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Effect of sulfur and temperature on ruthenium-catalyzed glycerol hydrogenolysis to glycols

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Abstract

The hydrogenolysis of glycerol to ethylene glycol and propylene glycol represents an initial system for the development of an improved mechanistic understanding of the conversion of the more complex higher polyhydric alcohols. Previous work in our laboratory demonstrated the effects that pH, product degradation, and competitive adsorption have on the reaction system. This work is an extension that studies the effects of temperature and sulfur loading. Batch reactor studies with ruthenium on carbon catalysts were performed at a temperature range of 205–240 °C and a sulfur loading range of 0–1.0 mol S/Ru. Previous Langmuir–Hinshelwood-type models were extended to include the data. Apparent activation energies for the glycerol reaction and the glycol degradation were determined. Previous studies for this system have focused on the aqueous-phase scission reactions and metal-catalyzed (de)hydrogenation reactions. Analysis of the reaction flux map with and without sulfur, however, leads to the conclusion that catalytic dehydration must also be occurring on the solid catalyst.

Keywords: Hydrogenolysis; Glycerol reaction; Propylene glycol selectivity; Sulfur-modified ruthenium

1. Introduction

Although the hydrogenolysis of sorbitol to propylene glycol and ethylene glycol has been examined for over 20 years [1–7], the majority of the studies have been empirical in nature, focusing on varying catalyst compositions and operating conditions. The practical goal of these studies was to optimize both glycol production rates and selectivities. Although either goal could be independently achieved, gains in production rate inevitably gave a loss in selectivity and vice versa. The highest combined selectivity for the two glycols with a reasonable production rate was 65% [1–5], which is not sufficient to be economically viable. Therefore, achieving the necessary improvement in glycol selectivity with a reasonable reaction rate requires a deeper understanding of the reaction mechanism, with the goal that a mechanistic understanding of the reaction will bring about a more rational approach to the development of improved catalyst systems.

The hydrogenolysis of higher polyols, such as sorbitol, xylitol, or glycerol, to form ethylene glycol and propylene glycol involves multiple steps [8]. In the prevailing literature mechanism, the polyol is first reversibly adsorbed and dehydrogenated by the catalyst, leading to a desorbed aldehyde or ketone species. The product of the dehydrogenation reaction can then undergo a C–C scission via either the retro-aldol mechanism and/or oxidation followed by decarboxylation or a C–O scission by dehydration. Both of these scissions pass through reaction intermediates and are proposed to occur in the aqueous phase by base catalysis. The product(s) of either of these scission mechanisms contains a total of two unsaturated bonds; the dehydrated species contains two such bonds, and the two species following the C–C scission contain one each. The unsaturated bonds are subsequently hydrogenated by the metal catalyst. The metal catalyst serves both hydrogenating and dehydrogenating functions; therefore, the initial formation of the aldehydes and ketones is reversible. It is has not been reported previously that the

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solid catalyst performs other functions under these reaction conditions.

To develop a better understanding of this complex reaction sequence, efforts need to be directed toward understanding the mechanism of the hydrogenolysis reaction and the interactions between the reactants, products, and catalysts. From the proposed overall model, two types of reactions occur, metal-catalyzed dehydrogenation/hydrogenation and hydroxyl-catalyzed C–C and C–O scissions. Previous work has examined the effect of pH, the degradation of products, and the competitive adsorption of products on the reaction rate of glycerol and selectivity for the glycols [9]. The pH of the system affected many of the intermediate reactions that occur within the hydrogenolysis reaction network and thus the product distribution. Product degradation was demonstrated to be important because of its impact on the overall selectivity for the glycols. Competitive adsorption of the products inhibited the reaction rate of glycerol. Because of the complexity of the hydrogenolysis system with higher polyols, these initial reaction studies were performed with glycerol, propylene glycol, and ethylene glycol.

Although the study gave insight into the reaction mechanism, further mechanistic development must necessarily consider the important role of sulfur modification on the ruthenium catalyst during the production of glycols from glycerol. Many groups have reported two primary effects that sulfur modification of the ruthenium has on the reaction [2,7,10]. The first effect is the reduction in the overall reaction rate, as sulfur is a well-known metal catalyst poison. However, in the case of the polyol products, a second effect occurs: the selectivity for specific products increases. For example, the selectivity for propylene glycol increases dramatically as sulfur loadings increase. Montassier et al. reported an increase in selectivity for propylene glycol from 10% without sulfur to 80% with 1 mole of sulfur per mole of ruthenium [5]. The work was performed at pH 6, which lowered the overall glycerol reaction rate.

The goal of the current work was to continue the development of a more detailed model for the portion of the hydrogenolysis process beginning with glycerol to ultimately help maximize yields to the desired glycols from higher polyols. The effect sulfur has on the reaction system and insights derived from these effects will be discussed. The work presented will discuss causality for the increased selectivity for propylene glycol from glycerol when the sulfur loading increases and the catalyst requirements for commercial application of this process.

