



Influence of copper on nickel-based catalysts in the conversion of glycerol



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ABSTRACT

The catalytic transformation of glycerol to value-added compounds was investigated over bimetallic Ni–Cu/ γ -Al₂O₃ catalysts with Ni/Cu atomic ratios of 8/1, 4/1, 2/1, 1/1, 1/2, 1/4, and 1/8. XPS analysis revealed that the surface composition of the catalyst exhibited progressive enrichment of Cu as its content in the catalyst increased. H₂-chemisorption indicated that the total number of exposed Ni atoms decreased as the Cu content increased. As a result, deep hydrogenolysis to produce CH₄ was inhibited by the addition of Cu to the Ni catalyst, yielding higher selectivity toward the dehydration products of glycerol such as hydroxyacetone.

FTIR spectra of adsorbed CO reveal that Cu asserts both geometric and electronic effects on the adsorption properties of Ni. The geometrical effect is visualized by the progressive disappearance of the bridge-bound adsorbed CO on metallic Ni by the incorporation of Cu. This suggests that the deep hydrogenolysis of glycerol to CH₄ formation requires an ensemble of adjacent active Ni atoms. The electronic effect of Cu on Ni is indicated by the red shift of the IR peak of adsorbed CO as the Cu content increases. The electronic interaction between Cu and Ni species was also substantiated by XANES results. HTREM revealed metal particles very well distributed on the support with particle size of 1.5 to 5 nm. The Ni–Cu samples were not a total intermetallic alloys.

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1. Introduction

Glycerol has been produced as a byproduct from saponification and hydrolysis reactions. Nowadays glycerol is also available as an inevitable by-product in biodiesel production generating approximately 10% of crude glycerol by volume [1]. Since biodiesel production worldwide is increasing, the availability of glycerol will also increase. In this respect, new applications for glycerol need to be developed [2,3] to overcome its excess. Efficient processes for glycerol transformation into valuable chemicals, such as hydrogenolysis, dehydrogenation, and dehydration are highly desirable [4,5].

The hydrogenolysis of glycerol is supposed to occur through two mechanisms: (i) the route of hydroxyacetone and (ii) the route of

glyceraldehyde. The route of hydroxyacetone [6] involves the glycerol dehydration to form hydroxyacetone which is sequentially hydrogenated to 1,2-propanediol (1,2-PDO). The most plausible mechanism reaction for the glyceraldehyde route was proposed by Montassier et al. [7] which involves a dehydrogenation of glycerol to glyceraldehyde followed by hydrogenation to form ethylene glycol (EG) and methanol. Finally, methane (CH₄) is formed by deep hydrogenolysis. The dehydration of glycerol to hydroxyacetone is catalyzed by acid sites and this reaction occurs via protonation of the terminal hydroxyl group with consecutive elimination of water molecule and formation of an enol intermediate [8,9].

The use of noble metal catalysts containing Ru [10,11], Pt [12–14], Rh [15–18], Pd [15,16,19], and Ir [20] have been reported in the hydrogenolysis of glycerol. Metallic systems based on noble metals can be a drawback to development of the hydrogenolysis process. The use of non-noble bimetallic catalysts has been proposed for hydrogenation and hydrogenolysis reactions. Replacement of noble metal catalysts with cheap and abundant

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metals is a major goal for a sustainable chemistry. Nickel (Ni) and copper (Cu) are cheap metals and, therefore, are ideal candidates. Jiménez-Morales et al. [21] reported that the hydrogenolysis of glycerol at 473 K and 2.4 MPa of H₂ on Ni supported on SBA-15 led to volatile products by C–C hydrogenolysis. Unlike Ni, Cu is effective at breaking C–O bonds and avoids C–C bonds cleavages [9]. Copper catalysts have been used to produce 1,2-PDO with high yield. Sato et al. [9] observed that the addition of acidic oxide support such as Al₂O₃, ZrO₂, Fe₂O₃ and SiO₂ to Cu enhanced the selectivity to hydroxyacetone.

Recently, we have studied the conversion of glycerol in gas phase at 573 K and atmospheric pressure over Ni based catalyst [22]. We proposed a general reaction pathway for glycerol conversion. Several routes of glycerol transformation such as dehydration, dehydrogenation and hydrogenolysis were observed producing mainly hydroxyacetone, pyruvaldehyde, pyruvic acid, methyl lactate, lactide, acetaldehyde and CH₄. Undesired side reactions such as coke formation were observed on 10% Ni/ γ -Al₂O₃ catalysts. Coke was the major cause of catalyst deactivation in the glycerol conversion. The use of a bimetallic catalyst can be an alternative to minimize the catalyst deactivation. The introduction of a second metal to the Ni catalyst may provide significant changes in the catalytic activity and selectivity as compared with the monometallic one, as observed in other works [23,24].

