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Ni(II)-Al(III) layered double hydroxide as catalyst precursor for ethanol steam reforming: Activation treatments and kinetic studies

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Abstract

The kinetic behaviour of the steam reforming reaction using Ni(II)-Al(III) layered double hydroxide (LDH) as catalyst precursor is studied. The carbonate form of Ni(II)-Al(III) LDH (takovite) was prepared using an homogeneous alkalinization procedure, by means of the thermal hydrolysis of urea. Different activation treatments of Ni(II)Al(III) precursor are analysed; it was found that the catalyst which presents the higher activity in methane steam reforming, is that obtained by pure H_2 reduction of precursor without previous calcination. The H_2 yield for ethanol steam reforming using the reduced LDH sample reaches values of 5 mol of H_2 per mol of ethanol in the feed. The others products obtained, operating between 823 and 923 K, are CO, CO_2 and CH_4. It is found that the reaction order respect to ethanol is lower than 1. It is verified that, for each reaction temperature, there is a water/ethanol molar ratio at which ethanol conversion has a maximum. It means that a competition between both reactants adsorbed on the same active sites is verified.

Keywords: Ethanol steam reforming; LDH; Ni Catalyst; Kinetic study

1. Introduction

Hydrogen will be a strategic energy vector, since feeding into a fuel cell allows the conversion of chemical energy into electric energy. Bioethanol produced by fermentation of sugar cane, corn or agricultural waste is very attractive as raw material for the hydrogen production due to its great content of hydrogen atoms, and to its renewable nature. The use of bioethanol to produce hydrogen also has an inherent environmental benefit, since it avoids the consumption of fossil fuel. For these reasons, ethanol steam reforming reaction is one of the technological alternatives to produce clean hydrogen through the following total reaction: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$. However, undesirable reactions can be produced affecting the hydrogen selectivity. Ethanol steam reforming has been studied using active elements as Ni, Co, Ni–Cu and noble metals such as Pd, Ru and Rh. [1–9]. The main interest of these works is to find an active catalyst which in turn inhibits coke formation. Analyzing the published results it can be inferred that the activity and the product distribution depend not only on the type of metal used (and its loading) but on the kind of support and the preparation method employed.

From Ross et al.'s researching works [10–13], several strategies to prepare and activate Ni(II)-Al(III)-LDHs for its use in steam reforming have been reported. LDHs solids allow an intimate distribution of two or more cations within a common crystalline structure [14], making them excellent precursors for the obtention of non-stoichiometrical mixed oxides, of tuned composition and crystallinity [15]. Typically, while carbonates containing Ni(II)-Al(III)-LDHs (takovite) are thermally decomposed, evolve into a biphasic solid consisting of an Al(III) containing ill crystallized bunsenite (NiO) coexisting with an amorphous Ni(II) containing alumina [16,17]. After reduction treatments, Ni(II) cations segregate as a Ni metallic phase dispersed within an alumina matrix [18].

Concerning to the preparation of LDHs, in recent years the urea method [19,20] demonstrated to be a useful procedure to

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obtain several well crystallized carbonate LDH, [21] including takovite [22].

In previous research [8,9] using a reduced takovite as catalyst for ethanol steam reforming at 773 K and a water/ethanol feed molar ratio of 6/1, it was proved that ethanol is totally converted, even at residence times as low as 0.15 mg min ml^{-1}, being CH_4, CO, CO_2 and H_2 the only products obtained. Moreover, a H_2 yield of around 5.2 was achieved, i.e. very close to the stoichiometric maximum 6.

On the other hand, there have been reported few kinetic studies employing Ni as catalyst in which power law [23] or an Eley Rideal model [24] were assumed. It should be pointed that as the catalytic reaction is an heterogeneous gas–solid process and the ethanol conversion rate is very fast, the reaction might be affected by both mass and heat diffusion limitations. This could explain the great discrepancy and the low energy activation values reported.

