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Reaction Kinetics of Glycerol Steam Reforming Using a Ru/Al₂O₃ Catalyst

Ravi Sundari and Prakash D. Vaidya*

Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Road, Matunga, Mumbai-400019, India

ABSTRACT: Hydrogen (H₂) production by steam reforming represents a candidate method for the utilization of the surplus amounts of biodiesel's crude glycerol. In this work, reaction kinetics of glycerol steam reforming is studied in a fixed-bed reactor, using a Ru/Al₂O₃ catalyst. The investigated reaction belongs to the kinetically controlled reaction regime systems. It is found that, in the studied ranges of temperature, 350–500 °C, and W/F_{AO} ratio, 0.4–1.98 g h/mol, the reaction order with respect to glycerol is one. At 500 °C, the first-order reaction rate constant equals 4.2×10^5 cm³/(g_{cat} h). From the temperature dependence of the rate constant, the activation energy (21.2 kJ/mol) is evaluated. Finally, it is found that a heterogeneous kinetic model described in a previous work also suggests first-order kinetics at the low glycerol partial pressures used for this study. Using Ru/Al₂O₃, we have reported reaction kinetics at low temperatures ($T \leq 500$ °C). Our work will facilitate the design and operation of reactors producing H₂ from glycerol.

1. INTRODUCTION

Because of increased biodiesel production, a large amount of crude glycerol byproduct is formed in biodiesel facilities. Commonly, crude glycerol has several impurities, e.g. methanol, water, inorganic salts, free fatty acids, unreacted mono-, di- and triglycerides, methyl esters, and other organic materials.^{1,2} Many smaller biodiesel plants send it to water treatment for digestion; however, this process is slow, expensive and has low yield.3 Crude glycerol is a poor fuel which does not burn in petrol or diesel engines.⁴ It is no longer blended with fuel oil and burnt as fuel.⁵ Therefore, the larger biodiesel facilities refine glycerol by distillation and sell the purified product to the food, cosmetics and pharmaceutical industries. Novel purification methods based on distillation are available;^{6,7} even so, purification by distillation requires high investment and operating costs.8 Increased availability of glycerol and limited commodity glycerol market has resulted in an expected fall in glycerol prices; therefore, finding-out ways for conversion into useful products is desirable.

Recently, Zhou et al.⁹ reviewed catalytic conversion of glycerol (e.g., by oxidation, hydrogenolysis, dehydration and steam reforming) into valuable commodity chemicals. Hydrogen (H₂) production by steam reforming represents a candidate method for the utilization of the surplus amounts of biodiesel's crude glycerol. According to Slinn et al.,¹⁰ reformation provides a viable alternative use for glycerol and is potentially a better option than purification. This process is represented by

$$C_{3}H_{8}O_{3} + 3H_{2}O \Rightarrow 3CO_{2} + 7H_{2}$$
$$\Delta H_{25^{\circ}C} = 128 \text{ kJ/mol}$$
(1)

 H_2 demand is continuously increasing in the chemical and energy industries. It is extensively used, e.g. in ammonia and methanol manufacturing, as a reactant in several refinery processes for producing liquid fuels and biofuels, and as an alternate fuel. Because of the opportunity to produce renewable H_2 and avoid using depleting fossil fuels (e.g., natural gas and naphtha), steam reforming of crude glycerol is attractive. In the context of the H_2 economy concept, production of this energy carrier (i.e., H_2) via glycerol reforming is promising. According to Sutton et al.,¹¹ the primary reactions in this process are glycerol decomposition and water gas shift reactions:

$$C_3H_8O_3 \rightleftharpoons 3CO + 4H_2 \quad \Delta H_{25^\circ C} = 251 \text{ kJ/mol}$$
 (2)

 $CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_{25^{\circ}C} = -41 \text{ kJ/mol}$ (3)

Because of the methanation of CO and CO_2 , the H_2 yield is reduced:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H_{25^{\circ}C} = -206 \text{ kJ/mol}$$

$$(4)$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{25^{\circ}C} = -165 \text{ kJ/mol}$$

(5) Commonly, H₂ yield is governed by the reaction variables, e.g. temperature, system pressure, and glycerol concentration in the

feed. By now, H₂ production from glycerol has been extensively studied; recently, Vaidya and Rodrigues¹² presented a comprehensive discussion on previous studies. Ni- and Ptbased catalysts which facilitate H₂ production from glycerol are widely investigated; however, there is only scarce information in the published literature on Ru-based catalysts. Hirai et al.¹³ investigated the efficacy of Ru using several supports, e.g., Y₂O₃, ZrO₂, CeO₂, SiO₂, MgO, and Al₂O₃, and reported complete glycerol conversion and high H₂ yield (90%) using Ru/Y₂O₃ at T = 600 °C and $W/F_{AO} = 13.4$ g h/mol. Using a Ru/Al₂O₃ catalyst, Adhikari et al.¹⁴ found that glycerol conversion and H₂ selectivity at T = 900 °C and GHSV = 51 000 1/h were 58 and 42%, respectively. By using Ru/Mg(Al)O catalyst at T = 550°C, Gallo et al.¹⁵ reported glycerol conversion, H₂ yield, and CO₂ selectivity close to 100% for a feed containing 10 wt %

