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Characterizations of nanostructured nickel aluminates as catalysts for conversion of glycerol: Influence of the preparation methods



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ABSTRACT

Three different preparation methods were applied to prepare nickel aluminates (i.e. nanocasting (NiAlN), coprecipitation (NiAlC) and wet impregnation (NiAlW) methods). All catalysts exhibited the NiAl₂O₄ phase besides that of NiO and γ -Al₂O₃. The NiAlN catalyst showed nanoparticles of the aforesaid oxides whereas NiAl_xO_y was the predominant phase found over NiAlW catalyst. The performances of the nickel aluminate-based catalysts were evaluated in glycerol dehydration to produce valuable chemical compounds through the dehydration of glycerol. The sintering effects were responsible for the decreased performance of NiAlC in glycerol dehydration. On the contrary, NiAlN is found to be deactivated due to the lesser stability of its supported nanoparticles, being the glycerol conversion of ca. 3.3% at the end of the reaction. Besides, the reaction efficiently proceeded on NiAlW, which had a high catalytic performance with 19.7% glycerol conversion to acetol and others products and no deactivation along of the time for 25 h of time on stream was observed. This was due to the stability of the NiAl_xO_y phase, which impeded phase transformation and was resistant to heavy coking.

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1. Introduction

Nickel aluminates can be synthesized by various preparation methods and they are very efficient catalysts or carries for the dehydration of a variety of alcohols: ethanol, glycerol, octanol, propanol, 4-hydroxy valeric, among other hydrocarbons [1–3]. It is a partially inverse spinel oxide structure with an ideal unit cell of a cubic system of NiAl₂O₄, being a class of chemically and thermally stable materials [2,3].

The role played by the structure of nickel aluminates for alcohol transformation reactions is not clear in the open literature, although several papers showed the Ni²⁺ centers are very efficient to convert the alcohols through the cleavage of the C–C, O–H and C–H bonds [4–6].

Moreover, the catalytic properties of the nickel aluminates depend on the preparation method, calcination temperature, among other aspects [5–7]. Therefore, the design of active, selec-

tive and recyclable nickel aluminate catalyst for glycerol dehydration is a challenging goal in the field of dehydration catalysis.

In this context, several attempts have been made by researchers for exploitation of uses for glycerol [8–11]. The dehydration of the tri-alcohol reaction constitutes an important research area because it represents the core of a variety of chemical processes to convert the trialcohol into valuable products such acrolein or acetol [12,13]. Acrolein (2-propenal) is a very useful chemical intermediate with widespread applications in antifreeze, polyester fibers, resins, pharmaceuticals, cosmetics, flavors and fragrances, among others whereas acetol (1-hydroxyacetone) is widely used as organic synthesis intermediate for polyols and used in food and cosmetic industry products [10].

The acetol formation through dehydration of glycerol is observed, when catalysis possessing Lewis acidity, or strong basic sites on their surface are used and this reaction occurs via protonation of the terminal hydroxyl group of glycerol with consecutive elimination of water molecule and formation of an enol intermediate [11,13]. Considering the acrolein production by dehydration of glycerol, catalysts having Brønsted acid sites give high acrolein selectivity [12]. In this direction, a variety of catalysts such as ox-

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des, sulfates, metal-based catalysts, phosphates, niobic acid, heteropolyacids, hydrotalcite-type compounds and silica and alumina supported solids, zeolites have been investigated [11,14–16]. Since these catalysts suffer from particle sintering, leaching of the active sites or even carbon deposition, there is a great interest for the development of alternative catalysts. This is a very important factor regarding a possible catalysts' commercial application.

In contrast with the huge research effort focused in the recent years to find out new catalytic applications of nickel aluminates material, almost no papers can be found in the open literature dealing with the nickel aluminate deactivation in dehydration of glycerol. As observed in steam reforming process and glycerol hydrogenolysis, the significant features of NiAl_2O_4 oxide catalysts includes elevated textural properties, profound redox and acid–base properties, high thermal stability and strong mechanical strength [2,3]. In addition, $\text{Ni}/\text{Al}_2\text{O}_3$ based catalysts have been used widely in glycerol steam reforming and *in situ* transformations lead to active $\text{Ni}^0/\text{NiAl}_2\text{O}_4$ phase [1,5]. However, the changes in Ni particle sizes and morphologies during the reaction and the interactions between the alumina carrier and the supported metal may result in detrimental effects such as coking and sintering for the catalyst.

Thus, in this paper, nanostructured nickel aluminates obtained by three preparation methods are evaluated in gas phase dehydration of glycerol. Many different synthetic procedures have been developed to obtain nickel aluminates. Among them, solid-state reaction (ceramic method) and aqueous solution (wet chemical method) such as coprecipitation and sol-gel methods are extensively studied [5,17,18]. The main advantages of wet chemical methods are increased homogeneity and high surface area of the resulting precipitate or gel, which lead to smaller particle size. Emphasis was given in the correlation between the structural properties of the solids after the reaction and their catalytic performance.

