CHAPTER VIII

Kinetics of steam reforming of glyoxal over Ru/Al$_2$O$_3$ catalyst
8.1. Introduction

Present work deals with steam reforming of Ethanedial, generally known as glyoxal with formula OCHCHO over Ru/Al2O3 catalyst. This yellow coloured liquid is smallest dialdehyde group present in bio-oil composition. Its tautomer acetylene diol is highly unstable. Glyoxal is supplied typically as a 40% aqueous solution. Like other small aldehydes, glyoxal forms hydrates. Furthermore, the hydrates condense to give a series of oligomers, the structures of which remain uncertain. Glyoxal is commercially prepared either by the gas phase oxidation of ethylene glycol in the presence of a silver or copper catalyst or by the liquid phase oxidation of acetaldehyde with nitric acid. The first commercial glyoxal source was in Lamotte, France, started in 1960 and currently owned by Clariant. The single largest commercial source is BASF in Ludwigshafen, Germany at ~ 60,000 tons/annum. Glyoxal represents a model compound present in bio-oil which is around 1-2%. Versatile properties of the intermediate glyoxal find its applications in textile manufacturing (efficient crosslinker decreases water uptake in crosslinking cellulose), in oil recovery (glyoxal crosslinks polymers increases the viscosity of fracturing fluids). Glyoxal is also used in the paper, leather, cosmetics, and epoxy industries. It finds its application as disinfectant and wood hardening. Beside known applications, glyoxal shows potential for new applications which are still in the early stages of development.

Extensive research studies on steam reforming, among aldehydic group (glucose) for production of H2 over wide range of temperature and catalyst is known. Glyoxal which is a dialdehydic group can be used to produce hydrogen via steam reforming. In the current work, ethanedial (or glyoxal) was selected as the model bio-oil compound. There is just scarce information in the published literature on this reaction system available. We investigated reaction kinetics in a fixed-bed reactor over the ranges in temperature, 573 to 773 K, glyoxal concentration, 1-5 wt%, and W/F ratio 4.6-18.3 g h/mol using a commercial Ru/Al2O3 catalyst. We selected Ru due to its high activity for C-C bond cleavage and water gas shift, and high thermal stability. Because Ru/Al2O3 has high efficacy for H2 production from other hydrocarbons such as glycerol (Soares et al., 2006) and ethylene glycol (Davda et al., 2005), we anticipated the stable conversion of glyoxal into H2 can be achieved using Ru/Al2O3 catalyst.
8.2. Experimental

8.2.1 Experimental Procedure

An aqueous glyoxal solution was charged from a feed vessel by using an HPLC pump, vaporized in a pre-heater (473 K) and passed over the catalyst placed inside the reactor at the desired temperature. The catalyst was kept between two beds of glass wool. 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 with an accuracy of ±1 cm³/min. The product vapours leaving the reactor were passed through a condenser, back-pressure regulator and gas-liquid separator. The non-condensable gases were analyzed by Gas Chromatography using a valve injection system. Besides, the liquid products were periodically collected and analyzed by Gas Chromatography too. The system pressure was maintained constant at 0.1 MPa. Before each experiment, the catalyst was reduced at 773 K for 1 h in the presence of pure H₂ employed at a flow rate of 50 cm³/min. Since a steady state condition was achieved within 1 h, the results reported here are after 1 h of reaction. Glyoxal conversion was defined as follows:

\[
\text{Glyoxal Conversion (\%)} = \frac{\text{Moles of glyoxal reacted}}{\text{Moles of glyoxal at inlet}} \times 100 \quad (8.1)
\]

H₂ yield, which is a measure of the amount of acetol converted into H₂, was defined as:

\[
\text{H₂ Yield} = \frac{\text{Moles of H₂ produced}}{3 \times \text{Moles of glyoxal reacted}} \quad (8.2)
\]

