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Selective hydrogenolysis of glycerol over Ir-Ni bimetallic catalysts

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ABSTRACT

The effect of the addition of Ni to Ir/γ-Al_2O_3 was studied for glycerol hydrogenolysis reaction. The catalysts were characterized by textural analysis, XRD, H_2-TPR, XPS and TEM. In all cases, the addition of Ni to Ir/γ-Al_2O_3 produced a significant increase in glycerol conversion, and a high selectivity to 1,2-PDO was maintained. TOF values increased from 0.4×10^{-2} s^{-1} for Ir monometallic catalyst, to 4.3×10^{-2} s^{-1} for bimetallic $IrNi_2$_C catalyst. The latter was the most active catalyst among the calcined bimetallic catalysts. Selectivity to 1,2-PDO had an insignificant decrease from 89.9% for Ir monometallic catalyst to 83.1% for $IrNi_2$_C catalyst. However, non-calcined $IrNi_2$ catalyst presented a TOF value of 1.3×10^{-2} s^{-1}. This result indicates that the calcination step was fundamental to obtain a strong Ir-Ni interaction that lead to better performances of the bimetallic catalysts. Ir-Ni interaction was evidenced by XPS analyses of the calcined series of catalysts, where the presence of an $Ir^{\delta+}$ species was observed ($0 < \delta < 4$), suggesting an electronic density transferring from Ni to Ir.

1. Introduction

The investigation of renewable energy alternatives has been an important concern recently and has led to the exploration of biodiesel as an alternative to fossil fuels. Biodiesel is obtained from fat oils by the transesterification with an alcohol [1], and crude glycerol is obtained as a by-product [2]. In this context, the search for synthesis routes aiming the transformation of glycerol into high value products has grown in the last years. Catalytic hydrogenolysis is an interesting route for obtaining high value materials such as 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), and other alcohols.

Different supported noble and non-noble metal catalysts have been employed for the selective hydrogenolysis of glycerol. Low activity for hydrogenolysis of glycerol with supported iridium catalysts have been reported [3–6]. Nakagawa et al. [3] reported a low conversion of glycerol for a 4% Ir/SiO_2 catalyst, however, a great increase in activity and selectivity for 1,3-PDO was observed when the catalyst was promoted with ReO_x. Ir-ReO_x/SiO_2 catalyst presented about 90% of glycerol conversion after 48 h of reaction and a maximum yield of 1,3-PDO of 38% at 36 h of reaction. Based in the results of this work, the authors proposed a reaction mechanism that involves the glycerol adsorption on the ReO_x cluster and the attack of an activated hydrogen on metallic Ir to explain the formation of 1,3-propanediol. Subsequently, other investigations have been developed by this research group to elucidate the effect of reaction parameters like Re/Ir rate, type of acid co-catalyst, as well as determining the structure of Ir-ReO_x/SiO_2 catalyst and the effect of the addition of Ru as a promoter [7–10]. Furtheremore, the activity of this bifunctional catalyst have been studied for C—O bonds hydrogenolysis of different biomass derived substrates using solvents as water and alkanes [11,12]. The activity of the catalyst was strongly depedent of the solvent used. Alkane solvent was advantageous on water in the hydrogenolysis of secondary mono-alcohols due the stronger adsorption of the substrate on the catalyst surface, leading to a two-setep indirect mechanism (acid-catalyzed dehydration and subsequent hydrogenation) [11]. In the presence of water, hydrogenolysis was promoted by the addition of acid cocatalysts, which was explained by the promoter effect of Re alkoxide formation under an acidic atmosphere, leading to the C—O bond hydrogenolysis by direct mechanism [12].

