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New molybdenum-based catalysts for dry reforming of methane in presence of sulfur: A promising way for biogas valorization

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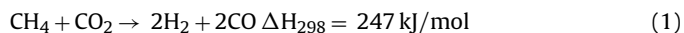
ABSTRACT

Mo-based catalysts supported on γ -Al₂O₃ were synthesized by an incipient wetness impregnation method. They have been tested in the methane dry reforming reaction in a fixed-bed reactor at temperatures from 650 to 800 °C. Additional tests have been carried out in presence of 50 ppm of H₂S to verify their stability towards sulfur poisoning. The influence of Mo loading and Ni promotion on the catalyst activity, stability, and coke deposition were investigated. The fresh and spent catalysts were characterized using N₂ physisorption, X-ray Diffraction, Temperature Programmed Reduction and Thermogravimetric Analysis. Carbon deposition was the major reason of deactivation of the molybdenum catalysts, while nickel catalysts rapidly lost their activity in the presence of sulfur. The optimized nickel-promoted molybdenum catalysts exhibit a synergetic effect conferring to them better reducibility, smaller carbon deposition and better stability in presence of sulfur.

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1. Introduction

In the current environmental context of both energetic and mineral resource scarcity, it is important to continually stimulate the research and development of new production sectors, from alternate and renewable resources, in order to prevent the climate risk and to reduce fossil fuel consumption. Biomass plays a key role as a source of renewable fuels [1,2]. Among all processes of biomass conversion into energy, anaerobic digestion, leading to the production of biogas (CH₄ + CO₂), is of great interest [3,4]. Among the technologies allowing the reforming of methane, one can put forward Steam Reforming, Partial Oxidation or Auto Thermal Reforming of Methane. However the Dry Reforming of Methane (DRM) (1) is considered as one of the most promising technologies [5].



Indeed, the dry reforming of the above-mentioned biogas leads to the simultaneous consumption of the two main greenhouse gases (methane and carbon dioxide) and results in syngas (H₂, CO), which is industrially attractive for Fischer-Tropsch process, eventually

setting up a promising waste-to-liquids substitutive way for fuel manufacturing.

Usually, syngas generation through hydrocarbon reforming requires nickel or noble metal-based catalytic systems [6]. Several attempts have been undertaken in order to improve the stability of nickel catalysts. For instance, catalyst doping with CeO₂ offers resistance towards coking thanks to the enhancement of oxygen mobility. Likewise, mesoporous zirconia also improves the catalyst stability [7,8]. On another hand, promotion by Ca, K, Fe or noble metals has been evaluated [9–11]. Finally, spinel structures were studied and have also demonstrated promising features [11]. However, the presence of sulfur in the biogas is one of the main obstacles of dry reforming and Ni is known to be particularly sensitive to this element [12–14]. Noble metals have shown to be very active for the DRM [5] and among them, Rh appears to be the most efficient species [15] in terms of both activity and stability towards carbon deposition. Among other noble metals, such as Pt, Ir and Ru, although they are active for the reaction, Pd and Pt are the most sensitive to carbon deposition [16,17]. Nevertheless, two key points concerning the use of noble metals for DRM are their high cost and more specifically, their affectability to sulfur which has not been resolved yet [18].

Moreover, Mo-based catalysts such as MoS₂ have demonstrated sulfur resistance in HDS reactions and more recently in the olefin and higher alcohol synthesis from syngas [19–22]. Finally, bulk MoS₂ catalysts have been tested and have shown noticeable activ-

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Table 1
Chemical composition of the Mo based catalysts measured by ICP analysis.

Catalyst	% mol Mo	% mol Ni
10Ni	–	–
5Mo	4.67	–
10Mo	10.04	–
20Mo	18.20	–
20Mo2Ni	25.30	1.15
20Mo5Ni	19.19	2.63
20Mo10Ni	18.64	5.39

ity in DRM [23]. Although supported Mo-based catalysts have not been tested yet for the DRM reaction in the presence of sulfur, they are known for their resistance towards sulfur in other reactions.

To this end, a new catalytic system has been set starting from alumina-supported Mo catalysts, on which the influence of nickel promotion was studied, and especially its effect on the catalytic performance in DRM [24,25]. This work focuses on the development and optimization of such catalysts, enabling the reforming of H₂S-containing biogas, primarily paying particular attention to the stability of the studied systems concerning carbon deposition and sulfur poisoning.

