Ir-Based Bimetallic Catalysts for Hydrogen Production through Glycerol Aqueous-Phase Reforming

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Abstract: Iridium, Iridium-Nickel and Iridium-Copper catalysts were prepared by incipient wetness impregnation and evaluated in the aqueous-phase reforming of glycerol using La2O3 or CeO2 as supports. The catalysts were characterized by N2 physisorption, XRD, H2-TPR, XPS, and EDS. The reactions were carried out in a fixed bed reactor feeding a solution of glycerol (10 wt %) in water, at 270 °C and 58 bar. All IrNi catalysts showed higher activity than Ir and IrCu, and in general, La2O3 catalysts showed a better performance when compared to CeO2 catalysts. The highest hydrogen production yield was reached by bimetallic IrNi catalysts with over 250 µmol min⁻¹ gcat⁻¹ for La2O3 and 150 µmol min⁻¹ gcat⁻¹ for CeO2.

Keywords: iridium; glycerol; aqueous-phase reforming; hydrogen production

1. Introduction

Fossil fuels have been the main energy source used to satisfy society’s needs since 1950, with a contribution of 64% of the global primary energy [1] and with 86% of global contribution registered in 2015 [2]. Issues related to the usage of fossil fuels such as depletion of reserves, rising of polluting gases and climate change have been addressed elsewhere [3–7]. Renewable energy is an alternative to the use of hydrocarbons. Among renewable energy types, hydrogen technology is a promising one. Hydrogen is not considered as an energy source but an energy carrier, and it can be harnessed for direct energy production through its use in fuel cells [8–11]. A drawback for hydrogen is that it must be obtained or produced from other sources such as water or biomass, for instance. Therefore, several methods have been studied for obtaining hydrogen, such as pyrolysis, electrolysis, biochemical processes with bacteria and algae, and reforming processes (using alcohols, oils) [12–15]. Among the different reforming processes, aqueous-phase reforming (APR) is a promising option. In APR, a substrate reacts in the presence of a catalyst at low-to-medium temperatures, splitting molecules and producing hydrogen, among other compounds. APR was investigated for the first time in 2002 by Dumesic and his workgroup, and since then they have explained the details on thermodynamics and the kinetics of the process [16]. Oxygenated hydrocarbons, such as alcohols have
been studied as APR substrate [17–20]. Otherwise, glycerol is a biodiesel production byproduct, about 10 wt% of fats and oils used in biodiesel production turn to glycerol. Therefore, glycerol has gained interest as it will be more available with the increase of the biodiesel industry. Despite its multiple uses in areas such as in medicine or the cosmetic industry, the market is limited, and then it is necessary to explore for potential additional uses that result in an added value for glycerol [20,21]. Iridium has been studied in the APR of methanol [22,23], ethylene glycol [24], and ethanol [25], and more extensively studied as a catalyst for other processes [26–33]. However, as far as the authors know, Iridium has never been analyzed using glycerol as a raw material under APR conditions. Iridium has shown high activity and H$_2$ selectivity when using ethanol [25]. Nevertheless, a drawback for the use of Ir in APR is the low activity in the water-gas shift reaction, a fundamental step in obtaining higher H$_2$ yields [24]. Therefore, it is necessary to conduct a study focused on overcoming that barrier to maximize the formation of H$_2$. Nickel has high activity on C-C bonds cleavage, although it also shows activity in the methanation process, which consumes hydrogen. On the other hand, Cu has shown significant activity mainly for the water-gas shift reaction. Therefore, in this work, the use of Ni and Cu as second metals in Iridium catalysts to produce a synergetic effects for hydrogen are proposed.

2. Results and Discussion

2.1. Catalysts Characterization

2.1.1. Physical Properties

Table 1 summarizes the textural properties of catalysts after calcination. The specific surface area of La$_2$O$_3$-supported catalysts is slightly bigger than CeO$_2$ catalysts. La$_2$O$_3$ catalysts have almost twice the pore volume than CeO$_2$ catalysts, causing a better metal dispersion.

