

KINETIC MODELING OF OXIDATION ETHYLENE GLYCOL TO GLYCOLIC ACID BY MONO AND BIMETALLIC PT BASED CATALYSTS

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Abstract

The selective oxidation of ethylene glycol (EG) to glycolic acid (GA) is industrially important and also challenging to understand the fundamentals of catalytic activity and selectivity. In this work, Pt-Fe bimetallic catalyst supported on CeO₂ was found to enhance the oxidation activity by 17-fold compared to the mono-Pt catalyst prepared by the same method. Concentration-time profiles were collected experimentally to understand the effect of various parameters on the rate of reaction, and validate the kinetic models based on different mechanisms. These results are helpful to discern the underlying reaction mechanisms on mono- and bimetallic Pt-based catalysts.

Keywords

selective oxidation, ethylene glycol, glycolic acid, kinetic modeling

Introduction

Ethylene glycol (EG) is the smallest polyol molecule that can be produced by hydration of ethylene oxide or hydrogenolysis of biomass (Sun and Liu 2011). Catalytic conversion of EG into glycolic acid (GA) is attractive since GA is an essential additive in skin care products, textile and food processing, and also a valuable commodity chemical precursor in polymer synthesis. The current industrial process for glycolic acid involves hydrolysis of monochloroacetic acid or carbonylation of formaldehyde (Case 2009). Approximately 94% GA yield is reported by reacting formaldehyde with CO and water (John 1939). However, the use of strong acid catalysts (concentrated sulfuric acid or chloric acid), and harsh reaction conditions (200 °C, 900 atm CO pressure) demand safer and greener alternative pathways. Currently, the oxidation of ethylene glycol to glycolic acid by heterogeneous catalysts has been studied only to a limited extent (Mitsui-Chemicals 1995, Berndt, Pitsch et al. 2003, Case 2009, Griffin, Rodriguez et al. 2013). The design of new catalysts is required to improve the oxidation rates and glycolic acid selectivity. Moreover,

systematic kinetics or mechanistic studies have also not been reported for this important reaction. This work reports new CeO₂-supported Pt-Fe catalysts that show remarkable glycolic acid yields during EG oxidation.

Experimental

The Pt/CeO₂ and Pt-Fe/CeO₂ were synthesized by a one-pot solvothermal method, as described in our previous publication (Jin, Zhao et al. 2016).

Experimental data for the kinetics study was collected from a 100 mL semi-batch reactor equipped with precise temperature and pressure control (Figure 1). The experimental conditions are: T = 50-100 °C; P_{O₂} = 15-60 bar; initial EG concentration = 0.15-0.60 mol/L in water solution; NaOH:EG molar ratio = 0-2 (NaOH is used as an alkali promoter); catalyst amount = 0.5-2 g; A software, Athena Visual Studio, was used to solve rate equations and mass balance equations simultaneously for determination of rate parameters, as well as the statistical analysis for model discrimination.

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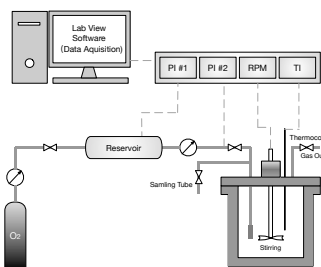


Figure 1. Batch slurry reaction setup for kinetic experiments (100 ml reactor vessel)

Preliminary results and discussion

As can be seen from Figure 2, the bimetallic PtFe catalyst gives a significantly higher activity compared to the monometallic Pt catalyst. Using PtFe catalyst, EG can be completely converted in only 4 hours while the Pt catalyst gives much less conversion in the same duration. The calculated initial TOF for PtFe is about 19.1 sec^{-1} which is more than 17 times higher than that of Pt catalyst ($\text{TOF}=1.11 \text{ sec}^{-1}$).

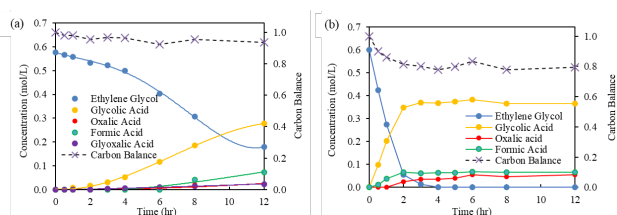


Figure 2. Concentration-time profile of (a) Pt/CeO₂ and (b) PtFe/CeO₂ on ethylene glycol oxidation in aqueous solution with addition of alkali promoter. Reaction conditions: 0.58 mol/L initial EG conc., initial pH=13.9 (NaOH added), EG:metal ratio = 5657:1 (mol:mol), 70 °C, 1atm O₂, 60 mL/min

Concentration-time profiles at different reaction conditions were collected for both Pt and Pt-Fe catalysts to understand the effect of various parameters on their reaction rates. These parameters include the initial EG concentration, reaction temperature, O₂ pressure, alkali concentration, and catalyst loading. An example of O₂ pressure effect and initial EG concentration effect for the mono Pt catalyst is shown as Figure 3. Before using the experimental data to determine rate equations and estimate intrinsic kinetic parameters, gas-liquid, liquid-solid and intraparticle mass transfer limitations were evaluated using standard criteria ((Chaudhari and Ramachandran 1980) to ensure that the reaction occurs in the kinetically controlled regime.

Based on temporal concentration profiles and proposed mechanism, microkinetic models are being developed for the bimetallic catalyst to discriminate different reaction pathways based on elementary steps involved in the catalytic cycle. Such results along with a proposed reaction mechanism will be presented.

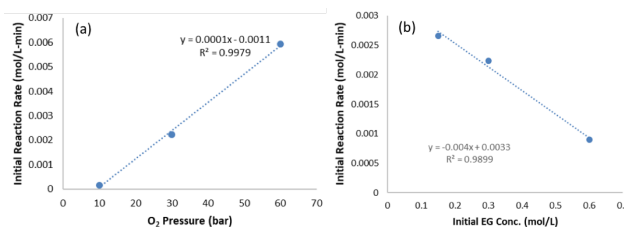


Figure 3. Effects of O₂ pressure and EG concentration on initial reaction rate

Conclusions

In this work, we developed a Pt-Fe bimetallic catalyst that gives high glycolic acid yield (62%) and activity ($\text{TOF} = 19.1 \text{ sec}^{-1}$, based on initial EG conversion). According to concentration-time profiles at different reaction condition, a plausible reaction mechanism was proposed. At the end of this work, a reliable kinetic model was obtained to describe the EG-to-GA oxidation in the aqueous phase which can be useful not only to reflect on the catalytic reaction mechanism but also provide rate parameters for design purpose.

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