

Kinetics of Hydrogenolysis of Glycerol to Propylene Glycol over Cu-ZnO-Al₂O₃ Catalysts^{*}

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Abstract A series of Cu-ZnO-Al₂O₃ catalysts with various metal compositions of Cu/Zn/Al were prepared by the co-precipitation method, and screened for glycerol hydrogenolysis to propylene glycol. The catalyst with a Cu/Zn/Al molar ratio of 1 : 1 : 0.5 exhibited the best performance for glycerol hydrogenolysis, and thus selected for kinetic investigation. Under elimination of external and internal diffusion limitation, kinetic experiments were performed in an isothermal fixed-bed reactor at a hydrogen pressure range of 3.0–5.0 MPa and a temperature range of 493–513 K. Based on a dehydration-hydrogenation two-step hydrogenolysis mechanism, a two-site Langmuir-Hinshelwood kinetic model taking into account competitive adsorption of glycerol, acetol and propylene glycol was proposed and successfully fitted to the experimental data. The average relative errors between observed and predicted outlet concentrations of glycerol and propylene glycol were 6.3% and 7.6%, respectively. The kinetic and adsorption parameters were estimated by using the fourth-order Runge-Kutta method together with the Rosenbrock algorithm. The activation energies for dehydration and hydrogenation reactions were 86.56 and 57.80 kJ·mol⁻¹, respectively.

Keywords kinetics, hydrogenolysis, glycerol, propylene glycol, catalyst

1 INTRODUCTION

The rapid development of biodiesel production by transesterification of vegetable oils or animal fats with methanol or ethanol yields large amounts of glycerol as a by-product. The influx of the biodiesel-derived glycerol into the commodity glycerol market leads to a rapid decline in the glycerol price, which in turn increases the production cost of biodiesel. Therefore, conversion of glycerol into high value-added chemicals is desirable, which will help to improve the economy of the biodiesel industry. Among the plentiful chemicals derived from glycerol, propylene glycol has attracted much attention from researchers in recent years because of its wide applications in pharmaceuticals, antifreezers, foods, agricultural adjuvants, *etc* [1–4].

The route of catalytic hydrogenolysis of renewable glycerol to propylene glycol is now being recognized as a green and sustainable process in comparison with the commercial petroleum-based route by which propylene glycol is produced by the hydration of propylene oxide [5]. Up to now, a lot of effort have been made for efficient hydrogenolysis of glycerol to propylene glycol [6–22]. Depending on catalysts and operating conditions, the reaction of glycerol hydrogenolysis is usually supposed to proceed through either dehydration of glycerol to acetol over acid catalysts followed by hydrogenation on metal catalysts [6–16] or dehydrogenation of glycerol to glyceraldehyde over basic catalysts or in basic solution followed

by dehydration to 2-hydroxyacrolein and hydrogenation to propylene glycol [17–22]. The representative studies on the dehydration-hydrogenation route were made by Suppes *et al.* [6–9] and Tomishige *et al.* [10–12], who used copper-chromite catalysts and hybrid Ru/C (Rh/SiO₂) + Amberlyst catalysts, respectively. As for the dehydrogenation-dehydration-hydrogenation route, Montassier *et al.* [17], Maris and Davis [18] made systematic investigation. Recently, Cu-ZnO-based catalysts were found to be highly efficient for catalytic hydrogenolysis of glycerol [13–16]. High conversion of glycerol and selectivity to propylene glycol was obtained over Cu-ZnO-based catalysts at proper conditions [15].

