

Structural investigation of the carbon deposits on Ni/Al₂O₃ catalyst modified by CaO-MgO for the biogas dry reforming reaction.

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Abstract: Ni catalysts based on Al₂O₃ and Al₂O₃ modified with CaO-MgO were tested for the dry reforming of biogas (BDR). Time-on-stream experiments were carried out between 600 and 800°C and the spent catalysts were examined using a variety of characterization techniques including, N₂ adsorption/desorption, thermogravimetric analysis (TGA), Raman spectroscopy, electron microscopy (STEM-HAADF and HR-TEM), and X-ray photoelectron spectroscopy (XPS). It was revealed that the carbon deposits consisted of carbon nanotubes and amorphous carbon for both samples. XPS studies showed the presence of Ni⁰ on both catalysts and Ni₂O₃/NiAl₂O₄ on the Ni/Al₂O₃ sample. The time-on-stream experiments showed that the Ni/CaO-MgO-Al₂O₃ catalyst is more resistant to deactivation and more active and selective for all temperatures under investigation. It was concluded that doping Al₂O₃ with CaO-MgO enhances catalytic performance as: (a) it helps to maintain highly dispersed Ni⁰ during the BDR as the interaction between metal and support is a stronger one, (b) it leads to the formation of carbon structures that are easier to oxidize, and (c) it facilitates the gasification of the carbon deposits because its increased surface basic sites enhance the adsorption of carbon dioxide.

Keywords: biogas dry reforming; syngas production; nickel based catalysts; catalytic deactivation; carbon deposition; CaO-MgO modifiers

1. Introduction

Biogas is a product of the anaerobic digestion of biomass. It contains mainly CH₄ and CO₂ and can be used for the production of syngas (H₂/CO) via dry reforming (BDR) [1]. Syngas is a valuable feedstock in the chemical industry used for the synthesis of oxygenated chemicals and hydrocarbons

via the Fisher-Tropsch process [2]. The major issue that must be overcome when using cheap Ni based systems is carbon deposition on the catalyst surface, which is produced via methane decomposition and carbon monoxide disproportionation. The carbon deposited on the catalyst surface can differ in nature and structure [3-5]. As is widely understood, the activity of a catalyst system depends on a number of factors which include the nature of the support and active metal, the catalyst preparation method and pretreatment. Popular metal oxides tested as supports for Ni based catalysts include Al_2O_3 , SiO_2 , ZrO_2 , rare earth metals (e.g., La_2O_3 and CeO_2) [6-9], or alkaline earth metals (e.g., Ba, Ca, Sr) [11,12] as promoters. The present work reports on the catalytic performance of Ni/Al and Ni/CaO-MgO-Al (Ni/modAl) catalysts using typical biogas mixtures ($\text{CH}_4/\text{CO}_2 = 1.5$). It examines the amount and/or the quality of deposited carbon after the time-on-stream experiments and relates this with catalyst deactivation. To achieve this aim, the time-on-stream experiments were performed at different reaction temperatures and the carbon deposited on the spent catalysts was examined by various characterization techniques (N_2 adsorption/desorption, TGA, Raman, STEM-HAADF, HR-TEM and XPS). The evolution of Ni oxidation states during the reaction was investigated using XPS.

2. Materials and Methods

2.1. Catalyst preparation

The alumina support was obtained from Akzo and the modified alumina (4.5% CaO, 1% MgO, 0.5% SiO_2) by Saint Gobain NorPro in pellet form. The supports were crashed and sieved to 350-500 μm and calcined at 800°C for 4 h. The catalysts were prepared via the wet impregnation technique using the appropriate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to give catalysts with a Ni content of 8 wt%. The catalysts were dried at 120°C for 12 h, calcined in atmosphere at 800°C for 4 h and in-situ activated for 1 h at 800°C under pure H_2 flow. The catalysts are denoted as Ni/Al and Ni/modAl.