2. Experimental

Glycerol, ethylene glycol, 1,2-propylene glycol (all 99+%), calcium oxide (96%), and sodium sulfide hydrate (60%) were purchased from Acros Organics. High-purity hydrogen (99.992%) was used to pressurize the reactor. The catalyst (Activated Metals & Chemicals, Inc.) was 5 wt% ruthenium supported on activated carbon. The catalyst was received in a reduced state with a metal dispersion of approximately 30% and was handled as a wet powder with a water content of about 50 wt%.

All reactions were performed in a 100-ml batch reactor (Autoclave Engineers) equipped with a stirrer, an electric temperature controller, and a sample port for liquid samples. For a typical reaction, 0.4–1.5 M solutions of glycerol, ethylene glycol, and/or propylene glycol were added with a 5 wt% Ru/C catalyst, 0–1.0 mole of sodium sulfide per mole of ruthenium, and a base for maintaining a constant pH. The predominant base used was 0.4 M CaO. The ex situ pH was measured after the reaction samples were stored at room temperature (20 °C) for 2 h to reduce the variance in pH measurements due to temperature. CaO in the 205 °C experiments resulted in an average pH in the cooled samples of 11.7, whereas in the 240 °C experiments the average measured pH was 11.2. Measurements on the samples taken throughout a reaction study showed that the measured ex situ pH did not vary significantly with time.

Initially, the reaction vessel was flushed consecutively with low-pressure nitrogen and low-pressure hydrogen. The system was then pressurized with 50 bar H_2 and heated to reaction temperature, which ranged from 205 to 240 °C. Two initial samples were taken, and the hydrogen pressure was subsequently increased to 100 bar. The stirring speed was set to 500 rpm. Experiments at higher mixing speed showed no change in reaction performance; therefore, there were no external mass transfer limitations. The temperature, pressure, and mixing speed were held constant during the reaction.

Samples were taken in 15-min intervals for 75 min. The samples were cooled to less than 40 °C, as they were taken through a cooling loop. After the pH was measured, the samples were diluted with 60 wt% acetonitrile in water to a final value of 40 wt% acetonitrile. We then analyzed the samples with a Hewlett–Packard HC-75 HPLC, using a Ca^{2+} cation exchange column from Hamilton with an RI detector. The column was run with a mobile phase of 40 wt% acetonitrile in water.

2.1. *Effect of temperature and sulfur on ethylene glycol and propylene glycol degradation*

A previous glycerol hydrogenolysis study, which was performed under isothermal conditions, demonstrated that knowledge of the kinetics of the ethylene glycol and propylene glycol degradation kinetics was a necessary step in understanding the overall glycerol hydrogenolysis reaction [9]. Therefore, further extension of the model required kinetic characterization of temperature and sulfur effects in the degradation of these products. The evaluation of the apparent activation energies and variation in competitive adsorption as a function of temperature for the product degradation reactions as determined from temperature studies allowed for the subsequent elucidation of the role of sulfur in the kinetics.

Table 1
Relative glycol degradation rates

Temperature (°C)	Individual glycol reaction			Equimolar reaction
	Ethylene glycol degradation rate (mmol/min)	Propylene glycol degradation rate (mmol/min)	Relative individual degradation rate EG/PG	relative degradation rate EG/PG
205	2.5	3.0	0.8	4.2
220	4.0	4.3	0.9	4.1
240	7.2	6.6	1.1	4.1

Experiments were first performed in which the temperature was varied with no sulfur introduction. When individually reacted, the degradation rate for both ethylene glycol and propylene glycol remained constant throughout the concentration range at each temperature level. Therefore, the zero-order reaction rate found for degradation of these compounds previously at 205 °C was found throughout the temperature range. The apparent activation energies measured for the degradation of the two glycols across the 205–240 °C temperature range were 62 kJ/mol for ethylene glycol and 45 kJ/mol for propylene glycol. The rate data for the two pure-component systems are listed in Table 1, as is their relative pure-component degradation rate.

The degradation rate for the two glycols when both are present depends on the pure component intrinsic rates and their relative adsorption behaviors. Therefore, degradation rate data were also obtained for an equimolar mixture (0.75 M) of each of the glycols. The results for the relative degradation rates of an equimolar glycol mixture are listed in the last column in Table 1.

The Langmuir–Hinshelwood model developed previously under the base case conditions of 205 °C [9] was extended to the nonisothermal conditions. The degradation reactions for the two glycols were modeled as a set of two equations:

$$-r_{i\mathrm{G}} = \frac{k'_{i\mathrm{G}}(i\mathrm{G})}{k_{\mathrm{EG}}\mathrm{EG} + k_{\mathrm{PG}}\mathrm{PG} + 1}, \tag{1}$$

where $r_{i\mathrm{G}}$ is the degradation rate for the glycol ($i = \mathrm{E}$ for ethylene glycol and P for propylene glycol), $k'_{i\mathrm{G}}$ is the degradation rate coefficient for each glycol, $i\mathrm{G}$ represents the respective concentrations of the glycols, and k_{EG} and k_{PG} are the respective adsorption constants for the glycols. The two glycol equations have eight parameters resulting from expressing each of the two degradation rate coefficients and the two adsorption coefficients in the Arrhenius form. Rather than fitting all of the experimental data with a multiple parameter regression, several constraining relationships were invoked.