However, it is noted that all the above investigations focused on catalyst preparation and characterization as well as optimization of process variables in order to increase glycerol conversion and selectivity to propylene glycol, and none was concerned with reaction kinetics of glycerol hydrogenolysis. In fact, to the best of our knowledge, very few results on the reaction kinetics have been reported so far. Lahr and Shanks [19, 20] developed a Langmuir-Hinshelwood-type model to describe glycerol hydrogenolysis, and addressed the importance of competitive adsorption between polyols. Unfortunately, just as pointed out by themselves, this model only provided an overall description for the reaction of glycerol hydrogenolysis, and did not capture all the steps involved in the detailed mechanism. Miller *et al.* [21] derived a kinetic model based on the dehydrogenation-dehydration-hydrogenation reaction mechanism. However, the kinetic investigation was

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conducted under the effect of mass and heat transport, which made the estimation of kinetic parameters intractable and intangible. In view of the deficiency in the reaction kinetics of glycerol hydrogenolysis in spite of its well-known importance, much work needs to be done in this field.

In this work, a series of Cu-ZnO-Al₂O₃ catalysts with different metal compositions are firstly prepared and tested for glycerol hydrogenolysis, and then the reaction kinetics is studied over the screened high-performance catalyst. The objective of this work is to develop a rigorous and reliable kinetic model for the hydrogenolysis reaction of glycerol to propylene glycol, which is qualified for simulation and optimization of different-scale reactors for glycerol hydrogenolysis.

2 EXPERIMENTAL

2.1 Reagents

Na₂CO₃ (99%), NH₃·H₂O (28%), glycerol (99%), *n*-butanol (99%), and the metal nitrate precursors, *i.e.*, Cu(NO₃)₂·3H₂O (99%), Zn(NO₃)₂·6H₂O (99%) and Al(NO₃)₃·9H₂O (99%), were purchased from Sino-pharm Group Chemical Reagent. Acetol (95%), 2-butanone (99%), ethylene glycol (99%), and propylene glycol (99%) were ordered from Alfa Aesar and used as standard chemicals for gas chromatographic analysis of products of glycerol hydrogenolysis.

2.2 Catalyst preparation

The Cu-ZnO-Al₂O₃ catalysts were prepared using the co-precipitation method. Firstly two mixtures were obtained by adding 10% NH₃·H₂O (prepared by dilution of a 28% NH₃·H₂O) into 1 mol·L⁻¹ Al(NO₃)₃ solution until pH 7.0, and by adding 0.5 mol·L⁻¹ Na₂CO₃ solution into a mixed solution of 1 mol·L⁻¹ Cu(NO₃)₂ and 1 mol·L⁻¹ Zn(NO₃)₂ until pH 7.5, respectively. Then the as-prepared two solutions were mixed under

vigorous stirring for 3 h at 343 K and kept at static condition for 2 h. After precipitation, the suspension was washed and filtered until the filtrate was neutral. The washed precipitate was dried at room temperature for 12 h and then at 393 K for 24 h. The catalysts were finally obtained by calcination of the precipitate in air at 723 K for 5 h. The catalysts prepared had various metal compositions of Cu/Zn/Al, as listed in Table 1.

2.3 Activity test

The catalytic activity of the catalysts for glycerol hydrogenolysis was tested in a tubular fixed-bed reactor (inner diameter of 10 mm and length of 450 mm). A schematic diagram of the experimental setup was shown in Fig. 1. Prior to each test, a certain amount of catalysts ($d_p = 0.34$ mm, or 40–60 mesh) were *in-situ* reduced in a flow of a mixture of hydrogen and nitrogen (50 : 50, by volume) from room temperature to 573 K (ramp of 5 K·min⁻¹) and kept at 573 K for 4 h. After reduction, the nitrogen feed was stopped, and temperature and pressure were adjusted to the desired values and stabilized for 2 h. Finally, the aqueous glycerol solution was fed into the reactor. Except where specified otherwise, the initial mass concentration of the glycerol feedstock was kept at 80%. After each run, the liquid product was collected from the sampling pipe and was analyzed by a gas chromatograph. Meanwhile, the effluent gas was also analyzed. Conversion of the reactants and selectivity of the products were calculated on carbon basis, which was proposed by Miyazawa *et al.* [10], *i.e.*,

conversion =

$$\frac{\text{sum of C - based mol of all products}}{\text{sum of C - based mol of reactant}} \times 100\% \quad (1)$$

selectivity =

$$\frac{\text{C - based mol of the specific product}}{\text{sum of C - based mol of all products}} \times 100\% \quad (2)$$

