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Nickel on alumina catalysts for the production of hydrogen rich mixtures via the biogas dry reforming reaction: Influence of the synthesis method

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ABSTRACT

Nickel on Al₂O₃ supported catalysts with low and high metal loading (8 and 16 wt. %) were synthesized, using the conventional incipient wetness and wet impregnation methods, as well as a slightly modified Equilibrium Deposition Filtration (EDF) technique. Calcined, reduced and used catalysts' properties were determined by applying several characterization techniques such as, N₂ adsorption-desorption, ICP-AES, XRD, TEM H₂-TPR and carbon analysis. The catalytic performance for the biogas dry reforming reaction was studied concerning CH₄ and CO₂ conversion, H₂ and CO yield and the produced gas mixture's H₂ to CO molar ratio. It was proven that the variation of the synthesis method, affects the catalyst's reducibility, as well as the nickel species' particle size. Catalysts with the low Ni loading present an improved performance when reduced at higher temperature (800 °C). Catalytic behavior was quite different for the 8Ni/Al-edf catalyst, in comparison to the samples prepared by the conventional incipient wetness or wet impregnation methods.

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Introduction

Hydrogen is envisioned as an alternative energy carrier in the future, and its potential serves as a fuel for more efficient energy conversion devices, such as fuel cells. With the increasing demand for hydrogen and the diminishing of fossil

fuels, hydrogen resources are also gaining increasing attention. Additionally, hydrogen production from renewable energy sources, such as *biogas*, is an important route in order to achieve zero emissions of carbon dioxide [1–4]. Due to the nature of the anaerobic digestion process by which biogas is produced, it can also serve as a decentralized source of energy. The main components of biogas are methane (CH₄) and

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carbon dioxide (CO₂), which are thought to be principal greenhouse gases (GHGs), leading to global climate degradation. However, the biogas produced can be converted into hydrogen or synthesis gas (syngas) via the dry reforming reaction and using the appropriate catalysts [2].

As a matter of fact, the biogas dry reforming reaction is quite similar with the methane dry reforming (DRM) or carbon dioxide reforming of methane reaction. The addition of a reforming catalyst enhances the yield to hydrogen or otherwise the production of syngas characterized by a high H₂/CO molar ratio. Among metals explored, like Ni, Co, Pt, Rh, etc, Ni appears to be the most suitable choice for both technical and economic reasons [5]. It has been demonstrated that if a strong nickel–support interaction exists initially in the catalyst, nickel sintering, as well as carbon deposition can be avoided [6,7]. Furthermore, supports play an important role in catalytic activity due to their probable chemical effect, besides their interaction with the 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 [8].

In general, nickel-based on alumina catalysts are reported to be deactivated, due to their coking and sintering problems. Moreover, although alumina has been commonly used as the supporting material, the nickel spinel phase (NiAl₂O₄) formed on its surface, seems to influence the whole process [8–12]. In order to improve the catalytic performance of the nickel/alumina catalysts, several parameters are modified, such as, improving the characteristics of the support by introducing structural or surface promoters or differentiating the active metal loading and the catalyst's preparation technique [13].

As it is well known, the dispersion and the physicochemical characteristics of the active species are the key factors determining the activity and the selectivity of the supported catalysts. Therefore, the maximization of the active phase dispersion and the optimization of the active species are major challenges for heterogeneous catalysis. A reasonable approach towards the solution of this problem is related with the selection of an appropriate methodology for catalysts' preparation. The deposition of the active species on the surface of the catalytic support, the most critical preparation step, usually takes place from electrolytic solutions [14], while metal incorporation is usually carried out following the conventional incipient wetness or wet impregnation techniques.

Over the past years, Papadopoulou et al., have developed both theoretically and practically the Equilibrium Deposition Filtration technique (EDF), otherwise called equilibrium adsorption [15]. The term EDF stresses the fact that species are deposited not only by adsorption but also by reaction with the receptor sites developed on the support surface during the whole process. This technique allows the preparation of supported catalysts with promising textural, structural, and catalytic properties. The main difference of this methodology from the conventional impregnation techniques (incipient wetness or wet impregnation) is that the deposition of the desired species, takes place through adsorption on and/or surface reaction with the receptor sites developed on the support surface (surface oxygens and surface hydroxyls) in the step of equilibration and not by precipitation during drying, as it is the case with conventional impregnation

techniques. Specifically, following EDF, the deposition also takes place in the step of the long time equilibration of quite dilute, impregnating suspensions via adsorption, which in certain cases is followed by surface oligomerization, polymerization or surface (more precisely interface) precipitation. Thus, the EDF technique is expected to provide supported catalysts with very small deposited crystallites in good contact with the support surface.

However, the incipient wetness and the wet impregnation are very simple techniques, well fitted to the industry requirements. Only sporadic studies have been reported dealing with efforts to improve the dispersion achieved following these techniques. On the other hand, it has been recently shown that a modified version of the EDF technique may meet industrial demands [16]. Moreover, having in mind that effective dispersion of the active phase on the support surface has to be achieved, several parameters must be controlled, such as the pH and the active species' concentration values of the impregnating solution, its ionic strength, the impregnation temperature, as well as, the impregnation time [17]. Finally, in several studies it has been shown that EDF catalysts allow high active phase dispersion and high thermal resistance to sintering, if they are compared to catalysts prepared using more conventional impregnation methodologies, achieving relatively high activity [14,17–19].

In the present study, several series of Al₂O₃-supported Ni catalysts' were prepared, with different nickel loadings (8 and 16 wt. %), using the above mentioned conventional methodologies (incipient wetness and wet impregnation) and a slightly modified EDF technique. The final catalysts' surface and bulk properties, at their calcined, reduced and used forms, were determined by applying several characterization techniques (XRD, ICP, BET, TEM, H₂-TPR, carbon analysis). Catalytic performance of all catalysts concerning the biogas dry reforming reaction, was studied in order to investigate the effect of the following parameters: (i) reaction temperature, (ii) WHSV, (iii) nickel loading, (iv) catalyst's preparation method and (v) catalyst's reduction temperature on methane (CH₄) and carbon dioxide (CO₂) conversion, hydrogen (H₂) and carbon monoxide (CO) yield and H₂/CO molar ratio of the produced gas mixtures at the outlet of the reactor. Moreover, the investigation of the influence of the catalysts' synthesis method on surface characteristics and catalytic performance will provide additional information on the correlation between the physicochemical and catalytic properties of the reforming catalysts under study.

Materials and methods

Catalysts preparation

A commercial γ -Al₂O₃ (Akzo, 350–500 μ m, SSA = 281 m² g⁻¹) was used as the support of all the nickel-based catalysts. The two EDF samples (labeled herein as 8Ni/Al-edf and 16Ni/Al-edf with 8 and 16 wt. % Ni respectively) were prepared at constant impregnating solution's temperature and pH value, equal to 25.0 \pm 0.1 °C and 7.0, respectively. It should be mentioned here that the Point of Zero Charge (PZC) of the γ -alumina used has been determined to be close to the value of 7.0 (at this pH value

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