Since the pure component degradation rates were zero order, two relationships were used to describe the limiting case of a single adsorbing glycol species, assuming complete saturation of the glycol adsorption sites:

$$k'_{\mathrm{PG}} = k_{\mathrm{PG}} r_{\mathrm{PG}}, \tag{2}$$

$$k'_{\mathrm{EG}} = k_{\mathrm{EG}} r_{\mathrm{EG}}, \tag{3}$$

Table 2
Calculated rate constants for the glycol degradation and glycerol reactions

Parameter	Preexponential factor	Units of PF	Apparent activation energy (kJ/mol)
k'_{G}	25000	$(\mathrm{L}^{3/2}/(\mathrm{min\,mol})^{1/2})$	45
k'_{EG}	4000	(L/min)	45
k'_{PG}	1000	(L/min)	45
k_{G}	230	(L/mol)	1
k_{EG}	0.27	(L/mol)	−17
k_{PG}	4	(L/mol)	0

where $k'_{i\mathrm{G}}$ are the degradation rate coefficients for the two glycols, $k_{i\mathrm{G}}$ are the inhibition constants for the two glycols, and $r_{i\mathrm{G}}$ are the degradation zero-order rates for each glycol as a function of temperature. In addition, the constant relative degradation rate for the glycols added one more constraint. Dividing the rate equations for the two glycols, which have the functional form given in Eq. (1), gave the competitive degradation ratio:

$$k_{\mathrm{r}} = \frac{k'_{\mathrm{EG}}\mathrm{EG}}{k'_{\mathrm{PG}}\mathrm{PG}}, \tag{4}$$

where k_{r} is the competitive degradation ratio, which was found to be 4.1 from the equimolar reactions.

Between the degradation rate equations for the two glycols and the constraining Eqs. (2)–(4), there is a set of five equations for fitting the eight kinetic parameters. With the available rate data, a statistically significant unique set of parameters could not be determined for the parameter set. The parameter estimation was insensitive to combinations of the pre-exponential and activation energy for the two glycol inhibition constants. From the previous isothermal experiments, k_{PG} equaled 4, so a further constraint imposed in the parameter estimation was to set k_{PG} equal to this constant value. This did not affect the quality of fit. Setting either k_{PG} or k_{EG} equal to a constant value while letting the other be fit did not affect the quality of the overall parameter fit. The selection of k_{PG} as the parameter to remain constant rather than k_{EG} was arbitrary. The values obtained from fitting the pre-exponential constants and the apparent activation energies for the ethylene glycol and propylene glycol degradation reactions are given in Table 2. The R^2 value resulting from fitting the 19 reaction points used in the estimation was 0.94.

Since the degradation rate for ethylene glycol increased with temperature relative to the propylene glycol, the model

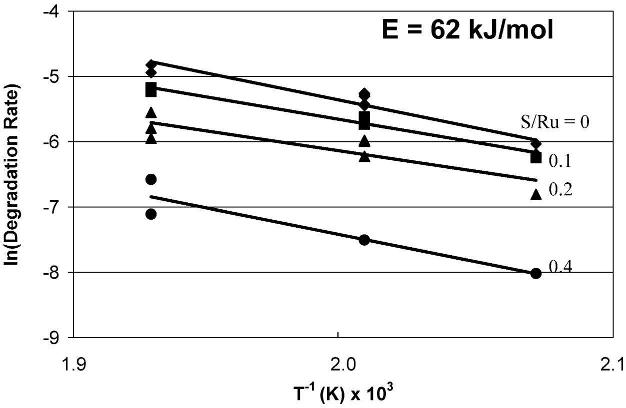

Fig. 1. Effect of sulfur loading on the apparent activation energy of ethylene glycol degradation.

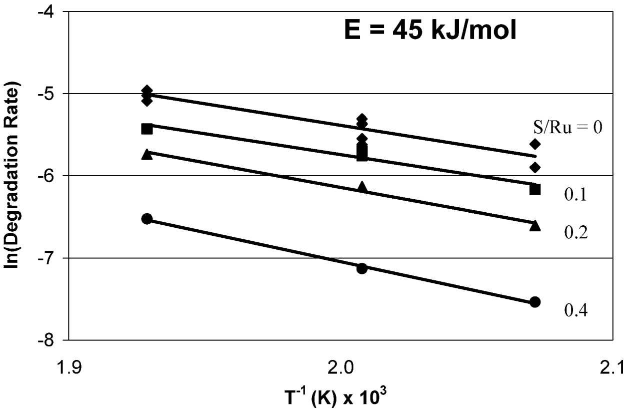

Fig. 2. Effect of sulfur loading on the apparent activation energy of propylene glycol degradation.