Thus, the main aims of this study are: (i) using a Ni(II)-Al(III) LDH as catalyst precursor for steam reforming reaction, synthesized through the urea method, determine the more appropriated activation conditions, with special emphasis on the calcination and/or reduction steps. (ii) To carry out a systematic study of the kinetic variables (concentration, temperature and residence time) in the ethanol steam reforming reaction in such condition which guarantee the absence of external and internal diffusional effects.

2. Experimental

2.1. Synthesis and characterization of Ni(II)-Al(III)-LDH

Ni(II)-Al(III)-LDH catalyst precursor, hereafter named NiAl, was prepared by the urea method, aging mixed aluminum(III)-nickel(II)-urea solutions at 363.0 ± 0.5 K in screw-capped plastic bottles, which were placed in a thermostatized water bath preheated at the working temperature for 24 h. After this time, the bottles were immersed in an ice–water bath to quench the reaction. Precipitated solids were collected by centrifugation, washed with cold water, and dried at 343 K overnight. The molar ratio Ni(II) to Al(III) was that of typical of takovite [25].

The different samples (fresh, calcined or/and reduced) were characterized by sorptometry in order to determine the BET specific area. The experiments were performed with nitrogen at 77 K in a Micromeritics Gemini 2360 equipment. Thermogravimetric analysis (TG) were carried out in Shimadzu TGA 51H apparatus, using a 3.0 K min^{-1} temperature ramp under an air flow of 50 cm^{3} min^{-1}. Also, X-ray diffraction spectra (XRD) were recorded for 2θ values between 5 and 70° in a Siemens D 5000 equipment using Cu Kα Ni filtered radiation, and 40 kV. Temperature programmed reduction (TPR) experiments were performed with a thermal conductivity detector, on samples of 30 mg in a 98% (molar) nitrogen and 2% (molar) hydrogen gas mixture, using a gas flow rate of 100 ml/min and a temperature range of 293–1173 K with a temperature ramp rate of 5 K min^{-1}. The experimental conditions were carefully selected following Monty and Baiker's recommendations [26]. Previous to the TPR experiments, NiAl sample was treated at 623 K in air stream (100 ml min^{-1}) during 0.5 h to avoid the elution and/or reduction of the compensated anions, simultaneously with the Ni(II) reduction, leading to an excess of H_2 uptake [18].

2.2. Catalytic evaluation

The catalytic evaluation was performed in a quartz reactor of 4 mm i.d., located in an electric oven. Reaction temperature is controlled by a thermocouple placed inside the catalytic bed. The reactants, a mixture of water and ethanol, are fed in liquid state by a syringe HPLC type pump. The mixture is evaporated in an electric oven at 623 K and afterwards diluted with a carrier-argon stream (350 ml min^{-1}). The catalyst was grinded to a diameter between 44 and 88 μm with the aim of avoiding any diffusion limitation in the interior of the particle and diluted with inert material of the same diameter to avoid any temperature gradient inside the catalytic bed. The liquid flow was varied in the range 1.32–6.80 × 10^{-2} ml min^{-1}, and the water–ethanol molar ratio ranged between 3.5 and 10. The catalyst was test in a temperature range of 823–923 K and a residence time of 5.5×10^{-6}–2.7×10^{-5} g min ml^{-1}. The feed and effluent pipes were heated to avoid any condensation. Stainless steel pipe was used with the aim of avoiding ethanol decomposition out of the catalytic bed. Previous to the catalytic evaluation experiments were carried out in order to verify negligible contribution of homogeneous phase reaction and absence of external and internal diffusion limitations.

2.3. Hydrogen activation of catalyst precursor

The fresh synthesized Ni(II)-Al(III)-LDH (NiAl) as well as a calcined sample were submitted to a reduction treatment in a flow hydrogen stream using different conditions of temperature and gas flow composition.

In all experiments, the temperature ramp rate was of 10 K min^{-1} to reach the activation temperature. Table 1 resumes the names, type of treatments and specific areas of the different samples.

