Highly Stable Ni-Al₂O₃ 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-Al₂O₃ catalyst derived from reduction of a Ni-Al layered double hydroxide precursor (LDH, Ni₆Al₂(OH)₁₆(CO₃)_{0.75}(OH)_{0.25}•4H₂O) is reported in this paper. *In-situ* X-ray adsorption spectroscopy show that reduction of Ni from the LDH precursor to form a highly loaded 80%Ni-Al₂O₃ catalyst (Ni-Al₂O₃-LDH) is faster than reduction of a 10% impregnated Ni-Al₂O₃ alumina (Ni-Al₂O₃-I) catalyst. The reduced Ni-Al₂O₃-LDH catalyst exhibits highly dispersed Ni nanoparticles (3-5 nm) distributed on top, partially *embedded nanoparticles*, and some encapsulated in the Al₂O₃ matrix. The nanoparticles impregnated on alumina (Ni-Al₂O₃-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-Al₂O₃-LDH exhibits only a slight deactivation during 100 h TOS, while the Ni-Al₂O₃-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-Al₂O₃-LDH catalyst, while a similar increase occurs after 2 h TOS on the Ni-Al₂O₃-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-Al₂O₃-LDH catalyst. Total surface area of the Ni-Al₂O₃-LDH catalyst increased during TOS, which may be supplying fresh surface Ni from the encapsulated Ni nanoparticles that sustain the high activity.

Key words: ethanol decomposition, Ni-Al₂O₃ supported catalysts, Ni-Al layered double hydroxide, activity, deactivation stability.

INTRODUCTION

Ethanol ($\text{C}_2\text{H}_5\text{OH}$) 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 (Eq. 3,4),

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, 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 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-Al₂O₃ catalysts in which small size (3-5nm) 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-Al₂O₃-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 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4.68 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (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 $\gamma\text{-Al}_2\text{O}_3$. Then, it was impregnated with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 hours, 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 Equations 5-6, where n_i is the molar flow rate:

$$X_{EtOH} = \frac{n_{EtOH,in} - n_{EtOH,out}}{n_{EtOH,in}} \times 100 \quad (5)$$

$$\chi_i = \frac{n_i}{\sum n_i} \times 100 \quad (6)$$

X-ray diffraction (XRD) patterns were obtained in a D8 Advance powder diffractometer (Bruker), using CuK α monochromatic radiation ($\lambda=0.1541$ nm) operated at 40 kV and 40 mA at a scan rate of 1° min^{-1} in angular range (2θ) from 20 to 80 degrees. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI VersaProbe II spectrometer with an

Al K α X-ray source operating at 1486.6 eV and a 90° take-off angle for near surface analysis of C 1s, Ni 2p_{3/2}, O 1s, Al 2p electronic transitions. Catalyst powders were adhered to stainless steel mounts and loaded into the analysis chamber. Samples were outgassed in the vacuum system maintained at a pressure less than $\sim 10^{-7}$ Pa. Binding energy values were referenced to the C 1s peak (284.8 eV) that resulted from the adventitious contamination layer. The spectra were analyzed using the Multipak XPS software package.

XANES measurements of *in-situ* reduction by hydrogen were made using X-ray absorption spectroscopy (XAS) at the Advanced Photon Source (APS) at Argonne National Laboratory as previously reported [24]. The measurements were obtained in transmission mode with ionization chambers optimized for the maximum current with linear response ($\sim 10^{10}$ photons detected/s). A cryogenically cooled double-crystal Si (111) monochromator with resolution (ΔE) better than 2.5 eV at 8.979 keV (Cu K edge) was used in conjunction with a Rh-coated mirror to minimize the presence of harmonics. 10 mg of the samples were loaded in a six chamber sample holder by pressing a pellet in a chamber. The sample holder was then placed in a quartz tube fitted with polyimide film on either end to allow X-rays to bombard the sample and to be run in transmission mode. The tube featured a gas inlet and outlet fittings to allow hydrogen flow through the samples. The tube was placed in a heater operated at temperatures up to 500 °C and adjusted to be in line with the X-ray beam. A Ni foil spectrum was simultaneously obtained with each sample for energy calibration. WinXAS and Athena software programs are used to analyze XAS spectra data. A linear combination between the height of the absorption edge of an elemental oxide state and its metallic state was used to determine the percentage of reduction of a given sample.

BET specific surface area determinations were made using nitrogen adsorption/desorption (-196°C) by an ASAP 2020 apparatus (Micromeritics). Before analysis, the samples were dried at room temperature and then vacuum degassed at 373 K for 12 hrs.

