

# KINETIC MODELING OF AQUEOUS PHASE GLYCEROL HYDROGENOLYSIS IN A BATCH SLURRY REACTOR

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## Summary

Catalytic hydrogenolysis of poly-hydroxy compounds, such as glycerol, is an important class of reaction in the conversion of biomass to fuels and chemicals. In this paper, we report the activity and selectivity of bimetallic Ru-Re catalyst for hydrogenolysis of glycerol and a detailed kinetic modeling of the complex multi-step reactions involved. For kinetic modeling, several experiments were carried out in a batch slurry reactor in which both gas and liquid phase product distributions were measured. Experimental data at different glycerol concentrations and catalyst loading, with and without external H<sub>2</sub> addition, over a temperature range of 453-493 K were obtained. The evaluation of different rate mechanisms based on model discrimination will also be discussed.

## Keywords

Biomass, bimetallic catalysts, multiphase slurry reactor, kinetics.

## Introduction

In our search for renewable resources for fuels and chemicals, conversion of biomass and vegetable oils to useful products has received particular attention. Biodiesel production via the transesterification of fatty acid methyl esters (FAME) is already at an advanced stage of commercialization, the economics of which depends on the utilization of the glycerol byproduct produced in large quantities. Since glycerol can also be derived from many other biomass sources, its conversion is generally considered as an important process. Among many possibilities, hydrogenolysis of glycerol to 1,2 propanediol (1,2 PDO) and ethylene glycol (EG) is an important example because of its attractiveness to obtain these commodity products not only cheaper than the petroleum routes but also from renewable feedstocks. The process involves catalytic hydrogenolysis in the aqueous phase, which represents a class of reactions useful in conversion of many other polyhydroxy compounds to industrial chemicals. The aim of this work was to investigate the aqueous phase hydrogenolysis of glycerol using bimetallic Ru-Re catalysts in a slurry reactor with the objective of understanding the catalytic activity and selectivity of this multi-step reaction system. A detailed kinetic study including discrimination of different rate models and evaluation of kinetic parameters will be presented.

Hydrogenolysis of glycerol has been reported previously using several supported transition metal catalysts such as Ru,<sup>1</sup> Pt,<sup>2</sup> Cu,<sup>3</sup> Ni<sup>4</sup> including some bimetallic catalysts consisting of Pt-Ru, Au-Ru<sup>5</sup> and Ru-

Re<sup>6</sup>. The activity of different supported metal catalysts for glycerol hydrogenolysis follows the order: Ru  $\approx$  Cu  $\approx$  Ni > Pt > Pd.<sup>7</sup> It is known that a series of reactions occur during hydrogenolysis leading to gas and liquid phase products and hence a challenge to achieve high selectivity to desired products like 1,2 PDO. Lahr et al<sup>8</sup> studied the kinetics of glycerol hydrogenolysis using 5% Ru/C under basic conditions (at pH 8 and 11.7). However, the interpretation of the kinetics is based on an empirical model and did not consider all the relevant reactions involved. In fact, there have been virtually been no detailed kinetic modeling investigations on any of these catalysts especially considering the complex reaction network in glycerol hydrogenolysis. Such an effort is essential to a reliable understanding of the catalytic activity-selectivity behavior.

In our recent study, we found that supported Ru-Re bimetallic catalyst outperforms the supported Ru catalyst (conversion: 43% and 52%; selectivity to 1,2-PDO: 50% and 20% respectively) for glycerol hydrogenolysis. In particular, the Ru-Re catalyst reduced the gaseous product formation (methane, ethane, etc.) compared to the Ru catalyst. A similar trend was reported earlier by Ma et al<sup>6</sup>, however, a detailed analysis of the liquid as well as gas phase products was not attempted in their work. Therefore, it was deemed worthwhile to study the hydrogenolysis using Ru-Re bimetallic catalyst which gives better selectivity to the desired 1,2-PDO product. The aim of this work was to study the activity and selectivity of Ru-Re

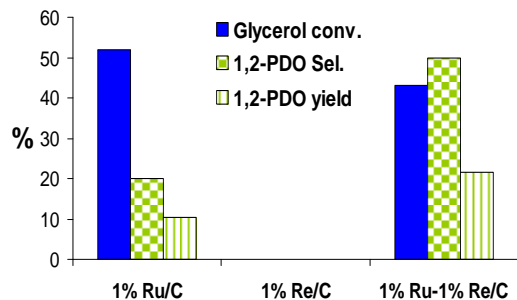
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bimetallic catalyst and to develop a batch slurry reactor model for analysis of the reaction kinetics.

