CO_2 methanation in a Ni-Fe based catalyst fixed bed reactor enhanced by selective water adsorption with LTA zeolites (Sorption Enhanced Sabatier Reaction – SESaR)

M. Rincón, 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 Fixed-Bed reactor improved by selective water adsorption LTA zeolites is proposed as an alternative to the conventional methanation reactors. This reactor produces methane from renewable H_2 (i.e. surplus electricity) and high CO_2 concentration sources, as could be municipal wastes derived biogas ($30\%^{v}$ CO_2 + $70\%^{v}$ CH_4). As catalyst, a supported (γ-Al_2O_3) Ni-Fe (7.5:2.5 $^{wt}/_{wt}$) was chosen.

Introduction

Nowadays the need of finding low CO_2 emission sources of energy is more critical than ever. Apparently how to produce the electricity is solved by renewable sources as solar energy and wind turbines, but an efficient energy storage is still missing. One of the trends about how to solve the energy storage and transportation goals are *Power to Gas* technologies (PtG). PtG is based on combining renewable H_2 with high CO_2 concentration streams into methane [1]. At the same time PtG is bringing an opportunity to decrease the CO_2 emissions of new energy sources such as biogas, since CO_2 from biogas (ca. $30\%^{v}$ CO_2+$70\%^{v}$ CH_4) can be trapped and transformed into methane through the *Sabatier* reaction (r.1) [2]. As a result, the upgraded biogas after the methanation process would have a concentration in methane close to 100%.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{r.1}$$

The reactor system anlyzed in this study is based on the *Sorption Enhanced Sabatier Reactor* (SESaR) with zeolites. SESaR technologies incorporate the use of water adsorbent solids in order to *in situ* remove the water produced by (r.1) trying to push up its thermodynamical equilibrium. Removing the water from the products, a behavior of reaction shift appears as result of *Le Chatelier*'s principle [3]. Thus, reaction shift to products increases the CO_2 conversion and warily the selectivity to CH_4. The catalyst selected was a lab-made Ni-Fe based catalyst supported on alumina. An LTA zeolite (5A) was chosen as water adsorbent. The goal of this study is to experimentally assess and quantify the effects of SESaR intensification in a fixed-bed reactor. The reactor consists in a fixed bed, 12 cm length and 13 mm inner diameter.

Experimental

The catalyst ($7.5^{wt.}\%$Ni, $2.5^{wt.}\%$Fe) was synthesized by incipient wetness impregnation from $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3) \cdot 9H_2O$, both from *Sigma Aldrich*. In addition, a commercial γ-Al_2O_3 (200 m^2/g, *Puralox, SASOL*) was selected as support material for the catalyst. After impregnation, the catalyst was dried at 65 ºC for 16 hours and then at 90 ºC for 8 hours. Afterward, the dry catalyst was calcined at 500 ºC for 9 hours (β= 1 ºC/min). Then the catalyst was crushed and sieved, obtaining a final particle diameter of 100-200 μm. Finally, the catalyst was activated at 500 ºC for 2 hours with a gas flow composed of 50% H_2, 45% Ar and 5% N_2.

On the solid characterization side the technologies applied were: adsorption-desorption isotherm by nitrogen adsorption (BET) pre-degassing at 200 ºC (specific area of 161 m^2/g for catalyst and 428 m^2/g for LTA zeolite), X-ray fluorescence (XRF) for the elemental quantification ($7.42^{wt.}\%$ Ni and $2.13^{wt.}\%$ Fe for the catalyst and $21.07^{wt.}\%$ Si, $19.37^{wt.}\%$ Al, $7.07^{wt.}\%$ Ca and $3.28^{wt.}\%$ Na for zeolite), X-ray diffraction (XRD) for the identification of cristallyne structures in the catalyst and the zeolite, temperature programmed reduction (TPR) was only used for the catalyst with a H_2/N_2 flow of 100 mL(STP)/min and partial pressure of 0.05 bar out of 1 bar (total pressure) carried out in an electric oven (β= 5 ºC/min). Results of TPR (not shown) demonstrate that the addition of Fe produced a decrease in the reduction temperature of the Ni/Fe alloy. The effect of diffusional constraints (internal and external) was also studied, fixing a volumetric flow of 250 mL(STP)/min enough to ensure kinetic regime.

