Enhanced methanation assisted by CO_2 adsorption on a bimetallic catalytic fixed bed reactor

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Abstract

This work studies the influence of introducing a CO_2 adsorbent in a bimetallic catalytic fixed bed reactor. The catalyst is a lab-made Fe-Ni alloy (2.5:7.5% $^{wt}/_{wt}$) supported on gamma alumina. Two CO_2 adsorbents were tested in this study, a lab made CaO and a Na_2O (10% $^{wt}/_{wt}$) supported on gamma alumina.

Introduction

During the last years CO_2 emissions achieved critical levels generating important environmental damages. If the carbon dioxide generation is not dramatically reduced, a hypothetic *Point of No Return* might arrive in an early future. Even though the need to reduce emissions is critical, some inevitable economical activities will continue producing CO_2. In addition, the energy supply is highly dependent on fossil fuels. In this line, hydrogen has been studied as an alternative energy vector, which could be produced with surplus electricity from renewables. However, hydrogen uses are still limited by its challenging store and transport. In order to solve the environmental problem and the hydrogen storage limitations, a set of new technologies have been proposed labelled as *Power to Gas* (PtG). PtG uses surplus electricity from renewables to generate green hydrogen from water electrolysis. That green hydrogen is 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 enriched in CH_4. Also, the resulting stream (i.e., *Synthetic Natural Gas*, SNG or even *upgraded biogas*) could be injected directly to the preexisting natural gas network [1].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \text{(r.1)}$$

The inclusion of an alkali or an alkaline-earth group species in the catalytic bed 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, two CO_2 adsorbents were synthesized including an alkali or alkaline earth supported on gamma alumina. Resulting adsorbents have a 10 ^{wt}% Na or 10 ^{wt}% Ca and were labelled as "Na_2O" and "CaO". Benefits of blending Fe with Ni in methanation catalysts were showed in previous CREG studies [3]. The goal of this study is to experimentally assess and quantify the effects of Sorption Enhanced Sabatier Reaction -*SESaR*- intensification in a fixed-bed reactor.

Experimental

Firstly the effect of diffusional constraints (internal and external) was studied, fixing a volumetric flow of 150 mL(STP)/min, enough to ensure kinetic regime. Experiments were carried out in a fixed bed reactor of approximately 12 cm length and 13 mm inner diameter, at atmospheric pressure. For the reaction experiments the mass of solids introduced in the column (pre-mixed) was 2 g of catalyst, 2g of CO_2 adsorbent (Na_2O or CaO) and 6.25g of γ-Al_2O_3. Before starting a methanation experiment, the catalyst was activated at 500 ºC for 2 h with a gas flow composition of 50% H_2, 45% Ar and 5% N_2 (by vol.). After the activation stage, the temperature was decreased to the experimental conditions. These were performed at 400 ºC. That temperature is adequate for the methanation reaction and this catalyst. Each methanation experiment (Table 1) includes three steps: first the reactor is fed with CO_2 diluted in inert (adsorption step); after that, CO_2 is exchanged in the inlet by H_2 (hydrogenation) and finally only inert gases are introduced as purge step. The concentration in the reactor outlet was measured with a micro chromatograph (*Agilent 490*) assisted by a continuous FTIR gas analyzer (*Servomex series 4000*).

Results and Conclusions

Reproducibility in the concentration measured at the outlet of the fixed bed reactor is presented in Figure 1. As it can be observed, results show a high reproducibility during the different repetitions of the experiment. In addition, "Cx" label indicates the number (and date) of the hydrogenation cycle, showing that the adsorbent and catalyst are stable along three adsorption-hydrogenation-purge steps.

On Figure 2 the intensification behavior for the hydrogenation step is presented. The inclusion of the CaO in the reactor bed improved the methane production by 40%. Meanwhile, the intensification for the Na_2O elevated the methane production by 60%.

As general conclusion, both adsorbents showed their potential to enhance the methanation reaction performed by adsorption followed by hydrogenation. Thus, they will continue being studied for forward potential uses in biogas upgrading.

Table 1. Experimental conditions

Catalyst load	2g
Adsorbent load	2g
Total volumetric flow	150 mL (STP) / min
CO_2 concentration (inlet flow)	40 ^{v}%
H_2 concentration (inlet flow)	5 ^{v}%
N_2 concentration (inlet flow)	5 ^{v}%
Inert gas (dilutant)	Ar
Pressure	1 bar
Adsorption steps duration	30 min (each one)
Methanation steps	1h and 30 min

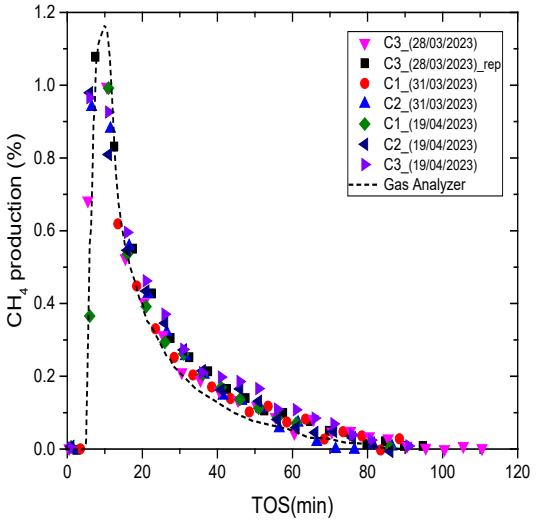

Figure 1. CH_4 production reproducibility of FeNi +CaO catalyst experiments carried out in the fixed bed reactor

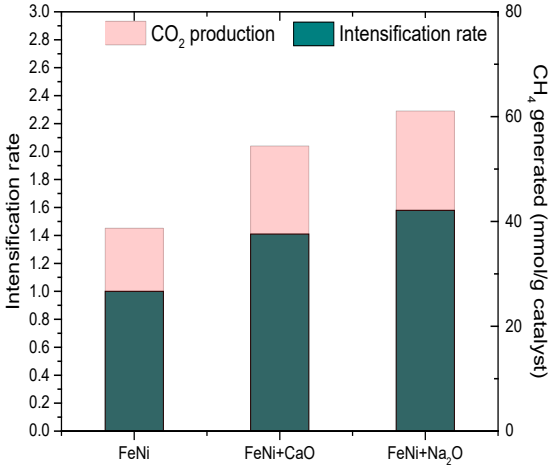

Figure 2. CH_4 generation and intensification rate referred to FeNi (mmol CH_4 generated with FeNi+adsorbent/ mmol CH_4 generated with only FeNi)

Acknowledgments

This work has been carried out with financing for grant PID2019-104866RB-I00 by MCIN/AEI /10.13039/501100011033. CREG research group (T43-23R) is being supported by Gobierno de Aragón (*Aragón, SPAIN*) through *European Social Fund* (FSE-FEDER). Also, V.D.M express his gratitude for the contract PRE2020-095679, and ASM for his contract BES-2017-082069.

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