A Titan 80-300 (FEI, USA) transmission electron microscope (TEM) with resolution of 0.136 nm and with 0.1 nm information limit in scanning TEM (STEM) and high resolution TEM mode, respectively, was used for structural and compositional characterization of the Ni crystallites at nm- and atomic levels. The Titan TEM was equipped with an energy dispersive X-ray spectrometer (EDS, Oxford Inc.) with a spectral energy resolution of 130 eV. Droplets of small catalyst particles dispersed by sonication in an ethanol solution were deposited on a holey carbon grid for TEM analysis.

A Costech ECS 4010 element analyzer was used to determine carbon content of catalysts. Prior to analysis, catalysts were wrapped in a tin foil capsules and deposited into an oxygen rich combustion zone, where the contents of the capsule combust. A capillary separation column (2 to 3 m in length) and a thermal conductivity detector were used to separate gas products of combustion and measure CO₂ concentration.

3. RESULTS AND DISCUSSION

3. 1 Precursor and catalyst characterization.

The Ni-Al₂O₃-LDH catalyst's precursor prepared by co-precipitation method was studied by XRD and FTIR spectroscopy. Figure 1 shows XRD and the transmission FTIR spectrum of the air dried precipitate. The XRD pattern (Figure 1A) shows that the dried precipitate exhibits major diffraction lines of the takovite-type structure (Ni₆Al₂(OH)₁₆(CO₃)_{0.75}(OH)_{0.25}•4(H₂O), (JSPDS #15-0087) shown as an inset in Figure 1A.

The FTIR spectrum of the precipitate in Figure 1B shows bands typical of CO_3^{2-} ion-intercalated LDH material, with a broad band at 3467 cm^{-1} (ν_{OH}), a peak at 1616 cm^{-1} ($\delta\text{H}_2\text{O}$), bands at $740, 563, \sim 400\text{ cm}^{-1}$ (due to Ni(Al)-O vibrations and Ni(Al)-O-H bending), and the sharp and strong band at 1362 cm^{-1} , which clearly shows the presence of the CO_3^{2-} ion in the sample.

The reduction of the both the catalysts prepared by co-precipitation ($\text{Ni-Al}_2\text{O}_3\text{-LDH}$) and by impregnation ($\text{Ni-Al}_2\text{O}_3\text{-I}$) methods were studied by XANES using $5\%\text{H}_2\text{-Ar}$ mixture at various temperatures. Spectra were taken approximately every 4 minutes as the temperature was increased to 500°C **at a rate of 3°C/min** . Both samples were reduced simultaneously in the beam-line and data was collected for each sample every other point switching between the two samples (a data point was taken every 8 min per each sample). The fraction of reduced Ni was calculated by linear interpolation between the height of the edge signal of NiO and a Ni reference. Figure 2 shows that the reduction of Ni(II) in either the $\text{Ni-Al}_2\text{O}_3\text{-LDH}$ or the $\text{Ni-Al}_2\text{O}_3\text{-I}$ did not occur before 300°C . Nickel in LDH precursor is reduced to $\sim 10\%$ metallic Ni at 380°C and becomes $\sim 80\%$ reduced Ni at 500°C . The catalyst prepared by impregnation, however, is reduced to $\sim 10\%$ metallic Ni at 400°C and is only reduced to 45% Ni at 500°C . Thus, at this temperature, $\text{Ni-Al}_2\text{O}_3\text{-I}$ is reduced at a lower rate, resulting in only half of the extent of reduction than in the LDH precursor. Such remarkable differences in the kinetics of reduction may be explained by the nature of the precursors. The Al_2O_3 support used in preparation of $\text{Ni-Al}_2\text{O}_3\text{-I}$ precursor has $160\text{ m}^2/\text{g}$ (Table 1), which is slightly higher than LDH one ($140\text{ m}^2/\text{g}$). Continuous structural rearrangement of the LDH precursor during reduction due to the removal of CO_2 and water molecules occurs at a higher rate than removal of oxygen from NiO in the impregnated catalyst. Table 1 shows that the BET surface area of reduced catalysts are 110

m²/g and 135 m²/g for Ni-Al₂O₃-LDH and Ni-Al₂O₃-I, respectively. Both catalysts exhibit similar broad pore sizes distribution ranging from 3 to 30 nm with an average size ~18 nm. Such large structural transformation affects the resulting location, crystallite size, and dispersion of the resulting Ni crystallites. The XANES results also justify the choice of 500°C in pure hydrogen for 1 h as the reduction conditions. Note that dilute hydrogen was used in the XANES experiments as per safety requirements set by the APS. Our XANES results are consistent with TPR experiments on the reducibility of LDH type structures reported in the literature [50].