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Figure 1. Schematic diagram of experimental setup (MFC = mass flow controller, LG = level gauge, PG = pressure gauge, PT = pressure transmitter, TI = temperature indicator, TE = temperature element, CV = control valve, NV = nonreturn valve, BPR = back-pressure regulator, TWV = three way valve, FP = feed pump, FV = feed vessel, GHT = gas holding tank, GC = gas chromatograph).

glycerol. At higher temperatures ($T \ge 550$ °C), this catalyst was stable for 20 h. May et al.¹⁶ investigated gasification of glycerol in supercritical water at T = 550 °C and P = 35 MPa and reported complete conversion at a residence time of 5 s using Ru/ZrO₂. Byrd et al.¹⁷ produced H₂ from glycerol by reforming in supercritical water at high temperature (700–800 °C), high feed concentration (up to 40 wt % glycerol), and low reaction time (<5 s) using a Ru/Al₂O₃ catalyst; this study is the only information available on reaction kinetics.

Ru, which is the least expensive among all noble metals,¹⁸ has high activity for steam reforming of several other hydrocarbons, viz. methane,¹⁹ ethanol,²⁰ acetic acid,²¹ and ethylene glycol.²² Much effort is now being put on the development of reforming catalysts containing Ru. Thus, a comprehensive study on glycerol using Ru-based catalysts appears desirable. By now, such a study is still missing, and we intend to close this gap. In this paper, we investigated the reaction mechanism and kinetics using a commercial 5% Ru/Al₂O₃ catalyst at low temperatures ($T \le 500$ °C) in a fixed-bed reactor. We anticipated that high H₂ yield can be achieved by using high Ru loading (5%). The outcome of this investigation will aid the design and operation of reactors producing H₂ from glycerol.

2. EXPERIMENTAL SECTION

2.1. Materials. Glycerol (analytical reagent grade), used in all experiments, was purchased from Merck India Pvt. Ltd., Mumbai. Air, H_2 , and nitrogen (N_2) cylinders (purity 99.995%) were acquired from Industrial Oxygen Company Ltd., Mumbai. Standard calibration gas mixtures containing carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), and propane (C₃H₈), were procured from Chemtron Laboratory Pvt. Ltd., Mumbai. A commercial

5% $\rm Ru/Al_2O_3$ catalyst was supplied by Johnson-Matthey Ltd., Delhi.

2.2. Experimental Setup. A SS-316 tubular fixed-bed upflow reactor (inner diameter 19 mm, height 200 mm), purchased from Chemito Technologies Pvt. Ltd., Mumbai, was used in all experiments (see Figure 1). The setup was supplied with a control panel, temperature-controlled furnace, gas chromatograph (GC 8610) unit, and a data acquisition system. The temperature was controlled by using a temperature controller (West, Germany). A pressure transducer (0–100 bar) enabled the measurement of pressure with an uncertainty of ± 0.1 bar.

2.3. Experimental Procedure. An aqueous glycerol solution was charged from a feed vessel by using an HPLC pump, vaporized in a preheater (350 °C) and passed over the catalyst placed inside the reactor at the desired temperature. The catalyst was kept between two beds of quartz wool. Because we worked at low temperatures, catalyst deactivation due to quartz wool was deemed insignificant. N2, used as a carrier gas in all experiments, was introduced from a gas reservoir at the predetermined flow rate by using a mass flow controller (0–500 cm³/min; Brooks, 5800 Series). The N₂ flow rate was adjusted to the desired value (100 cm³/min) with an accuracy of ± 1 cm³/min. The product vapors leaving the reactor were passed through a condenser, back-pressure regulator, and gas-liquid separator. The noncondensable gases were analyzed by GC using a valve injection system. Besides, the liquid products were periodically collected and analyzed by GC, too. The system pressure was maintained constant at 0.1 MPa. Before each experiment, the catalyst was reduced at 500 °C for 1 h in the presence of pure H_2 (50 cm³/ min). The results reported here are after 2 h of reaction. We considered the residual glycerol content of the liquid product for finding glycerol conversion; the latter was defined as follows:

$$Glycerol Conversion\% = \frac{Moles of glycerol reacted}{Moles of glycerol at inlet} \times 100$$
(6)

The effect of water consumption on glycerol concentration was not considered in this study. At low water/glycerol ratios in feed (i.e., 3), this effect could be significant. For much more dilute solutions, this problem may however be neglected. H_2 yield, which is a measure of the amount of glycerol converted into H_2 , was defined as:

$$H_2 \text{Yield} = \frac{\text{Moles of } H_2 \text{ produced}}{7 \times \text{Moles of glycerol reacted}}$$
(7)