| Catalyst          | S$_{BET}$/m$^2$ g$^{-1}$ | V$_p$/cm$^3$ g$^{-1}$ | Pore Size (Average Radius/Å) |
|-------------------|-------------------------|----------------------|-----------------------------|
| La$_2$O$_3$       | 9.1 ± 0.5               | (2.5 ± 0.3)$ \times 10^{-2}$ | 55.4 ± 0.1                  |
| Ir/La$_2$O$_3$    | 10.2 ± 0.6              | (2.2 ± 0.2)$ \times 10^{-2}$ | 42.5 ± 0.1                  |
| IrCu/La$_2$O$_3$  | 6.7 ± 0.4               | (1.3 ± 0.1)$ \times 10^{-2}$ | 39.2 ± 0.1                  |
| IrNi/La$_2$O$_3$  | 10.1 ± 0.6              | (2.4 ± 0.3)$ \times 10^{-2}$ | 47.0 ± 0.1                  |
| CeO$_2$           | 7.7 ± 0.5               | (2.8 ± 0.3)$ \times 10^{-2}$ | 67.8 ± 0.1                  |
| Ir/CeO$_2$        | 4.2 ± 0.2               | (6.7 ± 0.7)$ \times 10^{-3}$ | 32.1 ± 0.2                  |
| IrCu/CeO$_2$      | 5.3 ± 0.3               | (7.9 ± 0.8)$ \times 10^{-3}$ | 29.8 ± 0.2                  |
| IrNi/CeO$_2$      | 4.8 ± 0.3               | (8.5 ± 0.9)$ \times 10^{-3}$ | 35.7 ± 0.2                  |

La$_2$O$_3$ is a hygroscopic material that changes its phase by exposure in air forming La(OH)$_3$ and La$_2$O$_2$CO$_3$ [34]. Despite the presence of other phases, catalysts with that support will be named as La$_2$O$_3$ for simplicity. For La$_2$O$_3$ catalysts, there is a small surface area increase with metal addition. It has been seen that an increase in the catalyst’s surface area can be related to the diffusion of metal species in support and formation of new pores as proposed by Said et al. [35]. For this material, increase in the surface area may occur due to the formation of species such as NiO and La$_2$NiO$_4$ as exposed by TPR results presented in Section 2.1.5. Thyssen et al. [36] also reported surface area increments for La$_2$NiO$_4$ after incorporating Ni. For CeO$_2$ support, the addition of metals caused a specific surface area decrease and reduced pore volume by one order of magnitude.
2.1.2. X-ray Diffraction

XRD pattern for Ir/CeO$_2$ is presented in Figure 1. CeO$_2$ diffraction peaks can be clearly seen, whereas for Ir, only one diffraction peak at around 34.5° was identified (Figure 1 inset), corresponding to IrO$_2$. It may be due to the low concentration and high dispersion of the metal on the support. This result was similar to those obtained with Ni and Cu as shown in Figures 2 and 3, respectively, where metal oxides can be seen in the insets with a logarithmic scale.

![Ir/CeO$_2$ diffraction pattern.](image1)

Figure 1. Ir/CeO$_2$ diffraction pattern.

![IrNi/CeO$_2$ diffraction pattern.](image2)

Figure 2. IrNi/CeO$_2$ diffraction pattern.
Figure 4 shows the XRD patterns of the La\textsubscript{2}O\textsubscript{3} supported catalysts. Due to the hygroscopic nature of the La\textsubscript{2}O\textsubscript{3}, the diffraction patterns shifted towards La(OH)\textsubscript{3} and La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, and it occurred because of exposure of the samples to the atmosphere previously or during characterization. Besides, La\textsubscript{2}O\textsubscript{3}-supported catalysts showed only one peak corresponding to IrO\textsubscript{2} diffraction patterns of the supported metals, and it may be due to equipment sensibility, due to good dispersion of the metals throughout the support and possible overlapping of La compound patterns with the rest of the Ir peaks.

Figure 4 shows the XRD patterns of the La\textsubscript{2}O\textsubscript{3} supported catalysts. Due to the hygroscopic nature of the La\textsubscript{2}O\textsubscript{3}, the diffraction patterns shifted towards La(OH)\textsubscript{3} and La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, and it occurred because of exposure of the samples to the atmosphere previously or during characterization. Besides, La\textsubscript{2}O\textsubscript{3}-supported catalysts showed only one peak corresponding to IrO\textsubscript{2} diffraction patterns of the supported metals, and it may be due to equipment sensibility, due to good dispersion of the metals throughout the support and possible overlapping of La compound patterns with the rest of the Ir peaks.

