst. The model predicted well the experimental results, and confirmed the high selectivity of this catalyst towards C-C cleavage products, as well as the deactivation phenomena, probably caused by leaching.

The present catalyst will be compared with other Ag-based ones by using a similar model. Moreover, the deactivation phenomena will be analysed in detail, in order to check whether or not the deactivation depends on any reactant or product.

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