Its maximum stoichiometric value equals 1 mol/mol. W/F_{AO} (g h/mol) was defined as the ratio of the mass of the catalyst to the molar flow rate of glycerol at the inlet; the space time (W/ Q_0 is much lower. The amount of catalyst (W) used in all experiments was kept constant at 0.1 g. Unless stated otherwise, a water-to-glycerol molar ratio of 9 was used (steam/carbon molar ratio = 3). The liquid feeding rate was varied from 0.2 to 1 cm³/min. The flow rate of the aqueous glycerol solution was varied in the range of 209 to 1045 cm³/min. The total volumetric gas flow rate (30 °C, 0.1 MPa), which is inclusive of the N₂ flow rate, was varied in the range $309 < Q_0 < 1145 \text{ cm}^3/$ min. All experiments were performed at diluted conditions and hence the volume change due to reaction was neglected. In all, 36 experiments were done. The reproducibility of results was checked by repeating one experiment at T = 500 °C and W/ F_{AO} = 1.98 g h/mol. From the variation in glycerol conversion (89.1 and 87.5%) and H₂ yield (0.49 and 0.51 mol/mol), we concluded that the error in experimental measurements was within the limits of engineering accuracy $(\pm 3\%)$. In one experiment at 500 °C, no catalyst was used; however, it was found that the H₂ yield was negligible.

2.4. Product Analysis. A MS 13X column was used for the detection of H₂ in the gaseous product stream, whereas a silica gel column was used for the analysis of CH₄ formed during reaction. CO₂ was detected by using H₂ as the carrier gas in a Porapak N column. From a comparison with the analysis of calibration gas mixtures, we found that concentrations of C₂ and C₃ hydrocarbons in the reformed gas were negligible. Because N2 was used as a carrier gas during experimentation and all kinetic experiments were done at diluted conditions, CO concentration in the product stream was below the detection level. Contrarily, when no carrier gas was used (T = 500 °C, W/F_{AO} = 4.6 g h/mol), CO was detected using Hayesep DB column with TCD. After 2 h, the exit gas composition (mol %) was $H_2 = 58.3\%$, $CO_2 = 34.2\%$, $CH_4 = 0.3\%$, and CO = 7.2%. Similar trends in the C1 product composition were reported by Hirai et al.¹³ and Gallo et al.¹⁵ using Ru-based catalysts. The residual glycerol content of the liquid samples was estimated by using a Tenax column. 1-Hydroxy-2-propanone was the major byproduct detected in the liquid samples; a few others (e.g., ethylene glycol, ethanol, acetaldehyde, acetone, and 2hydroxypropanoic acid) were detected in trace amounts, too, and their identity was confirmed by using GC-MS technique (QP-2010 Shimadzu).

2.5. Catalyst Characterization. BET specific surface area of the Ru/Al_2O_3 catalyst was determined using a Micromeritics ASAP 2100 surface area analyzer. N₂ adsorption-desorption

isotherms were obtained at -195.5 °C over a wide range of relative pressures on samples previously outgassed at 150 °C for 12 h. It was found that the surface area using BET method equals 111.3 m²/g. The surface morphology of the catalyst was studied by using the scanning electron microscopy technique (JEOL-JSM 6380 LA SEM). Two SEM images of the unused catalyst are shown in Figure 2. Several particles with different



Figure 2. SEM images of the fresh Ru/Al₂O₃ catalyst.

sizes are shown; the presence of a predominantly porous region is evident. Using energy dispersive X-ray spectroscopy (EDS) technique, it was found that the Ru content was 5%.

Powder X-ray diffraction patterns of the Ru/Al₂O₃ catalysts were obtained using a Rigaku Miniflex D500 diffractometer and monochromic Cu K α radiation. The unused and used catalysts exhibit similar XRD patterns (see Figure 3). Weak diffraction peaks of Ru species are observed ($2\theta = 37^{\circ}$ and 44°), thereby indicating that Ru species is well dispersed on Al₂O₃. Very small diffraction peaks ($2\theta = 28^{\circ}$, 34° , and 54°), hardly distinguishable from the background noise, indicate very small amounts of RuO₂. The peak centered at 67° , caused by the Al₂O₃ support, is quite evident. The used catalyst does not exhibit new diffraction lines, thereby suggesting that no new phase is formed in the catalyst. A comprehensive characterization of Ru/Al₂O₃ catalyst by XRD technique was earlier presented by Lanza et al.²³ and Ma et al.²⁴

TPR experiments were conducted using a Micromeritics 2920 TPD/TPR apparatus. In this test, 100 mg of catalyst and a



Figure 3. XRD patterns of the fresh and spent Ru/Al₂O₃ catalysts.

mixture of H₂ and Ar (10% v/v, 20 cm³ (STP)/min) were used. The sample was previously heated to 150 °C under dry N₂ (30 cm³ (STP)/min) for 1 h and subsequently cooled to room temperature. The temperature was then increased under the hydrogen mixture at 10 °C/min and the TPR profiles were recorded. The temperature was raised to 500 °C. The volume of H₂ absorbed was 13.80 (cm³/g STP). The TPR profile is displayed in Figure 4. A sharp signal located at a temperature at