3. Results and discussion

The thermal decomposition in air of the NiAl sample is reported in Fig. 1. The decomposition proceeds in two endothermic steps, typical of carbonate (LDHs). The transition at low temperatures is a continuous mass loss in the range 305–500 K. The broad peak corresponds to the reversible release of interlamellar water. The second step occurs between 500 and 700 K, and the peak at 631 K corresponds to the dehydroxylation of the brucite-like layers overlapped with the irreversible loss of carbonate anions [27].

Fig. 2 shows the XRD pattern of the fresh NiAl sample. It can be observed the characteristic reflections of (0 0 3), (0 0 6), (0 1 2), (0 1 5) and (0 1 8) planes of a crystalline LDH. In the zone close to $2\theta = 60°$–$62°$, the typical doublet of d (1 1 0)-d (1 1 3) planes of LDH was also observed. No signals of other

Table 1
Summary of samples used in this work: denomination, type of treatments and specific area (Sg)

Sample	Reduction H_2/N_2 (10/90) $T = 923$ K	Reduction pure H_2 $T = 923$ K	Air calcination $T = 773$ K	Reduction pure H_2 $T = 923$ K	Sg (m^2/g)
NiAl					66
NiAl-R10	×				102
NiAl-R100		×			100
C-NiAl			×		177
C-NiAl-R100				×	84

crystalline phases are detected. Besides, in Fig. 2, the XRD pattern of air calcined sample at 773 K (C-NiAl) is shown. It must be noted that only a very low intensity signal is detected, indicating an incipient formation of a bunsenite type phase (NiO).

On the other hand, Fig. 3 shows the XRD patterns of hydrogen-reduced samples according to the different reduction protocols described in Section 2. It must be noted that in all cases, independently of the reduction treatments, only very low intensity signals characteristic of metallic nickel are present (▼). These results are in agreement with the incipient formation of NiO that it can be observed in the calcined sample at 773 K (C-NiAl), which XRD is also included in Fig. 3. The mean size of the Ni crystallites was estimated using Scherrer's equation, being close to 5 ± 1 nm for both samples directly reduced without previous calcination treatment (NiAl-R100 and NiAl-R10, respectively), independently of the H_2 concentration used. The mean size of the Ni crystallites value obtained for the sample reduced after calcination in air (C-NiAl-R100) was 11 ± 1 nm. In all the cases, the low intensity of the XRD signals suggests a high metal dispersion after reduction treatments.

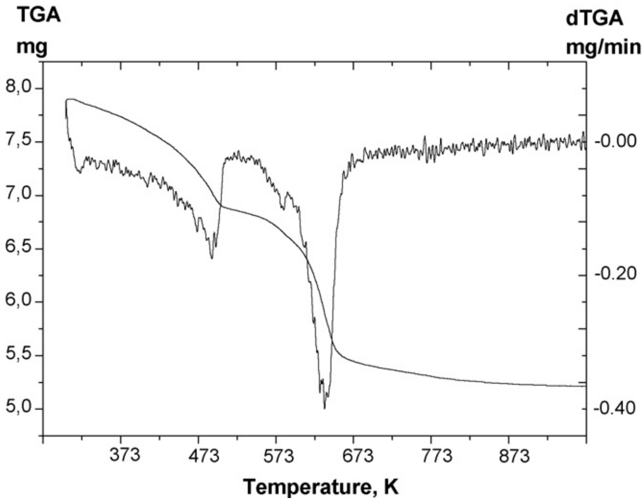

Fig. 1. TGA profile of Ni(II)-Al(III)-LDH (NiAl) under air stream.

