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Short Communication

Biogas reforming over La-NiMgAl catalysts derived from hydrotalcite-like structure: Influence of calcination temperature

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ABSTRACT

Hydrotalcite-like compound with general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n})\cdot mH_2O$, where A^{n-} is the compensation anion, has been used as precursor of active catalysts for biogas reforming. This precursor was calcined at six different temperatures between 250 and 750 °C and the resulting catalysts were tested in order to evaluate the influence of the calcination temperature on the catalytic activity and stability. XRD characterization showed that from 250 °C the hydrotalcite structure is no longer detected, leading to Mg(Ni,Al)O solid solutions, where no peaks related to lanthanum appear. An increase on the calcination temperature increased the grain size and cell parameter value. 50 h-catalytic tests were carried out at 700 °C, CH_4:CO_2 molar ratio of 1:1 and a mass/feed alimentation ratio (W/F) of 0.4 mg min cm^{-3}. Used catalysts were characterized by temperature programmed oxidation (TPO), scanning electron microscopy (SEM) and Raman spectroscopy in order to obtain information about coke deposition. Catalytic tests highlighted the great influence of calcination temperature over catalytic activity and stability, having found that, as a general trend, calcination temperatures below 750 °C decrease both the stability and catalytic activity, with the exception of the catalyst calcined at 550 °C, where a higher activity was achieved but with a comparatively low stability.

1. Introduction

Biogas is a renewable gas that constitutes an alternative fuel that can reduce fossil fuel dependency and emissions of greenhouse gasses. There are different technologies to convert the chemical energy of biogas into electricity, the most common being gas turbines and internal combustion engines [1]. However, these processes generate pollutants as NO_x, SO_x and dioxins, while their efficiencies are low, around 35%, and limited by the Carnot cycle [2]. A process commonly used to obtain hydrogen from biogas is the steam reforming [3–5]. It requires the evaporation of great quantities of water, which is an energy demanding step [6] as well as the CO_2 removal from the inlet stream. Although a cheaper alternative to this process is CO_2 reforming of methane, an important drawback is also present: catalyst deactivation mainly produced by carbon formation. Many different catalysts have been studied so far, indicating that noble metal-based catalysts are less sensitive to coking than those based on Ni [7]. However, considering their high cost and limited availability, Ni-based catalysts seem to be more appropriated. Different supports and promoters have been tested in order to minimize coke formation [8–14]. Hydrotalcites have been studied as precursors which after calcination lead to catalysts with good activity. Since small and highly dispersed particles of the active metal are formed, a hindered sinterization process may be expected. They also show high surface areas and basic properties which improve CO_2 chemisorption and consequently the resistance to coke formation [15–17]. In addition, in a previous work [18], after calcination at 750 °C, an increase in stability and a decrease in activity were reported when lanthanum was added. Lanthanides can also strengthen CO_2 adsorption on the support, which hinders the formation of deposited carbon via reverse disproportionation [12]. They also favor metal dispersion and the oxycarbonate on the La_2O_3 support might be considered as a dynamic oxygen pool, favoring coke removal [19]. Different calcination temperatures have been reported in the literature. It is known that high calcination temperatures tend to strengthen the interaction inside Mg(Ni,Al)O solid solution, leading to a considerable amount of nickel diffusing from the catalyst surface to the bulk, where it becomes irreducible and therefore ineffective for catalysis [20]. Lucredio et al. [21] and Daza et al. [22] calcined at 500 °C, while Olafsen et al. [23] calcined at 750 °C. However, Perez-Lopez et al. [24] reported that calcination temperature had little influence over catalytic activity.

The aim of this work is to study whether calcination temperature affects catalytic activity and stability and the subsequent determination of an adequate range of calcination temperatures.

