

BIOGAS VALORIZATION FOR SYNGAS PRODUCTION VIA THE DRY REFORMING REACTION USING NICKEL ON MODIFIED ALUMINA CATALYST

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ABSTRACT

Raw biogas contains 55–65% methane (CH₄), 30–45% carbon dioxide (CO₂), traces of hydrogen sulphide (H₂S) and fractions of water vapour. Since both methane and carbon dioxide are the main greenhouse gases, the reformation between these two gases is of significance; not only in tackling global warming, but also in providing a renewable fuel as hydrogen or synthesis gas (syngas) that is generally used as a feed for various chemicals production. The biogas reforming reaction is essentially the well known carbon dioxide reforming or dry reforming of methane (DRM) reaction, except of the different CH₄/CO₂ molar ratio in the feed. Ni-based catalysts have been tested for their methane or biogas reforming performance, since these catalysts exhibit huge potential for various industrial applications. However, one of the main limitations of Ni-based catalysts encountered is the deposition of carbon on their surface which can cause deactivation. The modification of the catalysts' supporting material using promoters is an efficient method to inhibit carbon formation [1, 2].

In order to have a deeper understanding of the aluminium oxide (Al₂O₃) modification with various dopants (CaO, MgO) mechanism and a much better control of the DRM reaction products, a comparative study of the Ni/m-Al and Ni/Al catalysts with a constant nickel loading (8wt%) is reported in this contribution.

The synthesized via the wet impregnation method Ni/Al and Ni/modified-Al samples, were characterized by the X-ray diffraction (XRD) and the N₂ adsorption-desorption techniques, at their calcined or/and their reduced forms. The chemical composition of the catalysts was determined using the inductively coupled plasma atomic emission spectroscopy (ICP) technique. Catalytic samples after calcination (fresh) and/or after reaction (used) were also characterized using the scanning electron microscopy (SEM) technique in order to examine their morphology and/or whether carbon was deposited on their surface.

Their catalytic performance for the biogas dry reforming reaction was studied in order to investigate the effect of the reaction temperature on methane (CH₄) and carbon dioxide (CO₂) conversion, hydrogen (H₂) yield and H₂/CO molar ratio of the produced gas mixtures at the outlet of the reactor. Time on stream experiments have also been conducted, in order to investigate catalysts' stability and possible deactivation.

It was concluded that the modification of γ -alumina, that was used as supporting material, with two basic oxides as calcium oxide (CaO) and magnesium oxide (MgO) improves the nickel catalysts' performance for the biogas dry reforming reaction, especially at the low temperature reaction range (550-750°C), while the carbon deposition on their surface was also suppressed.

Keywords: biogas dry reforming, nickel catalysts, catalyst's synthesis, hydrogen, syngas

1. Introduction

Synthesis gas (syngas) is a well known gas mixture consisting of hydrogen (H₂) and carbon monoxide (CO) with varying composition. In the case that its H₂/CO molar ratio is very close to 1,

syngas is more useful for the production of hydrocarbons and oxygenates through the Fischer-Tropsch process. For the biogas dry reforming reaction, the active metals that have been explored include Ni, Co, Pt, Rh, etc, with Ni appearing as the most suitable choice for both technical and economic reasons. The main drawback of nickel catalysts' is their deactivation due to coking and sintering. It should be mentioned that the supporting material plays an important role in catalytic performance due to its possible chemical effect, besides its interaction with the metal active phase. It is also known that supports with large surface area and usually small or medium pores, such as alumina, normally exhibit additional mass transfer limitation issues of the reactant [3]. Moreover, according to the literature [2, 4] the modification of alumina with calcium oxide (CaO) and magnesium oxide (MgO) significantly increases the stability and coke inhibition of Ni-based catalyst for hydrocarbon reforming reactions.