Table 1 Effect of the metal composition of Cu-ZnO-Al₂O₃ catalysts on glycerol hydrogenolysis^①

Cu/Zn/Al molar ratio	Glycerol conversion/%	Selectivity/%			
		Propylene glycol	Acetol	Ethylene glycol	Others ^②
2 : 1 : 0.67	33.2	93.9	2.3	1.9	1.9
2 : 1 : 1.5	65.1	85.4	1.8	1.6	11.2
2 : 1 : 3	78.8	87.4	1.2	1.4	10.0
2 : 1 : 6	38.3	71.9	2.7	1.0	24.4
1 : 1 : 0.25	70.0	90.8	2.1	3.2	3.9
1 : 1 : 0.5	81.5	93.4	1.2	2.7	2.7
1 : 1 : 1	75.5	91.5	1.1	2.4	5.0
1 : 1 : 2	73.3	90.5	1.1	2.8	5.6
1 : 2 : 0.5	69.7	84.5	0.9	2.4	12.2

① Reaction conditions: 3.0 g catalyst ($d_p = 0.34$ mm, 40–60 mesh), LHSV (liquid hourly space velocity) = 4.6 h⁻¹, $T = 493$ K, $P_H = 4.0$ MPa, H₂/glycerol = 5 : 1 (molar ratio). ② Others: C₁, methanol, ethanol, propanol and unknown products.

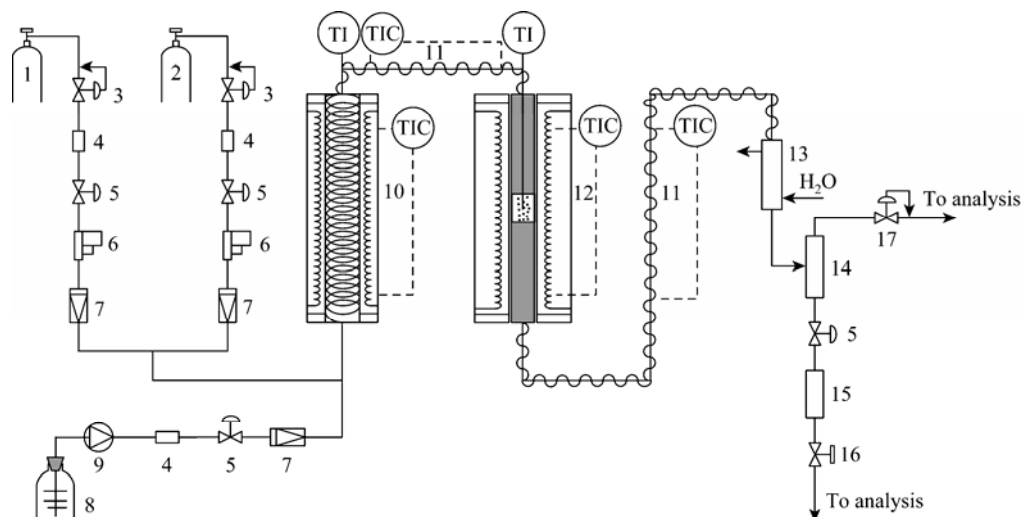


Figure 1 Schematic diagram of the experimental setup

1—nitrogen; 2—hydrogen; 3—pressure regulator; 4—filter; 5—ball valve; 6—mass flow controller; 7—check valve; 8—liquid feed; 9—metering pump; 10—preheater; 11—heater and thermal insulator; 12—reactor; 13—condenser; 14—gas-liquid separator; 15—sampling pipe; 16—needle valve; 17—back-pressure regulator