In the inset graph in Figure 2, besides IrO\textsubscript{2} diffraction peaks at 34.7° and 54.20°, NiO peaks at 37.1°, 43.03°, and 62.6° are shown. In the inset graph in Figure 3, peaks at 35.5° and 38.6° belong to CuO.

Figure 4 shows the XRD patterns of the La\textsubscript{2}O\textsubscript{3} supported catalysts. Due to the hygroscopic nature of the La\textsubscript{2}O\textsubscript{3}, the diffraction patterns shifted towards La(OH)\textsubscript{3} and La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, and it occurred because of exposure of the samples to the atmosphere previously or during characterization. Besides, La\textsubscript{2}O\textsubscript{3}-supported catalysts showed only one peak corresponding to IrO\textsubscript{2} diffraction patterns of the supported metals, and it may be due to equipment sensibility, due to good dispersion of the metals throughout the support and possible overlapping of La compound patterns with the rest of the Ir peaks.
2.1.3. Energy Dispersive Spectroscopy

Figure 5 shows the micrographs of both CeO$_2$- and La$_2$O$_3$-supported Iridium catalysts. The images show an adequate dispersion of Ir on both supports. Metal presence in synthesized catalysts was confirmed by EDS and presented in Table 2.

![Figure 5. EDS Mapping of (a) Ir/CeO$_2$; and (b) Ir/La$_2$O$_3$.](image)

| Catalyst       | Ir  | Ni | Cu |
|----------------|-----|----|----|
| Ir/La$_2$O$_3$ | 3.3 | -  | -  |
| IrNi/La$_2$O$_3$ | 2.8 | 2.2 | -  |
| IrCu/La$_2$O$_3$ | 2.8 | -  | 2.5 |
| Ir/CeO$_2$     | 3.4 | -  | -  |
| IrNi/CeO$_2$   | 3.4 | 2  | -  |
| IrCu/CeO$_2$   | 2.4 | -  | 2.7 |

2.1.4. X-ray Photoelectron Spectroscopy

Deposition of Ir on the supports was confirmed through XPS analysis. In Figure 6, XPS results for Ir 4f components of all catalysts are shown. Ir has previously been found to be in oxidation state +4, with a doublet of the components 4f 7/2 with binding energy between 61.1 and 62 eV; and 4f 5/2 with binding energy between 64.9 and 65.9 eV, with a difference between components of 2.9 eV [37]. XPS spectra for Cu 2p in La$_2$O$_3$ show low intensity, but the peak corresponding to component 3/2 at ~933 eV can be seen, which is equivalent to Cu$^{1+}$ oxidation state. For CeO$_2$, a peak was found at 932.2 eV, confirming the presence of Cu$_2$O. These results can be seen in Figure 7. On the other hand, for La$_2$O$_3$ no peak could be found that was related to Ni due to overlapping with other peaks; 2p 3/2 binding energy values for Ni species are between 852 and 856 eV [38], and La 3d 3/2 component values are located between 850 and 860 eV [39]. Ni 2s is located around 1000–1010 eV for NiO [40,41] but it could not be found. For CeO$_2$, Ni 2p 3/2 peak was found at 854.54 eV (Figure 8) corresponding to NiO.
Figure 6. Ir 4f components for catalysts: (a) Ir/CeO$_2$; (b) IrCu/CeO$_2$; (c) IrNi/CeO$_2$; (d) Ir/La$_2$O$_3$; (e) IrCu/La$_2$O$_3$; (f) IrNi/La$_2$O$_3$.

Figure 7. Cu 2p 3/2 components for catalysts: (a) IrCu/CeO$_2$; (b) IrCu/La$_2$O$_3$. 
2.1.5. \( \text{H}_2 \) Temperature Programmed Reduction

