



A comprehensive kinetic model for Cu catalyzed liquid phase glycerol hydrogenolysis



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ABSTRACT

Hydrogenolysis of biomass-derived glycerol has been investigated as an alternative route for the production of value-added chemicals, such as 1,2-propanediol, also commonly denoted as propylene glycol (PG). Intrinsic glycerol hydrogenolysis kinetics have been acquired experimentally on a stable, commercial copper-based catalyst in an isothermal trickle-bed reactor at 463–513 K, hydrogen pressures from 6.5 to 8 MPa and space times (W/F_0) from 25 to 340 kg s mol⁻¹ resulting in glycerol/PG conversions from 1 to 75 mol%. The selectivity to PG amounts to at least 90%. For a given conversion, the lowest selectivity is observed at the highest temperature. Glycerol is predominantly dehydrated to acetol which is subsequently converted to PG. Co-feeding reaction products, *i.e.*, PG and water, does not affect the rate of glycerol conversion. Additionally, glycerol can lead to minor side reactions forming products such as 1,3-propanediol, ethylene glycol while PG can degrade to ethanol, methanol and propanol. A comprehensive kinetic model accounting not only for the formation of main reaction products but also of side products was constructed. The activation energy of the rate-determining step for glycerol dehydration towards acetol was estimated at 84 kJ mol⁻¹, exceeding that of the rate-determining step of the consecutive hydrogenation into PG by about 25 kJ mol⁻¹. The high selectivity towards PG is attributed to (1) the relatively lower surface reaction rates for the parallel and the consecutive side reactions and (2) its low affinity for adsorption on the catalyst surface compared to glycerol at the investigated experimental conditions.

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1. Introduction

Growing concerns about global climate change and the diminishing fossil reserves have been important driving factors for the development of technologies starting from renewable biomass resources instead of traditional petroleum [1,2]. In this regard the implementation of fatty acid methyl esters (biodiesel) as an automotive fuel has been gaining prominence, especially in the US and Europe. While biodiesel is more expensive to produce than petroleum-derived diesel, the formers' renewable nature and lower emissions have encouraged governments around the world to subsidize its production [3]. The energy policies around climate change are anticipated to further enhance the demand for bio-fuels in the short and long term [4]. These factors have thus lead to a widespread increase in the biodiesel production in the past decade and, as a corollary, to an over supply of the by-product glycerol. The latter is unavoidably produced with a yield of about 10%wt of the biodiesel, resulting in a decline in its price. The current price

for the highest quality glycerol is about \$1100/metric ton and that for lower grades between \$180–\$540/metric ton [5]. Consequently, one way to increase the sustainability and profitability of a biodiesel plant is to investigate potential new applications of glycerol as low-cost feedstock for functional derivatives or as a precursor of high value fine chemicals. This is even more relevant in the current scenario with sub \$40 per barrel oil prices, which increases the price difference between petroleum-derived diesel and biodiesel even further [6].

Glycerol valorization can be achieved through various routes [7]. An effective pathway to this purpose is situated in the production of chemicals which are conventionally derived from fossil resources through the petrochemical industry, hence, replacing a currently non-renewable production route with one which is renewable, environmentally friendly and potentially carbon neutral. Propane-1,2-diol (propylene glycol) is an example of such a non-toxic added-value chemical with applications in cosmetics, pharmaceuticals, polyester resins, de-icing, *etc.* It is conventionally produced through propylene oxide hydration, the latter being obtained from petroleum derived propylene [8]. However, an interesting alternative route is through the catalytic hydrogenolysis of glycerol.

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Nomenclature

Roman symbols

a_i	activity for component i (-)
C_t	total concentration of active sites ($\text{mol kg}_{\text{cat}}^{-1}$)
cn	carbon number (-)
E_a	activation energy (kJ mol^{-1})
Er_i	relative experimental error for response i corresponding to a 95% confidence level (-)
F_i	molar flow rate of component i (mol s^{-1})
f_i	fugacity for component i (MPa)
h	Planck constant (J s)
k_B	Boltzmann constant (J K^{-1})
K_i	equilibrium coefficient (reaction dependent)
k_i	rate coefficient (s^{-1})
L	molar flow rate in liquid phase (mol s^{-1})
n_{exp}	number of experiments (-)
n_p	number of parameters (-)
n_{rep}	number repeat experiments (-)
n_{resp}	number of responses (-)
p_t	total pressure (MPa)
R	universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
R_i	net rate of formation of component i ($\text{mol s}^{-1} \text{kg}_{\text{cat}}^{-1}$)
S	selectivity (-)
T	temperature (K)
V	molar flow rate in vapor phase (mol s^{-1})
w_j	weighing factor of response j during regression (-)
X	conversion (-)
x_i	mole fraction of i in liquid phase (-)
Y	yield (-)
y_i	mole fraction of i in vapor phase (-)
ΔG^0	standard Gibbs energy (kJ mol^{-1})
ΔH^0	standard enthalpy change (kJ mol^{-1})
ΔS^0	standard entropy change ($\text{kJ mol}^{-1} \text{K}^{-1}$)
W	catalyst mass (kg)
SSQ	residuals sum of squares (-)