Scanning TEM images (STEM) of both reduced catalyst are shown in Figure 3. These results indicate that reduction of LDH precursor yields a Ni-Al₂O₃-LDH catalyst with highly dispersed Ni nanoparticles. Statistical analysis shows (see inset in Figure 3) that the size distribution of Ni nanoparticles is narrow with mean size of 4 nm. A high magnification STEM image inserted in Figure 3A shows that near cubic shape Ni nanoparticles are partially embedded in the Al₂O₃ matrix. Note that in this mode of STEM imaging, the bright images are the metal particles and the dark ones are the alumina matrix. Figure 3B shows Ni nanoparticles on the alumina support prepared by impregnation (Ni-Al₂O₃-I). On average these particles are larger (~11 nm) compared to those prepared from the LDH precursor.

3.2 Conversion, selectivity, and time on stream (TOS) results

Figure 4 shows ethanol conversion vs TOS results obtained at 250°C on Ni-Al₂O₃-LDH, Ni-Al₂O₃-I and Al₂O₃-diluted Ni-Al₂O₃-LDH (with 10% Ni content) catalysts. During 100 h of TOS, the Ni-Al₂O₃-LDH catalyst only shows slight deactivation from 100% to approximately 91% ethanol conversion (curve a), while the Ni-Al₂O₃-I catalyst shows rapid deactivation with no conversion after 2 h TOS (curve b). While we expect that Ni-Al₂O₃-LDH will eventually

deactivate, it will require too long time to observe deactivation on this high Ni content catalysts. Because of the scaling down of the Ni concentration on the diluted catalyst the breakthrough of the activity decrease on the 10% diluted Ni-Al₂O₃-LDH catalysts takes 12 h TOS to completely deactivate. These results indicate that depositing Ni on Al₂O₃ by impregnation leads to higher rate of carbon formation and hence a higher rate of deactivation than on the Ni-Al₂O₃-LDH catalyst.

The selectivity of the reaction over the stable Ni-Al₂O₃-LDH catalyst is shown in Figure 5. There is an initial change of the effluent concentration due to the transient startup of the reaction. These changes are attributed to structural changes caused by the reactants that led to the formation of the special active sites exhibiting resistance to deactivation obtained from the LDH precursor.

However, after several hours, hydrogen selectivity (curve a) increases throughout the reaction from 35 to 52% while methane (curve b) and carbon monoxide selectivity (curve c) decrease from 40 to 25% and 25 to 20%, respectively. This indicates a reaction pathway occurring according to reaction 4. The change on the hydrogen production with TOS that can be attributed to decomposition of methane and to structural changes as indicated by the increase in reduction time.

Over Ni-Al₂O₃-I catalyst, ethanol reacts to yield acetaldehyde, hydrogen, and small amounts (~10%) of CO and CH₄ before a rapid decrease of conversion to zero. The higher concentration of H₂ obtained over the Ni-Al₂O₃-LDH demonstrates the high activity/stability of this catalyst. It should be noted that due to the synthesis requirement, Ni-Al₂O₃-LDH has a higher Ni content than the 10% on Ni-Al₂O₃-I. In the later catalyst, it is not possible to load such

a large amount of Ni, hence the advantage of Ni-Al₂O₃-LDH catalysts. It should also be noted that unsupported Ni deactivates even faster than the impregnated Ni catalyst [24], so adding more Ni does not prevent deactivation by carbon unless it is embedded into the alumina matrix.

XRD analysis of the reduced and spent Ni-Al₂O₃-LDH catalysts after various TOS are shown in Figure 6. It can be seen that the XRD lines tend to broaden with increasing TOS. Several NiO diffraction peaks become more visible on the spent catalyst, while others disappear. The second peak in Figure 6a is the overlap of the NiO peak and the Ni(111) peak, so the former looks stronger than the latter, but actually is the opposite. This result may be related to partial surface oxidation of Ni particles upon exposure to air in the XRD diffractometer operating in a standard ex-situ mode. The surface area of Ni-Al₂O₃-LDH catalyst increases with TOS (Table 1), indicating that structural transformations have taken place during reaction.

