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Highly stable Ni–Al_2O_3 catalyst prepared from a Ni–Al layered double hydroxide for ethanol decomposition toward hydrogen

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ABSTRACT

The preparation, characterization, activity, and stability of a Ni–Al_2O_3 catalyst derived from reduction of a Ni–Al layered double hydroxide precursor (LDH, $Ni_6Al_2(OH)_{16}(CO_3)_{0.75}(OH)_{0.25}\cdot 4H_2O$) are reported in this paper. In-situ X-ray adsorption spectroscopy shows that reduction of Ni from the LDH precursor to form a highly loaded 80% Ni–Al_2O_3 catalyst (Ni–Al_2O_3–LDH) is faster than reduction of a 10% impregnated Ni–Al_2O_3 alumina (Ni–Al_2O_3–I) catalyst. The reduced Ni–Al_2O_3–LDH catalyst exhibits highly dispersed Ni nanoparticles (3–5 nm) distributed on top, partially embedded nanoparticles, and some encapsulated in the Al_2O_3 matrix. The nanoparticles impregnated on alumina (Ni–Al_2O_3–I) are larger (~7–15 nm) and appear on top of the alumina support. Conversion vs time on stream (TOS) results during ethanol decomposition at 250 °C on Ni–Al_2O_3–LDH exhibits only a slight deactivation during 100 h TOS, while the Ni–Al_2O_3–I catalyst shows rapid deactivation with no conversion after 2 h TOS. X-ray photoelectron spectroscopy shows that the carbon content increases up to 48% after 100 h TOS on the Ni–Al_2O_3–LDH catalyst, while a similar increase occurs after 2 h TOS on the Ni–Al_2O_3–I catalyst. TEM shows that after 100 h TOS either a thin layer of amorphous carbon or carbon nanotubes forms on Ni on top of the alumina matrix and on partially embedded Ni nanoparticles on the Ni–Al_2O_3–LDH catalyst. Total surface area of the Ni–Al_2O_3–LDH catalyst increased during TOS, which may be suplying fresh surface Ni from the encapsulated Ni nanoparticles that sustain the high activity.

1. Introduction

Ethanol (C_2H_5OH) is a potential candidate as a hydrogen chemical carrier for fuel cell applications [1–3]. Ethanol is non-hazardous compared to methanol and can be produced readily by the fermentation of sugar cane, corn grains, and other starch-rich materials [4–7]. In addition, several novel technologies are being developed to produce bioethanol from agricultural wastes and forestry residues [1,6,8].

The following reactions are possible routes for hydrogen production from ethanol: steam reforming (Eq. (1)), partial oxidation (Eq. (2)), and ethanol decomposition (Eqs. (3) and (4)),

$$C_2H_5OH + 3H_2O = 2CO_2 + 6H_2 \tag{1}$$

$$2C_2H_5OH + 3O_2 = 4CO_2 + 5H_2 \tag{2}$$

$$C_2H_5OH = CH_3CHO + H_2 \tag{3}$$

$$C_2H_5OH = CH_4 + CO + H_2 \tag{4}$$

Although the steam reforming of ethanol provides a high hydrogen yield, it is a highly endothermic reaction. Therefore, high operating temperatures are necessary in order to achieve high conversion [2,7–15]. The partial oxidation of ethanol is an exothermic reaction that exhibits fast start-up and response times [16–23], both of which are critically important for vehicle fuel cell applications. Drawbacks for the partial oxidation of ethanol include lower selectivity and yields due to hydrogen combustion and the difficulty in controlling the reaction due to hot-spot formation. Ethanol decomposition is another reaction pathway for hydrogen generation from ethanol [16,24–28], and relatively less literature is available for this reaction as compared to steam reforming and partial oxidation pathways. A main drawback of ethanol decomposition is the formation of carbon that deactivates the catalyst,

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and to a lesser extent, the formation of undesirable byproducts such as acetaldehyde and carbon monoxide. Regardless of economic considerations, this reaction was selected in this study as a probe reaction to examine catalyst deactivation using a novel catalyst preparation method. Detailed mechanistic discussion of the various reaction pathways and the role of Ni in the activity and selectivity of the reaction have been presented in detail in the literature [1,16,24,29] so they will be not be discussed hereafter except in connection to specific issues related to the results obtained.

Catalytic stability towards deactivation, however, is one of the most important challenges for hydrogen production from ethanol. Regardless of the metal and support used, significant deactivation has been reported in the literature for applications involving Pt [30,31], Pd [32,33], Rh [33], Ru [10,31], Co [34–37] and Ni-based [38–41] catalysts. Deactivation aspects of catalysts during ethanol conversion were thoroughly reviewed in the recent article by Mattos et al. [1]. Catalyst deactivation is attributed to the deposition of carbonaceous species as well as sintering and/or oxidation of metal crystallites.

Filamentous and amorphous carbons are two general types of carbonaceous species that form on metal catalysts. The nature of the carbon formed depends both on the operating conditions (primarily the reaction temperature), and the nature of the metal. Polymerization of ethylene intermediates and the disproportionation of carbon monoxide (i.e., the Boudouard reaction) are the main carbon formation (coking) reactions at low temperatures. At higher temperatures, decomposition of intermediate hydrocarbons (e.g., methane, ethylene) and byproducts (e.g., acetaldehyde) are the main pathways to form carbon.

On Ni- and Co-supported catalysts, at high temperatures, the deposited carbon species diffuse into the metal particles to nucleate the growth of filaments or nanotubes at the metal-support interface. Depending on the microstructure of the crystallite, in some cases, the nanotubes can lift the metal particles off the support [42]. However, the surface at the tip of the metal particle may still remain accessible to reactants, without deactivation albeit of significant carbon formation. At lower temperatures, the catalyst may deactivate through deposition of amorphous coke. The amorphous carbon may cover both the metal particles and the support [1,34,43].