2. Experimental

2.1. Preparation of the catalysts

Three wet methods were used for the preparation of the catalysts containing about 10–12 wt% of Ni: coprecipitation, nanocasting and wet impregnation.

The NiAlC catalyst was prepared by the coprecipitation of metal nitrates method. Under stirring, a 10% aqueous solution of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Reagen, 99 wt%) and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Vetec, 99 wt%) were added slowly with vigorous stirring into a sodium carbonate and sodium hydroxide solutions at room temperature. Then, the pH of the final mixture was adjusted to 11 by dropping a $1 \text{ mol} \cdot \text{L}^{-1}$ aqueous solution of sodium hydroxide. After stirring and standing the colloidal mixture for 1 h, the resulting precipitate was aged at 60°C for additional 2 h and then was filtered, washed with deionized water several times until the pH reached 7, dried at 80°C overnight and calcined in air flow at 700°C using a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$ for 6 h.

In case of NiAlW, the catalyst was prepared by the incipient wetness impregnation method studied [5]. For this purpose, aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99% Merck) was prepared and $\gamma\text{-Al}_2\text{O}_3$ (Rhone Poulenc) was used. The $\gamma\text{-Al}_2\text{O}_3$ was impregnated with 10% of Ni and the subsequent drying of the samples was performed in a muffle at 120°C for 6 h, followed by the calcination from room temperature to 700°C using a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$ and held at 700°C for 6 h.

For nanocasted NiAlN, the preparation method was based on previous work [19]. The synthesis was performed at constant pH

in the presence of 10 g of each metal source e.g., nickel acetate and tri-sec butoxide, which were dissolved in isopropanol, under vigorous stirring. After adding the solutions, about 1.0 g of silica template was dispersed in 40 mL of n-hexane with stirring for 3 h. Then, the obtained slurry was added dropwise to 1 mL of the metal precursor solutions with vigorous stirring for 24 h. The resulting mixture was then isolated by filtration and washed with water, being dried afterwards. The prepared solid was calcined at 700°C with a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$ and maintained at that temperature for 6 h, under nitrogen flow. The template was partially removed by stirring the composite in a 5% HF solution and further washed with ethanol, filtered and dried to obtain the resultant oxide sample.

2.2. Characterization of the catalysts

The NiAlC and NiAlN catalysts were characterized by chemical analysis (ICP-OES), X-ray diffraction (XRD), N_2 adsorption isotherms, Raman spectroscopy, and Transmission Electron Microscopy (TEM) techniques.

The chemical analyses of the solids were performed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The analyses were carried out with a Shimadzu ICPS-7500 spectrometer. About 100 mg of the solid was prepared by dissolution in concentrated nitric acid. The precipitated formed was diluted again in a 1% nitric acid solution to perform the measurements.

XRD analyses of fresh solids were performed on a Rigaku (DMAXB model) diffractometer with $\text{Cu K}\alpha$ radiation (40 kV and 30 mA). The diffractograms can be found in the papers published elsewhere [3,19,20]. The spent solids used in the reaction were also characterized by XRD and the diffraction pattern was identified through comparison with those included in the ICDD (International Center of Diffraction Data) database. Moreover, characterizations of fresh NiAlW catalyst (XRD and chemical analyses) are found in a previous paper [20].

The nitrogen adsorption isotherms at -196°C were carried out using a Bel Japan, BELSORP Mini II. Before adsorption measurements, samples (ca. 0.05 g) were heated at 200°C for 4 h under nitrogen flow. Surface areas of the fresh and spent solids were calculated by the Brunauer–Emmett–Teller (BET) method and pore diameters were obtained by BJH method. The surface areas of the microporous solids were measured by t-plot method.

Raman spectra of the fresh and spent catalysts were obtained using a T64000 Jobin Yvon spectrometer. Approximately, 10 mg of each sample was used with an argon laser at 514.5 nm and a power of 10 mW. Raman spectrum of NiAlC and NiAlW samples were obtained in a Horriba Jobin Yvon Labram1000 microscope with a 514.5 nm laser line. The power of 10 mW using a 100 times objective and a 600 mm^{-1} grating were applied.

The Transmission Electron Microscopy (TEM) images of the spent solids were obtained on a FEI Tecnai transmission electron microscope at 120 kV with a resolution of 0.17 nm. Previously, samples were dispersed in ethanol and placed in the grids to perform the analyses.

2.3. Activity testing

The gas-phase dehydration of glycerol was typically conducted at 250°C , $P = 1 \text{ atm}$, using 100 mg of catalyst. The reactant 20wt% of aqueous solution of glycerol was introduced in the in a fix bed reactor and the reaction was carried out at 250°C . The products of the reaction were analyzed by a G-Crom chromatograph. The products were identified by gas chromatography coupled to mass spectrometry (GC–MS). According to the findings [21–23], conversion of glycerol and selectivities to the products can be obtained as follows:

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