2.4 Kinetic study

The kinetic experiments were carried out in the same reactor as mentioned above. Preliminary tests were conducted in order to determine the experimental conditions for the kinetic investigation, under which effects of external and internal diffusion can be eliminated. The external diffusion effect was tested at various space times by changing the flow rate of the reactant, while the internal diffusion effect was checked by varying the particle size of the catalyst. Based on the preliminary tests, kinetic experiments were performed by varying the flow rates of hydrogen and aqueous glycerol as well as the molar ratio of hydrogen to glycerol at a hydrogen pressure of 3.0–5.0 MPa over a temperature range of 493–513 K.

The service time of the Cu-ZnO-Al₂O₃ catalyst used for the kinetic study was about 100 h, during which time the catalyst activity was stabilized. Under the same reaction condition, the glycerol conversion and the product distribution observed at the end of kinetic experiments were almost the same as those obtained at the beginning of the experiments.

2.5 Chemical analysis

The liquid products were analyzed by a Hewlett-Packard (HP) 6890 gas chromatograph equipped with a Supelcowax 10 capillary column (30 m×0.32 mm×

0.25 μm) and a flame ionization detector (FID). 2-butanone and *n*-butanol were used as the internal standard and the dilution solvent, respectively. The effluent gas was analyzed by two Agilent 4890 gas chromatographs, one with a HP-PLOT Al₂O₃ capillary column (30 m×0.53 mm×15 μm) and a FID used for the analysis of C₁–C₃ hydrocarbons, and the other with a Porapak Q (80–100 mesh) stainless steel packed column (3 m×2 mm) and a thermal conductivity detector (TCD) to analyze H₂, CO, CO₂, and CH₄.

3 KINETIC MODEL

The reaction mechanism of glycerol hydrogenolysis to propylene glycol has been investigated by many researchers [6, 7, 10, 11, 17, 18]. Among these researches, a two-step mechanism originally proposed by Suppes *et al.* [6], *i.e.*, glycerol is firstly dehydrated to acetol, and then acetol is hydrogenated to propylene glycol (shown in Fig. 2), has been widely proved and accepted for Cu-based catalysts [13–16].

Based on the two-step mechanism, a two-site Langmuir-Hinshelwood (L-H) kinetic model is proposed for glycerol hydrogenolysis. Organic molecules such as glycerol, acetol and propylene glycol adsorb on one type of the active sites, and dissociative hydrogen adsorption occurs on the other type. The two-site model and the dissociative hydrogen adsorption on the metal surface have been widely adopted in

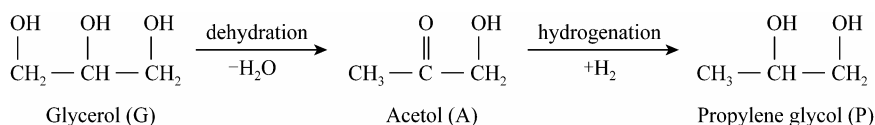
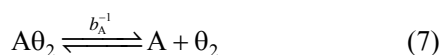
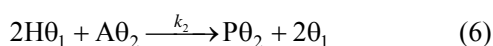
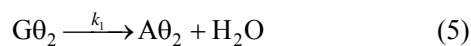
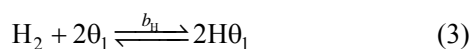


Figure 2 Reaction mechanism of glycerol hydrogenolysis to propylene glycol

the literature [23–25]. The competitive adsorption between polyols, such as glycerol and propylene glycol, was also evidenced by Lahr and Shanks [19, 20]. The reaction mechanism is thus given by



where θ_1 and θ_2 denote the active sites for hydrogen and organic molecules, respectively. b_H , b_G , b_A , and b_P are the adsorption constants of hydrogen, glycerol, acetol and propylene glycol, respectively. k_1 and k_2 represent the rate constants of glycerol dehydration to acetol and acetol hydrogenation to propylene glycol, respectively. Taking into account the steady-state assumption for adsorbed intermediates, the rate expressions for the above two reactions can be finally derived as follows:

$$r_1 = \frac{k_1 b_G c_G}{1 + b_G c_G + b_A c_A + b_P c_P} \quad (9)$$

$$r_2 = \frac{k_2 b_A c_A b_H P_H}{(1 + b_G c_G + b_A c_A + b_P c_P)(1 + \sqrt{b_H P_H})^2} \quad (10)$$

where c_G , c_A , c_P are the molar concentrations of glycerol, acetol and propylene glycol, respectively. P_H is the hydrogen pressure. The temperature dependences of rate constants and equilibrium constants can be expressed as follows:

$$k_i = k_i^0 \exp[-E_i / (R_g T)], \quad i = 1, 2 \quad (11)$$

$$b_j = b_j^0 \exp[Q_j / (R_g T)], \quad j = \text{G, A, P, H} \quad (12)$$

where E_i is the activation energy of the i th reaction, and Q_j is the adsorption activation energy of species j . For the fixed-bed reactor, the mass balance for glycerol and propylene glycol are given by

$$\frac{dF_G}{dm_C} = -r_1 \quad (13)$$

$$\frac{dF_P}{dm_C} = r_2 \quad (14)$$

where F_G and F_P are the molar flow rates of glycerol and propylene glycol, respectively, and m_C is the catalyst mass. Eqs. (13) and (14) correlate the operation conditions with the kinetic model, Eqs. (9) and (10).

Twelve kinetic and adsorption parameters in Eqs. (11) and (12) involved in the kinetic model need to be determined from the experimental data, which are

collected from 36 experimental runs. The ordinary differential equations are solved by the fourth-order Runge-Kutta method, and the twelve unknown parameters are estimated by the Rosenbrock algorithm [26], which minimizes the residual sum of squares, f , between the experimental concentrations of glycerol and propylene glycol at the exit of the reactor and the calculated values obtained from the above model, *i.e.*,

$$f = \sum_{i=1}^N \left[(c_{G,\text{exp}}^i - c_{G,\text{cal}}^i)^2 + (c_{P,\text{exp}}^i - c_{P,\text{cal}}^i)^2 \right] \quad (15)$$

The physical properties that are used in this work, *i.e.*, density and vapor pressure, are provided by Yaws [27] and Reid *et al* [28].

4 RESULTS AND DISCUSSION

4.1 Catalyst screening

As listed in Table 1, a series of Cu-ZnO-Al₂O₃ catalysts with different metal composition are prepared and tested for glycerol hydrogenolysis. Glycerol conversion varies from 33.2% to 81.5% and selectivity to propylene glycol varies from 71.9% to 93.9%. The high selectivity to propylene glycol demonstrates that Cu-ZnO-Al₂O₃ is an effective catalyst for the hydrogenolysis reaction of glycerol to propylene glycol. Besides glycerol and propylene glycol, methane, methanol, ethanol, ethylene glycol, propanol, acetol, and some unknown compounds are more or less detected in the product. The presence of trace amounts of acetol further validates the dehydration-hydrogenation two-step reaction mechanism for glycerol hydrogenolysis over Cu-ZnO-Al₂O₃ catalysts.