Another deactivation route [1,44] is the oxidation of ultra-small metallic crystallites, leading to a lower activity and selectivity of the oxidized metal surface. This problem may be controlled by careful balancing of the oxygen-to-ethanol ratio above the value in which oxidation of the metal occurs [45]. Yet, another pathway of catalyst's deactivation during ethanol reforming is the sintering of metal particles. High reaction temperatures or the exothermic nature of partial oxidation reaction can significantly contribute to the sintering of catalysts nanoparticles [1]. To prevent sintering, supports, such as ceria, or zirconia that exhibit a strong interaction with the small metal nanoparticles have been studied [19,46].

Previously, we prepared Ni catalysts for the ethanol reforming reaction using a simple combustion synthesis method [28]. Here, we demonstrate a different strategy of catalyst preparation for ethanol reforming using a Ni–Al layered double hydroxide (LDH) as precursor. Recent review articles suggested that reduction of LDHs permits formation of highly dispersed metal particle-oxide nanomaterials that could be used as catalysis [47–49]. Our results show that short thermal treatment of LDH under a reductive atmosphere produces in-situ a highly porous 80% Ni–Al_2O_3 catalysts in which small size (3–5 nm) metal crystallites on the surrounding alumina matrix. Here we investigated the time on stream (TOS) stability towards deactivation of LDH-derived catalyst during ethanol decomposition and compared it with a Ni catalyst prepared by impregnation. Textural and spectroscopic characterization of the Ni–Al_2O_3–LDH catalyst are presented to explain the high activity and stability of this catalyst for the ethanol decomposition reaction.

2. Experimental methods

The Ni–Al–LDH precursor was prepared by the co-precipitation method. Briefly, an aqueous solution (50 mL) containing 10.89 g of $Ni(NO_3)_2{\cdot}6H_2O$ and 4.68 g of $Al(NO_3)_3{\cdot}9H_2O$ (the total concentration of cations was 1 mol/L with a Ni/Al molar ratio of 3:1) was added dropwise into a 50 mL continually stirred solution containing 4.24 g of Na_2CO_3 (0.8 mol/L) and 2.40 g of NaOH (1.2 mol/L), while the pH value of the suspension was adjusted to 10 using 3 mol/L NaOH aqueous solution. The suspension was then kept at 65 °C for 24 h to obtain a precipitate with Ni–Al–LDH structure. The precipitate was recovered by filtration and repeatedly washed with deionized water. After drying at 80 °C, the resulting material was reduced at 500 °C for one hour in pure hydrogen to get the Ni–Al_2O_3–LDH catalyst with a Ni loading of 80 wt%. It should be noted that no LDH structure was detected at lower Ni concentration, so to compare results with a typical impregnated catalysts two alternative formulations were prepared.

A catalyst with 10 wt% of Ni loading was prepared by incipient wetness impregnation of Al_2O_3 support. The Al_2O_3 support was prepared by the same precipitation method described above, but without addition of nickel nitrate. The washed precipitate was heated to 500 °C for one hour in hydrogen to get a transition γ-Al_2O_3. Then, it was impregnated with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ followed by drying at 80 °C for 8 h and reduction at 500 °C for 1 h in pure hydrogen. This catalyst is referred as Ni–Al_2O_3–I and to compare its activity and stability with the LDH-derived catalysts, we prepared a physical mixture of the Ni–Al_2O_3–LDH and Al_2O_3 with a 10% Ni content, referred as 10% Ni–Al_2O_3–LDH/Al_2O_3. The physical mixture avoids introducing chemical changes during preparation, but it allows to scale down of Ni content so that deactivation could be observed in a shorter TOS.

FTIR spectra of catalyst precursors were measured on a Bruker Tensor 27 spectrometer after 64 scans within 4000–400 cm^{-1} at a resolution of 4 cm^{-1} by measuring the infrared absorbance of sample using diffuse reflection sampling technique.

Catalytic activity and selectivity during ethanol decomposition were measured in a continuous flow fixed bed quartz reactor at atmospheric pressure as described elsewhere [25,28]. The Ni–Al–LDH precipitates were ground into a fine powder, pressed into a wafer, ground again, and then sieved to select particles from 0.6 to 1 mm in size to eliminate mass transfer diffusion. 0.4 g of the precursor was placed into the reactor and reduced with hydrogen at 500 °C for 1 h. After purging with nitrogen for 2 h, the nitrogen flow was diverted into a bubbler filled with ethanol and sent to the reactor, operating at 250 °C. The products in the reactor effluent were analyzed using two gas chromatographs connected in parallel to measure the resulting gas concentrations. Conversion and product selectivity were calculated as described elsewhere [28] in Eqs. (5–6), where n_i is the molar flow rate:

$$X_{\mathrm{EtOH}} = \frac{n_{\mathrm{EtOH,in}} - n_{\mathrm{EtOH,out}}}{n_{\mathrm{EtOH,in}}} \times 100 \tag{5}$$

$$X_i = \frac{n_i}{\Sigma n_i} \times 100 \tag{6}$$

X-ray diffraction (XRD) patterns were obtained in a D8 Advance powder diffractometer (Bruker), using CuKα monochromatic radiation (λ = 0.1541 nm) operated at 40 kV and 40 mA at a scan rate of 1^0 min^{-1} in angular range (2θ) from 20 to 80°. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI VersaProbe II spectrometer with an Al Kα X-ray source operating at 1486.6 eV and a 90° take-off angle for near surface analysis of C 1s, Ni 2p3, O 1s, Al 2p electronic transitions. Catalyst powders were adhered to stainless steel mounts and loaded into the