3.3. Carbon Formation Pathway

The catalytic results of ethanol conversion (Figure 4) indicate that high activity and stability of the Ni-Al₂O₃-LDH catalyst is related to the high concentration (80%) and structure of dispersed Ni nanoparticles and their interaction with and the location on the alumina matrix. We used ultrahigh vacuum-XPS (UHV-XPS, requiring transfer to the spectrometer sample holder in air), carbon analysis, and high resolution TEM to explore carbon formation on the catalyst's surface and its relation to decrease in activity.

XPS results. Ni-Al₂O₃-LDH and Ni-Al₂O₃-I catalysts after reduction and extended TOS were studied by ex-situ XPS, and even though precautions were taken to minimize air exposure, some oxidation due to air can not be ruled out. All peaks (Ni 2p^{3/2}, O 1s, C 1s, Al 2p) were deconvoluted and the calculated surface concentrations are reported in Table 2. The large difference in Ni concentration, which is due to the higher loading in the Ni-Al₂O₃-LDH (80% Ni)

compared to 10% in Ni-Al₂O₃-I, is reflected in the Ni 2p^{3/2} peak of these catalysts (Figure 7A and B). The intensity of these peaks in Ni-Al₂O₃-LDH (Figure 7A) is approximately 12 times larger than in Ni-Al₂O₃-I (19 to 1% Ni on the surface as reported in Table 2, respectively). Metallic Ni peaks are observed at 852.5, while NiO peaks appear at ~856 eV. In the Ni-Al₂O₃-LDH catalyst (Figure 7A), no surface metallic Ni is observed on the reduced catalyst whereas the surface concentration of metallic Ni increases slightly after reaction from 29 to 34%. XRD analysis of these catalysts, however, shows that the intensity of some NiO-related peaks increases (Figure 6). As XPS is near-surface sensitive, it detects *surface* oxidation of the reduced catalyst due to its higher reactivity towards oxygen, and hence the disappearance of the reduced Ni from the XPS spectra. SEM micrographs, show that the spent catalyst is partly covered with layered structures that protects it from deactivation. This film protects the catalyst from further reduction and thus, reduced Ni is observed in the XRD patterns. The spent catalyst is further reduced during reaction, which explains the increase in the Ni⁰ signal in the XPS spectra with TOS. Figure 7B shows (note the different scales with Fig. 7A) that the 1% surface concentration of Ni (Table 2) of Ni-Al₂O₃-I is mostly metallic Ni, which is related to larger particles of this catalyst.

The main C peak (284.5 eV) of the Ni-Al₂O₃-LDH catalyst, shown in Figure 8A and Table 2, increased from 24 to 48% total concentration after 100 h TOS. Figure 8B shows a similar increase of the C signal on the Ni-Al₂O₃-I catalyst but at *only after 2 h TOS*, increasing from 21 to 43% C (Table 2). Therefore, the LDH synthesis does not completely protect Ni from carbon formation but the amount of carbon formed is much lower than on the impregnated Ni catalysts, and it does not seem to affect the conversion. Obviously this is partly due to the higher Ni loading of the Ni-Al₂O₃-LDH catalyst, but loading is not the only factor involved as an

unsupported Ni catalyst with a similar loading deactivates very rapidly [24]. The secondary carbon peak (at 288 eV) is due to C-O or C-N bond formation and is attributed to residual precursors of carbonate left on the catalyst surface during synthesis as it remains constant. Carbon formation seen on Ni-Al₂O₃-LDH by UHV-XPS in Figure 8 after 100 h TOS does not seem to contribute to deactivating the catalyst as a similar increase (106%) in total elemental surface carbon is detected on Ni-Al₂O₃-I but only after 2 h of reaction, at which point this catalyst is nearly completely deactivated. The diluted 10% Ni-Al₂O₃-LDH catalyst has a higher resistance to deactivation than the impregnated catalysts with similar loading as it does not deactivate until 12h TOS. Therefore, the rate of carbon formation on the Ni-Al₂O₃-LDH is slower than on the impregnated catalyst wherein crystallites are deposited on top of the support completely exposed to the reactants. The surface oxidation detected by XPS, results in the formation of a surface layer that protects the surface from further oxidation. Exposure of catalysts to air resulted in an increase of temperature less than 50°C rather than sudden ignition affecting surface carbon. The location of the Ni crystallites on the alumina matrix clearly has an effect on carbon formation and deactivation.

Elemental analysis. The percentage of carbon measured by elemental analyzer for the catalyst after various TOS is shown in Table 3. These results clearly indicate that carbon quantity for Ni-Al₂O₃-LDH catalysts increase from 0 to 9.45 wt.% after 100 h TOS, whereas on Ni-Al₂O₃-I ~11 wt.% carbon builds-up onto the catalyst after only 2 h of reaction.