Understanding the mechanism of the cleavage of the C–C and C–O bonds which modulates the routes in the glycerol conversion (dehydration, dehydrogenation, and hydrogenolysis) is the key to control the selectivity to valuable products such as hydroxyacetone and lactic acid. A good example of the modification of catalytic activity with composition is the use of bimetallic Ni–Cu catalysts [25]. The hydrogenolytic capacity of Cu to the cleavage of C–C bonds is poor. However, Cu is an efficient catalyst for the cleavage of C–O bonds which can dramatically affect the Ni based catalysts in the product distribution of the glycerol conversion. In particular, bimetallic Ni–Cu systems can present advantages with respect to monometallic Ni catalysts. Gandarias et al. [26] used Ni–Cu/Al₂O₃ in the glycerol hydrogenolysis to 1,2-PDO under N₂ pressure and formic acid as hydrogen donor molecule. These authors observed that the Ni/Cu atomic ratio and acid sites affected the yield to 1,2-PDO. In addition, the reduction of Ni–Cu/Al₂O₃ led to formation of Ni–Cu alloy inhibiting the activity for C–C bond cleavage. The effect of Cu on Ni in the reaction routes of glycerol (dehydration, dehydrogenation, hydrogenolysis) may be rationalized by the formation of different chemisorbed intermediates on the catalyst surface, resulting in different products [27,28]. The present work is devoted to study the effect of Cu introduction into Ni in the catalytic conversion of glycerol. Catalysts with different Ni/Cu atomic ratios were prepared and tested. The physical and chemical properties of Ni–Cu and monometallic samples were examined by X-ray diffraction (XRD), X-ray absorption near edge structure (XANES), in situ FTIR of adsorbed CO, H₂-chemisorption, temperature programmed desorption of NH₃ (TPD-NH₃), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR), high resolution transmission electron microscopy (HRTEM), N₂-physisorption and temperature programmed oxidation (TPO).

2. Experimental

2.1. Catalyst preparation

Commercial γ -Al₂O₃ was purchased from Degussa. It was calcined at 463 K for 4 h before use. The Ni–Cu catalysts containing 10 wt.% of total metal loading were prepared by wet co-impregnation of γ -Al₂O₃ with an aqueous solution containing the Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·6H₂O precursors, which were

mixed to obtain the following Ni:Cu atomic ratios: NiCu81, NiCu41, NiCu21, NiCu11, NiCu12, NiCu14 and NiCu18. It was also prepared the monometallic Ni sample and the monometallic Cu sample. After co-impregnation, each sample was dried by rotavapor at 373 K for 12 h and it was then reduced at 723 K in a flow of 20 mL/min with pure H₂ for 4 h.

2.2. Catalyst characterization

2.2.1. Thermal decomposition of Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·6H₂O co-impregnated over γ -Al₂O₃ under hydrogen flow

The decomposition temperature of Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·6H₂O precursors was investigated by TGA-MS over all dried co-impregnated samples. TGA were recorded in a Sensys evo apparatus from 323 K to 1023 K, at a heating rate of 10 K/min under a flow of 5% H₂/Ar. The off-gas was simultaneously analyzed with a Pfeiffer Vacuum QME 220 mass spectrometer (MS).

2.2.2. Temperature programmed reduction (TPR)

TPR experiments were performed in a ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector (TCD). The samples were then purged with Ar flow before the TPR analysis. The analysis was carried out using a 5% H₂/Ar gas flowing at 20 mL/min by heating from room temperature (RT) to 1173 K with a heating rate of 10 K/min. The evolved species during TPR were monitored by an on-line mass spectrometer Pfeiffer Vacuum QME 220. Soda lime was used as trap in order to stop NO_x gases in the carrier gas before they enter the detector.

2.2.3. N₂-adsorption-desorption

The specific surface area, cumulative pore volume and average pore diameter of the samples were measured by the BET method using N₂ adsorption/desorption at 77 K in a Quantachrome Autosorb-1. Before measurement, each sample was degassed under vacuum at 393 K overnight. The BET specific surface area was calculated from the range $P/P_0 = 0.05$ – 0.35 in the adsorption branch while the pore size distribution was calculated from the desorption branch.

2.2.4. Temperature programmed desorption of NH₃ (TPD-NH₃)

The total acidity measurements of the fresh catalysts were determined by TPD of NH₃ on a Micromeritics AutoChem II equipped with a TCD detector. Each sample (50 mg) was pretreated with Ar at 353 K during 1 h in a tubular down flow quartz reactor and then cooled to RT. The sample was then treated with NH₃ flow (5% NH₃ in He) at RT for 1 h. The NH₃ desorption was measured by heating the sample from RT to 973 K at a heating rate of 10 K/min in He flow. The total number of acid sites was calculated by using pulses of a known amount of NH₃.

2.2.5. X-ray diffraction (XRD)

The XRD analysis of the materials was recorded using a Siemens D5000 diffractometer (Bragg–Brentano for focusing geometry and vertical θ - θ goniometer) with an angular 2θ -diffraction range between 5° and 90°. The samples were dispersed on a Si(5 1 0) sample holder. The data were collected with an angular step of 0.03° at 5 s per step and sample rotation. Cu K α radiation ($\lambda = 1.54056$ Å) was obtained from a copper X-ray tube operated at 40 kV and 30 mA. For some of the samples, the angular 2θ -diffraction range was between 3° and 60°.

2.2.6. High resolution transmission electron microscopy (HRTEM)

HRTEM was carried out with a JEOL J2010F electron microscope equipped with a field emission gun operating at an accelerating voltage of 200 kV. The samples were prepared by dispersing the

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