## Results

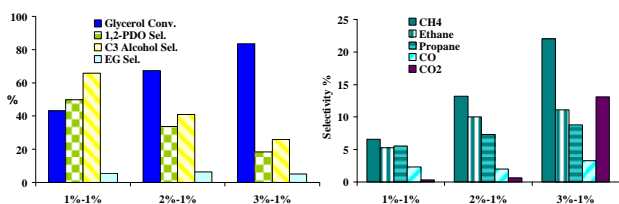
In a few preliminary experiments, catalysts consisting of only ruthenium and only rhenium were evaluated against the bimetallic ruthenium-rhenium supported catalyst as shown in Figure 1. Rhenium was found to have a prominent effect as a promoter on the selectivity of liquid products. Another important characteristic observed with Re promoted catalyst was that by itself, it has no activity in hydrogenolysis of glycerol.



**Figure 1.** Conversion and selectivity data for monometallic and bimetallic Ru-Re/C catalysts.

Reaction conditions: glycerol: 1 kmol/m<sup>3</sup>; catalyst: 0.25 g; P<sub>H<sub>2</sub></sub>: 41 bar; solvent: H<sub>2</sub>O; Liq. Vol.: 30 ml; batch time: 6 h.

The effect of ruthenium loading is shown in Figure 2. Increasing ruthenium content promotes aqueous phase reforming (APR) leading to a higher amount of gas phase products.

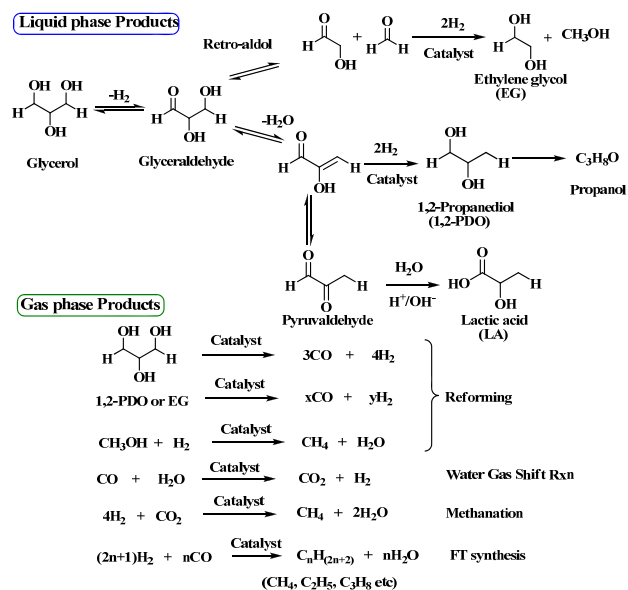


**Figure 2.** Effect of Ru loading on conversion and liquid (left) and gas (right) phase products selectivity. Reaction conditions as given in Figure 1.

The kinetic experiments were carried out using Ru-Re catalyst in a multiple slurry reactor system wherein six reactions can be carried out in parallel under different temperature-pressure conditions. Several diagnostic experiments were carried out with each identified product to understand the reaction network. The possible reactions in aqueous phase glycerol hydrogenolysis are shown in Figure 3.

For the kinetic study, the effects of glycerol concentration, H<sub>2</sub> pressure, catalyst loading, and temperature (453-493K) on concentration vs. time profiles were investigated. A detailed analysis of the kinetic models following the rigorous model discrimination procedure will be presented using a batch slurry reactor model, which

describes the concentration-time profiles of all the gas and liquid phase products.



**Figure 3.** Possible reactions in glycerol hydrogenolysis

The results from this study will be useful in understanding the mechanism of the reactions involved in hydrogenolysis as well as the modeling of slurry and fixed bed reactors.

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