CO₂ and H₂O adsorption-desorption cycles for multifunctional Ni-Fe based catalyst in the production of Synthetic Natural Gas

V.D Mercader*, A. Sanz-Martínez, P. Durán, E. Francés, J. Herguido, J.A. Peña

Grupo de Catálisis, Separaciones Moleculares e Ingeniería de Reactores (CREG)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Tel. +34-976762707, e-mail: vmercader@unizar.es

Abstract

A study of the affinity of lab-made multifunctional catalysts to adsorb-desorb CO_2, H_2 and H_2O has been carried out by thermogravimetry in the *Hydrogen Technologies Laboratory* of I3A. Higher CO_2 affinities were showed by multifunctional catalyst in comparison with the nonfunctionalized FeNi catalyst.

Introduction

Power to Gas (PtG) technologies has been proposed as an interesting alternative to generate an energy vector able to cover the energy intermittency of renewables [5]. The surplus electricity from renewables could be used to generate green hydrogen from water electrolysis [5]. That green hydrogen would be combined with a concentrated CO_2 flow (e.g. biogas -30%ᵛ CO_2 and 70%ᵛ CH_4- through *Sabatier* reaction (r.1), generating a stream rich in CH_4 [4]. Also, the resulting CH_4 (so called *Synthetic Natural Gas*, SNG) or even upgraded biogas could be injected directly to the preexisting natural gas network. Thus, PtG technologies are able to provide safety an energy vector easy to carry and store, whereas H_2 storage and transportation is a challenge with the actual technology limitations. For example, preexisting natural gas network is limited by the fragility of materials in presence of H_2, the actual natural gas network could transport a maximum concentration 10%v H_2 [1]. This also applies for domestic burners for which a limit in the proportion of H_2 is still present. However, SNG could be used to supply energy to the electric network during the intermittent periods of renewables.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad (r.1)$$
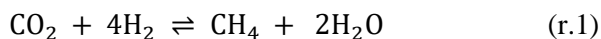
The inclusion of an alkali or an alkaline group in a nickel-based catalyst could improve the CO_2 affinity of the catalyst, creating chemical bonds between the basic groups and CO_2 [2]. As result, the interaction between the fixed CO_2 with H_2 could be improved. Thus, the selectivity and conversion to methane might increase. In order to study the previously mentioned assumptions, three nickel-based catalysts supported on gamma alumina were synthesized including an alkali or alkaline earth in their composition. Resulting catalysts were named "NaNi" (10ʷᵗ% Na, 10ʷᵗ% Ni), "NaNiFe" (10ʷᵗ%Na, 7.5ʷᵗ·%Ni, 2.5ʷᵗ·%Fe) and "CaNiFe" (10ʷᵗ% Ca, 7.5ʷᵗ·%Ni, 2.5ʷᵗ·% Fe). Benefits of blending Fe with Ni in methanation catalysts were showed in previous CREG studies [3]. Thermogravimetric analysis was selected as characterization method for CO_2, H_2 and H_2O adsorption-desorption behavior. In such studies, the catalyst is exposed to a gas flow. Its surface interacts with the gas species, generating bonds between the gas molecules and the catalyst surface. As result, an increase in the catalyst mass is generated and registered by the TGA device.

Experimental

The multifunctional catalysts were synthesized by incipient wetness impregnation from their nitrate or carbonate metallic precursors. In addition, a commercial γ-Al_2O_3 (200 m²/g, *Puralox, SASOL*) was selected as support material for the catalysts.

A *STA 449 F3 Jupiter* (Netzsch) was used for the experiments. A 20.0±0.1 mg sample of each catalyst was introduced in the STA chamber on a crucible plate. The adsorption-desorption cycles included the following steps: a) Preconditioning: the catalysts were heated at 500 ºC in inert atmosphere for 1h. b) Activation of the catalyst with a 50%ᵛ flow of H_2 for 1 hour. c) Decreasing the temperature until 400 ºC and keeping it constant for 1 hour in inert atmosphere. The objective of the adsorption-desorption cycles is to spot the interaction of different gaseous species in the adsorption on the catalyst. Adsorption-desorption sequence: d) The catalyst is exposed to a gas flow of 40%ᵛ of CO_2 diluted in inert. Later, a stream with 10 %ᵛ of H_2O is added to the previously CO_2 flow. Later the CO_2 is removed from the gas inlet, remaining only the 10 %ᵛ of H_2O flow. Following, the 40%ᵛ of CO_2 is reintroduced in the inlet along with the water.

Subsequently, the H_2O is removed from the gas flow, keeping only the 40%^{v} of CO_2 as inlet. Finally, the desorption (regeneration) step was carried out with a 100% of inert at 400 ºC. Experimental condition details can be found in **Table 1** and the results of the adsorption-desorption cycles are showed in **Figure 1**.

Results

As it can be observed in **Figure 1,** multifunctional catalysts presented higher CO_2 mass gain in comparison to plain Ni-Fe catalyst (6 times lower than results from multifunctional catalysts). Adsorption of CO_2 in water presence showed similar behavior for all samples, increasing the same percentage in mass. In the third sequential step (H_2O), multifunctional catalysts totally released the CO_2 stored, keeping similar values of mass gain than in Ni-Fe. After introducing CO_2 to the H_2O feeding (i.e., fourth step), the mass gain rose to values lower than in the previous CO_2+H_2O second step. Finally, during the last CO_2 step the values of mass gain returned to similar ones than in the first CO_2 adsorption step, but slightly higher than in step 1.

Conclusions

The inclusion of alkali and alkaline earth metals significantly improved the CO_2 adsorption capacity of multifunctional catalysts. CO_2 was totally removed in step 3rd as effect of temperature (400 ºC). Water and CO_2 partially compete for the adsorption sites of the catalysts, as it can be observed in the reduction of the mass gain in the 4th step in comparison with the 2nd one. H_2O competes partially with CO_2 for the adsorption centers. CO_2 adsorption capacity was recovered after removing the H_2O from the gas inlet.

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Table 1. TGA analysis conditions

Catalyst load	20.0 ± 0.1 mg
Total volumetric flow	100 mL (STP) / min
CO_2 concentration (inlet flow)	40 ^{v}%
H_2O concentration (inlet flow)	10 ^{v}%
H_2 concentration (activation)	50 ^{v}%
Inert gas (dilutant)	N_2
Pressure	1 bar
Adsorption steps duration	30 min (each one)
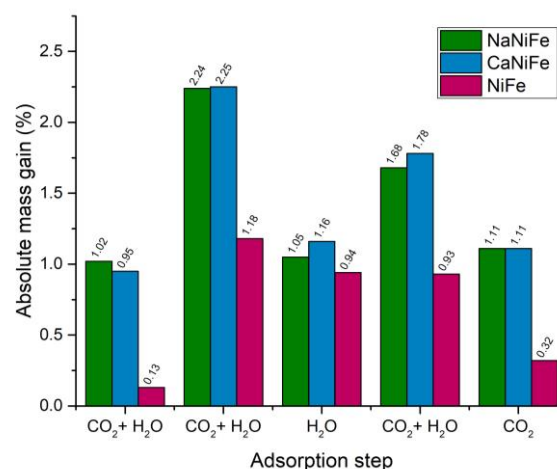
Figure 1. TGA mass gain for catalyst samples subjected to different atmospheres.