



Long-term stability test of Ni-based catalyst in carbon dioxide reforming of methane



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ABSTRACT

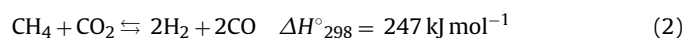
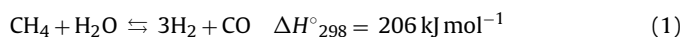
A La-NiMgAlO catalyst, obtained after calcination of a hydrotalcite precursor, was evaluated in dry reforming of methane at 650 and 700 °C and compared with a previous test performed at 750 °C. At 700 °C the catalyst showed no sign of deactivation during 200 h, while it deactivated slowly afterwards. However, at 650 °C conversion decay was detected from the beginning of the test. In both tests, CH₄ and CO₂ conversion were higher than thermodynamic equilibrium estimation which suggests the participation of other reactions such as methane decomposition or steam reforming of methane. The occurrence of reverse water-gas-shift reaction (RWGS) was responsible for the H₂/CO ratios below unity and for the higher CO₂ conversion compared with CH₄.

Used catalysts were characterized by several techniques (TEM, ²⁷Al MAS NMR, XRD, TPO and Raman spectroscopy) in order to study catalyst structure and to establish whether carbon was deposited and its nature. Ni particle diameter increased when reaction temperature decreased but no differences in ²⁷Al MAS NMR or XRD results were observed. A higher coke deposition rate was detected when the temperature was increased. At 700 and 650 °C carbon species were mainly graphite ribbons, coating carbon and graphite nanoencapsulates, while at 750 °C there were multi-walled carbon nanotubes (MWCNT), fibres and graphite ribbons. The deactivation of the catalysts tested at 650 and 700 °C can be related to: (i) the presence of coating carbon, graphite nanoencapsulates and Ni particles embedded inside the carbon nanotubes (CNT); (ii) partial sintering and (iii) a lower hydrogen production what makes that carbon transportation away the surface was less favoured.

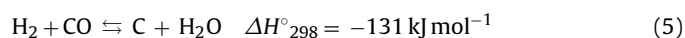
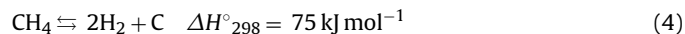
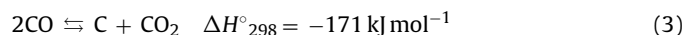
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1. Introduction

The CO₂-reforming of CH₄ with CO₂ has been intensively studied due to its important application in the industry for producing synthesis gas [1–5]. Synthesis gas (H₂ + CO) is an important feed for the petrochemical industry (e.g. in methanol synthesis and the Fischer–Tropsch process). Although the commercial method most commonly employed by industry to produce syngas is the steam reforming of methane (1), this process produces a rather high H₂/CO ratio for the methanol and Fischer–Tropsch syntheses. On the contrary, CO₂-reforming of CH₄ (2) produces a lower H₂/CO ratio and the separation of CO₂, which is an energy intensive and a rather costly process, is not necessary. In addition, it introduces some other environmental benefits such as: upgrading of biogas (a renewable resource mainly composed by CH₄ and CO₂) and the removal of two greenhouse gases



The major drawback of this reaction is the rapid deactivation of nickel catalysts as a result of carbon deposition via the Boudouard reaction (3), CH₄ decomposition (4) and/or the reverse carbon gasification reaction (5) [6]



In addition to operation parameters [7–9], catalyst structure and properties affect carbon deposition. It is supposed to occur more easily on larger nickel particles than on smaller ones [10,11]. Furthermore, it is favoured by acidic supports. It has been suggested that carbon deposition can be attenuated or even suppressed when the metal is supported on a metal oxide with a strong Lewis basicity [12] or when a promoter is added [13,14]. This occurs because the ability of the catalyst to chemisorb CO₂ is enhanced, and the adsorbed CO₂ reacts with C to form CO, resulting in the reduction of coke formation. Ni/MgO possess good coke resistance ability due to formation of solid solution Ni–Mg–O [15,16], but the surface area

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and activity of Ni/MgO is low compared with other catalysts under the same reaction conditions [17].

The synthesis method is another important parameter to take into account. The use of precursors in which the metal is homogeneously distributed, may result, after calcination and reduction, in the formation of highly dispersed and stable metal particles on the surface [18]. Catalysts obtained after calcination of hydrotalcite-like precursors have shown high surface area and basic properties as well as high dispersion of the active metal [19]. However, they do not provide a sufficient degree of stability which is required by an industrial process. Previous works [20–22] reported the addition of lanthanum as a way to enhance catalytic stability in dry reforming of methane when calcined at 750 °C. Lanthanides favour metal dispersion [23,24] and strengthen CO₂ adsorption on the support [25]. The presence of oxycarbonates over La₂O₃ also facilitates coke removal since it seems to act as a dynamic oxygen pool [14,26]. The aim of this work is to study the influence of reaction temperature over catalyst deactivation, as well as to evaluate and characterize the deposited carbon.

2. Experimental

2.1. Catalyst preparation

The catalyst was obtained after calcination at 750 °C of a hydrotalcite precursor, which was prepared by co-precipitation, according to a previously reported method [20,21]. The final measured Mg/Al molar ratio was 2.3, whereas Ni and La contents were 2.8% and 1.9%, respectively.