Figure 4. TPR profile of the fresh Ru/Al_2O_3 catalyst.

peak maximum ($T_{\rm m}$) of 141.8 °C was detected; it may be related to the reduction of unknown Ru species present on the catalyst surface. A shoulder at 169 °C is associated with the reduction of dispersed RuO_x species.²³ The $T_{\rm m}$ for the hightemperature peak at 224 °C corresponds to reduction of RuO₂.²⁵

Coke deposition on the catalyst surface was ascertained by thermo-gravimetric analysis TG/DTA. The maximum temperature (i.e., 500 °C) used for catalyst activity trials was used for the TGA test too. The catalyst was heated from 50 to 500 °C at 10 °C/min under air flow and the coke deposition rate was measured. The TGA profiles for the unused and used catalysts are shown in Figure 5. At 300 °C, coke deposition for the unused catalyst was negligible. It was found that the coke deposition rate for the spent catalyst equals 36.6 mg C/(g_{cat} h). This may be associated with the decomposition or oxidation of carbonaceous species from the catalyst surface. The reaction conditions for the spent catalyst used for this measurement



Figure 5. TG-DTA weight loss profiles of fresh and spent $\rm Ru/Al_2O_3$ catalysts.

were T = 500 °C, $W/F_{AO} = 0.4 \text{ g h/mol}$, steam/carbon ratio = 3, and reaction time = 2 h.

Surface metallic atom characteristics (such as dispersion and particle diameter) were investigated by H_2 chemisorption (Micromeritics 2920 unit). Metal dispersion and active particle diameter were found to be 3.44% and 38.4 nm, respectively.

3. RESULTS AND DISCUSSION

3.1. Reaction Pathway. According to Byrd et al.,¹⁷ the following processes occur in presence of Ru/Al_2O_3 : adsorption of glycerol on the catalyst surface primarily through one or more oxygen atoms, glycerol dehydrogenation on the surface, and cleavage of C–C or C–O bonds. C–C bond cleavage and subsequent dehydrogenation results in the formation of adsorbed CO, which may either desorb, water-gas shift, or undergo methanation. This is represented as

$$CH_{2}OH - CHOH - CH_{2}OH$$

$$\xrightarrow{-H_{2}} *CHOH - *COH - CH_{2}OH$$

$$\xrightarrow{-H_{2}} *CO$$
(8)

$$*CO \xrightarrow{H_2 \odot} CO_2 + H_2 \tag{9}$$

$$*CO \xrightarrow{H_2} CH_4 + H_2O$$
(10)

C-O bond cleavage results in the formation of smaller alcohols and alkanes.²⁶ Rearrangement and dehydrogenation reactions may possibly lead to the formation of alkenes and carboxylic acids. Ru has high activity for C-C bond scission.²⁷ In a previous study, Slinn et al.¹⁰ described a similar reaction pathway on another noble metal surface, viz. Pt. Recently, Pompeo et al.²⁸ described plausible reaction mechanisms for glycerol steam reforming over Pt-based catalysts. After the initial dehydrogenation step (to 1,3-dihydroxy-2-propanone or 2,3-dihydroxy-propanal), two pathways were proposed. The first pathway involves 1,3-dihydroxy-2-propanone dehydration (to 1-hydroxy-2-propanone), dehydrogenation (to propanol-2oxo) and subsequent C-C cleavage (to acetaldehyde). Reactions of hydration-dehydrogenation of acetaldehyde could lead to acetic acid formation, which yields H₂, CO, CO_{2} , and CH_4 by C-C bond cleavage. The second pathway does not involve dehydration reactions, but it mainly involves

C–C cleavage and dehydrogenation, thereby resulting in the formation of H_2 and CO. Pompeo et al.²⁸ reported low contribution of the first pathway in their results; however, it is evident from our results that this pathway is predominant, due to the fact that 1-hydroxy-2-propanone and acetaldehyde are formed during reaction.

3.2. Mass Transfer Considerations. Glycerol steam reforming is a heterogeneous gas—solid catalyzed reaction system, which involves the following transfer processes: diffusion of the reactants from the bulk gas phase to the catalyst surface, intraparticle diffusion followed by chemical reaction at the active centers and diffusion of the products. Any of these mass transfer processes (external or internal) can influence the rates of reaction. To determine the kinetic parameters, it is essential to ensure the absence of mass transfer limitations.

