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Research paper

Preparation of NiAlZr-terephthalate LDHs with high Al and Zr content and their mixed oxides for cyclohexane dehydrogenation

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ABSTRACT

Hydrotalcite-like materials were synthesized by pH-controlled precipitation method with Ni^{2+} and Al^{3+} cations and terephthalate as the compensation anion. Ni/Al ratios were 1.0 and 0.3, both high in aluminum content for what has been commonly reported in the literature for this type of materials. The incorporation of Zr(IV) in the structure of the materials was evaluated substituting Al(III) for Zr(IV), using Al/Zr ratios of 3.0 and 0.3. Characterization techniques, such as X-ray diffraction, thermogravimetric analysis, infrared spectroscopy and chemical analysis, demonstrated that NiAlZr-terephthalate hydrotalcite-like materials were obtained simultaneously with amorphous phases of ZrO_2 and $Al(OH)_3$. The mixed oxides, produced by the calcination of the hydrotalcites, had interesting characteristics that could be useful for potential unsupported mesoporous nickel catalysts, with high surface areas, nanoparticles, variable reducibility temperature, thermal stability and different kinds of interaction of nickel with aluminum and zirconium, depending on the metal content. These NiAlZr oxides were evaluated as catalysts for cyclohexane dehydrogenation reaction after a reduction process. The resulting catalysts presented a high cyclohexane conversion and in some cases selectivity to benzene close to 90%, especially when zirconium was added and nanosized cristallites of NiO were formed.

1. Introduction

Mixed oxides are widely used in the industry as heterogeneous catalysts or supports for selective oxidation reactions (e.g., methanol oxidation to formaldehyde, propylene and propane oxidation/ammoxidation to acrolein/acrylonitrile, and n-butane oxidation to maleic anhydride), fuel cell electrocatalysts and hydrogen production (Wachs and Routray, 2012). For the efficient preparation of oxides with a homogeneous distribution of elements, precursors known as layered double hydroxides (LDHs) or hydrotalcite-like compounds have been commonly used (Qu et al., 2016; Mishra et al., 2018).

Hydrotalcites are anionic clays represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}_{x/n}].mH_2O$, in which M(II) and M(III) are respectively divalent and trivalent cations in octahedral sites, forming layers in the presence of hydroxyl anions (OH^-); x is the M(III) metallic molar fraction. A^{n-} is a compensation anion located between the layers (Vaccari, 1999; Rives, 2006). The oxides obtained from the decomposition of LDHs have a high specific surface area and high thermal stability (Forano et al., 2006).

There are numerous combinations of layer composition that can be found from not only divalent M(II) and trivalent M(III) cations, but also cations with other valences such as lithium (I), silicon (IV), zirconium (IV), tin (IV) and titanium (IV) (Velu et al., 1998; Fogg et al., 2002; Intissar et al., 2003; Evans and Slade, 2006; Saber, 2006; Seftel et al., 2008). Similarly, the layer composition is not restricted exclusively to combinations of a pair of cations, as reported in a number of works on the synthesis of ternary and even quaternary systems (Forano et al., 2006).

The divalent and trivalent metal ratio determines the density of charge on the layer of the LDH, influencing important properties such as crystallinity and ion exchange capacity. It is frequently stated that pure phases of hydrotalcite can only be formed with x-values in the range of 0.2–0.33 (Cavani et al., 1991). In LDH materials with higher values of x, containing Al^{3+} as a trivalent cation, the content of octahedral aluminum is so high that $Al(OH)_3$ may form a segregated phase. Similarly, for low values of x, the high density of divalent cations in

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octahedral geometry would lead to the formation of the segregated respective hydroxides M(II)$(OH)_2$ (Forano et al., 2006).