The experiments were carried out in the above-described fixed bed reactor, at atmospheric pressure. For the reaction experiments the mass of solids introduced in the column (pre-mixed) was 0.25 g of catalyst and 10.25g of 5A zeolite. Before starting an methanation experiment, the catalyst was activated at 500 ºC for 2 hours with a gas flow composition of 50% H_2, 45% Ar and 5% N_2. After the activation stage, the temperature was decreased to the experimental conditions. These were performed in the range between 450 and 250 ºC. For the methanation of CO_2, the reactor was fed with a total volumetric flow of 250 mL(STP)/min and different molar rations H_2/CO_2 (2/1, 4/1 and 6/1) diluted with a $5\%^{v}$ of Ar and $5\%^{v}$ of N_2. On the other hand, for the synthetic biogas (CO_2+CH_4) methanation the feed included a CH_4/CO_2 molar ratio=7/3 and H_2/CO_2 =4/1 diluted with a 5% of Ar and 5% of N_2.

Results

Figure 1 shows a comparison between the conversion of CO_2 vs time for three different consecutive cycles, each one of them followed by a desorption step. The improvement in the conversion of CO_2 introducing the zeolite in the packed bed is shown by the colored areas, being the values marked by the upper grey rectangles the conversion attainable without the contribution of the zeolite. Thus, M1, M2, and M3 are the methanation intervals, that were interspersed by D1 and D2 showing the desorption steps. D1 was carried out at the same temperature than the reaction-adsorption (350 ºC), while D2 was tested for a higher temperature (500 ºC). Comparing M1 with M2, it has been observed a decrease in the conversion of CO_2 enhancement (proportional to the areas under the curves). Moreover, M3 shows a conversion enhancement partially recovered after operating in D2 at higher temperature desorption conditions. The initial CO_2 conversion rose from 28% to 76% by working with the zeolite as the diluent solid in the packed bed.

For the simulated sweetened biogas feed tests, it was observed a similar behavior than for the conventional methanation feed (CO_2 + H_2) in terms of conversion enhancement. However, a decrease in the absolute conversion values was observed at each temperature. Thus, methane present in the biogas did not act as an inert, interfering somewhat in the methanation reaction process unlike any other inert species.

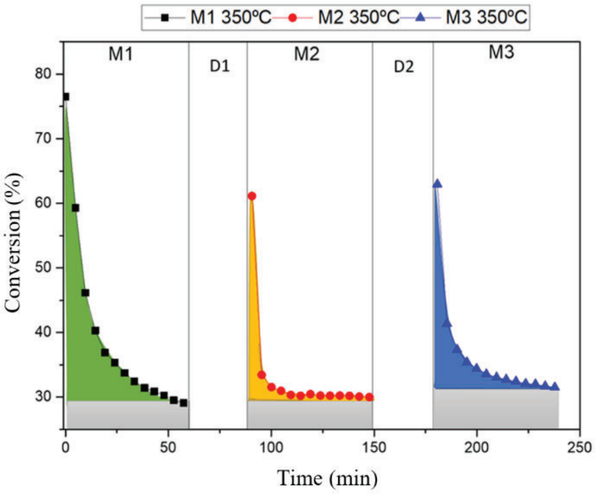

Figure 1. Comparison of SESaR enhanced methanation (colored) with conventional (upper grey) methanation

Conclusions

The Ni-Fe catalyst showed a good conversion to CH_4 allowing to decrease the operational cost in comparison with a conventional nickel catalyst. An important improvement in the CO_2 conversion has been shown by replacing the inert solid in the packed bed with 5A LTA zeolite. Increasing temperature on the desorption steps (e.g., D2) has been observed as a feasible way in the recovery of the adsorption capacity of the zeolite. The conversion enhancing effect is also observed when methane is fed simulating biogas upgrading experiments.

REFERENCIAS

[1]. ANGELIDAKI, I., TREU, L., TSAPEKOS, P., LUO, G., CAMPANARO, S., WENZEL, H., and KOUGIAS, P.G. Biogas upgrading and utilization: Current status and perspectives. *Biotechnology Advances.* 2018, 36(2), 452-466. Available from: doi:10.1016/j.biotechadv.2018.01.011.

[2]. SABATIER, P., and SENDERENS, J.B. New Synthesis of Methane. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* 1902, 134, 514-516. Available from: doi:10.1039/CA9028200333.

[3]. VAN KAMPEN, J., BOON, J., VAN BERKEL, F., VENTE, J., and VAN SINT ANNALAND, M. Steam Separation Enhanced Reactions: Review and Outlook. *Chemical Engineering Journal.* 2019, 374, 1286-1303. Available from: doi:10.1016/j.cej.2019.06.031.