In the kinetically controlled reaction regime, the conversion of the reactant should not depend on the total gas flow rate for a fixed value of the W/F_{AO} ratio. This effect was experimentally studied at 500 °C using a steam/carbon ratio of 3 and a catalyst weight of 0.1 g. It was found that there was practically no change in the glycerol conversion (50%), while varying the N_2 flow rate from 50 to 200 cm³/min, and hence, the total volumetric flow rate (Q_0) from 1095 to 1245 cm³/min at a W/ F_{AO} ratio equal to 0.4 g h/mol. Thus, it was established that the external mass transfer resistance was absent over the entire temperature range studied. To ascertain the absence of pore diffusion limitation, the effect of catalyst particle size on conversion was studied at T = 500 °C, $W/F_{AO} = 0.4$ g h/mol, and N_2 flow rate = 100 cm³/min. The total gas flow rate was 1145 cm³/min. It was found that the conversion (50%)obtained while using larger particles in the size range 150-210 μ m was exactly identical to that obtained using particles in the range 23–69 μ m (50%). Therefore, it was concluded that the intraparticle diffusion resistance was negligible. All further experiments were conducted using particles in the size range 23-69 μ m. Because the reaction rates are not influenced by mass transfer processes at the highest temperature used for this study (i.e., 500 °C), the absence of diffusion limitations at lower temperatures (i.e., 350 °C) is inevitable.

The Madon-Boudart method is a useful technique to establish the prevalence of the kinetically controlled reaction regime.²⁹ In this method, catalysts with different loading but similar metal dispersion are employed. If the values of TOF (mol H₂ produced per mole of surface metal per min) at identical conversion values are alike, it can be concluded that the reaction rates are not influenced by the rates of mass transport. To ensure large variation in Ru loading, we used 0.5% Ru/Al₂O₃ catalyst (Johnson-Matthey Ltd., Delhi). Using H₂ chemisorption, we estimated metal dispersion and particle size. The properties of both catalysts (viz. 0.5 and 5% Ru) and their performance at T = 500 °C and $W/F_{AO} = 0.4$ g h/mol are shown in Table 1. Certainly, the surface metallic atom characteristics of the two commercial catalysts were similar. From our results, we concluded that at the same conversion, the values of TOF (H_2) were similar. Thus, the Madon-Boudart test for the absence of transport limitations was satisfied.

3.3. Glycerol Conversion Kinetics. In the present work, reaction kinetics of glycerol steam reforming was investigated over the ranges in temperature 350-500 °C, water/glycerol ratio 3-12 mol/mol, and W/F_{AO} ratio 0.4 to 1.98 g h/mol. The experimental kinetic data are represented in Table 2. As the W/

Table 1. Properties of Ru/Al ₂ O ₃ Catalysts and Their
Performance at $T = 500$ °C and $W/F_{AO} = 0.4$ g h/mol
(water/glycerol molar ratio = 9, steam/carbon ratio = 3,
catalyst weight = 0.1 g, system pressure = 0.1 MPa)

metal loading (%)	crystallite size d _p (nm)	dispersion ^a D (%)	glycerol conversion (%)	H ₂ formation rate (mol/ min/g _{cat})	$\begin{array}{c} \text{TOF} \\ (\text{H}_2) \\ (1/\text{min}) \end{array}$
0.5	36.5	3.63	47.6	0.0037	2060.9
5.0	38.4	3.44	50.0	0.0345	2025.8
$^{a}D = ((2$	$2 \times H_2$ ads	orption)/red	uced Ru) ×	100. $D = ((n_1 + n_2)^2)$	umber of

 $D = ((2 \times R_2 \text{ adsorption})/\text{reduced Kd}) \times 100.$ $D = ((\text{number of surface atoms})/(\text{total number of atoms of specified catalytic phase})) \times 100.$

 $F_{\rm AO}$ ratio increased from 0.4 to 0.66 g h/mol, there was marginal increase in the glycerol conversion; thereafter, this effect was more prominent at all temperatures. Using a water/ glycerol ratio equal to 9 mol/mol at 500 °C, the highest values of glycerol conversion (89.1%) and H_2 yield (0.49 mol/mol) were achieved at W/F_{AO} equal to 1.98 g h/mol. Values of TOF (H_2) at various temperatures are represented in Table 2; certainly, these values are high. The effect of the space time on glycerol conversion at 350, 400, 450, and 500 °C is represented in Figure 6. The increase in temperature and space time caused the expected increase in % glycerol conversion. Certainly, the efficacy of a catalyst is enhanced at high temperature; then again, catalyst deactivation, e.g., due to sintering, may be accelerated. As evident from Table 2, the decrease in Q_0 results in the expected increase in conversion. The dependence of the H_2 yield on temperature at different values of W/F_{AO} ratio is shown in Figure 7. It is, thus, obvious that H₂ production is favored at high temperatures. The W/F_{AO} ratio was varied by changing the flow rate of the liquid feed. At 500 °C, it was found that as the W/F_{AO} ratio increased from 0.4 to 1.98 g h/ mol, the H_2 yield increased from 0.23 to 0.49 mol/mol.