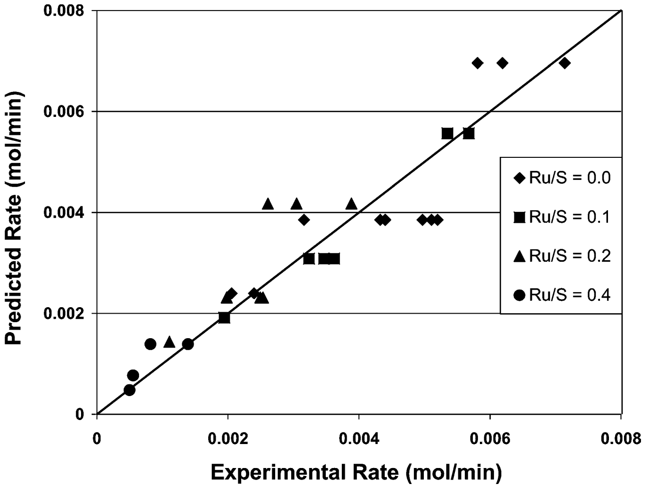

Fig. 3. Parity plot for the ethylene glycol degradation reaction.

suggested that the relative adsorption coverage of ethylene glycol on the catalyst must have decreased to account for the lack of change in the competitive degradation ratio. The less reactive propylene glycol then occupied more active sites as the temperature increased, negating the higher relative reaction rate of ethylene glycol. Therefore, the glycol degradation reaction was a relatively simple system. The glycols adsorbed on the same sites and more sites were covered with propylene glycol as the temperature increased because of the lower relative reactivity of propylene glycol. Despite its reduced coverage, the higher reaction rate for ethylene glycol caused the relative degradation rate to remain constant. Therefore, the glycols were independent of each other on the catalyst.

Glycol degradation experiments were then performed in the presence of sulfur with sulfur/ruthenium molar (S/Ru) ratios of 0–0.8. Within the experimental temperature range the rate of degradation for the glycols became immeasurable for S/Ru ratios greater than 0.5. For both glycols at a sulfur loading of 0.4, the reaction rate decreased to less than 15% of the original sulfur-free reaction rate. The apparent activation energies found for the pure component studies with ethylene glycol and propylene glycol are shown in Figs. 1 and 2. As can be seen from the figures, the apparent activation energies for the degradation reactions appeared to be independent of the S/Ru ratio used. When equimolar initial glycol concentrations were used, the relative degradation rate for the glycols was also independent of the S/Ru ratio. Therefore, Eq. (1) was modified by a linear sulfur factor as follows:

$$-r_{i\mathrm{G}} = \frac{k'_{i\mathrm{G}}(i\mathrm{G})(1-2S)}{k_{\mathrm{EG}}\mathrm{EG}+k_{\mathrm{PG}}\mathrm{PG}+1}, \tag{5}$$

where S is the molar ratio of sulfur to ruthenium. This equation, which fit the degradation data without further adjustment to the sulfur-free parameters given in Table 2, was valid only to a ratio of 0.5, as higher ratios led to no glycol degradation. Fig. 3 shows a parity plot of the observed ethylene glycol degradation rate versus the predicted rate, which confirms the independence of the apparent activation energy from the S/Ru ratio. A parity plot for propylene glycol degradation rates gave a similar result.

Since the apparent activation energies and relative rates for glycol degradation remained constant as sulfur was added, sulfur was not affecting the reaction chemistry but was merely acting to block active sites for the glycol dehydrogenation reactions. If sulfur had a broader affect on the reaction, such as interacting with the glycols or changing the surface chemistry of the catalyst, the apparent activation energy of the degradation reaction would have changed. Once the glycol degradation reactions were thoroughly characterized, the hydrogenolysis reaction behavior of glycerol was determined.

2.2. *Effect of temperature and sulfur on the glycerol reaction*

In a fashion similar to that of the glycols, the glycerol was reacted over a range of temperatures and sulfur loadings at an initial molar concentration range of 2.5–10 wt% (0.3–1.1 M) under mixing with no external mass transfer limitation. Unlike the glycols, the glycerol reaction was not

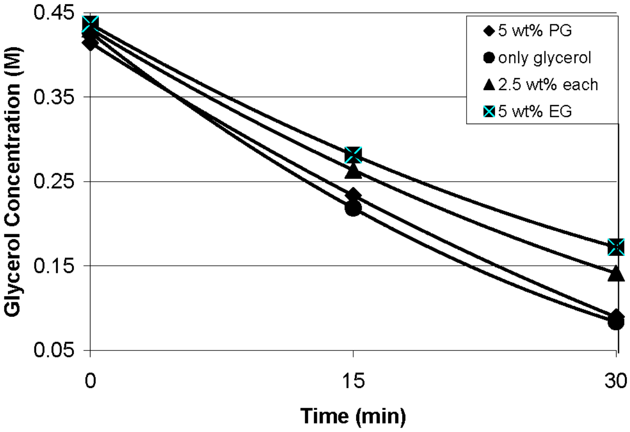

Fig. 4. Glycerol reactivity as a function of glycol concentration at 240 °C.