Its maximum stoichiometric value equals 1 mol/mol. W/Fₐₒ (g h/mol) was defined as the ratio of the mass of the catalyst Ru/Al₂O₃ to the molar flow rate of glyoxal at the inlet; the space time W/Qₒ is much lower. The amount of catalyst (W) used in all experiments was kept constant at 0.3 g. Unless stated otherwise, an initial glyoxal concentration of 10 wt % was used. The liquid feeding rate was varied from 0.25 to 1.0 cm³/min. A nitrogen flowrate of 100 cm³/min was used in all experiments. The total volumetric gas flow rate (303 K, 0.1 MPa) was varied in the range 520 < Qₒ < 1800 cm³/min. All experiments were performed at diluted conditions and hence the
volume change due to reaction was negligible. At 773 K, we reported the values of glyoxal conversion (21%) and H₂ yield (0.12 mol/mol) in the absence of the catalyst.

8.2.2 Product Analysis

The concentrations of H₂, CO, CO₂, and CH₄ were analyzed by thermal conductivity detector with Hayesep DB 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. The condensate was analyzed by using flame ionization detector with OV-101 column.

8.2.3 Catalyst Characterization

BET specific surface area of Ru/Al₂O₃ catalyst was determined using Micromeritics Model ASAP 2100 surface area analyzer. Using N₂ adsorption-desorption isotherms were obtained at 77.5 K over a wide range of relative pressures on samples previously out gassed at 423 K 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 Figs. 8.1. (a) and (b). Irregular particles with different sizes are seen. Certainly, the solid has a porous structure, and there is a presence of granules distributed on the solid surface. The granular characteristics of the catalyst are distinctly seen. Besides, a predominantly porous region with a solid phase distributed on its top is evident. Using energy dispersive X-ray spectroscopy (EDS) technique, it was found that Ru content was 5%.

TPR experiments were conducted using a Micromeritics 2920 TPD/TPR apparatus. In this test, 100 mg of catalyst and a mixture of H₂ and Ar (10% v/v, 20 cm³ (STP)/min) were used. The sample was previously heated to 423 K under dry N₂ (30 cm³ (STP)/min) for 1 h and subsequently cooled at room temperature was then increased under hydrogen mixture at 283 K/min and the TPR profiles were recorded. The temperature was raised to 773 K. The volume of H₂ absorbed was 13.80 (cm³/g STP). The TPR profile is displayed in Fig. 8.2. A sharp signal located at a temperature at peak maximum (Tₘ) of 414.8 K was detected; it may be related to the reduction of unknown Ru species present on the catalyst surface. A shoulder at 442 K
is associated with the reduction of dispersed RuOx species. The $T_m$ for the high
temperature peak at 497 K corresponds to reduction of RuO$_2$.

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. All
properties of the catalyst are summarized in Table 8.1.

8.3. Results and Discussion

Glyoxal steam reforming is a heterogeneous gas solid catalyzed reaction system
which involves following transfer processes: diffusion of the reactants from the bulk
gas phase to the catalyst surface, intra-particle diffusion followed by chemical
reaction at the active centres and diffusion of the product. Any of these mass transfer
processes (external or internal) can influence the rate of the reaction. To investigate
the kinetics parameters, it is essential to ensure mass transfer limitations.

In kinetically controlled reaction regime, the conversion of the reactant should not
depend on the total gas flow rate for a fixed value of W/F ratio. This effect was
studied experimentally at 773 K, S/C ratio of and a catalyst weight of 0.3 g. Glyoxal
conversion was determined to be nearly constant when N$_2$ flow rate was varied at
constant $W/F_{A_0} = 4.57-18.27$ g h/mol. The values are represented in Table 8.2. Thus,
it was confirmed that over the entire range of temperature studied, external mass
transfer resistance was absent.