Recently, other properties of Ir-Re catalysts have been studied as suport [13] and structural [14,15] effects. It was found that Ir-Re supported on alumina-silica material (ASA) was nearly inactive,

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which was attributed to the strong Re-support interaction that promotes the dispersion of Re species, difficulting the sinegy between Ir and Re. However, Ir-Re supported on de-aluminated ASA (ASA treated with 0.05 or 0.5 M HNO_3) showed an enhanced activity and selectivity to 1,3-PDO, as a result of the formation of active Ir-Re alloy nanoparticles [13]. This Ir-Re alloy was shown to be more active than Ir-ReOx structure (both supported on mesoporous silica KIT-6). Besides the enhanced activity, Ir-Re alloy presented double 1,3-PDO formation rate, and enhanced resistance against particle sintering [14].

Previously, we have studied the activity and selectivity of Al_2O_3, SiO_2 and ZrO_2 supported iridium catalysts in C—C and C—O cleavage in cyclohexane conversion and glycerol hydrogenolysis [16]. The effect of support, H_2 initial pressure and temperature reaction on glycerol conversion and products selectivity were explored. When reaction was performed at 200 °C, glycerol conversion was 8.3% for Ir/ZrO_2 catalyst, 7.7% for $Ir/\gamma\text{-}Al_2O_3$ catalyst and 3.9% for Ir/SiO_2 catalyst, and a maximum selectivity for 1,2-PDO of 86.7% was obtained with Ir/SiO_2 catalyst. For a higher reaction temperature (250 °C), higher values of conversion were obtained, however, a decrease in selectivity to 1,2-PDO was also observed. At this temperature, several undesired products as short and long chain alcohols, ketones, esters, ethers and aldehydes were formed. The results showed that both C—O and C—C hydrogenolysis were influenced by acidic properties of the support, the electronic state of the active phase and the different metal-support interactions [16]. Consequently, the present manuscript addresses the addition of Ni as a second metal to $Ir/\gamma\text{-}Al_2O_3$ aiming the increase of the catalyst activity with a high selectivity to 1,2-PDO. Mono- and bimetallic Ni based catalysts have shown activity for glycerol conversion reactions [17–19].

The performances of bimetallic Ni-Ir catalysts have been investigated in several reactions involving C—H cleavage like methane dissociation [20], and H_2 production by hydrated hydrazine decomposition [21] and partial oxidation of methane [22]. Additionally, the addition of Ir to TiO_2 supported Ni catalysts produced an activity increase in the cinnamaldehyde hydrogenation due the strong interaction between Ni and Ir that modified the electronic structure of the surface Ni [23]. A similar effect was obtained in the ammonia decomposition, where the addition of Ir to a $Ni/\gamma\text{-}Al_2O_3$ catalyst caused an increase of 40% in conversion, suggesting the presence of a synergic effect that reduces the interaction of the active phase with the support and favors the formation of more active sites [24]. On the other hand, the addition of Ni to $Ir/\gamma\text{-}Al_2O_3$ catalysts was shown to be efficient in suppressing substituted C—C cleavage in 1,3-dimethylcyclohexane ring opening, allowing the formation of products with better cetane number and moderate vapor pressure [25].

In this work, the effect of the addition of different amounts of Ni to an $Ir/\gamma\text{-}Al_2O_3$ catalyst for glycerol hydrogenolysis reaction was investigated. The effect of the Ir-Ni interactions on glycerol conversion and selectivity to 1,2-PDO was studied.

2. Experimental

2.1. Catalyst preparation

Commercial $\gamma\text{-}Al_2O_3$ (Puralox HP-14) calcined at 600 °C (5 °C/min during 4 h) was used. The monometallic iridium and nickel catalysts were prepared by incipient wetness impregnation technique, using solutions of $H_2IrCl_6{\cdot}xH_2O$ (Sigma-Aldrich) and $Ni(NO_3)_2{\cdot}9H_2O$, to yield 2 wt.% Ir and 3 wt.% Ni, respectively. "Ni_C" catalyst was obtained after drying of the impregnated solid at 100 °C for 16 h, and calcination at 500 °C during 4 h (10 °C/min). Iridium impregnated solid was dried at 70 °C for 16 h due the low melting point of the $H_2IrCl_6{\cdot}xH_2O$ (65 °C), this solid was denoted as "Ir" catalyst. Finally, "Ir_C" catalyst was prepared by calcination of "Ir" catalyst at 400 °C during 4 h (10 °C/min).