zero order. The reaction order at 240 °C as determined from initial rate data was 0.5, which was consistent with that reported previously for 205 °C [9]. The reaction order remained constant with all sulfur loadings as well. The relative inhibition effect of the glycols on the glycerol reaction at 240 °C is shown in Fig. 4. The effect shown in this figure is very similar to what was found previously at 205 °C. In both cases, ethylene glycol affected the reaction rate of glycerol in proportion to the amount of ethylene glycol added. In contrast, the addition of propylene glycol had a minimal effect on the reaction rate of the glycerol. Analogous to the development of Eq. (1), parameters for the glycerol reaction were found:

$$-r_{\mathrm{G}} = \frac{k'_{\mathrm{G}}\mathrm{G}^{1.5}}{k_{\mathrm{G}}\mathrm{G} + k_{\mathrm{EG}}\mathrm{EG} + k_{\mathrm{PG}}\mathrm{PG} + 1}, \tag{6}$$

where r_{G} is the glycerol reaction rate, k'_{G} is the glycerol reaction rate coefficient, and k_{G} is the adsorption constant for glycerol. As seen for ethylene glycol and propylene glycol degradation, the relative rates for glycerol reaction and glycol degradation did not vary with temperature. Since the apparent activation energy for the glycerol reaction was lower than that for the degradation of glycols, the fraction of adsorbed glycerol compared with that of the glycols increased with temperature.

The values for the glycerol reaction rate and adsorption constants, which are listed in Table 2, were found from fitting Eq. (6) to glycerol reaction data. In this fitting procedure, the ethylene glycol and propylene glycol adsorption constants were held fixed at the values determined from the pure component degradation reactions. The resulting fit of 80 glycerol reaction data points gave an R^2 of 0.94 for the parameter set listed in Table 2. In a separate parameter estimation, the values in Table 2 were taken as initial guesses, and the glycerol reaction data were refit while all of the parameters were allowed to float. The resulting regressed parameters were not significantly different from those listed in Table 2 and gave an R^2 of 0.94, which was identical.

Eq. (1) gave the rate equations for the degradation of the glycols. The overall rate expressions used to determine the glycol selectivities must also include a generation term resulting from glycerol conversion. It was shown previously that a form of Eq. (6) suitable for the glycols is as follows:

Table 3
Calculated selectivities of propylene and ethylene glycol

	Temperature (°C)	Selectivity	Data points	R^2
Propylene glycol	205	0.19	120	0.79
	220	0.27	27	0.92
	240	0.34	37	0.79
Ethylene glycol	205	0.09	120	0.74
	220	0.11	27	0.67
	240	0.07	37	0.79

$$-r_{i\mathrm{G}} = \frac{k_{i\mathrm{G}}\,i\mathrm{G} - s_{i\mathrm{G}}k'_{\mathrm{G}}\mathrm{G}^{1.5}}{k_{\mathrm{G}}\mathrm{G} + k_{\mathrm{EG}}\mathrm{EG} + k_{\mathrm{PG}}\mathrm{PG} + 1}, \tag{7}$$

where the $i\mathrm{G}$ concentrations correspond to $i = \mathrm{E}$ for ethylene glycol and P for propylene glycol and the $s_{i\mathrm{G}}$ factors are the respective selectivity factors [9]. The selectivity factors were defined simply as the fraction of the glycerol converted into either ethylene glycol or propylene glycol. Since glycerol could also react to form chemical species other than the desired glycols, the selectivity factors for the glycols will not necessarily sum to a value of one. The only glycerol reaction products that were measured were the two glycols. The selectivity factors represent the fraction of glycerol that forms each glycol, separate from the degradation of the glycols. Within the scatter of the data, no change in the selectivity factors was observed over the course of a reaction.

A regression fit of the selectivity factor at the each of the three temperatures studied is given in Table 3. As can be seen, the selectivity for propylene glycol increased as the temperature increased, whereas the ethylene glycol selectivity was essentially constant. At 205 °C, the selectivity for propylene glycol was 0.19, and, at 240 °C, it was 0.34. In contrast, the selectivity for ethylene glycol remained at about 0.09 across the temperature range.

The glycerol reaction was also characterized upon sulfur addition to the reaction system. Unlike with the glycol degradation reactions, sulfur affected the apparent activation energy for the glycerol reaction; the apparent activation energy increased with sulfur concentration, as shown in Fig. 5. The Weisz–Prater number was estimated to be 1.4 at the highest reaction rate, which would correspond to the transition to internal diffusion limitation. However, a concomitant decrease in the observed reaction order from 0.5 to 0 was not observed, indicating kinetic control. Similar to glycol degradation, the glycerol reaction rate decreased with increasing sulfur. However, the glycerol reaction rate was not diminished to the extent that was found for glycol degradation. At a sulfur level of 0.4 S/Ru, the glycerol reaction rate was about 50% relative to the sulfur-free base case and about 30% at a S/Ru of 1.0. Whereas the sulfur effect on glycol degradation could be explained by sulfur blocking only active sites, sulfur played a more complex role in the