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2. Experimental

2.1. Precursor and Catalysts Preparation

A precursor denoted as LaHT2 where number 2 indicates nominal Mg/Al molar ratio, was prepared by co-precipitation at pH = 8 and 60 °C, under continuous stirring by dropwise adding an aqueous solution containing $Mg(NO_3)_2 \cdot 6H_2O$ (Panreac, 98% assay), $Al(NO_3)_3 \cdot 9H_2O$ (Panreac, 98.0–102.0% assay), $Ni(NO_3)_2 \cdot 6H_2O$ (Panreac, 99% assay) and $La(NO_3)_2 \cdot 6H_2O$ (Panreac, 99,0% assay) to a saturated aqueous solution containing $NaHCO_3$ (Panreac, 99.7–100.3% assay) at pH = 8, followed by aging for 90 min at 60 °C. pH was adjusted with a mixture of $NaHCO_3$ and NaOH solution (Riedel-de-Haën, 99% assay). Special care of filtering and precipitate washing was taken in order to eliminate Na^+ ions completely. It was dried overnight at 110 °C and calcined at 250, 350, 450, 550, 650 and 750 °C. The calcination was performed at a rate of 5 °C min^{-1} and maintained for 2 h. After calcination, catalysts denoted as LaHT2-x were obtained. Letter x represents the calcination temperature. The final measured Mg/Al molar ratio was 1.7 whereas Ni and La contents are 2.1 and 1.1%, respectively.

2.2. Catalysts Characterization

Catalyst composition was determined after acid digestion by an ICP-MS Elan 6000 Perkin-Elmer Sciex equipped with an autosampler AS 91. X-ray diffraction of the calcined catalysts was performed by an X-ray diffractometer (XPERT-PRO, PANanalytical) using Cu Kα radiation (λ = 0.154 nm). Temperature programmed reduction (TPR) was carried out, though not shown here, in order to establish the appropriate reduction temperature. Carbon deposition was determined by temperature programmed oxidation (TPO) over post-reaction catalysts with a Mettler-Toledo TGA/SDTA 851 thermo-balance and STAR 8.10 software coupled to a mass spectrometer detector Pfeiffer Thermostar. TPO tests were performed between 25 and 950 °C (10 °C min^{-1}) using a mixture of O_2/N_2 10/40 mL N min^{-1}. CO_2 desorption in the mass spectrometer detector (m/z = 44) was used to determine coke gasification temperatures. SEM measurements were performed on a Hitachi S-3000N Scanning Electron Microscope coupled to an INCAx-sight energy-dispersive spectrometer, using a Sputter Caoter SC502 to pre-treat the samples. Raman spectroscopy of used catalysts was performed on a PerkinElmer Raman 400F, using 100 mW laser power of 785 nm excitation, a CCD detector and with a spectral resolution of 4 cm^{-1} and a total exposure time of 20 s.

2.3. Catalytic Testing

Catalytic tests were carried out in a Microactivity Reference PID Eng&Tech equipment. They were performed in a tubular fixed-bed quartz reactor at 700 °C and at CH_4:CO_2 molar ratio of 1:1. In order to validate the comparison with previous reported results [18], the same conditions were tested, briefly, a catalyst mass of 40 mg with a particle size between 0.5 and 0.42 mm, chosen to avoid excessive pressure drop, a mass/feed alimentation ratio (W/F) of 0.4 mg min cm^{-3} and 50 h duration. The testing protocol includes catalyst heating up to the reduction temperature in N_2 (100 mL min^{-1}), followed by reduction in H_2 (100 mL min^{-1}) for 1 h. LaHT2-250 and LaHT2-350 were reduced at 600 °C, while 650 °C was chosen for the rest. After reduction, the reactor was heated up to 700 °C in N_2 (100 mL min^{-1}) followed by the start of the catalytic test by feeding CH_4 and CO_2. Reaction products were analyzed with an Agilent chromatograph 6890N connected in line, equipped with a TCD detector and Chromosob 102 and Porapak P5 Q columns. CH_4, N_2, H_2, and CO_2 gasses were fed from Praxair gas bottles with a purity of 99.5 for CH_4 and 99.999% for the rest.