TEM analysis: The structure and composition of Ni-Al₂O₃-LDH and Ni-Al₂O₃-I catalysts and their changes after TOS was studied by TEM. Figure 3 shows typical STEM images of reduced Ni-Al₂O₃-LDH (A) and Ni-Al₂O₃-I (B) catalysts. Some Ni crystallites are observed located on the surface while others appears embedded in the alumina matrix and just partially exposed to

the atmosphere (Figure 3A). Other crystallites may be encapsulated by the alumina matrix. The location of the particles may have substantial effect on their behavior during reaction. High resolution TEM images of Ni-Al₂O₃-LDH catalyst after 24 h TOS are shown in Figure 9. Ni crystallites exhibit a bimodal distribution with some nanoparticles distributed on top of the Al₂O₃ (Figure 9A), whereas others are embedded in Al₂O₃. The electron diffraction pattern (inset) shows weak diffraction rings that could be attributed both to Ni and NiO phases. A HRTEM image of the Ni-Al₂O₃-LDH catalysts after 100 h TOS is shown in Figure 9B and 9C. A carbon layer covering Ni nanoparticles (Figure 9B) is observed on the exposed crystallites on top of Al₂O₃. The carbon was identified by EDS analysis. Figure 9C shows a carbon nanotube (ordered) structure, such carbon filaments or nanotubes structures on Ni are well documented in the literature, albeit at higher temperatures and from other more stable reactants such as methane [51]. We have examined many samples and observed similar features of carbon overlayers further supporting the results presented in Figure 9. The growth of carbon filaments (or nanotubes) around Ni particles at the tip has been known in catalysis for many years so these observations are in agreement with the previous literature [42].

The TEM results of the used catalysts again show evidence that there are at least two types of active Ni nanoparticles in the Ni-Al₂O₃-LDH catalysts: free-standing Ni nanoparticles and crystallites partially embedded into Al₂O₃ and. It is also possible that some Ni nanoparticles are completely encapsulated inside the Al₂O₃ matrix but these are not initially accessible to the reactants.

Based on the characterization results, we propose the following model to explain the stability of the DHL catalyst. The free standing Ni particles on the surface of the alumina matrix interact more weakly with it and could be lifted from the surface by growing carbon material, as

shown in many TEM studies (41). Eventually, these particles will be completely covered by carbon that would prevent transport of the reactants to the surface and therefore, will no longer participate in the reaction. On the other hand, the Ni particles that were partially embedded in the Al_2O_3 matrix are strongly interacting with it, which would decrease the rate of formation of carbon and carbon nanotubes around them and delay coverage of Ni by carbon. This model is consistent with the characterization results and explains the long activity of the Ni- Al_2O_3 -LDH catalyst. In addition, the Ni particles encapsulated by the matrix may be another source of surface Ni, refreshing it when these particles are partially exposed to reactants after structural transformation occurring during reaction. These complex structural transformations occurring on Ni- Al_2O_3 -LDH during TOS, are evidenced by the increase in the BET surface area of this catalyst from 110 to 155 m^2/g (Table 1), and by the increase in hydrogen selectivity during reaction. The phenomena of spalling, or the break up of the support by carbon formation which is known to occur on Ni alumina catalysts at high temperatures, may contribute to these structural transformations and supply fresh Ni nanoparticles to the surface that sustain the high activity for such a long period of time compared with the catalyst made by impregnation.

4. CONCLUSIONS

In summary, we show that Ni- Al_2O_3 catalysts prepared from a LDH precursor is an effective way to obtain a catalyst with high Ni loading in a similar volume occupied by the impregnated catalysts. This results in a significant increase in its lifetime during hydrogen production from ethanol decomposition. The LDH precursor reduces at lower temperature than a 10% Ni impregnated on a similar alumina support with comparable surface area. Ni- Al_2O_3 -LDH catalysts exhibit highly dispersed Ni nanoparticles (3-5 nm) located on the surface, partially embedded or encapsulated by Al_2O_3 the alumina matrix. Ni nanoparticles impregnated on alumina are larger