Figure 9 shows the TPR profile for CeO\(_2\)-supported catalysts. For monometallic Ir catalyst, the peak at around 187 °C corresponds to IrO\(_2\) in the bulk of the support, and also shows a shoulder between 100 and 140 °C, corresponding to IrO\(_2\) species at the surface. Typically, CeO\(_2\) TPR profile shows two peaks at around 500 °C and 800 °C related to reduction at the surface and bulk, respectively [42]. Addition of noble metals promotes the reduction of oxygen species at the surface of CeO\(_2\) at temperatures where the noble metal oxide reduces due to the spillover effect [43, 44]. This phenomenon results in a reduction of Ce(IV) in the bulk, and it can be observed in the broad peak starting at 600 °C. For IrNi/CeO\(_2\), besides the peak and shoulder between 100 and 200 °C corresponding to the reduction of IrO\(_2\), a second peak can also be seen between 200 and 300 °C that belongs to NiO species reduction at the surface and the bulk [45]. In the case of IrCu/CeO\(_2\), the first peak at 130 °C corresponds to CuO dispersed at the support surface, whereas the second peak is a contribution of IrO\(_2\) and CuO at the bulk, showing a broad shoulder from 200 °C to 400 °C [45].
TPR profiles corresponding to La₂O₃-supported catalysts are shown in Figure 10. When compared to CeO₂ catalysts, the interaction between Ir and La₂O₃ is more complex. The presence of multiple peaks in the range of 80 °C and 280 °C is visible, and they correspond to the reduction of exposed and bulk IrO₂ species. There is also a broad peak from 460 °C to 650 °C corresponding to La(OH)₃ decomposition [46]. For IrNi/La₂O₃, it can be seen that IrO₂ species reduction peaks are more defined; the first peak belongs to the reduction of IrO₂ at the surface, and peaks between 200 °C and 300 °C are a contribution of IrO₂ reduction in the bulk and reduction of NiO species. The slight shift of reduction temperatures for iridium to higher temperatures, and the shift to lower reduction temperatures for Ni suggest a direct metal–metal interaction because NiO is normally reduced between 350 and 400 °C [47,48]. Peaks found in the range of 400 to 550 °C are attributed to a stronger interaction of NiO, and also to the formation of a perovskite-like structure LaNiO₃ and La₂NiO₄ [49]. For IrCu/La₂O₃, peaks below 400 °C are contributions of the reduction of both metal oxides. The first peak in the range of 100 to 200 °C belongs to the reduction of Ir and Cu dispersed at the surface of support, whereas peaks in the range of 200 to 360 °C correspond to species of high support interaction, such as reduction from Cu²⁺ to metallic Cu in the La₂CuO₄ phase [47,50].

Figure 10. La₂O₃-supported catalysts TPR profile.

2.2. Catalytic Activity

Figure 11 shows the hydrogen production rate for all catalysts at 270 °C and 58 bar. Bimetallic IrNi catalysts excel among the others with 150 µmol min⁻¹ g⁻¹ cat for CeO₂ and over 250 µmol min⁻¹ g⁻¹ cat for La₂O₃. These results are due to high activity on the C-C bonds cleavage of Ni. Synthesized IrNiLa₂O₃ is competitive with others catalyst using Pt, as reported by Wen et al. [51]. They prepared different Al₂O₃-supported catalysts with metals such as Pt, Ni, Co, Cu. Best performance was achieved by Pt (4.38 wt %), with a stable rate of H₂ production around 550 µmol min⁻¹ g⁻¹ cat. Ni, Co, and Cu showed catalyst deactivation and a decrease of H₂ production over time. Ni/Al₂O₃ achieved around 250 mmol in the first hour, but after 200 min, it decreased below 100. Deactivation for Al₂O₃ was related to carbon deposition during reaction. Besides, C to gas conversion was 18.9%, 15.8% and 2% for Pt, Ni and Cu catalysts, respectively. Other Pt catalysts reported were Pt (4.34 wt %)/SiO₂, Pt (4.23 wt %)/AC, Pt (9.84 wt %)/MgO, Pt (5.1 wt %)/HUSY, Pt (5.31 wt %)/MSAPO-11 with 369.4, 307.7, 431.9, 337, and 221.1 µmol min⁻¹ g⁻¹ cat respectively. Guo et al. [52] achieved 159.6 and 104.1 µmol min⁻¹ g⁻¹ cat using a Ni-B amorphous alloy and Raney Ni catalysts, respectively, with C to gas conversion below 12% for both catalysts.
The support also plays an essential role in hydrogen production. Almost every La$_2$O$_3$ supported catalyst achieved a higher H$_2$ production yield than CeO$_2$-supported catalysts, due to a higher pore volume and a better metal-support interaction. As discussed before, La$_2$O$_3$ is highly hygroscopic and interacts with moisture and the air of the environment during its manipulation, forming other phases (La(OH)$_3$ and La$_2$O$_3$CO$_3$). Furthermore, aqueous-phase reforming is carried out in the presence of water, and CO$_2$ is also formed during reaction. La$_2$O$_2$CO$_3$ phase in La$_2$O$_3$ catalysts interacts with carbon deposits on the catalyst surface, giving place to CO formation. This compound is harnessed in the water-gas shift reaction, forming more H$_2$. This effect results in a higher hydrogen production. On the other hand, a higher resistance to deactivation was observed for the IrNi/La$_2$O$_3$ catalyst. This can be attributed to the removal of carbon formed on Ni sites by oxygen species from the carbonate as mentioned above [36,53]. It can also be seen that monometallic Ir catalysts exhibited a better H$_2$ production than bimetallic IrCu catalysts, although it was expected to have a synergetic performance due to Cu activity in water-gas shift reaction. This may be caused by a Cu sintering while reducing the catalyst, thus covering Ir particles and lowering the metal-substrate contact area.