2.2. Materials characterization

The spent catalysts were examined using the following instruments/techniques: (a) Leco TGA 701, (b) S-Twin Tecnai (200 kV G2 20) and Tecnai G2-F30 Field Emission Gun microscope (STEM-HAADF & HR-TEM), (c) ThermoFisher Scientific Instruments K-Alpha+ spectrometer (XPS), (d) WITEC alpha 300R micro-Raman system, and (e) high-resolution 3Flex Micromeritics porosimeter (N_2 adsorption/desorption).

2.3. Catalysts tests

The experimental apparatus used was a continuous flow fixed bed tubular reactor. The tests were carried out at atmospheric pressure. The gas mixture fed into the system was 55% CH_4 , 35% CO_2 and 10% Ar (CH_4/CO_2 molar ratio = 1.57). Short (10 h) time-on-stream experiments were carried out at different temperatures. The WHSV was 40,000 $\text{mL g}^{-1} \text{h}^{-1}$. The analysis of the reactants and products was carried out by gas chromatography in a CG-Agilent 7890A.

3. RESULTS AND DISCUSSION

3.1. Characterization of spent catalysts

3.1.1. Textural characterization

The N_2 adsorption/desorption isotherms for the Ni/Al and Ni/modAl catalysts after their in-situ reduction and after reaction at 600, 700 and 800°C are presented in Figure 1. The respective pore size distribution curves are also presented as insets on the corresponding figures. The isotherms for both samples are type IVa. The hysteresis loop for the reduced Ni/Al sample is type H2(b) (typical of mesoporous materials), but after reaction this loop is transformed to an H3 type (usually found in materials with macropores). Regarding the Ni/modAl samples, the hysteresis loop is H3 type. This is

because although the adsorption branch resembles a Type II isotherm, the lower limit of the desorption branch is located at the cavitation-induced P/P_0 .

Regarding the pore size distribution, for the Ni/Al samples, these are single modal types in the mesopore range, centered around 10-20 nm. However, a shift to the micropore range is observed for the samples used at 600 and 700°C. This is opposing to what can be concluded for the Ni/modAl samples, which show that the majority of the population of pores is in the meso-range. Also noticeable for the spent catalysts is a shift to a bigger mean diameter, which provides an indication that pore blocking occurs at the meso-range. It can be deduced that for both spent catalysts, the carbon deposition that took place at lower reaction temperatures (600 and 700 °C) covered the mesopores.

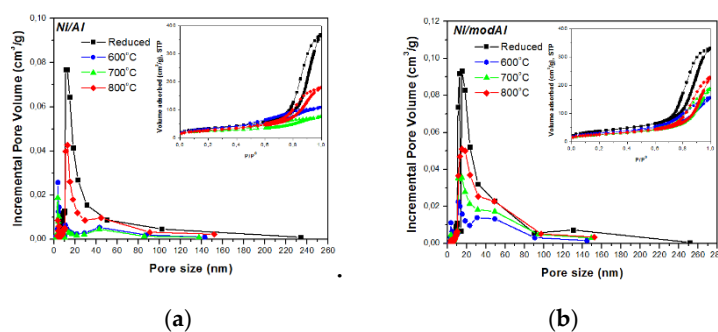


Figure 1. Pore size distribution and N_2 adsorption-desorption isotherms (inset) of the reduced and spent catalysts at 600, 700 and 800°C.

3.1.2. TGA analysis

From the TGA analysis (not shown herein) it was observed that the oxidation process was different between the two catalysts. For the Ni/Al, the main thermal event was found between ≈ 450 –700°C for the samples tested at low reaction temperatures (600 and 650°C), but it included up to 800 °C for the catalysts tested at higher reaction T_s . In contrast, for the Ni/modAl, the main thermal event was ≈ 450 –800°C. According to the literature, amorphous carbon combusts between 200–500°C, carbon nanofibers (CNFs) and/or carbon nanotubes (CNTs) combust between 500–600°C, and more graphitic structures, such as multi wall carbon nanotubes (MWCNTs) combust between 600–800°C [13]. Although these results show that different carbon structures were deposited on the catalysts during the reaction, it appears that a bigger fraction of graphitic coke was deposited on the Ni/Al, especially at higher reaction temperatures. Thus, it can be concluded that the addition of MgO and CaO on the alumina supporting material led to a less graphitic type of carbon, due to the higher rate of carbon oxidation, which could lead to a catalyst with improved stability characteristics.