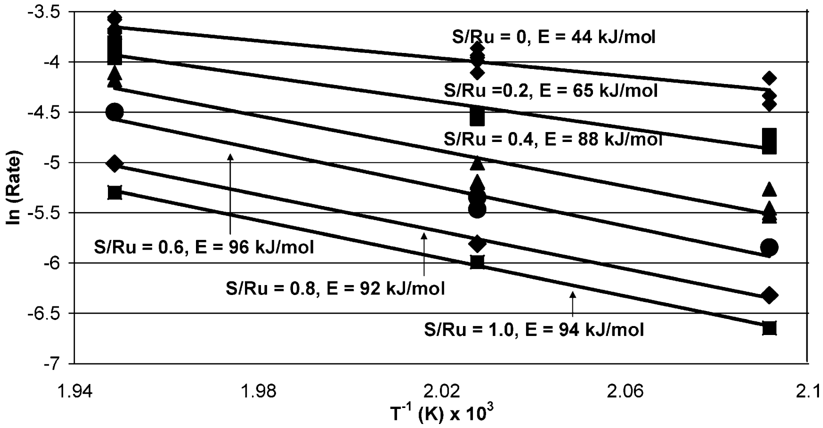

Fig. 5. Apparent activation energy of the glycerol reaction as a function of sulfur loading.

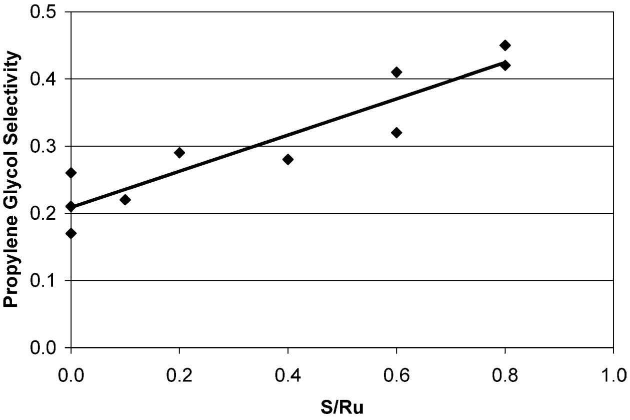

Fig. 6. Effect of sulfur loading on propylene glycol selectivity at 205 °C.

Table 4
Calculated linear effect of sulfur on propylene glycol selectivity

Temperature (°C)	Slope	Intercept	R^2
205	0.27	0.21	0.86
220	0.22	0.26	0.85
240	0.18	0.30	0.70

glycerol reaction. Because of the change in apparent activation energy, there was a reaction step where sulfur affected the active intermediate or there were multiple reaction pathways, one of which is preferentially limited by sulfur.

The propylene glycol selectivity was significantly affected by sulfur loading, but the selectivity for ethylene glycol was not. The initial selectivity for propylene glycol as a function of sulfur loading at 205 °C is shown in Fig. 6. The reaction rate at 205 °C with a sulfur loading of 1.0 S/Ru was too small to produce a measurable selectivity value. The glycol selectivities were determined 15 min after initiation of a reaction, thereby limiting the effect degradation or competitive adsorption had on the results. For all three temperatures studied, the selectivity for propylene glycol increased with sulfur loading. The slope and intercept of the lines for propylene glycol selectivity as a function of sulfur loading are listed in Table 4. For the experimental temperature range, the change in propylene glycol selectivity with sulfur addition was attenuated as the reaction temperature was increased. In a previous study at a low pH of 6, the selectivity for ethylene glycol decreased with increasing sulfur loading [5]. Since the selectivity for ethylene glycol decreases with increasing pH and is at a low value under the high pH conditions [9], a significant change in ethylene glycol selectivity as a function of sulfur loading was not detectable in the current study.

Although the selectivity for propylene glycol increased with the S/Ru ratio, the overall flux toward propylene glycol decreased because of the decreasing glycerol reaction rate. At a S/Ru of 1.0, the flux toward propylene glycol was 60% of its value without sulfur. The higher selectivity for propylene glycol meant that the rest of the products, which were mostly degradation products with some ethylene glycol, had a flux of only 30% of the sulfur-free flux.

3. Discussion

The overall reaction model that has been proposed for the glycerol hydrogenolysis reaction is shown in Fig. 7. Glycerol is first adsorbed and dehydrogenated reversibly on the metal catalyst to form glyceraldehyde. The glyceraldehyde then desorbs from the catalyst and can react through four different paths in the basic media: the retro-aldol mechanism to form the precursor of ethylene glycol (glycolaldehyde), oxidation and subsequent decarboxylation to also form glycol aldehyde, dehydration to the precursor of propylene glycol (2-hydroxypropionaldehyde), or degradation to unwanted side products. The two glycol precursors could potentially also degrade to unwanted side products. Finally, the respective glycol precursors are hydrogenated by the metal function to the product glycols.