Figure 12 shows the catalyst selectivity towards H$_2$ at 270 °C and 58 bar. For La$_2$O$_3$ catalysts, IrNi/La$_2$O$_3$ shows a stable H$_2$ selectivity even in the small decrease in its activity during the reaction tests, while Ir/La$_2$O$_3$ and IrCu/La$_2$O$_3$ exhibit a significant decrease from over 100% to 30–50%, related to a higher catalyst deactivation. H$_2$ selectivity values are higher than 100% because they are compared against gaseous C products as stated in Equation (2). For CeO$_2$ support, all catalysts showed a low but stable selectivity along the reaction at around 20–45%. Carbon to gas conversion at 270 °C and 58 bar is presented in Figure 13. Once again, bimetallic Ni catalysts had the highest value among all catalysts. The low C to gas conversion of the rest of the catalysts indicates that they are not active enough to break the glycerol molecule and its liquid byproducts to produce hydrogen. Liquid products of reactions include compounds such as acetaldehyde, acetone, acetic acid, methyl alcohol, ethanol, 1-hydroxy-2-Propanone, R-(-)-1,2-propanediol, 1,2-Ethanediol, and propylene glycol.

Figures 14 and 15 show CH$_4$ and CO selectivity of catalysts, respectively. Bimetallic Ni catalysts showed less CH$_4$ selectivity than monometallic Ir catalysts, resulting in higher CO selectivity. It may suggest that even though Ir is less active in the methanation reaction, when Ni is added, a synergetic effect occurs and methanation reduces. This result is of particular interest because not only Ni increases H$_2$ production of Ir catalysts, it also decreases the formation of CH$_4$. This phenomenon can be attributed to the increase of metal-support interaction after the addition of Ni to Ir catalysts due to a better active species dispersion [54].
Figure 12. H$_2$ Selectivity at 270 °C and 58 bar.

Figure 13. C to gas conversion at 270 °C and 58 bar.

Figure 14. CH$_4$ Selectivity at 270 °C and 58 bar.
were synthesized using a mixture of IrCl$_3$·H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O (purum p.a.) or Cu(NO$_3$)$_2$·3H$_2$O (puriss, p.a.), dissolved in ethanol. The solutions were added dropwise to the support and calcined at 110 °C overnight and calcined in flowing oxygen at 550 °C for 4 h. Bimetallic IrNi (Ir 3 wt %, Ni 3 wt %) and IrCu (Ir 3 wt %, Cu 3 wt %) catalysts were synthesized using a mixture of IrCl$_3$·H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O (purum p.a.) or Cu(NO$_3$)$_2$·3H$_2$O (puriss, p.a.), dissolved in ethanol. The solutions were added dropwise to the support and calcined following the same procedure.

Table 3 summarizes average glycerol conversion, C to gas conversion, yield rate of H$_2$ production and selectivities (to H$_2$, CH$_4$, CO, CO$_2$) for all catalysts. The best catalyst was IrNi/La$_2$O$_3$. Although this catalyst has the lowest H$_2$ selectivity, it is remarkable regarding glycerol and C to gas conversion. For instance, Manfro et al. [55] prepared Ni/ CeO$_2$ catalysts by different methods. NiCe-Com (prepared by combustion) achieved 30% glycerol conversion after 12 h of reaction (1 wt % glycerol, 543 K), against 24% for NiCe-Imp. (prepared by impregnation).

