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Stable reduced Ni catalysts for xylose hydrogenation in aqueous medium

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ABSTRACT

Precursor materials with 20 wt.% nickel content and formula mater $Nd_{1\text{-}x}Ce_xAl_{0.162}Ni_{0.838}O_3$ (x = 0.0, 0.1, 0.5, 0.7) were successfully used to prepare reduced Ni nanoclusters to be used as catalysts in the catalytic hydrogenation of xylose to xylitol. Reduction at 500 °C led to large reduced nickel content with almost no changes in the structure of the started mixed oxide precursors. The catalytic performance of the Ni-reduced catalysts did not show a clear relation with Ce content while a close dependence of the hydrogenated products with Ni° crystal size and the isomerization product with acidity was obtained. The well-known Ni leaching in aqueous medium was absent in the prepared Ni-reduced catalysts corroborating the promising use of crystalline mixed oxides as precursors to prepare stabilized Ni-reduced catalysts for aqueous-phase processing of biomass-derived compounds.

1. Introduction

Mixed oxides have been widely used as support for the synthesis of reduced metal catalysts to be used in hydrogenation and reforming reactions [1,2]. Nevertheless, impregnation methods for the synthesis of supported nickel catalysts could be not fully reproducible and can lead to non-homogeneity of metal distribution. For these reasons, the so called solid phase crystallization (SPC) method [3–5] appears to be a better alternative to prepare Ni reduced catalysts from well-known crystalline structures i.e., spinels and perovskites-type structures. Indeed, several reports can be found focusing on such approach for a wide variety of reactions [6–10]. Alvarez et al. [6] used LaNiNb-based perovskites for dry reforming of methane, Bedel et al. synthesized $LaCo_xFe_{1\text{-}x}O_3$ perovskites as precursors for Co° metal catalysts for Fischer-Tropsch synthesis [7], de Lima et al. obtained Ni catalysts from $La_{1\text{-}x}Ce_xNiO_3$ for steam reforming of ethanol [8] and Escalona et al. used the same approach for guaiacol HDO reaction [9] while Franchini et al. exploited it for glycerol steam reforming [10]. Furthermore, lanthanides and their derivative oxides have been reported as support [11], promoters [12] and even as precursors for some metal catalysts [13]. In hydrogenation reactions, their employment as promoters consists one strategy to tailor catalyst selectivity. Ceria, a well-known promoter with outstanding redox and acid-base properties, has been exploited in this regard [14,15].

Catalytic hydrogenation of aldoses is an important process in the synthesis of polyhydric alcohols, which have long been used as an alternative for saccharose in the food industry. Xylitol, obtained by the hydrogenation of xylose, is a sweetener molecule, which has been increasingly commercialized [16] due to its attractive properties as high solubility in water, stability upon storage and does not caramelize at elevated temperatures. Moreover, the sweetening capacity of xylitol exceeds that of saccharose by 20–25% with no insulin requirement [17,18]. Xylitol is produced normally by catalytic hydrogenation of xylose in triphasic batch reactors, where reagent and catalysts are dispersed in an aqueous medium. The most used catalyst for this reaction is Raney Ni, due to its high activity and lower price compared to noble metal catalysts [18,19]. Nevertheless, the main drawback of this kind of catalysts is the rapid deactivation and metal leaching in aqueous medium [20]. In the search for obtaining high dispersed metal catalysts, which are at the same time resistant to metal leaching in water, mixed oxides have been taken as catalyst precursors. Indeed we have recently reported the use of ceria doped La-Ni perovskite-type structures as precursors of Ni-reduced catalysts for aqueous-phase hydrogenation of xylose to xylitol. We succeeded to improve the stability of the catalyst, accomplishing a high resistance to Ni leaching [21]. Despite such an achievement, the stabilization of Ni nanoclusters demanded the use of lanthanum cations in the A-site of the perovskite-type structure. This requirement brings the possibility of dissolution of La-based oxides in aqueous phase by formation of $La(OH)_3$, which may impose another technical barrier to use alternative Ni systems.