2.2. Catalytic tests

Catalytic tests were carried out in a Microactivity Reference PID Eng&Tech equipment, in a tubular fixed-bed stainless steel (Ni free) reactor with a CH₄:CO₂ molar ratio of 1:1. Excessive pressure drop was avoided by choosing a catalyst particle size between 0.50 and 0.42 mm. A more detailed description of the testing protocol can be found elsewhere [20]. 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. CH₄, N₂, H₂, and CO₂ gases were fed from Praxair gas bottles with a purity of 99.5 for CH₄ and 99.999% for the rest. The catalyst was pre-treated in situ at 650 °C with pure hydrogen (100 mL min⁻¹) during 1 h, in order to only reduce the segregated NiO [22].

The influence of reaction temperature was evaluated testing the catalyst at 650 and 700 °C and comparing the results with an experiment performed at 750 °C which has been already reported [27]. These tests were performed at the highest space velocity necessary to achieve the maximum conversion, i.e. 4800 cm³ g_{cat}⁻¹ h⁻¹. Therefore, deactivation would not be hidden as a consequence of an excess of active sites.

2.3. Characterization

X-ray diffraction of tested catalysts was performed by an X-ray diffractometer (XPRT-PRO, PANanalytical) using Cu K α radiation ($\lambda = 0.154$ nm). ²⁷Al MAS NMR analysis was carried out in a BRUKER AV 400 WB spectrometer, equipped with a CPMAS 4-mm probe, at room temperature and 15 kHz. TEM studies were carried out in a JEOL Model JEM-1200 EXII transmission electron microscope equipped with an emission source of electron at 200 kV. Samples were ultrasonically dispersed in ethanol and a few drops were placed on a holey-carbon-coated copper grid, allowing the solvent to evaporate in air before TEM observation. Temperature programmed oxidation (TPO) were conducted in a Mettler-Toledo TGA/SDTA 851 thermo-balance with STAR 8.10

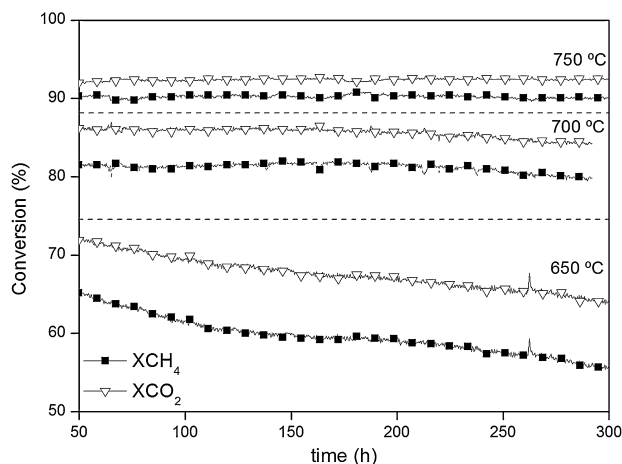


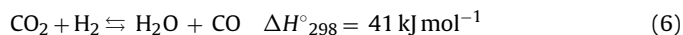
Fig. 1. CH₄ and CO₂ conversion vs. time in dry reforming of methane at 650, 700 and 750 °C. Testing conditions: CO₂:CH₄ = 1 and space velocity equal to 4800 cm³ g_{cat}⁻¹ h⁻¹.

software. The thermobalance was coupled to a mass spectrometer (MS) detector Pfeiffer ThermoStar GSD 301 T3. The test was performed between 25 and 900 °C (5 °C min⁻¹) using a mixture of O₂/N₂ 10/40 mL N min⁻¹. Carbon gasification was monitored by CO₂⁺ signal ($m/z = 44$). Raman spectra were collected in a Renishaw System 1000 spectrometer equipped with Ar ion laser (Spectra Physics, $\lambda = 514$ nm, power 19 mW, 1 mW on sample), a cooled CCD detector (−73 °C) and a holographic super-Notch filter to remove the elastic scattering. The spectral resolution was ca. 3 cm⁻¹ and spectrum acquisition consisted of 10 accumulations of 30 s. The spectra were recorded at ambient temperature.

3. Results and discussion

3.1. Catalyst testing

Fig. 1 shows the evolution of CH₄ and CO₂ conversion (X_{CH_4} and X_{CO_2} , respectively) at different reaction temperatures versus time. The experiments were kept for almost 300 h. All the tests started at 700 °C in order to check that catalyst conversion achieved the expected value, and to complete the activation process of the catalyst which may be ascribed to the formation of new active sites when the catalyst was exposed to the reaction mixture [4,28]. Fig. 1 shows the catalytic performance afterwards. In all cases CO₂ conversion was higher than CH₄ conversion what may be due to reverse water shift reaction (RWGS) (6) [20]



Moreover, both conversions were higher than thermodynamic equilibrium estimation (650 °C: 60%, 700 °C: 76%, 750 °C: 86%), what suggests that other reactions were taking place. These reactions could be methane decomposition (3) or methane steam reforming (1) which will consume water formed by means of RWGS reaction (6) [9].

When the catalyst was operated at 750 °C no sign of deactivation occurred [27]. However, when reaction temperature decreases deactivation phenomena become evident. At 700 °C the catalyst was stable during the first 200 h and afterwards methane and carbon dioxide conversions slightly decreased from 82% and 86% to 80% and 84%, respectively. The deactivation rate (k_d) was 2.3×10^{-4} h⁻¹. This rate was calculated according to a previously reported procedure [21]. At 650 °C a higher deactivation was observed from the beginning of the test, being the deactivation rate $k_d = 4.3 \times 10^{-4}$ h⁻¹.

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