3.1.3. Raman spectroscopy analysis

The results obtained using Raman spectroscopy are shown in Figure 2. This technique allows the investigation of the nature (graphitization) of the carbon deposits. Both samples show peaks between 1000 and 2000 cm^{-1} (first order region) and between 2300 and 3300 cm^{-1} (second order region). In the first order region are located two broad bands; these are termed the G-band (between 1500 and 1600 cm^{-1}), and D-band (between 1300 and 1400 cm^{-1}). Deconvolution of the Raman spectra showed that the G and D-band peaks were centered at 1565 and 1345 cm^{-1} corresponding to CNTs. The extent of graphitization of the coke can be gauged by the relative intensity of the D and G-bands (I_D/I_G), namely lower I_D/I_G values are correlated with higher crystallinity due to the higher contribution of the G-band [14]. For all catalysts tested for the present work it is obvious that the degree of crystallinity increased with an increase of the reaction temperature however, this increase was more significant for the unmodified nickel catalyst. To illustrate the point, the I_D/I_G ratio for the Ni/Al sample followed the order $1.32 > 0.72 > 0.45 > 0.44 > 0.35$ and for the modified catalyst $1.42 > 1.18 > 1.06 > 0.98 > 0.86$ at 600, 650, 700, 750 and 800 °C, respectively.

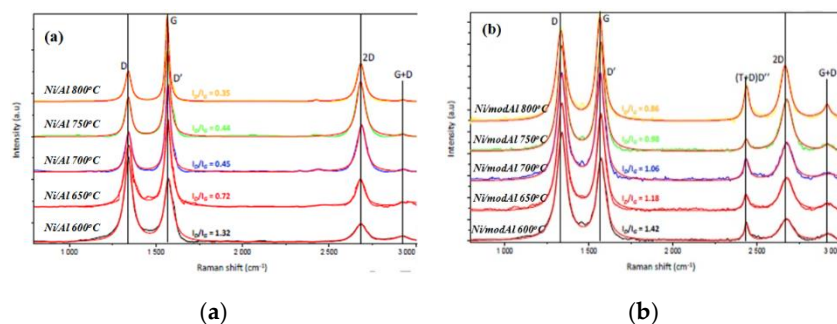


Figure 2. Pore size distribution and N₂ adsorption-desorption isotherms (inset) of the reduced and spent catalysts at 600, 700 and 800 °C.

3.1.4. Electron microscopy analysis

At 600 °C both samples exhibited crystalline carbon allotropes shaped as carbon nanotubes and amorphous carbon; coke encapsulating Ni particles can also be observed. In contrast, at high reaction temperatures (800 °C), no amorphous carbon was detected on the Ni/Al catalyst; only coke encapsulating the active metallic Ni nanoparticles (NPs) could be observed. This was in contrast to the conclusion drawn regarding the Ni/modAl spent catalyst, where amorphous carbon could be observed even after reaction at 800 °C [15]. Another interesting observation was that at 800 °C the Ni/Al catalyst showed the formation of core-shell carbon coated Ni NPs with highly graphitized CNTs formed. This provides a good explanation for the very low I_D/I_G ratios discussed above. From HR-TEM, a plethora of defects on the CNTs formed onto the Ni/modAl system could be observed. These defects can be explained by the transfer of oxygen and its insertion in the graphitic lattice during CNT growth, which inhibits the formation of CNTs with continuous, straight walls.