In this work, we synthesized a series of $Nd_{1\text{-}x}Ce_xAl_{0.162}Ni_{0.838}O_3$ (x = 0.0, 0.1, 0.5, 0.7) mixed oxides as precursors to prepare Ni-

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reduced catalysts for the catalytic hydrogenation of xylose to xylitol. The strategy to use Nd in the A-site position was selected for a better stabilization of the Ni-reduced catalysts in aqueous medium reaction. To ensure a nominal Ni loading of 20 wt.%, a non-reducible metal (aluminum) was also used in the B-site. A fully structural and textural characterization of the synthesized partial substituted Nd-Ce mixed oxides was carried out to explain the activity and selectivity of the reduced catalysts.

2. Experimental

2.1. Preparation of the catalysts

$Nd_{1-x}Ce_xAl_{0.162}Ni_{0.838}O_3$ ($x = 0.0, 0.1, 0.5, 0.7$) materials with 20 wt.% of nominal Ni loading and different Ce and Nd contents were prepared by the self-combustion method [22]. $Nd(NO_3)_{3x}6H_2O$ (Sigma-Aldrich), $Ce(NO_3)_{3x}6H_2O$ (Sigma-Aldrich), $Al(NO_3)_{3x}9H_2O$ (Sigma-Aldrich), $Ni(NO_3)_{2x}6H_2O$ (Sigma-Aldrich) and glycine (Sigma-Aldrich) were used as reagents for synthesis and using deionized water. Table S1 shows the mass needed of each reagent in order to obtain 3 g of precursor solid. Glycine ($H_2NCH_2CO_2H$), used as ignition promoter, was added to an aqueous solution of metal nitrates with the appropriate stoichiometry to get a metal/glycine (molar ratio) = 0.5. HNO_3 was added to obtain a glycine/NO_3• ratio of 0.6. The resulting solution was slowly evaporated at 120 °C under constant agitation until a green vitreous gel was obtained. The gel was heated up to over 265 °C, temperature at which the ignition reaction occurs producing a powdered precursor. After the combustion process, the powders were ground and subjected to air thermal treatment calcination to eliminate the remaining organic precursors. Solids were crushed and sieved to obtain the required particle size (< 200 μm) and then finally calcined at a heating rate of 1 °C min^{-1} up to 700 °C and maintained for 5 h.

Since hydrogen was used to activate the solids prior to catalytic activity measurements, the calcined samples were first reduced under pure hydrogen flow (50 mL min^{-1}) at 500 °C for 2 h to carry out *ex-situ* characterization. After reduction, the reactor was purged with nitrogen, cooled down until room temperature and then placed in a cryostatic bath (liquid nitrogen and isopropyl alcohol mixture at −70 °C). Once reached that temperature, a flow of 5% O_2/N_2 was admitted into the reactor for 1 h. Finally the bath was removed and the catalysts were stabilized at room temperature for 1 h. These materials are referred to as Ni-reduced solids hereinafter.

Samples were labeled according to their Ce content, all of them with nominal loading of 20 wt.%Ni and 2 wt.% Al. The $x = 0.0$ sample corresponds to the Ce free $Nd_{1.0}Al_{0.162}Ni_{0.838}O_3$ while $x = 0.1$ (10%Ce) refers to $Nd_{0.9}Ce_{0.1}Al_{0.162}Ni_{0.838}O_3$ and $x = 0.5$ (50%Ce) and 0.7 (70%Ce) to $Nd_{0.5}Ce_{0.5}Al_{0.162}Ni_{0.838}O_3$ and $Nd_{0.3}Ce_{0.7}Al_{0.162}Ni_{0.838}O_3$, respectively.

2.2. Characterization

Chemical analysis was conducted by atomic absorption spectrometry (AAS) using a Perkin Elmer instrument 3100. Samples were heated up in an open Teflon beaker with 2.5 mL of HNO_3, 2.5 mL of HCl and 5.0 mL of HF (all in high concentration). Once samples were dissolved, HF was evaporated to minimum volume. Finally, a spatula tip of $H_3BO_3(s)$ and up to 50 mL total volume of water was added in a plastic volumetric flask.