2. Materials and methods

2.1. Catalysts preparation

A commercial γ -Al₂O₃ (Akzo, 350-500 μm , $S_{\text{BET}}=290 \text{ m}^2\text{g}^{-1}$) and a commercially modified γ -Al₂O₃ (Saint-Gobain, 350-500 μm , $S_{\text{BET}}=278 \text{ m}^2\text{g}^{-1}$, containing 4.5 wt% CaO, 1 wt% MgO, 0.5 wt% SiO₂) were used as supports for the nickel-based catalysts. The two catalysts (labeled herein as Ni/Al and Ni/modified Al) were prepared following the wet impregnation method and by using aqueous solutions of Ni (NO₃)₂ 6H₂O with the proper concentration, in order to obtain final catalysts with a nominal Ni content of about 8 wt%. All the catalyst samples were dried at 120°C overnight and calcined at 800°C for 4h.

2.2. Catalysts characterization

Catalysts' specific surface area (SSA) was measured by applying the BET method from the N₂ adsorption-desorption isotherms obtained using a Micromeritics Tristar apparatus with Micromeritics VacPrep 061 Sample Degas System. The total metal loading (wt%) of the final catalysts' was determined by the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) technique using a Perkin-Elmer Optima 4300DV apparatus. The catalysts' crystalline structure was determined by applying the X-ray diffraction (XRD) technique, using a ThermoAl diffractometer with Cu-K α radiation. The diffraction patterns were identified by comparison with those of known structures in the JCPDS (Joint Committee of Powder Diffraction Standards) database. It should be noted that the XRD technique was applied for both fresh and reduced samples. Morphological examination of both fresh and used catalysts was done using the Scanning Electron Microscopy (SEM) technique (JEOL 6610LV). The elemental analysis, by means of Energy Dispersive Spectroscopy (EDS) was carried out using a large area (80mm²) silicon drift detector (X-Max 80 Oxford Instruments). Images, elemental maps and spectra were acquired and analyzed with the AZtech Nanoanalysis software (Oxford Instruments).

2.3. Catalysts testing

The biogas dry reforming reaction was carried out at atmospheric pressure, in a fixed-bed reactor at temperature ranging from 500-850°C. The feed total flow rate was 100 ml min⁻¹, consisting of a gas mixture with 30% v/v CH₄ and 20% v/v CO₂ diluted in helium, corresponding to a Gas Hourly Space Velocity (GHSV) of 120,000 ml g⁻¹ h⁻¹. The reaction temperature was controlled by a K-type thermocouple placed in the middle of the catalytic bed. The amount of catalyst used in the catalytic bed was 50mg. In addition, stability of samples in dry reforming of biogas reaction was investigated at 750°C and CH₄/CO₂=1.5 for 28h time on stream (TOS). The gaseous products were analyzed on-line by a gas chromatographer (Agilent 7890A), with two columns in parallel, HP-Plot-Q (19095-Q04, 30 m length, 0.530 mm I.D.) and HP-Molesieve (19095P-MSO, 30 m length, 0.530 mm I.D.), equipped with TCD and FID detectors. Prior to performing any catalytic reaction measurements, catalysts were in situ activated (reduced) by flowing 70ml min⁻¹ hydrogen (H₂) for 1 hour at 800°C.

3. Results and discussion

3.1. Characterisation

In Table 1 the physicochemical properties of all samples are presented. As can be observed, the specific surface area (SSA) for the supported nickel on Al₂O₃ catalyst is significantly lower than

the one of the supporting material (γ -Al₂O₃, 195 m² g⁻¹, after calcination at 800°C), whereas the pore volume was not significantly altered. The lower surface area can be attributed to the fact that the internal surface area of the support pore system is probably progressively covered by nickel species adsorbed on alumina active sites forming a layer and blocking micropores. However, it should also be noted that both catalytic samples (Ni/Al and Ni/modified Al) have comparable SSA's. The ICP results (metal loading) indicate that the desired metal level was achieved for both catalysts.