In Figure 8, a plot of H₂ yield vs glycerol conversion at 500 °C is shown. The higher the extent of reaction (glycerol conversion), the higher is the relative yield of H_2 . The effect of temperature on the CH_4/H_2 ratio was studied; these results are shown in Figure 9. As the temperature increased from 350 to 500 °C, the CH₄/H₂ ratio decreased from 0.89 to 0.23. While steam methane reforming occurs in the studied range of temperatures, this reaction is limited by thermodynamics. Finally, the effect of initial water/glycerol molar ratio on the conversion and yield was studied (see Table 3). The liquid feeding rate was kept constant (1 cm³/min), whereas the W/ F_{AO} ratio was varied. The overall tendency observed when the steam/carbon molar ratio was increased was that the H₂ yield was improved. At 500 °C, H₂ yield increases from 0.14 to 0.28 as the water/glycerol ratio in the feed increases from 3 to 12 mol/mol. It is, thus, obvious that high water content in the feed facilitates H₂ production. However, it is worthy of note that a higher water-to-glycerol ratio in the feed will result in increased energy requirement for the evaporation of water. We used a short reaction time (i.e., 2 h) for this work; however, further work at prolonged time is essential to demonstrate stable catalyst operation.

The glycerol disappearance rates at various temperatures were estimated using the following expression:

$$=\frac{\mathrm{d}X}{\mathrm{d}\left(\frac{W}{F_{\mathrm{AO}}}\right)}\tag{11}$$

Table 2. Kinetic Data at Various Temperatures (Water/Glycerol Molar Ratio = 9, Steam/Carbon Ratio = 3, Catalyst Weight = 0.1 g, System Pressure = 0.1 MPa)

temp. (°C)	liquid feeding rate (cm³/min)	glycerol conversion (%)	H ₂ yield (mol/mol)	TOF (H ₂) (1/ min)	Q _o (cm ³ /min)	W/F _{AO} (g h/mol)	mole fraction of glycerol in feed
350	1.0	21.4	0.09	328.1	1145	0.40	0.091
350	0.8	30.9	0.12	544.6	936	0.50	0.089
350	0.6	38.2	0.13	515.5	727	0.66	0.086
350	0.4	47.3	0.18	599.7	518	0.99	0.081
350	0.2	61.9	0.27	575.3	309	1.98	0.068
400	1.0	32.4	0.11	637.1	1145	0.40	0.091
400	0.8	35.6	0.20	983.6	936	0.50	0.089
400	0.6	42.0	0.22	960.4	727	0.66	0.086
400	0.4	53.1	0.22	807.2	518	0.99	0.081
400	0.2	68.1	0.37	861.0	309	1.98	0.068
450	1.0	41.0	0.21	1498.4	1145	0.40	0.091
450	0.8	45.4	0.22	1375.8	936	0.50	0.089
450	0.6	52.4	0.26	1433.8	727	0.66	0.086
450	0.4	61.4	0.34	1437.8	518	0.99	0.081
450	0.2	78.6	0.47	1286.3	309	1.98	0.068
500	1.0	50.0	0.23	2025.8	1145	0.40	0.091
500	0.8	56.0	0.24	1893.9	936	0.50	0.089
500	0.6	64.1	0.32	2159.3	727	0.66	0.086
500	0.4	71.9	0.37	1859.8	518	0.99	0.081
500	0.2	89.1	0.49	1499.7	309	1.98	0.068



Figure 6. Effect of the space time on glycerol conversion at 350, 400, 450, and 500 °C; points: experimental data; curves: predictions from eq 12 (water/glycerol molar ratio = 9, steam/carbon ratio = 3, catalyst weight = 0.1 g, system pressure = 0.1 MPa).

The reaction order with respect to glycerol was determined by using the integral method of analysis. Using this simple technique, Vaidya and Rodrigues³⁰ reported first-order kinetics for the steam reforming of another oxygenate—ethanol—using Ru/Al_2O_3 catalyst. Sutar et al.³¹ established that the steam reforming reaction is of the first order with respect to glycerol over a Pt/C catalyst. Therefore, we anticipated first-order kinetics for this work, too. For a first order reaction, the following relation holds:

$$X = 1 - e^{-kW/Q_0}$$
(12)

Equation 12 can be rewritten in the following form:

$$\ln(1-X) = -\frac{kW}{Q_0} \tag{13}$$



Figure 7. Effect of temperature on the H_2 yield (water/glycerol molar ratio = 9, steam/carbon ratio = 3, catalyst weight = 0.1 g, system pressure = 0.1 MPa).

Water is in large excess and, therefore, the reaction order with respect to water is assumed to be zero. Hence, eq 13 does not account for the water concentration. The plots of $\ln (1 - X)$ vs W/Q_0 at various temperatures are shown in Figure 10. Since the data reasonably fall on a straight line, the investigated reaction is of the first order with respect to glycerol.

There are few papers on power-law kinetics of glycerol steam reforming available;^{31–36} these works are summarized in Table 4. Cheng et al.^{32–34} found that the reaction order is less than unity for other Al_2O_3 -supported catalysts. Similarly, Adhikari et al.³⁵ and Dave and Pant³⁶ reported fractional dependence on glycerol concentration between 0 and 1, using Ni-based catalysts.