Temperature programmed reduction profiles obtained for NiAl and C-NiAl samples (fresh and calcined at 773 K, respectively) showed a broad peak indicating that the reduction occurs in a wide range temperatures attributed to the reduction of Ni (II) species contained in the different oxidic phases derived from the takovite's decomposition [18,28]. The maximum hydrogen consumption was obtained at 710 K for the fresh sample. Nevertheless for the sample calcined at 773 K, this maximum occurs at 850 K. Besides, the hydrogen consumption for this sample diminished 20% with respect to the fresh one, indicating that those non reducible Ni(II) ions migrated towards the increasing Al(III) rich amorphous phase. It is known that Ni(II) species present in the decomposed

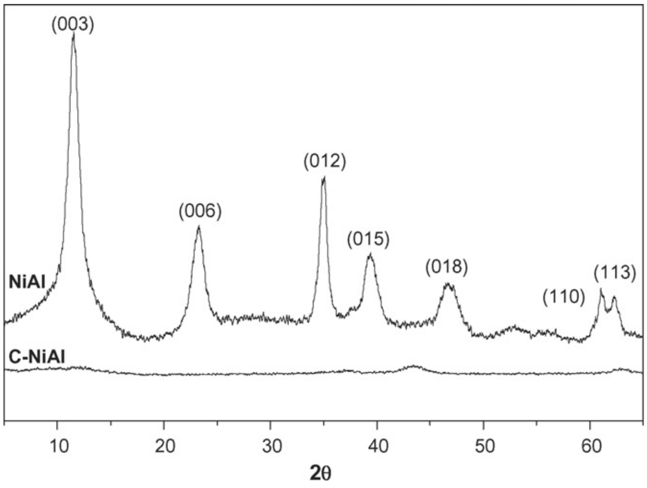

Fig. 2. XRD patterns of fresh NiAl and C-NiAl (calcined at 773 K) samples.

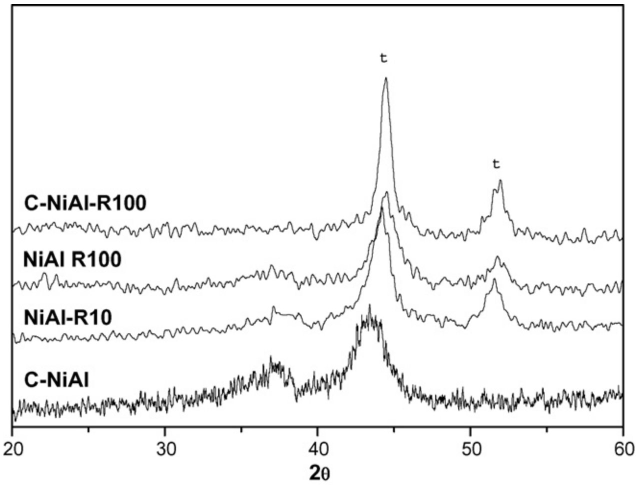

Fig. 3. XRD patterns of different reduced samples in hydrogen stream. The XRD pattern of calcined sample (C-NiAl) is also included.

Table 2
Methane conversion values for the samples submitted at different activation treatments

	NiAl-R10	NiAl-R100	C-NiAl-R100
X_{CH4} (%)	29.5	43	20

takovite are more difficult to reduce as the calcination temperature increases [29]. It has been reported that takovite's decomposition (dehydroxilation–decarboxilation) proceeds in a similar way in the presence of H_2 or O_2, in the former case Ni(II) reduction starts around 720 K [30]. Then, the higher Ni dispersion and surface area achieved in sample NiAl-R100 respect to C-NiAl-R100 sample, mainly obeys to the lower annealing treatment applied over that sample.

Hence, with the aim of determine the more adequate activation conditions for the precursor, directly or with a calcination previous to reduction, the steam reforming of methane was performed as a reaction test. Taking into account that the reaction test was carried out under operating conditions which guarantee absence of diffusion limitations, the methane conversion obtained is roughly proportional to the metal surface area [31]. In Table 2 it can be observed the methane conversion values for the catalysts submitted to different activation conditions. The reaction test was carried out under the following conditions: T: 773 K, atmospheric pressure; catalyst mass, w_{cat}: 0.012 g dried base; CH_4 wet molar fraction: 0.1; dried feed flow: 200 ml min^{-1}; water/CH_4 molar ratio: 2.2 (N_2 balance). It must be mentioned that all the catalysts were stable during the operation time (10 h) and for all the experiments the carbon balance closed satisfactory.

