CHAPTER 6:

CATALYST ACTIVITY TESTS FOR

GLYCEROL AND ETHYLENE GLYCOL CONVERSION
6.1. Introduction

In this chapter, catalytic steam reforming of glycerol and ethylene glycol is investigated using several noble metal and Ni based catalysts.

Glycerol is an oxygenated hydrocarbon having one hydroxyl group on each carbon atom and a carbon-to-oxygen ratio equal to 1. It is nontoxic, non-flammable and high-boiling, and is a poor fuel which does not burn in petrol or diesel engines (Scharmer, 2006). Glycerol can be obtained as a by-product in soap manufacture, biodiesel production (Zhou et al., 2008). With the increase in the production of biodiesel and the reduction in glycerol price, glycerol is expected to become a major platform for chemicals. Crude glycerol by-product with an estimated 50% purity has few direct uses and is of low value. Its disposal is difficult and its high methanol content renders as hazardous. However, this crude glycerol stream has a good potential for H₂ production and the reforming of this aqueous stream is attractive (Vaidya and Rodrigues, 2009). The glycerol steam reforming reaction is represented as:

\[ C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad \Delta H_{25^\circ C} = -128 \text{ kJ/mol} \] (6.1)

Ethylene glycol (EG) is the simplest diol and is similar in structure to the larger polyols contained in biomass oxygenated compounds. Its concentration in the bio-oil aqueous fraction is as high as 2% (Dielbold, 1999). It is an important building block for chemical synthesis in several industrial processes. It used as antifreeze and raw material in the production of polyester fibres. EG is a sustainable chemical since it can be generated from sugars, sugar-alcohols (Blanc et al., 2000; Sun and Liu, 2011) and cellulose (Zhang et al., 2010; Zheng et al., 2010). For this reason, it is considered as a promising feedstock for H₂ production via reforming (Cortright et al., 2002). The EG steam reforming reaction represented as:

\[ C_2H_6O_2 + 2H_2O \rightarrow 5H_2 + 2CO_2 \quad \Delta H_{25^\circ C} = 86.2 \text{ kJ/mol} \] (6.2)
In this chapter, steam reforming of glycerol and ethylene glycol was investigated at low temperature \( T = 500 \, ^\circ\text{C} \) using commercial alumina and carbon supported catalysts such as Ni/Al\(_2\)O\(_3\), Ru/Al\(_2\)O\(_3\), Pt/C, Pd/C and Ru/C and steam-to-carbon ratios (S/C) between 14.3 and 15.5 mol/mol.

### 6.2. Catalyst Characterization

All catalysts used for this study were characterized by using BET, TEM, SEM-EDX and XRD techniques. The properties of Ru/Al\(_2\)O\(_3\) were earlier discussed in Chapters 4 and 5. The physicochemical properties of all catalysts are summarized in Table 6.1. N\(_2\) adsorption–desorption isotherms were obtained at -195.5 \(^\circ\text{C} \) over a wide range of relative pressures using a SMART SORB 93 automatic device on samples previously out gassed at 150 \(^\circ\text{C} \) for 12 h. BET specific surface areas were calculated from these isotherms using the BET method.

Transmission electron microscopy (TEM) characterization was carried out using a JEOL 2010 instrument with a point-to-point resolution better than 0.19 nm. TEM specimens were prepared by ultrasonically dispersing the catalyst in acetone, and then placing a drop of the suspension on a carbon coated grid. The surface morphology of the catalyst was examined by scanning electron microscopy (SEM) on a JEOL 6300 microscope, coupled with energy-dispersive X-ray analysis for determination of elemental composition.