From the values of the slopes, the specific reaction rate constant *k* at various temperatures was estimated. The values of *k* at 350, 400, 450, and 500 °C were found to be 1.9×10^5 , 2.3



Fractional glycerol conversion

Figure 8. Plot of H_2 yield vs glycerol conversion at 500 °C (water/ glycerol molar ratio = 9, steam/carbon ratio = 3, catalyst weight = 0.1 g, system pressure = 0.1 MPa).



Figure 9. Effect of temperature on the CH_4/H_2 ratio (water/glycerol molar ratio = 9, steam/carbon ratio = 3, catalyst weight = 0.1 g, system pressure = 0.1 MPa).

× 10⁵, 3.0 × 10⁵, and 4.2 × 10⁵ cm³/(g_{cat} h), respectively. The Arrhenius plot is shown in Figure 11. The activation energy was evaluated as 21.2 kJ/mol. We ensured the absence of diffusion resistances; even so, our value of E_{act} is lower than those reported by other researchers (see Table 4). The problem of the low value of the apparent activation energy may lie in the uncertainty in the calculation of reaction rate (integral reactor data are used), the usage of a rather simplistic approach to data analysis (first-order kinetics is a coarse approximation), and the enhanced catalyst activity (due to high loading level of Ru) even at low reaction temperatures. Further investigation on reaction kinetics using mechanistic models is essential before one can deduce reasons for the low value of E_{act} . Recently, Pant et al.³⁷ reported low activation energy (36.5 kJ/mol) for glycerol steam reforming over Ni/CeO₂.

The experimental and predicted conversions (Figure 6) were compared, and there exists good agreement between them. From knowledge of mole fraction of glycerol in feed, system Table 3. Effect of Water/Glycerol Molar Ratio in Feed on Glycerol Conversion and H_2 Yield (Catalyst Weight = 0.1 g, Liquid Feeding Rate = 1 cm³/min, System Pressure = 0.1 MPa)

temp. (°C)	water/glycerol in feed (mol/mol)	steam/ carbon molar ratio	W/F _{AO} (g h/mol)	glycerol conversion (%)	H ₂ yield (mol/mol)
350	3	1	0.22	22.7	0.04
350	6	2	0.30	24.8	0.06
350	9	3	0.40	21.4	0.09
350	12	4	0.49	39.1	0.14
400	3	1	0.22	26.7	0.07
400	6	2	0.30	28.9	0.08
400	9	3	0.40	32.4	0.11
400	12	4	0.49	48.5	0.19
450	3	1	0.22	36.5	0.08
450	6	2	0.30	38.9	0.10
450	9	3	0.40	41.0	0.21
450	12	4	0.49	51.5	0.26
500	3	1	0.22	35.6	0.14
500	6	2	0.30	40.6	0.16
500	9	3	0.40	50.0	0.23
500	12	4	0.49	61.8	0.28



Figure 10. Plots of $\ln(1 - X)$ vs W/Q_0 (water/glycerol molar ratio = 9, steam/carbon ratio = 3, catalyst weight = 0.1 g, system pressure = 0.1 MPa).

 Table 4. Power-Law Kinetic Modeling of Glycerol Steam

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catalyst	temp. (°C)	order wrt glycerol	order wrt steam	E _{act} (kJ/mol)	reference
$\rm Ru/Al_2O_3$	350-500	1.0		21.2	this work
Pt/C	350-400	1.0			31
Co/Al_2O_3	450-550	0.10	0.40	67.2	32
Ni/Al ₂ O ₃	450-550	0.48	0.34	60.0	33
Co–Ni/ Al ₂ O ₃	500-550	0.25	0.36	63.3	34
Ni/CeO_2	600-650	0.233		103.4	35
Ni-ZrO ₂ / CeO ₂	700	0.3		43.4	36

pressure and conversion, the values of glycerol partial pressures were evaluated. The values of r were estimated using eqs 11 and 12. The variation in the reaction rate with glycerol partial



Figure 11. Arrhenius plot.

pressures is shown in Figure 12. The linear dependence of the rates on the partial pressure is in good agreement with the first-



order kinetic model earlier discussed. While the first-order reaction kinetics is valid at low glycerol concentrations, it should however be noted that less dilute solutions will be used in reformers during actual operation, where the assumption of a first-order reaction may be no longer valid. It is, therefore, necessary to exercise caution during reactor design.