Table 1: Characterization results of supports and catalysts after calcination or reduction

Sample	S _{BET} (m ² g ⁻¹)	V _p (ml g ⁻¹)	Crystalline phases	Metal loading (Ni, wt%)
Al (Calcined)	195	0.65	Al ₂ O ₃	-
Modified Al (Calcined)	n/a	n/a	n/a	-
Ni/Al (Calcined)	168	0.59	Al ₂ O ₃ , NiAl ₂ O ₄	7.14
Ni/Al (Reduced)	-	-	Al ₂ O ₃ , NiAl ₂ O ₄ , Ni	-
Ni/modified Al (Calcined)	158	n/a	NiAl ₂ O ₄ , Al ₂ O ₃ , CaO, NiO	7.40
Ni/modified Al (Reduced)	-	-	NiAl ₂ O ₄ , Al ₂ O ₃ , CaO, Ni	-

Figure 1 depicts the XRD patterns of the Ni/Al catalyst after calcination and after reduction. Characteristic peaks at $2\theta=35.2^\circ$, 47.2° and 67.6° assigned to γ -Al₂O₃ and peaks of the spinel nickel aluminate phase (NiAl₂O₄), indicated by the diffraction lines at $2\theta=19^\circ$, 32° , 37° , 45° , 60.2° και 65.9° can be observed for both samples. The formation of NiAl₂O₄ is most probably caused by the reaction of NiO and Al₂O₃ due to the high calcination temperature (T=800°C) [2]. For the case of the Ni/Al (Reduced) sample the appearance of two small peaks at $2\theta=44^\circ$ and 51.2° indicate the presence of metallic Ni⁰. Figure 2 depicts the XRD patterns of the Ni/modified Al catalyst after calcination and after reduction. Peaks of NiAl₂O₄ ($2\theta= (19.2^\circ, 31.4^\circ, 37.2^\circ, 46.26^\circ, 59.64^\circ$ and $65.59^\circ)$), Al₂O₃ ($2\theta=35.1^\circ, 46.81^\circ, 61.82^\circ$, and 66.83°) and CaO ($2\theta=31.36^\circ, 52.55^\circ$) can be observed for both samples. NiO (with peaks at $2\theta=43.44^\circ$ appears only on the calcinated sample, while metallic Ni⁰ ($2\theta=44.42^\circ, 51.86^\circ$) is present only on the reduced sample.

Figures 3(a) and (b) show the SEM images of the two catalysts, i.e., Ni/Al and Ni/modified Al after calcination. Both catalysts are composed of micro and nano particles however, for the Ni/modified Al they appear agglomerated into larger particles. SEM was also being used in order to identify the presence of carbon deposits on the surface of the catalysts. In Figure 3(c) and (e) the morphology of the used Ni/Al and the used Ni/modified Al (plane particles and others with rugged appearance) is shown respectively. Carbon quantification revealed that in the Ni/Al catalyst, carbon is concentrated in specific areas, probably those where metallic Ni⁰ is to be found, leading to the catalyst's deactivation as observed during the stability tests (fig. 3d). In the Ni/ modified Al catalyst, SEM results indicate that the formation of carbon was lower and more widely dispersed, which can be attributed to the presence of CaO and MgO in the support (fig. 3f).