(~7-15 nm) and appear mainly on top of the support. Conversion vs TOS results at 250°C show that Ni-Al₂O₃-LDH exhibits only a slight deactivation during 100 h TOS, while catalysts prepared by impregnation shows rapid deactivation with no conversion after 2 h TOS. The hydrogen selectivity on the Ni-Al₂O₃-LDH catalyst increases with TOS from 35 to 52%, while methane and carbon monoxide selectivity decrease from 40 to 25% and 25 to 20%, respectively. Such changes are attributed to further methane decomposition and structural transformation of the catalyst. Catalyst prepared by impregnation exhibits conversion of ethanol to acetaldehyde, hydrogen, and small amounts (~10%) of CO and CH₄ before a rapid decrease to zero conversion. XPS analysis show that the carbon content increases from 24 to 48% after 100 h TOS on Ni-Al-LDH whereas a similar increase is seen on the impregnated Ni catalysts but at only 2 h TOS. High resolution TEM analysis of Ni-Al₂O₃-LDH after 100 h TOS show a carbon layer covering some of the Ni nanoparticles on top of Al₂O₃, and Ni nanoparticles on top of nanotubes.

The results suggest that encapsulated Ni crystallites, which initially might not participate in the reaction, may refresh the surface when exposed by spalling. The high concentration of Ni in the Ni-Al₂O₃-LDH catalyst assists in maintaining the high activity during long TOS as more Ni surface is available. This model was tested by designing a 20wt.%Ni-SiO₂ catalyst using combustion synthesis and obtained a 100 % conversion in ethanol which exhibited no deactivation for 100 hrs [29], similar to the results reported here. Such results (manuscript in preparation) give us confidence in the validity of the model proposed in this work.

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FIGURE CAPTIONS

Figure 1. (A) XRD pattern and (B) FTIR spectrum of Ni-Al₂O₃-LDH

Figure 2. Ni % reduction from in-situ XANES vs. reduction temperature for: (a) Ni-Al₂O₃-LDH and (b) Ni-Al₂O₃-I.

Figure 3. Scanning TEM images of reduced: (A) Ni-Al₂O₃-LDH and (B) Ni-Al₂O₃-I catalysts

Figure 4. Ethanol conversion on: (a) Ni-Al₂O₃-LDH, (b) Ni-Al₂O₃-I, and (c) Al₂O₃-diluted Ni-Al₂O₃-LDH catalysts over 100 h TOS

Figure 5. Selectivity for: (a) hydrogen, (b) methane and (c) carbon monoxide on Ni-Al₂O₃-LDH catalysts after 100 h TOS.

Figure 6. XRD patterns of reduced (a) Ni-Al₂O₃-LDH, (b) spent catalyst after 24 h, and (c) 100 h TOS.

Figure 7. UHV-XPS Ni 2p^{3/2} spectra for: (A) Ni-Al₂O₃-LDH and (B) Ni-Al₂O₃-I.

Figure 8. UHV-XPS C 1s spectra for: (A) Ni-Al₂O₃-LDH and (B) Ni-Al₂O₃-I at various TOS

Figure 9. High resolution TEM micrographs of Ni-Al₂O₃-LDH catalyst after A) 24 h, and B) and C) 100 h of TOS.

Table 1. BET surface area of catalyst precursors and reduced and spent catalysts

	Precursor/support	Surface area, m ² /g			
		Reduced	TOS		
			2 h	25 h	100 h
Ni-Al ₂ O ₃ -LDH	140, Ni-Al ₂ O ₃ -LDH	110	-	115	155
Ni-Al ₂ O ₃ -I	160, Al ₂ O ₃	135	133	-	-

Table 2. UHV-XPS catalyst’s surface concentration

	Ni-Al ₂ O ₃ -LDH, (BE eV)				Ni-Al ₂ O ₃ -I, (BE eV)			
	C (284.5)	O (531)	Ni (852)	Al (74.4)	C (284.5)	O (531)	Ni (852)	Al (74.4)
Reduced	24	44	19	12	21	58	1	20
5 h	-	-	-	-	43	44	1	12
24 h	24	45	18	14	-	-	-	-
100 h	48	31	10	11	-	-	-	-
% change	94	-29	-45	-14	106	-25	-22	-40

Table 3

Table 3: Quantity of carbon at different TOS

Catalyst	Reduced	Quantity, wt. %		
		2 h	25 h	100 h
Ni-Al ₂ O ₃ -LDH	0	-	2.5	9.45
Ni-Al ₂ O ₃ -I	0	11.2	-	-

Figure 1

Figure 1

Figure 2

Figure 2

Figure 3

Figure 4

Figure 4

Figure 5

Figure 6

Figure 6

Figure 7

Figure 7

Figure 8

Figure 8

Figure 9

Figure 9