3. Results and Discussion

3.1. Catalysts Characterization

Ni and La nominal contents measured by ICP-MS are summarized in Table 1. It can be seen that they increase below a calcination temperature of 550 °C, which agrees with TPO experiments over the precursor [18], where almost all H_2O and CO_2 were eliminated after 550 °C. The higher the amount of H_2O and CO_2 on the sample is the less the relative nickel content the sample contains.

XRD characterization of the calcined catalysts (Fig. 1) showed that from 250 °C, hydrotalcite structure is no longer present, leading to diffraction bands at 37, 43, 63, 75 and 79°. These bands can be identified as MgO phase (JCPDS 00-045-0946), but if cell parameters *a* are calculated (Fig. 2) values lower than the MgO cell parameter (4.21 Å) are obtained, which can be explained by Mg(Ni,Al)O formation, since cell parameter decreases as Al^{3+} ionic radius is smaller than Mg^{2+} and Ni^{2+} ones. Cell parameter *a* was calculated by plotting the cell parameter *a* (calculated as $d\sqrt{h^2 + k^2 + l^2}$) *vs.* $\frac{cos^2\theta}{sen\theta} + \frac{cos^2\theta}{\theta}$ (the Nelson–Riley factor) for peaks at 43, 63 and 79°. This procedure minimizes error sources like absorption of the X-ray beam, displacement of rotation axis or inaccurate determination of camera constants [25].

As above mentioned, from 250 °C hydrotalcite structure is lost. According to Vaccari et al. [26], hydrotalcite decomposes from 300 °C. Hibino et al. [27] established 350 °C as the decomposition temperature. Constantino et al. [28] reported that at temperatures below 250 °C hydrotalcite structure is retained. These differences among reported results may be a consequence of the differences on thermal stabilities due to the synthesis method or as Constantino et al. [28] proposed, due to the rehydration and reconstitution of hydrotalcite structure. Since we detected this reconstitution process in our laboratory, DRX measurements were carried out immediately after calcination.

No peak related to lanthanum can be seen in Fig. 1, probably due to its low concentration (1.1–1.6%) or high dispersion. XRD pattern of LaHT2-250 catalyst shows intermediate features between hydrotalcite and Mg(Ni,Al)O solid solution structures, since hydrotalcite peaks at 11 and 24° are still present, while peaks at 35 and 60° show higher intensities than peak at 43°. From 350 °C, the higher the calcination temperature is, the sharper the peaks are obtained, suggesting an increase in grain size.

An increase of cell parameter between 450 and 650 °C is observed (Fig. 2), an approach to pure MgO cell parameter as the calcination temperature rises. This could be a result of Al^{3+} cations leaving the lattice, since the presence of Al^{3+} ions in the Ni–Mg–O cubic lattice is expected to reduce this value. However, no presence of possible crystalline phases of Al_2O_3 was detected. Preliminary results obtained by XPS characterization (not shown), show that surface and bulk chemical compositions differ. The surface is enriched on Al, which supports the hypothesis of Al^{3+} leaving Ni–Mg–O cubic lattice and migrating to the surface.

By TPR experiments (not shown), an appropriate reduction temperature was chosen for each catalyst. TPR showed two reduction peaks, one at high temperature and one below 700 °C. We established the reduction temperature at the end of the first peak, since we have observed that reducing the nickel that is more strongly interacting with the support decreases the catalytic stability. Since the applied

Table 1
Ni and La nominal contents determined by ICP-MS for hydrotalcite-based catalysts calcined from 250 to 750 °C.

Catalyst	Ni nominal content/%	La nominal content/%
LaHT2-250	2.3	1.3
LaHT2-350	2.7	1.5
LaHT2-450	2.8	1.6
LaHT2-550	3.1	1.6
LaHT2-650	3.0	1.6
LaHT2-750	3.0	1.6