Absence of pore diffusion limitation was determined by the study of effect of
catalyst particle size on conversion. Experiments was conducted at T=773K. To show
that intra particle diffusion was negligible, experiments were performed by using
larger particles in the size range of 150-210 µm and smaller particles size in the range
of 23-69 µm. Experimental results demonstrate that there was practically no change in
glyoxal conversion. Glyoxal conversion for 150-210 µm and 23-69 µm was
respectively. Thereby, absence of intra particle diffusion was inferred. Since the
reaction rates was not influenced by mass transfer process at highest temperature used
in current study (i.e., 773 K), the absence of diffusion limitation at lower temperature
(i.e., 573 K) was anticipated. Hence, subsequently all experiments was performed by
using particle size in the range of 23-69 µm. The results are summarized in Figs. 8.3
and 8.4, and in Table 8.3. Fig. 8.3 shows plot of $X$ vs. $W/Q_o$ at different temperatures, whereas Fig. 8.4 shows effect of temperature on $H_2$ yield.

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

$$r = \frac{dX}{d(W/F_{A_0})}$$  \hspace{1cm} (8.3)

The reaction order with respect to glyoxal was determined by using the integral method of analysis. Using this simple technique, Vaidya and Rodrigues (2006) reported first-order kinetics for the steam reforming of another oxygenate – ethanol – using Ru/Al$_2$O$_3$ catalyst. Sutar et al. (2010) established that the steam reforming reaction is of the first order with respect to glycerol over a Pt/C catalyst. Therefore, it was anticipated first-order kinetics for this work, too. For a first order reaction, the following relation holds:

$$X = 1 - e^{-kW/Q_0}$$  \hspace{1cm} (8.4)

Eq. 8.4 can be rewritten in the following form:

$$\ln(1 - X) = -\frac{kW}{Q_0}$$  \hspace{1cm} (8.5)

Water is in large excess and, therefore, the reaction order with respect to water is assumed to be zero. Hence, Eq. 8.5 does not account for the water concentration. The plots of $\ln (1 - X)$ vs. $W/Q_o$ at various temperatures are shown in Fig. 8.6. Since the data reasonably fall on a straight line, the investigated reaction is of the first order with respect to glyoxal.

From the values of the slopes, the specific reaction rate constant $k$ at various temperatures was estimated. The values of $k$ at 573, 673 and 773 K were found to be $1.2\times10^5$, $1.9\times10^5$ and $3.0\times10^5$ cm$^3$/(g$_{cat}$ h) respectively. The Arrhenius plot is shown in Fig. 4.10. The activation energy was evaluated as 15.5 kJ/mol. It was ensured the absence of diffusion resistances; even so, our value of $E_{act}$ is lower than those reported by other researchers. 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 $E_{act}$.

The experimental and predicted conversions (Fig. 8.5) were compared, and there exists good agreement between them. From knowledge of mole fraction of glycerol in feed, system pressure and conversion, the values of glyoxal partial pressures were evaluated. The values of $r$ were estimated using Eqs. 8.4 and 8.5. The variation in the reaction rate with glycerol partial pressures is shown in Fig. 8.7. 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 glyoxal 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.

8.4 Conclusions

Glyoxal represents a di-aldehydic fraction in bio-oil. In this work, the kinetics of the glyoxal steam reforming reaction was investigated in a fixed-bed reactor over wide ranges in temperature (573-773 K), glyoxal concentration (1 & 5 wt %) and $W/F_{A_o}$ ratio (4.6–18.3 g h/mol) using a commercial 5% Ru/Al$_2$O$_3$ catalyst. It was found that high temperature and space time facilitate H$_2$ production from glyoxal. The absence of mass transfer resistances (external and internal) was ascertained. Kinetic data was summarized. The influences of reaction variables on H$_2$ production were investigated.
Figure 8.1: SEM image of unused Ru/Al₂O₃
Figure 8.2: TPR profile of unused Ru/Al₂O₃
**Figure 8.3:** Effect of the Temperature (K) ratio on glyoxal fractional conversion at