The C-NiAR-100 shows both the lower hydrogen consumption in TPR experiments and specific area (see Table 1) as well as presents the lower methane conversion (Table 2). On the other hand, the NiAl-R100 shows the higher methane conversion. Considering that both samples NiAl-R10 and NiAl-R100 have similar specific surface area, the activation in hydrogen excess would lead to a small size metallic nickel particles. Several authors have reported the relevance of the preparation conditions and pretreatments of nickel-alumina catalysts before reaction [32,33]. In fact, Bartholomew and Farrauto reported that the decomposition of nickel-alumina samples in hydrogen atmosphere (without previous calcination) tends to maximize nickel surface area, dispersion and reduction to nickel metal [32].

From these latter results a kinetic study of ethanol steam reforming reaction was performed using the NiAl-R100 catalyst. Temperature, residence time and ethanol and water concentration were varied systematically. All the experiments were carried out under diluted conditions and ethanol conversion was always less than 100% with the aim of obtaining significant kinetic results. Dilution conditions (water/ethanol/argon molar ratio: 8.8/1.6/89.6) were so that the variation in molar number due to the stoichiometry of the reaction could be neglected. The experiments at different feed molar ratio were conducted at the same residence time by means of modifying the inert-argon flow. The following definitions were used:

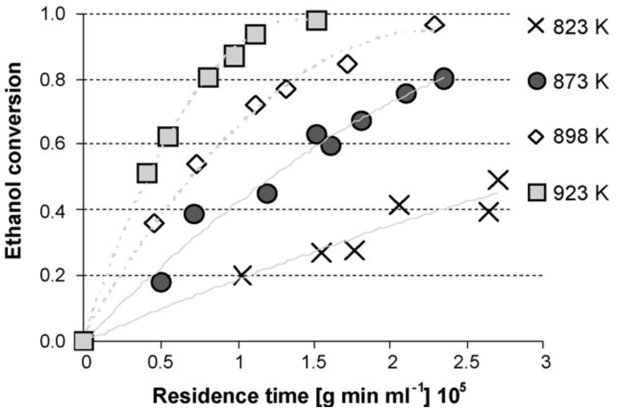

Fig. 4. Ethanol conversion vs. residence time for different reaction temperatures. Ethanol molar fraction: 0.016. Water molar fraction: 0.09.

Ethanol conversion (x): *(mole of ethanol in the feed – mole of ethanol in the effluent)/mole of ethanol in the feed.*
Residence time: *mass of catalyst/total volumetric flow.*
Yield: *molar product flow/molar ethanol flow in the feed.*

Ethanol conversion and H_2 yield increase with the increasing of temperature and residence time as it can be seen in Figs. 4 and 5. The behaviour at different temperatures is linked to the endothermic character of the reaction. It can be observed that when the conversion reaches values near to 100%, H_2 yield approximates to a value of 5, being 6 the stoichiometric limit. The other products obtained are CO_2, CO and traces of CH_4.

Ethanol conversion vs. ethanol and water molar fractions in the feed are shown in Figs. 6 and 7, respectively. As it can be seen, ethanol conversion decreases as ethanol concentration increases, indicating, if a power law kinetic expression is assumed, that the reaction order is lower than 1. Regarding ethanol conversion as a function of water molar fraction, a maximum is observed. This fact illustrates the existence of a competition between ethanol and water to be adsorbed on the same active site. At 898 K, the maximum ethanol conversion was observed at a water–ethanol molar ratio value of 5.