Table 3. APR performance of catalysts at 270 °C and 58 bar. Average of six hours of reaction.

| Catalyst      | Yield Rate of H$_2$ Production (µmol min$^{-1}$ g$_{cat}$$^{-1}$) | Glycerol Conversion (%) | S-H$_2$ (%) | S-CH$_4$ (%) | S-CO (%) | S-CO$_2$ (%) | C to GAS Conv. (%) |
|---------------|---------------------------------------------------------------|------------------------|-------------|-------------|---------|-------------|---------------------|
| Ir/La$_2$O$_3$ | 21.2                                                          | 58.2                   | 95.4        | 48.8        | 8.8     | 42.4        | 0.7                 |
| IrCu/La$_2$O$_3$ | 16.9                                                         | 76.5                   | 54.5        | 37.1        | 7.3     | 55.6        | 0.9                 |
| IrNi/La$_2$O$_3$ | 317.7                                                        | 92.0                   | 23.1        | 40.8        | 11.0    | 48.2        | 43.6                |
| Ir/CeO$_2$    | 16.0                                                          | 52.6                   | 39.3        | 40.6        | 9.0     | 50.4        | 1.3                 |
| IrCu/CeO$_2$  | 4.7                                                           | 35.5                   | 23.7        | 43.3        | 9.4     | 473         | 0.6                 |
| IrNi/CeO$_2$  | 162.9                                                         | 55.7                   | 34.8        | 27.8        | 14.7    | 57.5        | 14.8                |

Figure 15. CO Selectivity at 270 °C and 58 bar.

3. Materials and Methods

3.1. Preparation of Catalysts

Iridium, iridium-nickel, and iridium-copper (Ir, IrNi, and IrCu from now on) catalysts were prepared by incipient wetness impregnation using two supports: CeO$_2$ (99.9% trace metals basis) and La$_2$O$_3$ (≥99.9%). All materials were purchased from Sigma-Aldrich.

For the preparation of monometallic iridium catalyst, the amount of IrCl$_3$·H$_2$O (reagent grade) corresponding to Ir 3 wt % of the catalyst was added to ethanol and stirred until it was dissolved. The solution was added dropwise to the support, heated at 110 °C overnight and calcined in flowing oxygen at 550 °C for 4 h. Bimetallic IrNi (Ir 3 wt %, Ni 3 wt %) and IrCu (Ir 3 wt %, Cu 3 wt %) catalysts were synthesized using a mixture of IrCl$_3$·H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O (purum p.a.) or Cu(NO$_3$)$_2$·3H$_2$O (puriss, p.a.), dissolved in ethanol. The solutions were added dropwise to the support and calcined following the same procedure.

3.2. Catalysts Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D8-Advance diffractometer with a CuKα radiation source operated at 40 kV and 30 mA (Billerica, MA, USA). X-ray photoelectron
spectroscopy (XPS) analysis was performed with a K-Alpha Thermo Scientific spectrometer (Waltham, MA, USA) using an AlKα X-ray monochromatic source of 1486.6 eV at 12 kV and 40 Watts. A copper adhesive tape was placed on a stainless-steel holder to fix the powder samples. The analyzed area was of 400 µm using an incident relative angle of 30°. Before analysis, the surfaces of samples were cleaned upon argon erosion for 30 s at 3 kV and 30 W. Survey spectra were obtained from 0 to 1350 eV using 1 eV/step and 100 eV pass energy, whereas 0.1 eV/step and 50 eV pass energy were used for high-resolution spectra. The binding energies (±0.2 eV) were referenced to C1s of adventitious carbon at 284.8 eV. Textural properties of catalysts were measured by N2 physisorption at 77 K using a Quantachrome Instrument NOVA 2200e equipment (Boynton Beach, FL, USA). Before the measurement, the samples were degassed at 573 K for 16 h under vacuum. The specific surface area was determined from the BET plot. The pore volume was calculated from the desorption branch of N2 physisorption isotherm. Energy-dispersive X-ray spectroscopy (EDX) analyses were performed with a JEOL JSM-6360LV (Peabody, MA, USA) High-Resolution Scanning Electron Microscope coupled to an Electron Dispersion Scanning X-Ray (EDX). TPR profiles were obtained using a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System (Norcross, GA, USA) with a Thermal Conductivity Detector. The particle size of catalysts was reduced to 40–60 mesh. Then, 100 mg were packed between glass wool in a quartz U-tube used as a reduction cell. The tube was then placed inside an oven connected to a CryoCooler system. Before analysis, 100 mg of fresh catalyst was pretreated in a 20% O2-N2 gas mixture at 300 °C for 60 min. Then, the temperature was reduced in the presence of argon (30 cm3/min). TPR profile was then measured from 30 to 800 °C at 10 °C/min under 5% H2/He flow.