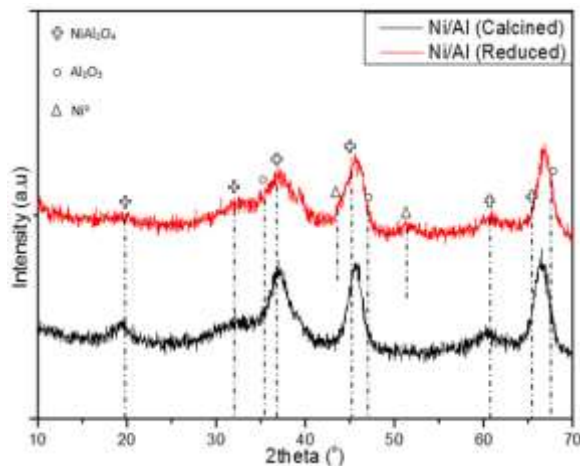


Figure 1: XRD patterns of calcined and reduced (at 800°C) Ni/Al catalysts

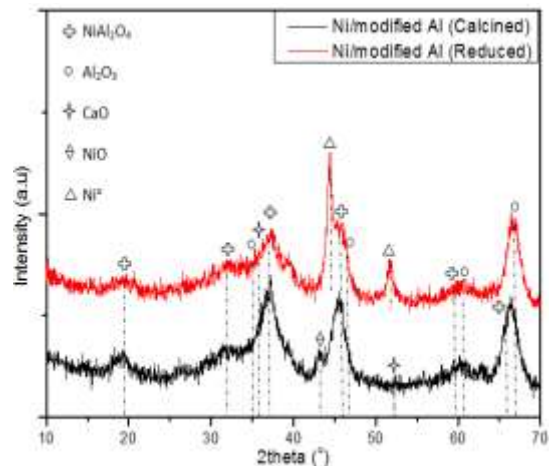


Figure 2: XRD patterns of calcined and reduced (at 800°C) Ni/modified Al catalysts

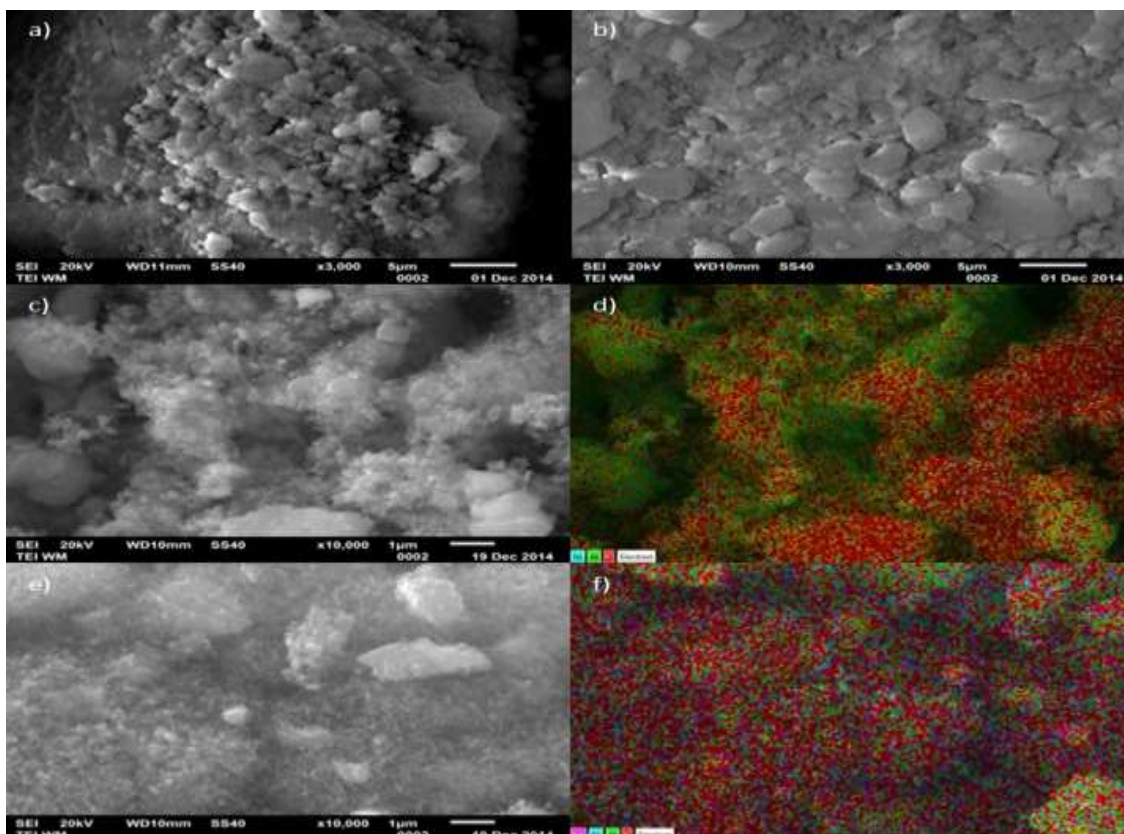


Figure 3: SEM images and mapping of fresh and used catalysts. a) Fresh Ni/Al, b) Fresh Ni/modified Al, c) Used Ni/Al, d) Mapping of used Ni/Al, e) Used Ni/modified Al, f) Mapping of used Ni/modified Al

