

Hydrogen production via biogas reforming over nickel-alumina catalysts: Effect of catalysts' synthesis method

M.A. Goula^{1*}, K.N. Papageridis¹, N.D. Charisiou¹, O.A. Bereketidou¹,
E. Pachatouridou², E.F. Iliopoulou²

¹Technological Educational Institute of Western Macedonia (TEIWM), Department of Environmental and Pollution Control Engineering, Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), GR – 50100, Koila, Kozani, Greece

²CPERI/CERTH, GR-57001 Thermi, Thessaloniki, Greece

*corresponding author: mgoula@teikoz.gr

Introduction

Biogas reforming is essentially carbon dioxide reforming or dry reforming of methane. Ni-based catalysts are mainly investigated for this reaction and are promising for future industrial application. However, one of the main limitations of Ni-based catalysts encountered is carbon deposition on the surface of catalyst, which can cause its deactivation [1]. Modification of the support characteristics, the metal content, the preparation method as well as the introduction of promoters, are practical ways to inhibit carbon formation [2]. In the present study Al₂O₃-supported Ni catalysts, prepared by different methods, were characterized and evaluated in biogas reforming reaction. Moreover, the influence of the catalysts' preparation method on their structure and catalytic activity was thoroughly investigated.

Materials and Methods

A commercial γ -Al₂O₃ (AKZO, 350-500 μ m, S_{BET} = 195 m²g⁻¹) was used as the support of all Ni-based catalysts of the present study. The incipient (dry) impregnation and the conventional wet impregnation method were applied for the synthesis of the 8Ni/Al-dry and 8Ni/Al-wet samples respectively using in both cases aqueous solutions of Ni(NO₃)₃·6H₂O as the precursor salt. An additional catalytic sample (8Ni/Al-edf) was prepared by a modified EDF method at pH=7.0 (after retaining the pH=7.0 for 2.5 h, the solution was removed using a rotary evaporator at 60°C) [2]. All the samples were dried at 120°C for 3 hr and calcined at 800°C for 5 hr. Prior reaction, the catalysts were reduced in hydrogen flow at 700 or 800°C for 1 hr. All catalysts were characterized via X-ray diffraction (XRD), surface area and porosity analysis (N₂ physisorption – BET method), H₂ temperature-programmed reduction and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Biogas reforming reaction was carried out at atmospheric pressure in a fixed-bed reactor at temperatures ranging from 550 to 850°C. The total flow rate used was 100 ml min⁻¹, consisting of a mixture of CH₄/CO₂/He, corresponding to a Gas Hourly Space Velocity (GHSV) of 120.000 mL g⁻¹ h⁻¹. Product gases were analyzed by online gas chromatography (equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID)).

Results and Discussion

Figs 1a illustrates the XRD patterns of the catalysts studied. Characteristic peaks at $2\theta=37, 45.9^\circ$ and 67.0° assigned to γ -Al₂O₃ can be observed for all of the samples. In addition, for all the calcined catalysts, characteristic peaks at $2\theta = 19.0^\circ, 31.0^\circ$ and 59.8° were depicted indicating the existence of the spinel nickel aluminate phase (NiAl₂O₄). Fig 2b presents the TPR curves of Ni-based catalysts. As obvious from Fig 2b two main peaks are observed for all

samples; one at 280-365°C possibly related with the reduction of NiO and one at 650-750°C, tentatively assigned to the presence of NiAl₂O₄. In the case of the edf sample the peak assigned to the NiAl₂O₄ phase is interestingly shifted to the lowest temperature (650°C).

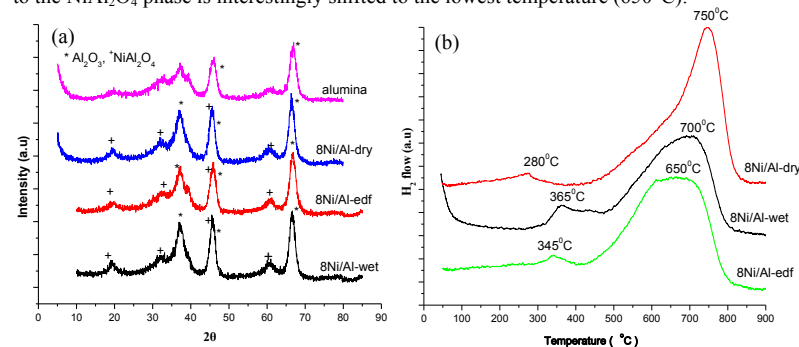


Figure 1. (a) XRD patterns and (b) TPR curves of all Ni-based catalysts

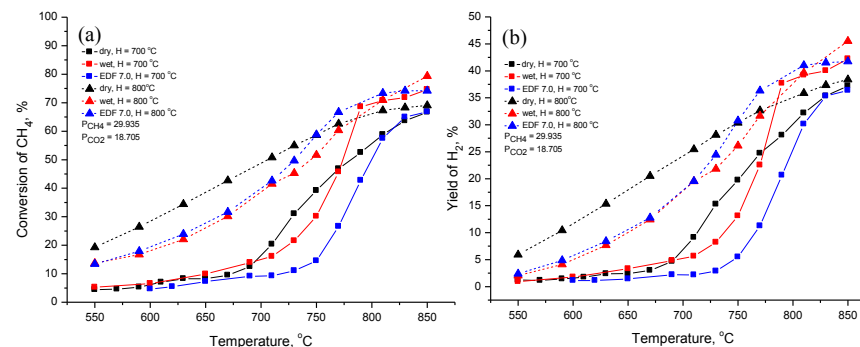


Figure 2. (a) CH₄ conversion and (b) H₂ yields vs reaction temperature

Figs. 2a and 2b illustrate the CH₄ conversion and H₂ yield as a function of the reaction temperature. Obviously, the catalytic activity increases with temperature, while pretreatment at 800°C significantly enhances the catalytic performance possibly due to the reduction of the undesired nickel aluminate phase.

Significance

The Ni/alumina catalyst synthesized via the EDF method and reduced at 800°C is relatively more active in the reforming reaction than the corresponding samples prepared by conventional techniques; the optimized activity of this edf sample can be attributed to its high surface area and its easier and more efficient reducibility of Ni-phases on the catalyst.

References

1. Xu J., Zhou W. Li Z., Wang J., Ma J., *Int. J. Hydrogen Energy*, **2009**, 34, 6646.
2. Bereketidou O.A, Goula M.A., *Catal.Today*, **2012**, 195, 93.