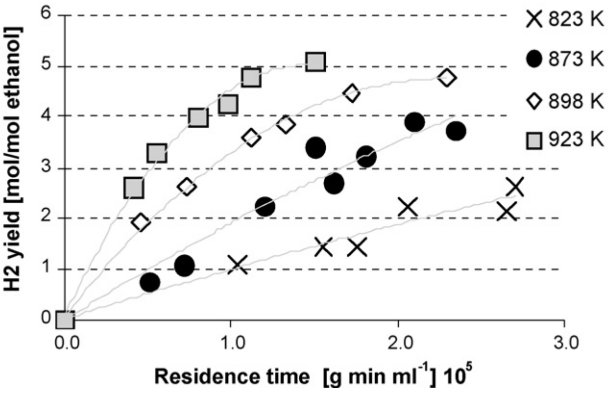

Fig. 5. H_2 yield vs. residence time for different reaction temperatures. Ethanol molar fraction: 0.016. Water molar fraction: 0.09.

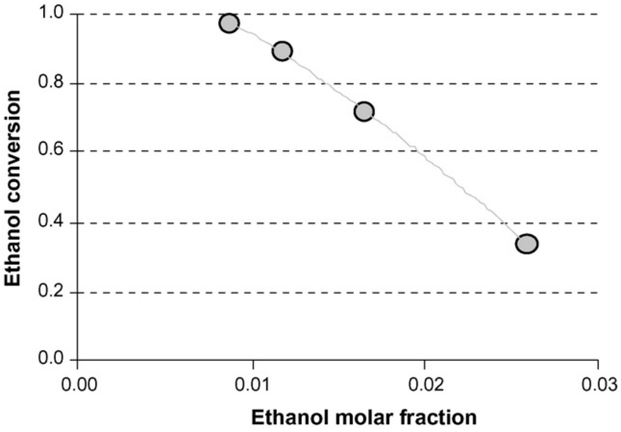

Fig. 6. Ethanol conversion vs. ethanol feed molar fraction. Water molar fraction: 0.09, temperature: 898 K.

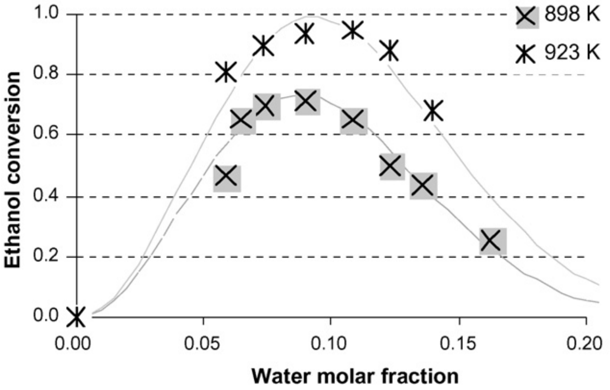

Fig. 7. Ethanol conversion vs. water feed molar fraction. Ethanol molar fraction: 0.016. Temperature: 898 and 923 K.

4. Conclusions

Activation steps which transform these Ni(II)-Al(III) precursors into steam reforming catalysts strongly affect the final particle size and therefore the catalytic activity and stability. It has been confirmed that the reduction of precursors using pure H_2 and without previous calcinations leads to a higher activity for methane steam reforming. H_2 yield from ethanol steam reforming reached a value of 5, being 6 the maximum stoichiometric. CO, CO_2, CH_4 and H_2 were the only products obtained even for ethanol conversion lower than 100%. Ethanol order was found to be lower than 1, assuming a power law kinetic expression. The dependence on water concentration is further more complex. A maximum value of ethanol conversion was found. Additionally, it was verified that the water/ethanol molar ratio value where the maximum conversion is observed depends on the temperature. This behaviour indicates that both reactants are adsorbed on the catalyst and both compete for the same active site.

Then a kinetic study considering a Langmuir–Hinshelwood type mechanism with surface reaction between both reactants adsorbed on catalyst surface as limiting rate step, was performed and the results will be presented in a next paper.

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