Effects of Cu and ZnO on glycerol hydrogenolysis have been comprehensively studied in the literature [13–16], revealing that ZnO catalyzes dehydration of glycerol to acetol and that acetol hydrogenation to propylene glycol occurs on Cu sites. As for Al₂O₃, it is observed from Table 1 that an increase in the amount of Al in the catalyst will on one hand make the glycerol conversion show a trend of first increase and then decrease, but on the other hand yield more byproducts. The incorporation of Al₂O₃ into the Cu/Zn mixed-metal oxide system changes the metal composition of the catalyst as well as its texture, which in turn modifies the acidic-basic property of the catalyst and finally results in the complex variation of the glycerol conversion and the selectivity of the products [13–16]. A dramatic decrease in glycerol conversion is observed when the Cu/Zn/Al molar ratio is 2 : 1 : 6, which might be due to the insufficient amount of Cu and ZnO in the catalyst considering the important roles of Cu (hydrogenation effect) and ZnO (dehydration effect) for the hydrogenolysis reaction. As shown in Table 1, the Cu-ZnO-Al₂O₃ catalyst with a Cu/Zn/Al molar ratio of 1 : 1 : 0.5 exhibits the best performance, glycerol conversion being 81.5% and selectivity of propylene glycol 93.4%. Therefore, this catalyst is selected for further kinetics investigation.

4.2 Kinetics

In order to obtain experimental data applicable to the intrinsic kinetic model, influences of internal and external diffusions have to be eliminated. Four sizes of catalyst powders, *i.e.*, 20–40 mesh (average particle size $d_p = 0.64$ mm), 40–60 mesh ($d_p = 0.34$ mm), 60–80 mesh ($d_p = 0.22$ mm) and 80–100 mesh ($d_p = 0.17$ mm), are used to check the effect of the internal diffusion resistance. It is found from Fig. 3 that the internal diffusion limitation can be ignored when the catalyst size is reduced to 0.22 mm. Fig. 4 shows that there is no difference in the glycerol conversion under two different catalyst loadings of 2.0 g and 3.0 g when the liquid hourly space velocity (LHSV) is higher than 10.5 h^{-1} , which indicates that at this point or higher the external mass transfer limitation can be neglected. Based on the aforementioned results, 36 reaction runs for the kinetic model development are performed under the following conditions: $T = 493\text{--}513 \text{ K}$, $P_H = 3.0\text{--}5.0 \text{ MPa}$, $\text{LHSV} = 10.5\text{--}15.1 \text{ h}^{-1}$, $\text{H}_2/\text{glycerol}$ (molar ratio) = 5–7, and $d_p = 0.17 \text{ mm}$ (80–100 mesh).

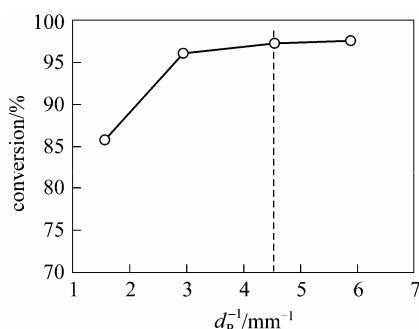


Figure 3 Effect of catalyst size on the glycerol conversion
 $T = 513 \text{ K}$, $P_H = 5.0 \text{ MPa}$, $\text{LHSV} = 4.6 \text{ h}^{-1}$, $\text{H}_2/\text{glycerol}$ (molar ratio) = 5 : 1

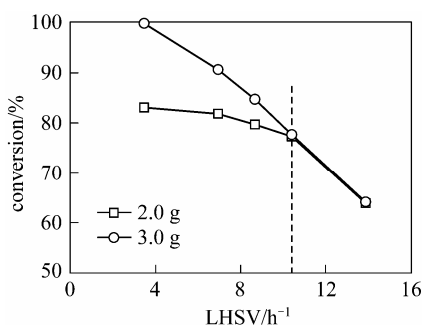
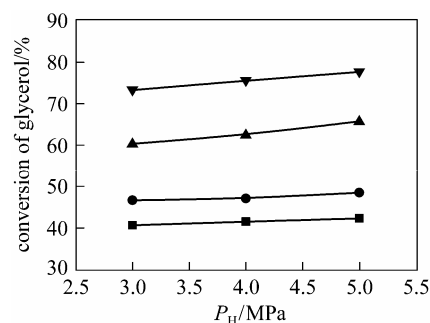
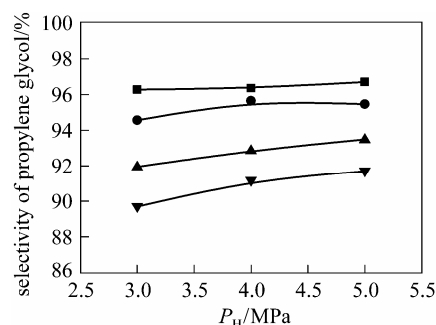