3.2. Catalytic performance

The methane (CH_4) and carbon dioxide (CO_2) conversion values, the hydrogen (H_2) yield, the molar ratio H_2/CO versus reaction temperature and time on stream for the catalysts are shown in figures 4 & 5. As can be deduced from figure 4, the Ni/modified Al catalyst exhibits higher activity and H_2 production than the Ni/Al catalyst at the temperature range of 550-750 °C. Moreover, it also shows (fig 5) a higher molar ratio of H_2/CO (a ratio of 1 is ideal). In addition, stability tests conducted over a 28hr period (figures 6 & 7) reveal that the presence of CaO and MgO in the

carrier of the Ni/modified Al catalyst significantly increases its lifetime and stabilizes its performance after approximately 10hrs.

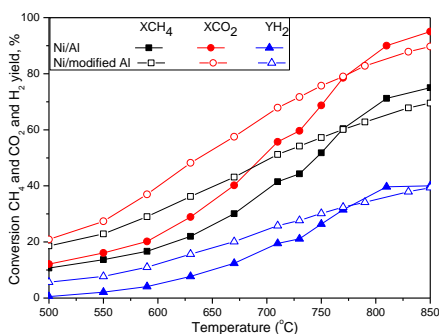


Figure 4: Conversion CH₄, Conversion CO₂ and Hydrogen yield vs temperature

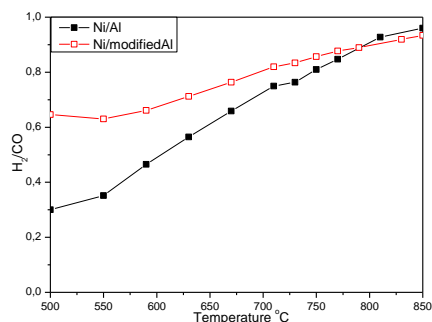


Figure 5: Molar ratio H₂/CO vs temperature

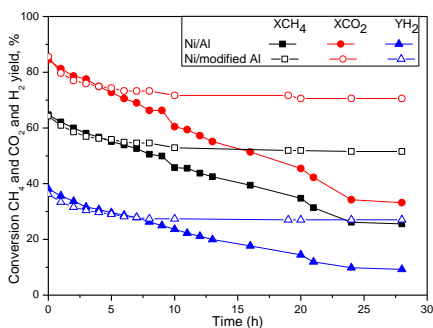


Figure 6: Conversion CH₄, Conversion CO₂ and Hydrogen yield vs time on stream (750°C)

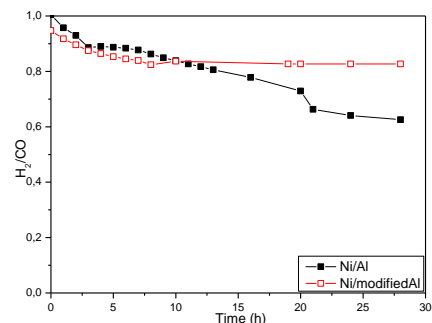


Figure 7: Molar ratio H₂/CO vs time on stream (750°C)

4. Conclusions

The modification of catalysts' support using CaO and MgO as promoters inhibits carbon formation that is the main cause of deactivation during the biogas dry reforming reaction, improves catalytic performance especially at low reaction temperature range (550-750°C) and enhances the lifetime of alumina based Ni catalysts.

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