Powder X-ray diffraction patterns were recorded in a Philips X’pert diffractometer equipped with a curved graphite monochromator. CuK\(_a\) (\( \lambda = 0.15406 \) nm) radiation was used. Scanning was done over the range 2\( \theta = 5 - 100^\circ \). The position and width of peaks were obtained by a standard profile fitting routine provided by Philips.
Fig. 6.1 represents the TEM photographs. TEM images of the spent catalyst samples show major differences in the way carbon was deposited on the catalyst surface. Figs. 6.1 A, C, E, G and I illustrate the image of fresh Pt/C, Pd/C, Ru/C, Ru/Al₂O₃ and Ni/Al₂O₃ catalyst respectively, whereas, Figs. 6.1 B, D, F, H and J demonstrate the images of the spent Pt/C, Pd/C, Ru/C, Ru/Al₂O₃ and Ni/Al₂O₃ and respectively. Images obtained from used catalyst were different from those obtained using the fresh catalyst. The used images of all the metal supported catalysts consist prominent dark spots which are absent in unused images. These dark spots may be due to carbon formation on the active surface site. In case of Ru/Al₂O₃, the support particles were of stick shape, whereas Ru on the surface of Al₂O₃ was in the form of fine spherical particles. Pd/C spent catalyst shows a distinct tube shaped structure thereby indicating formation of carbon particles.

In order to investigate the influence of metal supported catalyst on alumina and carbon catalyst XRD analysis was used to determine the phase composition. The fresh catalyst sample of Ru/Al₂O₃ and Ru/C was reduced using pure H₂ prior to XRD analysis. The fresh and spent catalysts exhibit similar XRD patterns (see Fig. 6.2). The peak at (2θ = 26.6°) is attributed to C, the peaks at 37° and 44° are characteristic of Ru (\(\text{Ru}^+\)). Diffraction peaks of Ru\(^+\) species were observed (2θ = 37° and 44°). Very small diffraction peaks (2θ = 28°, 34° and 54°), hardly distinguishable from the background noise, indicate very small amounts of RuO₂. The used catalyst does not exhibit any new diffraction lines, thereby signifying that no new phase is formed in the catalyst in during reaction.
6.3. Results and Discussion

6.3.1. Glycerol Reforming

The performance of Ru/Al₂O₃, Ni/Al₂O₃, Ru/C, Pd/C and Pt/c was investigated at T=500 °C. The results are shown in Figs. 6.3 a, b, c and d.

As can be seen in Fig. 6.3a H₂ selectivity using Ni/Al₂O₃ and Ru/Al₂O₃ catalyst was equal to 92.7% and 67.6% respectively. Due to C-C Cleavage on catalytic surface The H₂ selectivity for the C-supported catalysts was of the order reaction at 500 °C was in the order: Ru/C > Pt/C > Pd/C. Thus, Ru promotes WGS reaction. Ru catalysts are known for their enhanced activity in WGS reaction (Hirai et al., 2005). It was found Pd/C exhibits high CO selectivity (52.6%). CO selectivity among all the C-supported catalyst decreased in order Pd/C> Pt/C> Ru/C. CH₄ selectivity was observed that low in using Ru/Al₂O₃ was 2.8%, whereas Ru/C (4.0%) catalysts.

Table 6.2 shows the values of glycerol conversion to gas phase products. As seen in in Table 6.2 gas phase conversion was 14.6% and 17.55% using Ni/Al₂O₃ and Ru/Al₂O₃ catalysts respectively. Whereas, 15.9%, 17.7% and 28.2% using Pd/C, Pt/C and Ru/C respectively, at W/Fₐo ratio equal to 4.6 g h/mol and steam to carbon ratio equal to 14.3 mol/mol. Thus, Ru/C catalyst facilities high carbon to gas phase conversions.

6.3.2. Ethylene Glycol Reforming

The performance of Ru/Al₂O₃, Ni/Al₂O₃, Ru/C, Pd/C and Pt/c was investigated at T=500 °C. The results are shown in Figs. 6.4 a, b, c and d.

As can be seen in Fig. 6.4a H₂ selectivity using Ru/Al₂O₃ and Ni/Al₂O₃ catalyst was equal to 49.6% and 79.1% respectively. The H₂ selectivity for the C-supported catalysts was of the order reaction at 500 °C was in the order: Ru/C > Pt/C > Pd/C. It was found Pd/C exhibits high
CO selectivity (32.6%). CO selectivity among all the C-supported catalyst decreased in order Pd/C > Pt/C > Ru/C. whereas, alumina supported catalysts are Ni/Al₂O₃ > Ru/Al₂O₃ respectively. CH₄ selectivity was observed that high in using Pt/C was 19.8%.