Previous studies have demonstrated that sulfur-modified ruthenium yields higher selectivity for propylene glycol and that sulfur interacts with metal catalysts such as ruthenium when operating at high pH. Yet, the previously postulated mechanism would suggest that changes in the relative selectivity for the two glycols would be dictated by solution-

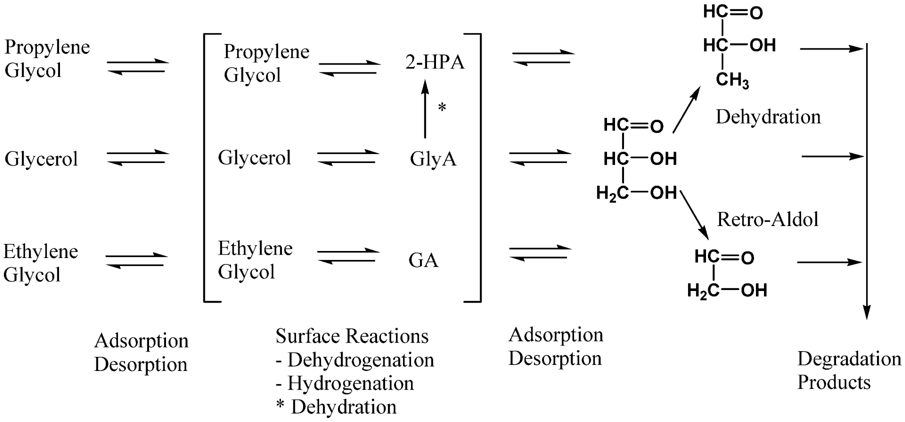

Fig. 7. Overall reaction pathway for the production of glycols from glycerol.

phase reactions, since it is unlikely that sulfur modification of ruthenium would lead to changes in the relative adsorption and reduction selectivity of 2-hydroxypropionaldehyde compared with glycolaldehyde. However, the relative degradation rates of the two glycols did not change with sulfur concentration, and the sulfur did not affect the liquid-phase reactions, since the pH of the solution did not change with the addition of sulfur. The molar ratio of calcium oxide to sulfur in the reaction system at high sulfur levels was 25:1, and the solubility of calcium oxide gave a pH 1 unit higher then the molarity of the sodium sulfide added. Therefore, the postulated model must be missing a key reaction mechanism feature, and this feature must be associated with the solid catalyst.

As manifested by the decreased glycerol reaction rate with increasing sulfur loading, sulfur appeared to block sites that led to the reaction of glycerol to glyceraldehydes, which subsequently desorbed and reacted further. However, the change in apparent activation for the glycerol reaction could not be explained merely by site blockage. There are two ways in which the sulfur could be interacting with the catalyst to produce this result. First, there may be two catalytic pathways that produced propylene glycol, one of which was preferentially blocked by sulfur, and the one being blocked had the lower activation energy. Second, sulfur could affect the active intermediate in the catalytic step that produces propylene glycol. Since sulfur is electronegative, it may attract the carbon atoms enough to weaken the carbon–oxygen bond, allowing for an easier dehydration.

The previously postulated glycerol hydrogenolysis mechanism had glyceraldehyde as a common reaction intermediate for either propylene glycol or ethylene glycol. Therefore, if sulfur interaction with the Ru was changing the energetics of the adsorbed intermediate, the selectivity of both glycols would have been affected. The fact that increased sulfur loading increased only the selectivity for propylene glycol led to the introduction of a proposed alternative dehydration reaction pathway on the catalyst. This added speculative reaction pathway would be represented by direct dehydration of the adsorbed glyceraldehydes, as shown by the arrow with asterisk in Fig. 7.

With this modified reaction network, the relative carbon selectivity through the desorbed glyceraldehyde path and the surface dehydration path could be determined. For this analysis, the end products were placed in three groups: (a) propylene glycol produced through surface dehydration, (b) propylene glycol produced through reaction of desorbed glyceraldehyde in solution, and (c) all other reactions that occur in solution, one of which is the reaction to produce glycolaldehyde and eventually ethylene glycol from glyceraldehyde. The total carbon selectivity of these three pathways sums to unity:

$$a+b+c=a'+b'+c'=1, \tag{8}$$

where a, b, and c represent the relative selectivities for the three groups discussed above without sulfur present and a', b', and c' would represent these selectivities with sulfur present. Eq. (8) can be rearranged to separate the propylene glycol-producing reactions from the remaining reactions:

$$\frac{1-a'-b'}{1-a-b}=\frac{c'}{c}=x, \tag{9}$$

where x is the carbon selectivity for non-propylene glycol products with sulfur relative to the selectivity without sulfur present.

At 205 °C and a sulfur loading of 1.0 S/Ru, x was 0.64. At this sulfur loading, the selectivity for the non-propylene glycol-producing reactions, which are presumed to progress through a common solution-phase glyceraldehye intermediate, were decreased by 36%. For route (b), propylene glycol would also proceed through the solution-phase glyceraldehydes, so the carbon flow through this path would also be expected to be attenuated by 36%. At higher temperatures with the same sulfur loading, this value was 0.74.