3.4. Heterogeneous Kinetic Modeling. We proposed a single-site reaction mechanism comprising the following steps: reversible adsorption of glycerol (here denoted as A) on the active site (S) of the catalyst, reaction between adsorbed glycerol and water to form the complex ABS, decomposition of ABS into intermediates, and further reaction to give products, CO_2 and H_2 . The above-mentioned elementary steps in this mechanism were represented as:

$$\mathbf{A} + \mathbf{S} \stackrel{k_1, k_{-1}}{\longleftrightarrow} \mathbf{A}\mathbf{S} \tag{14}$$

$$AS + B \xrightarrow{\kappa_2} ABS \tag{15}$$

ABS
$$\xrightarrow{k_3}$$
 Intermediates $\xrightarrow{k_4}$ CO₂ + H₂ (16)

Applying stationary steady state hypothesis to the complexes AS and ABS and assuming that decomposition of ABS is ratedetermining, the reaction rate was expressed as

$$r = \frac{k_1 k_2 p_{\rm A} p_{\rm B}}{[k_{-1} + k_1 p_{\rm A} + k_2 p_{\rm B} + (k_1 k_2 p_{\rm A} p_{\rm B} / k_3)]}$$
(17)

Since water was in large excess and pressure was constant, $p_{\rm B}$ was assumed to be nearly equal to $p_{\rm B0}$. Equation 17 was expressed in a simpler form as

$$r = \frac{k_{\rm R} p_{\rm A}}{1 + b p_{\rm A}} \tag{18}$$

where $k_{\rm R}$ and b are defined by:

$$k_{\rm R} = \frac{k_1 k_2 p_{\rm B0}}{k_{-1} + k_2 p_{\rm B0}}; \quad b = \frac{k_1 + (k_1 k_2 p_{\rm B0}/k_3)}{k_{-1} + k_2 p_{\rm B0}}$$
(19)

At low values of p_A similar to those used in this study, $bp_A \ll 1$; thus, the reaction is of the first order with respect to glycerol ($r = k_R p_A$). This is in line with our result obtained by using the integral method of analysis.

This kinetic model was earlier reported by Vaidya and Rodrigues³⁰ to elucidate the pathway of ethanol steam reforming at low temperatures ($350 \le T \le 500$ °C) using Ru/Al₂O₃ catalyst. Byrd et al.¹⁷ used the same model for describing glycerol reforming kinetics in supercritical water at high temperatures ($700 \le T \le 800$ °C). Because we anticipated similar pathways for the Ru-catalyzed steam reforming reactions of ethanol and glycerol at identical temperatures, we applied this model for this study.

3.5. Some General Remarks. We investigated reaction kinetics using pure glycerol; even so, further investigation using crude glycerol byproduct is essential. As of now, there exists no information in the literature on the mechanistic features of reaction kinetics. The exact composition of raw glycerol depends on the method of biodiesel production. If the impurity levels are high, the performance of the reforming catalyst may be adversely affected. Slinn et al.¹⁰ reported slightly poorer performance of Pt/Al₂O₃ when byproduct glycerol was used as feed. The H₂ yield was 70% of that obtained using pure glycerol under the same reaction conditions; then again, the amount of carbon deposited on the catalyst surface was higher. They attributed the increased catalyst coking to the long-chain fatty acid impurities, which are resistant to reformation. Thus, it is clear that more severe reaction conditions (e.g., higher temperature, higher W/F_{AO} ratios and longer residence times) will be needed to achieve high H_2 yield.

4. CONCLUSION

In the present work, reaction kinetics of glycerol steam reforming was investigated in a fixed-bed reactor in the range of temperatures 350-500 °C, and $W/F_{\rm AO}$ ratio 0.4-1.98 g h/mol, using a Ru/Al₂O₃ catalyst. The increase in temperature, water/glycerol ratio in feed and space time caused the expected increase in the values of the H₂ yield. It was found that the investigated reaction system belongs to the kinetically controlled reaction regime systems. Using the integral method of analysis, we established that the reaction order with respect to glycerol is one. Based on the temperature dependence of the reaction rate constant, the activation energy was evaluated as

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21.2 kJ/mol. Finally, it was found that a heterogeneous kinetic model described in a previous work also suggests first-order kinetics at the low glycerol partial pressures used for this study. This study has contributed to the design of reactor systems for the production of H_2 by steam reforming of glycerol.

AUTHOR INFORMATION

Corresponding Author

*Fax: +91-22-33611020. Tel.: +91-22-33612014. E-mail: pd. vaidya@ictmumbai.edu.in.

Notes

The authors declare no competing financial interest.

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NOMENCLATURE

- A = glycerol
- B = water

b = parameter defined by eq 19

D = metal dispersion, %

 $d_{\rm p}$ = crystallite size, nm

 \vec{E}_{act} = activation energy, kJ/mol

 F_{A0} = molar flow rate of glycerol at inlet, mol/h

k =first order reaction rate constant, cm³/(g_{cat} h)

 k_{1}, k_{-1} = forward and backward reaction rate constants in eq 14

 k_2 = reaction rate constant in eq 15

 k_3 , k_4 = reaction rate constants in eq 16

 $k_{\rm R}$ = parameter defined by eq 19

 $p_{\rm A}$ = partial pressure of A, atm

 $p_{\rm B}$ = partial pressure of B, atm

 $p_{\rm B0}$ = partial pressure of B at inlet, atm

 Q_0 = volumetric flow rate at reactor inlet, cm³/h

 $r = reaction rate, mol/(g_{cat} h)$

S = active site

T =temperature, °C

TOF = turnover frequency, 1/min

W = weight of catalyst, g

X = fractional glycerol conversion

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