2. Experimental

2.1. Catalyst preparation

Commercial alumina (Puralox) was used as support. All the catalysts were prepared via the incipient wetness impregnation method: the exact amount of ammonium heptamolybdate (AHM) salt (NH₄)₆Mo₇O₂₄ · 4H₂O (Sigma-Aldrich) to obtain 5, 10 and 20 mol% loaded catalysts was dissolved into the exact volume of water corresponding to the porous volume of the alumina. For the promoted catalysts, nickel nitrate Ni(NO₃)₂ · 6H₂O (Sigma-Aldrich) precursor was dissolved alongside with the AHM, in the calculated proportions to obtain 2, 5 and 10 mol% promoted Ni catalysts. As for the Ni/Al₂O₃ catalyst, only the nickel nitrate salt was dissolved in the solution prior to the impregnation step. This solution was then added dropwise to the support.

The materials were next dried for 12 h at 120 °C. Finally the catalysts were calcined at 600 °C for 4 h (heating ramp of 2 °C/min). The chemical composition of the catalysts is listed in Table 1.

2.2. DRM reaction

The catalytic tests were carried in a fixed bed quartz reactor with an inner diameter of 1 cm. Prior to the reaction, the catalyst was pretreated *in situ* with a reductive flow of H₂ (20 mL/min) for 10 h at 650 °C. Then the catalyst was exposed to the reactant gas stream: CH₄ and CO₂ at equimolar ratio and diluted in N₂ (CH₄:CO₂:N₂ = 1:1:1.6), as for the GHSV to be 6800 h⁻¹. The tests were performed at different temperatures from 650 °C to 800 °C (50 °C steps, 1 h holding time at each target temperature). Randomly, some tests were repeated several times to confirm the reproducibility of the catalytic results.

The stability tests were carried out during at least 25 h at 750 °C. The catalyst performance has been evaluated in presence of 50 ppm H₂S in the feed and without the presence of sulfur. For the latter, the catalyst has been submitted to a lesser N₂ dilution rate: CH₄:CO₂:N₂ = 1:1:0.6.

The product gas mixture was analyzed with an Agilent 3000 A μGC. Two columns mixed the reactants: the first one, a molecular sieve type (5 Å, 10 m × 0.32 mm × 12 μm), held back H₂, N₂, CH₄ and CO and the second column, a PLOT U type (8 m × 0.32 mm × 30 μm), held back N₂, CH₄ and CO₂.

To measure the catalytic efficiency of each material, the CH₄ and CO₂ conversions, as well as the H₂/CO ratios, were calculated as follow:

$$\text{Conv CH}_4 (\%) = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100$$

$$\text{Conv CO}_2 (\%) = \frac{\text{CO}_{2,\text{in}} - \text{CO}_{2,\text{out}}}{\text{CO}_{2,\text{in}}} \times 100$$

$$\text{H}_2/\text{CO} = \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of CO produced}}$$

2.3. Characterization

2.3.1. ICP analysis

Quantitative elemental analyses of the catalysts were performed by inductively coupled plasma-optic emission spectroscopy 720-ES ICP-OES (Agilent) with axially viewing and simultaneous CCD detection. The quantitative determination of metal content was carried out on the basis of the certified standard solution. The ICP Expert™ software (version 2.0.4) provided the concentration of metal in sample allowing estimating the weight percentage of components.

2.3.2. BET analysis

The specific surface of the catalysts along with other textural parameters were recorded on an ASP 2000 apparatus (Micrometrics), at the N₂ boiling temperature (-196 °C), using the BET method in the 0.05–0.2 *p/p*₀ pressure range. Previously, all samples were purged for 3 h at 250 °C. The results were treated through the ASAP 2010 3.0 software.

2.3.3. X-ray diffraction analysis

The XRD measurements were realized with a D8 advance diffractometer equipped with an energy dispersive type detector and a monochromatic Cuα radiation source. The patterns were recorded from 20° to 80° with a step of 0.02°. The size of the particles was determined through the features width by the Debye–Scherrer equation applied at the maximum half-height (FWMH) of the most intense and resolved peaks.

2.3.4. Temperature programmed reduction experiments

Temperature Programmed Reduction analysis was conducted on an Autochem II apparatus (Micrometrics). The gas composition was analyzed by a TCD detector. The masses from 0.1 to 0.5 g were submitted to a temperature ramp of 3 °C/min to the target temperature, under a 5 vol% H₂/Ar flow of 50 mL/min.

2.3.5. Thermogravimetric analysis

TGA analyses were performed through a SDT Q600 V20.9 Build 20, on a 10–15 mg sample, submitted to a temperature ramp of 5 °C/min until 600 °C under air.

3. Results

3.1. Pre-testing characterization

3.1.1. Influence of Mo loading

First of all, a set of alumina-supported catalysts was synthesized with Mo loading of 5, 10 and 20 mol%, corresponding to alumina surface coverage values of respectively 2.2, 4.3 and 8.6 at./nm². The ICP analyses (Table 1) show good agreement between the theoretical and experimental compositions of the Mo-based catalysts. From the literature, it is well known that the monolayer surface

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