Table 6.2 shows the values of ethylene glycol conversion to gas phase products. As seen in Table 6.2 gas phase conversion was 49.1% and 45.7% using Ni/Al₂O₃ and Ru/Al₂O₃ catalysts respectively. Whereas, 36.4%, 44.1% and 41.1% using Pd/C, Pt/C and Ru/C respectively, at W/Fₘ ratio equal to 3.1 g h/mol and steam to carbon ratio equal to 15.5 mol/mol. Thus, Ni/Al₂O₃ catalyst facilities high carbon to gas phase conversions.

6.4. Conclusions

In the present work, reactions of glycerol and ethylene glycol steam reforming was investigated in a fixed-bed reactor T=500 °C, and W/Fₘ ratio 4.6 and 3.1 g.h/mol and S/C ratio was 14.3, and 15.5 mol/mol respectively, over a carbon supported catalyst such as Ru/C, Pt/C and Pd/C and alumina supported catalyst such as Ru/Al₂O₃ and Ni/Al₂O₃. It was observed that alumina supported catalyst especially Ni/Al₂O₃ ≥ Ru/Al₂O₃ was given a best catalytic performances towards H₂ selectivity and gas phase conversions and C-supported catalysts was in order Ru/C > Pt/C > Pd/C. In fact that Ru/C catalyst was shows a stable performance long time over than other carbon supported catalyst.
Fig. 6.1 TEM images of the used and unused metal supported catalyst.
Fig. 6.1 TEM images of the used and unused metal supported catalyst.
Fig. 6.2 XRD patterns of the fresh and spent Ru/C and Ru/Al₂O₃ catalysts.
Fig. 6.3 Product selectivity as a function of time on steam (♦)-Ru/Al$_2$O$_3$, (□)-Ru/C, (×)-Pt/C, (○)-Pd/C, (Δ)-Ni/Al$_2$O$_3$ catalyst, at T=500 °C, pressure =0.1 MPa, W/F$_{AO}$=4.6 g h/mol, S/C ratio=14.3 mol/mol.
**Fig. 6.4** Product selectivity as a function of time on steam (♦)-Ru/Al$_2$O$_3$, (□)-Ru/C, (×)-Pt/C, (○)-Pd/C, (Δ)-Ni/Al$_2$O$_3$ catalyst, at T=500 °C, pressure =0.1 MPa, W/F$_{AO}$=3.1 g h/mol, S/C ratio=15.5 mol/mol.
Table 6.1 Physiochemical properties of all the investigated catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni/Al₂O₃</th>
<th>Ru/Al₂O₃</th>
<th>Ru/C</th>
<th>Pt/C</th>
<th>Pd/C</th>
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<tr>
<td>Metal loading (wt.%)</td>
<td>20</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>aSurface area (m²/g)</td>
<td>150.08</td>
<td>78.51</td>
<td>669.50</td>
<td>950.07</td>
<td>1069.82</td>
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<tr>
<td>aTotal Pore Volume (cc/g)</td>
<td>0.117</td>
<td>0.19</td>
<td>0.3765</td>
<td>0.5359</td>
<td>0.5071</td>
</tr>
<tr>
<td>aAverage pore diameter (Å)</td>
<td>31.183</td>
<td>96.80</td>
<td>22.494</td>
<td>22.562</td>
<td>18.960</td>
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</table>

aBET-surface analysis
Table 6.2 Efficacy of metal supported catalysts for steam reforming of glycerol and ethylene glycol. Reaction conditions: P=0.1 MPa, T =500 °C, catalyst Wt.=0.3 g, reaction time =1 h.

<table>
<thead>
<tr>
<th>Feed stock</th>
<th>S/C (mol/mol)</th>
<th>W/F&lt;sub&gt;AO&lt;/sub&gt; (g h/mol)</th>
<th>Gas phase conversion (%)</th>
<th>Ni/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Ru/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Ru/C</th>
<th>Pt/C</th>
<th>Pd/C</th>
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<tr>
<td>Glycerol</td>
<td>14.3</td>
<td>4.6</td>
<td></td>
<td>14.6</td>
<td>17.5</td>
<td>28.2</td>
<td>17.7</td>
<td>15.9</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>15.5</td>
<td>3.1</td>
<td></td>
<td>49.2</td>
<td>45.7</td>
<td>41.1</td>
<td>44.1</td>
<td>36.4</td>
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