Greek symbols

β	model parameter
μ_i	chemical potential of component i (J mol^{-1})
ϕ	fugacity coefficient (-)
θ_i	fractional site coverage of component i (-)

Superscripts

\wedge	model calculated
l	liquid phase
v	vapor phase

Subscripts

A	acetol
G	glycerol
i, j	components
PG	propylene glycol

In the past few years, glycerol hydrogenolysis has been investigated extensively [9–18] in both gas and liquid phase. Investigations thus far have been performed towards developing the process [18] and effective catalysts [9–12]. Transition and noble metals have been dealt with, Cu, Ru and Ni being most popular [19–21]. Although the activity of the noble metal catalysts was found to exceed that of the transition metals, the selectivity towards side products such as 1,3-propanediol and ethylene glycol was reported to be higher on the former compared to the latter [11]. Among transition metals, Ru catalysts exhibit a lower

selectivity towards propylene glycol due to more pronounced C–C bond scissions, hence, yielding more ethylene glycol and gaseous by-products as compared to Cu based catalysts [13]. The latter are known for their selective C–O bond scission performance [14] and, hence, exhibit a superior performance in terms of selectivity towards propylene glycol.

Depending on the catalyst and the operating conditions used, glycerol hydrogenolysis can proceed through two principle mechanisms: a dehydration–hydrogenation mechanism occurs with 1-hydroxyacetone (acetol) as the intermediate [18,15] and a dehydrogenation–dehydration–hydrogenation reaction with 2,3-dihydroxy-propanal (glyceraldehyde) as the intermediate [14,10]. Acetol being observed as an intermediate in the presence of Cu-based catalysts such as copper-silica [16] and copper-alumina [17] supports the former, i.e., the dehydration–hydrogenation mechanism. A bi-functional route has been suggested by various authors with the dehydration step catalyzed by acid sites (usually from the support) and hydrogenation catalyzed by the metal [22,15,23]. However, among other things based on a widely reported linear relation between the active Cu surface area and hydrogenolysis activity [17,16,24–26], the unique role of metallic copper in promoting both glycerol dehydration and hydrogenation has been generally accepted.

Although glycerol hydrogenolysis has received significant research interest in the past decade, few studies have been performed on understanding the detailed kinetics of the reaction. Liquid phase experiments have been preferred for kinetic studies. Lahr and Shanks [27] developed a Langmuir–Hinshelwood type model for kinetics acquired on a commercial Ru/C catalyst and indicated the importance of the competitive adsorption of the main reaction products. However, the model did not explicitly account for the intermediate reaction steps and, hence, could not provide adequate mechanistic insights. Zhou et al. [28] derived a Langmuir–Hinshelwood type model over a Cu–ZnO–Al₂O₃ catalyst using a fixed-bed tubular reactor. Essential features of this model were the slow nature of the glycerol dehydration towards acetol and the weak adsorption of propylene glycol. Torres et al. [29] derived power law rate equations to quantify the relative importance of the side reactions over a bimetallic Ru–Re catalyst. Finally, Vasiliadou and Lemonidou [16] derived power law kinetics over a Cu–SiO₂ catalyst using a batch reactor based on the dehydration–hydrogenation mechanism. A weak PG formation rate on the glycerol concentration and a first order dependence of hydrogen concentration was reported.

The present work aims at investigating the liquid phase glycerol hydrogenolysis kinetics over a stable, commercial Cu based catalyst in a fixed bed tubular reactor. Intrinsic kinetic experiments have been performed by varying operating conditions such as temperature, hydrogen pressure and feed concentration at different space times, W/F_G^0 in order to investigate their effect on the catalytic performance. Based on the experimental observations an intrinsic kinetic model is developed, aiming at a quantified understanding of the catalytic chemistry both for the main and the side products in a wider range of operating conditions, including feedstock composition.

2. Procedures

2.1. Catalyst and materials

Commercial glycerol and propylene glycol with 99.5% purity was used. 99.99% nitrogen and hydrogen were obtained from Air-Liquide. A commercial, Cu based catalyst on an inert support was used which exhibited the following typical properties: BET surface area of $60 \text{ m}^2 \text{ g}^{-1}$, Cu particle diameter of 10 nm, Cu surface

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