The specific areas were calculated using the BET method from the nitrogen adsorption isotherms obtained on a Micromeritics ASAP 2010 apparatus at −196 °C. Samples were previously pretreated at 150 °C under nitrogen atmosphere for 2 h to dehydrate and clean catalysts surface from adsorbed gases, followed by vacuum. Isotherms were recorded taking 25 relative pressure points ranging from 0.0 to 1.0 for the adsorption branch and 23 points for desorption process.

X-ray powder diffraction (XRD) patterns were obtained with nickel-filtered CuKα_1 radiation ($\lambda = 1.5418$ Å) using a Rigaku diffractometer and collected in the 2θ range of 20 − 70° in steps of 2 °C min^{-1}.

Temperature programmed reduction (TPR) experiments were performed in a TPR/TPD 2900 Micromeritics system with a thermal conductivity detector (TCD). Prior to the reduction experiments the samples (50 mg) were thermally treated under air stream at 700 °C to remove any contaminants on catalysts surface. The reduction profiles were recorded under 10% H_2/N_2 flow at 25 mL min^{-1} at a heating rate of 5 °C min^{-1} from room temperature to 1000 °C.

NH_3-TPD experiments were carried out on the reduced samples (2 h at 500 °C) on a TPR/TPD 2010 apparatus, saturating the catalyst surface at 100 °C with ammonia pulses. Then the sample was cooled down to room temperature and, once the baseline was restored, the temperature linearly increased up to 500 °C.

The XPS measurements were performed using a VG Escalab 200R electron spectrometer equipped with a hemispherical electron analyzer and Mg Kα (1253.6 eV) X-ray source. Prior to analysis, the samples were reduced *in situ* under hydrogen at 500 °C for 1 h and transported to the analysis chamber without contact with air. Charging effects on the samples were corrected by taking the C1s peak of adventitious carbon at 284.8 eV. The peaks were decomposed into several components assuming a Gaussian/Lorentzian shape.

2.3. Catalytic activity

The evaluation of the catalytic activity in aqueous-phase hydrogenation of xylose was performed in a semi-batch Parr reactor at conditions (catalyst weight and agitation speed) to ensure absence of any transport limitations, evaluated by the Weisz-Prater parameter. Catalysts were reduced previous to the reaction in a conventional fixed bed reactor at 36 mL min^{-1} of H_2 and heating of 5 °Cmin^{-1} up to 500 °C and maintained at this temperature for 2 h. Afterwards, reducing gas was switched to nitrogen stream and catalyst was cooled down to room temperature.

Reaction conditions were previously determined and described elsewhere [21]. In a typical run, the reactor was fed with 80 mL of water, 100 mg of catalyst, and xylose to obtain a concentration of 41.5 mmol L^{-1}. Reactor was sealed and purged five times with N_2 and at last with H_2 to avoid contamination with other gases. The reactor was heated up to 100 °C with no stirring. Once reached the desired temperature, hydrogen pressure was adjusted and kept constant at 25 bar, and stirring was settled to 600 rpm. Samples were taken periodically during the reaction and analyzed in duplicate by a Waters HPLC chromatograph model Alliance e2695, coupled to a PDA detector model 2998 at wavelength of 280 nm and a RID detector model 2414 at 50 °C using a Biorad Aminex HPX-87H column maintained at 65 °C. H_2SO_4 aqueous solution at 5 mmol L^{-1} was used as mobile phase at 0.7 mL min^{-1}. Reactions with all four catalysts were performed in duplicate to ensure reproducibility.

The conversion of xylose (X_{Xylose}) was calculated from (Eq. (1)):

$$X_{Xylose}(\%) = \frac{n^0_{xylose} - n^i_{xylose}}{n^0_{xylose}} \times 100 \tag{1}$$

where n^0_{xylose} is the initial moles of xylose in the solution (mol) and n^i_{xylose} stands for the moles of xylose at time *i* (mol). The initial reaction rate r_o (mol g^{-1} min^{-1}) was calculated from the initial slope (*b*) of the conversion vs. time plot (min^{-1}) and the mass of the catalyst *m* (g) according to (Eq. (2)):

$$r_o = \frac{b \times n^0_{xylose}}{m} \tag{2}$$

The selectivity was calculated from (Eq. (3)):

$$Selectivity(\%) = \frac{n_{productj}}{n_{xylose\ converted}} \times 100 \tag{3}$$