Assuming the Fig. 7 flux map is accurate, propylene glycol could be produced from either a purely catalytic route (a) or through a liquid-phase route (b) or a combination of the two. Determining the relative fluxes through these pathways would be useful for catalyst design. Although higher

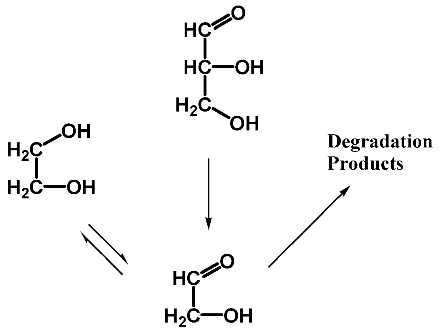

Fig. 8. Glycolaldehyde production and reaction.

sulfur loadings caused the relative selectivity through path (a) to increase, the value of the absolute selectivity through each path is important. Both the dehydration and retro-aldol mechanisms are known to convert solution-phase glyceraldehyde to the two glycol intermediates under reaction conditions; therefore, there is likely to be at least some flux through (b).

In previous work, the selectivity for ethylene glycol was found to vary as a function of pH [9]. At a moderate pH of 8, the instantaneous selectivity for ethylene glycol was 0.26; at a pH of 11, the selectivity dropped to 0.09. Glycolaldehyde, an intermediate in the production of ethylene glycol as shown in the Fig. 8 reaction sequence, has two labile protons on the hydroxyl carbon that are prone to deprotonation. Even though the rates of glycolaldehyde production and reduction toward ethylene glycol are increased at higher pH, the rate of degradation increased more. The degradation reaction is likely more dependent on pH than the production reaction or the catalytic adsorption, because of these labile hydrogen atoms.

The pH dependence on selectivity was not found for propylene glycol [9]. The instantaneous selectivity modeled for both pH levels was constant at 0.19 with a standard deviation of 0.06. The hydrogenolysis reaction selectivity for propylene glycol did not vary with pH through the pH range of 5–11 (as determined with five bases) at either 205 °C or 240 °C. The degradation of the propylene glycol intermediate would likely be pH-dependent; however, this was not found in the regression model, since the selectivity did not change. Thus, two possibilities exist in which there may be little flux toward 2-hydroxypropionaldehyde, or most of the flux that passes through this intermediate also degrades even at moderate pH. If the second situation occurred, it would be difficult to detect a pH dependence on the selectivity for propylene glycol because the ratio of degradation versus reduction of 2-hydroxypropionaldehyde would be high even at moderate pH values. In either situation, the majority of the flux to propylene glycol even without sulfur present must come via dehydration on the catalyst instead of in solution, or else a noticeable difference in selectivity would exist as a function of pH.

Given the preponderance of propylene glycol production through the proposed catalytic dehydration pathway, the increased selectivity for propylene glycol on sulfur-modified ruthenium should focus on the absorbed species. At ambient temperatures, the diffusion of hydrogen on a ruthenium catalyst surface was found to decrease by a factor of 30 upon the addition of sulfur [10]. This effect was caused by both geometric blocking and other long-range electronic effects. Polyols adsorb to ruthenium through oxygen, and for dehydrogenation to occur two hydrogen atoms must diffuse away from the adsorbed polyol. The adsorbed sulfur may slow such diffusion, allowing the more activated dehydration process to occur preferentially. The limiting step in the catalytic dehydrogenation of polyols was the surface reaction, whereas the adsorption and desorption steps were fast [9], so diffusion of hydrogen away from the polyol is required for the catalytic reaction to occur. Although sulfur would decrease the recombination of hydrogen atoms because of a lower diffusion rate and occupation of recombination sites, the desorption of H_2 from ruthenium is not affected by sulfur [11].

The postulate that glycerol can react to form propylene glycol but not ethylene glycol on the catalyst is reasonable, given that different mechanisms are used to convert glycerol into the two glycols. Ethylene glycol can be produced through either a retro-aldol or decarboxylation reaction, the first step of which involves a deprotonation on the hydroxyl group on the β-carbon in relation to aldehyde carbon. Propylene glycol can be produced via dehydration, the first step of which involves a deprotonation of the labile hydrogen for the carbon α from the aldehyde. Whether the catalyst converts an adsorbed glyceraldehyde into propylene glycol through the same mechanism is not known, but it is commonly known that dehydrogenating catalysts can also function as dehydration catalysts.

4. Conclusions

Despite significant interest in hydrogenolysis of higher polyols to glycols, little information is available in the literature for the reaction system because of its complexity. Previous work on the effect of pH on glycerol hydrogenolysis and the degradation of the product glycols was extended to include the effects of temperature and sulfur. Empirical Langmuir–Hinshelwood-type models were developed to characterize the reaction system to improve the understanding of this complex system. Because of competitive adsorption, the relative degradation rates of the glycols were independent of temperature. Sulfur modification of the ruthenium catalysts did not change the activation energy of the degradation reactions, but did dramatically suppress the reactions. Sulfur affected the apparent activation energy of the glycerol reaction, which led to the postulate that dehydration to propylene glycol may be occurring on the catalyst and not just in solution. Previous models for the reaction systems could not reconcile the results. It is not known whether the retro-aldol mechanism is occurring on the catalyst as well as in solution. The selectivity for propylene glycol increased with sulfur loading because of this catalytic reaction. The results suggest that selectivity for propylene glycol relative to ethylene glycol and degradation products can be enhanced in the glycerol hydrogenolysis reaction if the catalyst is active for dehydration.

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