Figure 4 Effect of liquid hourly space velocity on the glycerol conversion
 $T = 513 \text{ K}$, $P_H = 5.0 \text{ MPa}$, $d_p = 0.17 \text{ mm}$, $\text{H}_2/\text{glycerol}$ (molar ratio) = 5 : 1

Typical experimental results for glycerol hydrogenolysis are presented in Fig. 5. It is observed that higher temperature and pressure result in higher conversion of glycerol, while lower temperature and higher pressure lead to higher selectivity to propylene glycol. Compared with pressure, reaction temperature



(a) Conversion of glycerol



(b) Selectivity of propylene glycol

Figure 5 Effects of reaction temperature and hydrogen pressure on glycerol conversion and selectivity of propylene glycol

[$\text{LHSV} = 10.5 \text{ h}^{-1}$, $\text{H}_2/\text{glycerol}$ (molar ratio) = 5 : 1]
 T/K : ■ 493; ● 500; ▲ 506; ▼ 513

Table 2 Estimated kinetic parameters from experimental data

	Parameter	
	Preexponential factor ^①	activation energy ^②
k_1	1.54×10^4	86.56
k_2	7.16×10^3	57.80
b_G	2.22×10^{-3}	36.42
b_A	8.73×10^{-3}	25.94
b_P	5.80×10^{-3}	25.77
b_H	1.86×10^{-5}	36.24

① The units for k_i and b_i (exclude H_2) are $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ and $\text{m}^3 \cdot \text{mol}^{-1}$, respectively; the unit for b_H is MPa^{-1} . ② The unit for activation energy is $\text{kJ} \cdot \text{mol}^{-1}$.

has a pronounced effect on glycerol conversion and selectivity of propylene glycol.

The estimated values for the twelve kinetic and adsorption parameters are summarized in Table 2. The activation energy for glycerol dehydration over the $\text{Cu-ZnO-Al}_2\text{O}_3$ catalyst is regressed to be $86.56 \text{ kJ} \cdot \text{mol}^{-1}$, which is consistent with the calculation data ($83.74\text{--}104.67 \text{ kJ} \cdot \text{mol}^{-1}$) based on quantum mechanism [29]. The activation energy for acetol hydrogenation is about 30 kJ lower than that of glycerol dehydration, indicating that the rate of the second step (acetol hydrogenation) is much faster than that of the first step (glycerol dehydration). Taking 493 K as an

example, the rate constants for the first and second step are 1.05×10^{-5} and $5.40 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$, respectively. This result is in accordance with that reported by Suppes and Sutterlin [8].

Based on the adsorption parameters listed in Table 2, it can be calculated that, under the experimental conditions in this study, the adsorption rate constants of glycerol, acetol and propylene glycol have the following order: $b_G > b_A > b_P$, which indicates that glycerol has the highest affinity for catalytic active sites among the three species, and propylene glycol is the most weakly adsorbed component. The strongly adsorbed glycerol and the weakly adsorbed propylene glycol guarantee the hydrogenolysis of glycerol to propylene glycol with high conversion and selectivity.

The average relative errors for glycerol and propylene glycol are individually calculated according to the following definition:

$$E(\%) = \frac{\sum_i^N \left| \frac{c_{\text{exp}}^i - c_{\text{cal}}^i}{c_{\text{exp}}^i} \right|}{N} \times 100\% \quad (16)$$

As shown in Fig. 6, the observed outlet concentrations of glycerol and propylene glycol are in good agreement with the predicted values, and the average relative errors for glycerol and propylene glycol are 6.3% and 7.6%, respectively. It demonstrates that the proposed two-site L-H model can describe very well the reaction kinetics of glycerol hydrogenolysis to propylene glycol over the Cu-ZnO-Al₂O₃ catalyst.