Some studies have reported hydrotalcite-like compound synthesis with x-values outside the ideal range with high aluminum contents (Kooli et al., 1996; Kukkadapu et al., 1997). In most cases the formation of low crystalline aluminum trihydroxide was observed. In other cases, it was possible to distinguish the formation of poorly crystallized LDH and other Al well crystallized phases, such as gibbsite or boehmite (Jitianu et al., 2000). Some authors have reported the synthesis of NiAl, CoAl, CoMgAl and NiMnAl LDHs with high aluminum content using terephthalate as the compensation anion (Arias et al., 2013; Coelho et al., 2015). In these cases, segregated phases of $Al(OH)_3$ were successfully quantified. Theoretical studies have supported the possibility of obtaining materials with x-value as high as 0.5, using the terephthalate anion (Nangoi et al., 2015; Nangoi et al., 2018).

The terephthalate anion provides a relatively large expansion of the interlayer space because of its size and the negative charges on the opposite sides of its structure. In this case, electrostatic repulsion energy can be reduced between the layers, stabilizing the structure. For this reason, this anion is widely used in the synthesis of hydrotalcites with high aluminum content (Arias et al., 2013; Coelho et al., 2015; Nangoi et al., 2015). This makes terephthalate a good candidate for inclusion in the layer of a cation such as zirconium.

The incorporation of Zr(IV) or other tetravalent metals into LDHs as a partial substitution for M(II) or Al(III) has often been thought to be difficult because of the higher valency of the Zr. Some studies have demonstrated that it is possible to incorporate Zr in hydrotalcites with carbonate and chloride intercalated anions. However, these anions have promoted the incorporation of a limited amount of Zr into the layers. Additional Zr was identified as amorphous phases segregated from the LDHs structure (Velu et al., 1998; Tichit et al., 2002; Curtius et al., 2009; Shen et al., 2011; Gao et al., 2013; Poonosamy et al., 2018).

Zirconium oxides, as potential carriers or promoters, have attracted growing attention in catalysts containing metal active sites for different reactions such as CO_2 methanation over Ni/ZrO_2 (Yamasaki et al., 2006), water gas shift (WGS) over Pt/ZrO_2 (Franchini et al., 2012), steam reforming (SR) of hydrocarbons over $Ni/CeO_2/ZrO_2$ (Park et al., 2010) and hydrodeoxygenation (HDO) over Pd/ZrO_2 (De Souza et al., 2015). On the other hand, nickel has been used in cyclohexane dehydrogenation reactions as a lower cost alternative to precious metals. The dehydrogenation of cycloalkanes has an important application in petroleum refining through catalytic reforming for the production of aromatics. However, Ni has the property of promoting undesired hydrogenolysis reactions by generating light hydrocarbons (Sinfelt et al., 1972). The introduction of a second metal or a promoter element into the Ni catalyst can increase its performance by reducing hydrogenolysis and increasing selectivity to aromatics (Xia et al., 2017).

In this work, novel nickel-aluminum-terephthalate hydrotalcites were synthesized with two Ni/Al ratios: 1.0 and 0.3 both with high aluminum content using terephthalate as the compensation anion. Terephthalate enabled expansion of the interlayer space and stabilization of the structure with high content of Al above ordinary values. The partial substitution of aluminum by zirconium (Al/Zr ratios of 3.0 and 0.3) and its effect on the formation of layered double hydroxides simultaneously with amorphous phases of Al and Zr segregated from the hydrotalcite structure were both evaluated. The mixed oxides obtained from the calcination of these hydrotalcites were characterized and evaluated for the dehydrogenation reaction of cyclohexane, after reduction treatment at 350 °C.

