Conversion of crude glycerin to formic acid: Use of iron oxide supported alumina in liquid phase system

Victor A. A. Freitas1*, Patterson P. Souza2, Márcio Portilho1, Henrique S. Oliveira1 and Luiz C. A. Oliveira1
1Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais (Brazil).
2Centro Federal de Educação Tecnológica de Minas Gerais (Brazil)
3CENPES-Petrobras, Cidade Universitária, Q7, Ilha do Fundão, Rio de Janeiro (Brazil)
*viktoraugusto.freitas@gmail.com

Introduction

Glycerol (1,2,3-propanetriol) is a molecule with wide possible reaction pathways, which depending on the route, could lead to value-added chemicals. One of those products is formic acid, which is a commodity chemical that is widely used in the chemical, agricultural, textile, leather, pharmaceutical, and rubber industries [1]. In addition, it may be employed as hydrogen source for fuel cells application. Noble metals as Pd, Ru, Rh over a range of supports like silica and alumina or in homogenous phase has been used for increase the rate of selective oxidation of glycerol in batch system [2]. However, cheaper catalysts compatible with flow system are desirable to turn this reaction route attractive for an industrial scale. We have synthesized a simple iron-based catalyst dispersed in alumina support capable of convert crude glycerin in liquid phase system into formic acid with a high selectivity.

Materials and Methods

Catalyst preparation

Iron oxide/alumina was prepared by classical impregnation of alumina with Fe(NO3)3·9H2O solution to promote catalyst with 5% wt of iron oxide. Iron salt was dissolved into water and mixed with alumina support at 60 ºC and stirred until dry. The red powder denominated FeO/Al2O3 was calcinated at 500 ºC/3 h. The catalyst was characterized by Mössbauer spectroscopy and N2 adsorption/desorption.

Flow reactions

Reactor was filled with CSi and the appropriate amount of catalyst. Feedstock solution was prepared with crude glycerin/H2O (35%) solution 50% v/v. The flow rate was 0.4 mL.min−1 and temperature 423 or 473 K. The products passed through a condenser, collected each 3 h into stainless steel vessel, and analyzed by GC-MS.

Results and Discussion

The iron oxide crystalline phase are finely dispersed at Al2O3 support as diagnosed by Mössbauer spectroscopy with central duplet with δ = 0.32 nm s−1, ε = 0.6 nm s−1 (Figure 1a). Nitrogen adsorption gave a specific area = 184 m² g⁻¹ estimated by BET method, whose isotherm lies in a type-2 with H2 hysteresis loop (Figure 1b). Hence, the catalyst shows porous at interparticle void.

Results and Discussion

The iron oxide crystalline phase are finely dispersed at Al2O3 support as diagnosed by Mössbauer spectroscopy with central duplet with δ = 0.32 nm s⁻¹, ε = 0.6 nm s⁻¹ (Figure 1a). Nitrogen adsorption gave a specific area = 184 m² g⁻¹ estimated by BET method,whose isotherm lies in a type-2 with H2 hysteresis loop (Figure 1b). Hence, the catalyst shows porous at interparticle void.

Figure 1 Mössbauer spectroscopy at 298 K (a) and Nitrogen adsorption/desorption and pore distribution (BJH) (b)

Table 1 summarizes the conversion and products distribution. The reaction was very selective for formic acid (FA) at 473 K reaching a conversion of 58.5 %. Other oxidation products such as butadiene (BDN), acetic acid (AA) and dehydration product hydroxypropanone (HPN) were obtained in small amounts. Absence of other oxidation intermediates as glycolic acid and dihydroxyacetone, indicates that glycerol oxidation in presence of H2O2 and FeO/Al2O3 was not interrupted. However the presence of glycerol formal (GF), a mix of 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane, shows formaldehyde production. This formaldehyde in presence of FA reacts with glycerol molecules, hindering further oxidation. The FA selectivity increased by decreasing the process temperature to 423 K (~76 % at 65 h) and a decrease in GF formation. Other oxidation and dehydration products were obtained in a smaller amount. This results indicate that at lower temperatures, the operating conditions (flow rate, [glycerol]/[H2O2]-[H2O2], temperature and catalyst mass) promote a higher crude glycerin conversion into formic acid rather than glycerol formals. Doubling the catalyst mass increased the conversion to 76% but it favored a decomposition of FA, probably into CO2.

Table 1 Crude glycerin conversion and products distribution of reactions carried at flow system with FeO/Al2O3 catalyst

<table>
<thead>
<tr>
<th>Temperature  (K)</th>
<th>Mass of catalyst (g)</th>
<th>Conversion (%)</th>
<th>Products distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>0.375</td>
<td>58.5</td>
<td>70.0  3.2  3.8  2.6  20.4</td>
</tr>
<tr>
<td>473*</td>
<td>0.750</td>
<td>66.7</td>
<td>60.4  0.6  2.8  1.7  34.5</td>
</tr>
<tr>
<td>423*</td>
<td>0.300</td>
<td>76.08</td>
<td>79.0  1.9  3.5  0.6  15.0</td>
</tr>
</tbody>
</table>

a = after 65 h; b = after 30 h

Significance

Obtain formic acid, which is an important commodity chemical, from a renewable source such as crude glycerol in flow system and mild conditions will strengthen the sustainable technologies and process.

References