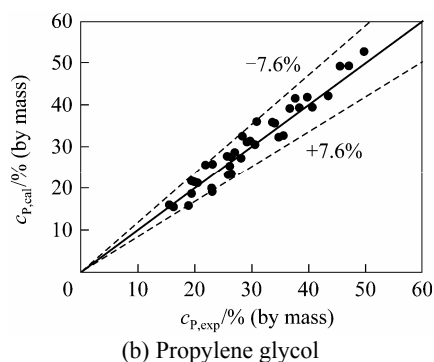
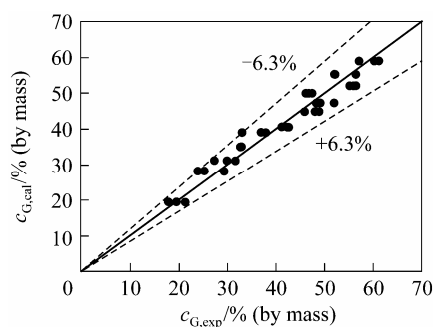


Figure 6 Comparison of experimental and calculated concentrations of glycerol and propylene glycol

The above results show that the intrinsic kinetic model is reliable for glycerol hydrogenolysis over Cu-ZnO-Al₂O₃. Combining this kinetic model with mass and heat transfer models, a mathematical model can be developed and used for simulation of the performance of a large-scale trickle-bed reactor. The corresponding experimental and theoretical work is being performed in the authors' laboratory.

5 CONCLUSIONS

Among a series of Cu-ZnO-Al₂O₃ catalysts prepared by co-precipitation method, the catalyst with a Cu/Zn/Al molar ratio of 1 : 1 : 0.5 showed the best performance for glycerol hydrogenolysis to propylene glycol. This catalyst was selected for kinetic studies on glycerol hydrogenolysis. Experimental results showed that high glycerol conversion can be obtained at high temperature and pressure, while low temperature and high pressure benefit selectivity to propylene glycol.

A two-site Langmuir-Hinshelwood kinetic model based on a dehydration-hydrogenation two-step mechanism was developed for the hydrogenolysis reaction of glycerol to propylene glycol. This model described well the experimental data, the average relative errors between observed and predicted outlet concentrations of glycerol and propylene glycol being 6.3% and 7.6%, respectively. Analysis of the kinetic and adsorption parameters revealed that the reaction of glycerol dehydration to acetol was much slower than the reaction of acetol hydrogenation to propylene glycol, and propylene glycol was the most weakly adsorbed species among glycerol, acetol and propylene glycol.

NOMENCLATURE

b_j	adsorption rate constant for species j , $\text{m}^3 \cdot \text{mol}^{-1}$
b_j^0	preexponential factor of adsorption rate constant for species j , $\text{m}^3 \cdot \text{mol}^{-1}$
c	molar concentration, $\text{mol} \cdot \text{m}^{-3}$
E_i	activation energy of the i th reaction, $\text{kJ} \cdot \text{mol}^{-1}$
F	molar flow rate, $\text{mol} \cdot \text{s}^{-1}$
k_i	rate constant of the i th reaction, $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$
k_i^0	preexponential factor of rate constant of the i th reaction, $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$
m_C	catalyst mass, g
N	number of experimental runs for kinetic study
P	pressure, MPa
Q_j	adsorption activation energy of species j , $\text{kJ} \cdot \text{mol}^{-1}$
R_g	universal gas constant, $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
r_i	rate of the i th reaction, $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$
T	temperature, K
θ_1, θ_2	active site

Subscripts

A	acetol
cal	calculated value
exp	experimental value
G	glycerol
H	hydrogen
P	propylene glycol

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