2. Experimental

2.1. Preparation of materials

For the synthesis of the materials the pH-controlled coprecipitation method was adapted from the procedure previously described by Arias et al., 2013, in which two solutions, were added dropwise into a flask containing 100 mL of previously boiled de-ionized water (in order to avoid the formation of the carbonate) under agitation at 50 °C, with the help of a magnetic stirrer and a temperature-controlled heating plate. One of the solutions contained the metal salts: nickel nitrate, $Ni(NO_3)_2.6H_2O$ (Vetec, 97%), aluminum nitrate, $Al(NO_3)_3.9H_2O$ (CEquímica, 98.5%) and zirconium oxychloride, $ZrOCl_2.8H_2O$ (Sigma-Aldrich, 99.5%) in the desired stoichiometric amounts. The other solution contained sodium hydroxide, NaOH (Merck, 99%), and terephthalic acid, $C_8H_6O_4$ (Acros Organics, 99.0%). All reagents were added in stoichiometric proportions according to the general formula $[M(II)_{1\text{-}x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}.mH_2O$, except the terephthalic acid that was in an excess of 10 mol%, to favor its incorporation as the compensation anion. pH was maintained at 6.5 ± 0.3, controlled by the speed of addition of the two solutions. To obtain the hydrotalcites, the pH value during co-precipitation needed to be below the pKa of the $Ni(OH)_2$ and $Al(OH)_3$ to avoid the formation of these segregated phases. The precipitated solids were aged under agitation for 4 h at 50 °C and 16 h at room temperature and then recovered by vacuum filtration after being washed with abundant previously boiled deionized water to remove Na^+ and $(NO_3)^-$ ions and to reach the neutral pH. Subsequently, the materials were dried in an oven at 70 °C for 12 h.

All reagent amounts were calculated taking into account x-values of 0.5 and 0.75 using the theoretical formula for the hydrotalcites. Materials containing zirconium were prepared by partially replacing Al(III) with Zr(IV) at Al/Zr molar ratios of 3.0 and 0.3. The materials were labeled by their metallic elements and their theoretical molar composition, so the material with x of 0.5 and Al/Zr ratio of 3.0 is $Ni_{0.5}Al_{0.38}Zr_{0.12}$. The mixed oxides were obtained by calcination of the precursor materials at 500 °C for 3 h, heating rate of 10 °C min^{-1} under static air. Thermogravimetric data show that above 500 °C there is no further mass loss. The oxides were identified here with the “cal” suffix after the precursor identification.

2.2. Characterization

Chemical analysis of the materials was performed with X-ray fluorescence by dispersive energy in a Shimadzu EDX-720 instrument under vacuum, using Ti (Rh 50 kV; 39 μA; 0.00 to 40.00; 0–40 keV; DT 39%) and Na-Sc (Rh 50 kV; 39 μA; 0.00 to 40.00; 0–40 keV; DT 40%) as standard analytes. Carbon contents of the hydrotalcites were obtained in a CHNS/O 2400 Series II – PerkinElmer apparatus using an ignition temperature of 975 °C; oven temperature of 84.5 °C and scan time of 6 min. X-ray diffraction patterns were obtained on a Shimadzu XRD-6000 diffractometer in the range of 2θ between 5 and 70°, at 2.0° min^{-1}, with a 0.02° increment using Cu-Kα radiation ($\lambda = 1.54056$ Å), 30 kV and 30 mA. Particle size was determined by the Scherrer equation. Thermogravimetric analysis (TGA) was carried out in a Perkin Elmer instrument model STA 6000. About 5 mg of each sample was placed in a platinum sample holder and heated from 30 to 800 °C at a rate of 10 °C min^{-1} under 20 mL min^{-1} of synthetic air flow. The infrared (FT-IR) spectra were collected using a Bruker apparatus model Tensor 27, with ATR (Attenuated Total Reflectance), using 30 scans in the range of 4000 to 500 cm^{-1}. The texture properties of the oxides were characterized by the BET method (Brunauer, Emmett, Teller) and BJH method (Barret, Joyner and Halenda) using a Micrometrics volumetric apparatus, model ASAP 2420 through adsorption/desorption isotherm of nitrogen at −196 °C. Temperature programmed reduction (TPR) analyses were obtained in a Multipurpose Samp3 analytical system instrument from Termolab Company. The materials were treated at 200 °C under nitrogen flow for 60 min to remove humidity. Final reduction temperature was 800 °C heating rate was 20 °C min^{-1}, and the flow rate of an Argon/Hydrogen (1.5 hydrogen vol%) mixture was close to 70 mL min^{-1}.