For bimetallic catalysts Ir content was maintained at 2 wt.%, and Ni content was adjusted for obtaining Ni/Ir = 0.5; 1.0 e 2.0 molar ratios.

For the preparation of these solids, first the support was impregnated with a $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) aqueous solution. Then, the precursors were dried at 100 °C during 16 h and calcined at 500 °C (10 °C/min) during 4 h. Finally, the solids were impregnated with an $H_2IrCl_6{\cdot}xH_2O$ (Sigma-Aldrich) aqueous solution, and the precursors were dried at 70 °C during 16 h. Finally, calcination of bimetallic catalyst was performed at 500 °C (10 °C/min) during 4 h.

Non-calcined and calcined solids ($IrNi_x$ and $IrNi_x$_C, respectively) were reduced and passivated in a fixed bed reactor prior to catalytic runs. The solids were dried at 150 °C for 30 min under He flow (30 mL/min) and cooled to room temperature. The reduction was performed at 500 °C in H_2 flow (30 mL/min) during 2 h, then catalysts were passivated with a 5% O_2/He flow at liquid N_2 temperature.

2.2. Catalyst characterization

Nitrogen adsorption isotherms of the samples were measured using a Micromeritics ASAP 2020 equipment. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. X-ray diffraction (XRD) experiments were performed using a Miniflex RIGAKU spectrometer (CuKα radiation). The diffractograms were obtained between $2\theta = 10°$ and 80° using a 0.02° step size (1 step/s).

Temperature programmed reduction (TPR) experiments were performed with a multipurpose unit coupled to a Prisma quadrupole mass spectrometer (Pfeiffer). The samples were dried at 150 °C for 30 min under He flow (30 mL/min) and cooled to room temperature, then the samples were submitted to a 5% H_2/Ar gas flow (30 mL/min) and the temperature was raised to 1000 °C at a heating rate of 10 °C/min.

CO chemisorption analyses were performed in a Micromeritics ASAP 2010 device by volumetric method. Samples (about 600 mg) were dried in He flow (30 mL/min) at 100 °C during 30 min, and reduced in H_2 (30 mL/min) at 500 °C during 2 h. A first outgas was performed at 500 °C during 60 min, followed by an outgas at 35 °C during 30 min. Total and reversible CO adsorption isotherms were measured at 35 °C and CO/Metal was calculated from irreversible CO uptake.

XPS analysis was carried out using an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) with monochromatic Al Kα X-rays (spot size of 900 μm). Surface charging of the electrically insulating materials was compensated using an integrated flood gun with approximate spot size of 900 μm. Survey spectra were obtained with a pass energy of 100 eV and region spectra (Ir4*f*, Al2*p*, Ni2*p*) using a pass energy of 25 eV. The base pressure of the analysis chamber was 7×10^{-10} mbar. Spectra were acquired, analyzed and peak fitted using the Avantage software with Lorentzian/Gaussian product function and a Shirley type background. Ir4*f* spectra were fitted with an energy constraint for $Ir4f_{5/2}$ within a 3 eV shift relative to the $Ir4f_{7/2}$ peak, an area ratio of 0.75:1, respectively, and a FWHM in the range 0.5–2.5 eV. Ni2*p* spectra were fitted with an energy constraint for $Ni2p_{3/2}$ within a 17.5 eV shift relative to the $Ni2p_{1/2}$ peak, an area ratio of 1:0.52, respectively, and a FWHM in the range 1.0–2.7 eV. The residual STD of the fitted spectra was around 0.9 for all catalysts. The binding energy (BE) calibration was done by adventitious carbon signal (C1*s* = 284.8 eV).

Morphological and nanostructural characterization of passivated catalysts were performed using a FEI Tecnai G2 Spirit Twin TEM with LaB6 filament operating at 120 kV.

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