3.3. Catalytic stability

As mentioned above time-on-stream experiments for the Ni/Al and Ni/modAl were carried out at a variety of reaction temperatures (600, 650, 700, 750, 800 °C). To allow fair comparison, a fresh catalytic sample was used for each experiment. The changes regarding X_{CH₄}, X_{CO₂} and Y_{H₂} during BDR are depicted in Figure 3. The Ni/Al catalyst shows a steep drop in the conversion and yield values during the first two hours of the reaction (except at 800 °C), which leads to the loss of approximately half of its activity. In contrast, it is obvious that the Ni/modAl catalyst is more stable, active and selective. These differences are less pronounced at high reaction temperature. As an example, at 650 °C, the Ni/modAl presents almost double the values for X_{CH₄} (40%) and Y_{H₂} (35%) over the Ni/Al.

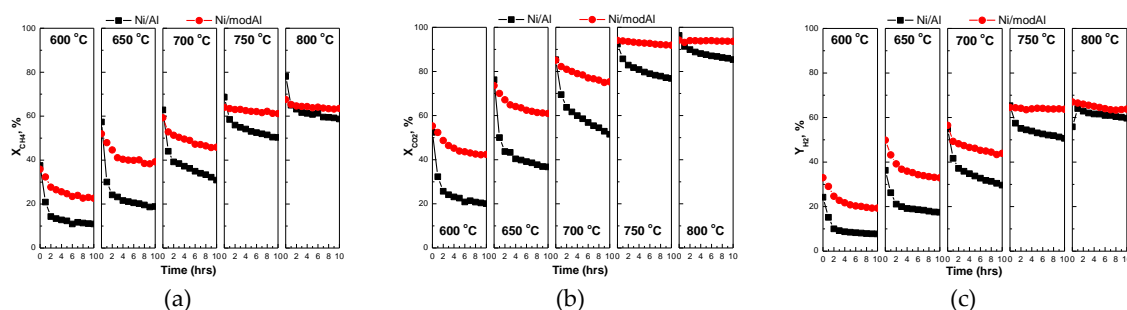


Figure 3. CH₄ and CO₂ conversion (%) for the Ni/Al and Ni/modAl catalysts for stability tests conducted at different temperatures.

Another observation is that for both catalysts the loss in activity loss decreases as test are carried out at higher reaction temperature. To be more specific, for the Ni/Al sample, the activity loss ($\Delta X(\text{CH}_4)\%$) is between 70% (600 °C) and 20% (800 °C) and for the Ni/modAl it is between 50% (600

°C) and ≈5% (800 °C). It is pointed out that XCO₂, YH₂, YCO are affected by the reverse water gas shift (RWGS) reaction and only the XCH₄ provides a true indication of the DRM activity.

Finally, regarding the H₂/CO molar ratio, its values are almost constant for the duration of the time-on-stream tests except for the first 2 h of operation in which elevated H₂/CO values (up to 1) were recorded. The high H₂/CO values point to a significant occurrence of the CH₄ cracking reaction, and/or Boudouard reaction. These reactions are mainly responsible for carbon deposition. The severe deactivation shown by both catalysts is also due to the harsh experimental conditions used in this study, i.e., the gas mixture used as feed had a high CH₄ to CO₂ ratio (equal to 1.57) and was almost undiluted.

4. Conclusions

In the present work, the time-on-stream stability of Ni/Al and Ni/modAl catalysts was examined for the reaction of the dry reforming of biogas. The study focused on the correlation between deactivation and carbon deposition. In particular, for both spent catalysts, TGA and Raman results proved that the degree of coke graphitization increased with higher reaction temperatures. The use of CaO and MgO as modifiers helped obtain coke deposits that were less graphitic in type. The TEM analysis showed that both catalysts contained graphitic structures in the shape of carbon nanotubes, and co-existent amorphous carbon. The HR-TEM images showed in a clear manner the defects of the CNTs formed onto the spent Ni/modAl catalyst. The time-on-stream tests showed that deactivation for the modified catalyst was less pronounced for all reaction temperatures. Thus, the modification of Al₂O₃ with CaO and MgO helped maintain the Ni⁰ phase during the reaction (due to stronger active phase-support interactions) and improved the deposited carbon gasification via the Reverse Boudouard reaction. The latter was achieved by an enhancement of CO₂ adsorption on the catalyst's increased surface basic sites.

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Conflicts of Interest: The authors declare no conflict of interest.

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