3.3. Activity Test

The evaluation of the catalytic behavior during the glycerol APR was performed in a down-flow fixed-bed reactor (Microactivity Reference, 0.9 cm diameter) operated at 543 K and 58 bar. Before the reaction, 612 mg of each catalyst were reduced at 550 °C under a hydrogen stream (50 mL/min, 1.5 h, heating ramp 5 °C/min) and then heated up to the reaction temperature in a nitrogen atmosphere at the desired pressure. A 10 wt % aqueous glycerol solution (glycerol ≥ 99.5%) was fed at 0.25 mL/min with a WHSV of 2.5 h−1 and a time-on-stream of 6 h. Reaction products were separated in a condensation cell. Gas products were stored in 0.6 l sampling bags (every hour, at reaction time = 30 min, a sampling bag was connected to the gas exit for 10 min, then it was changed for another sampling bag. In total, three sampling bags were used every hour of reaction), then they were analyzed in a Portable Syngas Analyzer ETG MCA 100 SYN-P (Montiglio, AT, Italy). According to the calibration of measuring equipment, errors in estimation are less than 1.2%; Liquid products were stored in 20 mL amber bottles and then analyzed by a Gas Chromatograph Young Lin GC-6500 (Anyang-si, Gyeonggi-do, Korea) using a Mass-selective Detector equipped with a MEGA-Wax column (internal diameter = 0.32 mm, length = 25 m). The method employed started at 31 °C for 3 min, and then it was heated to 200 °C at 15 °C/min.

Acquired data were processed according to the following definitions [56]:

\[
Conversion = \left( \frac{\text{glycerol moles fed} - \text{glycerol moles in products}}{\text{glycerol moles fed}} \right) \times 100\%,
\]

\[
S_{H_2} = \left( \frac{\text{H}_2 \text{ molecules produced}}{\text{C atoms in gas product}} \right) \times \left( \frac{1}{R} \right) \times 100\%,
\]

where \( R \) is the H2/CO2 reforming ratio of glycerol (7/3);

\[
S_i = \left( \frac{\text{moles of } i \text{ species produced experimentally}}{\text{C moles in gas products}} \right) \times 100\%,
\]
where $i$ is for CH$_4$, CO or CO$_2$, and

$$C \text{ conversion to gas} = \left( \frac{C \text{ in gas products}}{C \text{ fed into reactor}} \right) \times 100\%.$$  \hspace{1cm} (4)

4. Conclusions

Experimental investigation of Ir and Ir-bimetallic catalysts performance for H$_2$ production using glycerol as a substrate under aqueous phase reforming conditions was performed for the first time.

Ir-based catalysts were synthesized using La$_2$O$_3$ and CeO$_2$ supports. Although H$_2$ selectivity was low, IrNi/CeO$_2$ and IrNi/La$_2$O$_3$ catalyst showed potential for hydrogen production. IrNi/La$_2$O$_3$ catalyst showed the highest glycerol conversion (92.02%) and rate of hydrogen production (317.65 $\mu$mol min$^{-1}$ g$_{\text{cat}}^{-1}$). Ir by itself was apparently not capable of breaking glycerol’s C-C bonds. Besides, despite the relative high glycerol conversion (~52 and 58% for CeO$_2$ and La$_2$O$_3$, respectively), there was low C to gas conversion (below 2% for both supports) meaning that low CH$_4$, CO$_2$ and CO is being produced. CO is important because it is part of the water-gas shift reaction and this step is fundamental for hydrogen production. The expected synergetic effect between the activities of Ir and Cu was not achieved due to possible sintering of the latter. Nevertheless, a reduction in CH$_4$ selectivity was observed while adding Ni to Ir regarding of the support. Ir (3 wt %) did not show relevance to H$_2$ production by itself, but when combined with other metals, or with a higher metal charge, it could be a promising material.

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