\[ \frac{W}{F_0} \] ratio ranging from 4.57-18.27 \( \text{g}_{\text{cat.h}}/\text{mol} \)
Figure 8.4: Effect of the temperature on the H₂ yield.
Figure 8.5: Effect of the space time on glyoxal conversion at 573, 673 and 773K; points: experimental data, curves: predictions from Eq. 4.10 (glyoxal = 5 wt%, catalyst wt.=0.3 g, system pressure = 0.1 MPa).
**Figure 8.6:** Plots of ln(1-X) vs. W/Q₀ (glyoxal 5 wt %, catalyst wt = 0.3 g, system pressure = 0.1 MPa).
Figure 8.7: Plots of reaction rate vs. glycerol partial pressure.
Table 8.1: Effect of total gas flow rate on glyoxal conversion at 773 K

<table>
<thead>
<tr>
<th>N₂ flow rate (cm³/min)</th>
<th>Qₒ (cm³/min)</th>
<th>Glyoxal Conversion (%)</th>
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<tbody>
<tr>
<td>50</td>
<td>1743.8</td>
<td>59.0</td>
</tr>
<tr>
<td>100</td>
<td>1793.8</td>
<td>60.3</td>
</tr>
<tr>
<td>150</td>
<td>1843.8</td>
<td>62.5</td>
</tr>
<tr>
<td>200</td>
<td>1893.8</td>
<td>64.7</td>
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Table 8.2: Kinetic data at various temperatures

<table>
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<tr>
<th>Temp. (K)</th>
<th>Liquid feeding rate (cm³/min)</th>
<th>Glyoxal conversion rate (cm³/min)</th>
<th>H₂ yield (cm³/min)</th>
<th>Q₀ (g/min)</th>
<th>W/Fₐ₀ (g h/mol)</th>
<th>Mole fraction of glyoxal in feed</th>
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<tr>
<td>573</td>
<td>0.25</td>
<td>0.71</td>
<td>0.66</td>
<td>523.5</td>
<td>18.27</td>
<td>0.0130</td>
</tr>
<tr>
<td>573</td>
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<td>0.49</td>
<td>0.57</td>
<td>946.9</td>
<td>9.13</td>
<td>0.0144</td>
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<td>0.0152</td>
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<td>0.75</td>
<td>523.5</td>
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<td>0.65</td>
<td>0.68</td>
<td>946.9</td>
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<tr>
<td>673</td>
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<td>0.55</td>
<td>0.60</td>
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<tr>
<td>773</td>
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<td>0.59</td>
<td>0.57</td>
<td>1793.8</td>
<td>4.57</td>
<td>0.0152</td>
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Table 8.3: Properties of Ru/Al₂O₃ catalyst and their performance at 773 K

<table>
<thead>
<tr>
<th>Metal loading (%)</th>
<th>Crystallite size d_p (nm)</th>
<th>Dispersion D (%)</th>
<th>Glyoxal Conversion (%)</th>
<th>H₂ formation rate (mol/min/g_cat)</th>
<th>TOF (H₂ l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>36.5</td>
<td>3.63</td>
<td>59.6</td>
<td>0.0037</td>
<td>217.3</td>
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<tr>
<td>5.0</td>
<td>38.4</td>
<td>3.44</td>
<td>53.0</td>
<td>0.0004</td>
<td>226.7</td>
</tr>
</tbody>
</table>

\[
D = \left(\frac{2 \times H_2 \text{ adsorption}}{\text{reduced Ru}}\right) \times 100
\]

\[
D = \left(\frac{\text{number of surface atoms}}{\text{total number of atoms of specified catalytic phase}}\right) \times 100
\]

\[
\text{TOF of } H_2 \ (\text{l/min}) = \frac{\text{Moles of } H_2 \text{ produced}}{(\text{Mole of surface metal } \times \text{ min})}
\]