Influence of operating pressure and H_2S presence on the stability and performance of commercial catalysts for CO_2 methanation

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Abstract

This study examines the use of the *Power-to-Gas* strategy to convert CO_2 from biogas and renewable H_2 into synthetic natural gas (SNG). It will analyse, using commercial catalysts (with a view toward industrial implementation), the influence of pressure as an intensification variable and in addition, the effect of the presence of H_2S in the feed [1].

Introduction

Main reaction consists in the catalytic methanation of CO_2 using the *Sabatier* reaction (r.1) [2].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_r^o = -165 \text{ kJ/mol} \quad \text{(r.1)}$$

The research focuses on three main objectives. First, to compare the CO_2 conversion, selectivity, and CH_4 yield of four commercial catalysts under identical operating conditions. Second, to evaluate the effect of pressure on the results of the process with the catalyst previously identified as optimal [3]. Finally, to assess catalyst stability under sulphur poisoning conditions. For this purpose, the catalyst active sites will be exposed to reactive streams containing H_2S in long-term tests, commonly referred as *in situ* experiments [4].

Experimental

A fixed-bed reactor made of stainless steel was used to carry out the experiments. They were performed using an H_2:CO_2 molar ratio of 4:1 in a feed stream with a total volumetric flow rate of 250 mL (SATP)·min^{-1}. Concentration of species coming out from the reactor were monitored by continuous NDIR and micro-chromatography.

The catalysts evaluated were obtained from different suppliers. All catalysts were based in nickel as their active phase. Since results are confidential and subjected to NdA, no details about composition or providers have been included. Catalysts A and B are commercial solids available for industrial-scale production. Catalysts C and D, on the other hand, were synthesised and distributed as lab-scale specimens. Finally, the experimental conditions are summarised in Table 1. [5]

Table 1. Experimental conditions.

Variable	Pressurized experiments	*In situ*
Inerts (%)	10	50
H_2S (ppm)	0	5
Temperature (ºC)	250-350 ($\Delta T = 25°C$)	300
Catalyst (g)	0.5	0.2
Pressure (bar)	1; 5; 6; 7	1

Results

In Figure 1 the CH_4 yield is compared for each temperature range at atmospheric pressure. As long as the temperature increases, the yield to CH_4 also increases due to faster kinetics for a fixed space time W/F_{Ao}. As expected, maximum conversion was reported at the highest temperature (300 °C), approaching the thermodynamic limit (upper dashed line). Catalysts B and D exhibited the highest CH_4 yields across the entire temperature range evaluated. According to that, catalyst B was selected to study the effect of pressure, as it has the potential for ready industrial-scale application, whereas catalyst D does not offer this capacity (no mass production for the time being).

The effect of pressure on CH_4 yield at different temperatures was subsequently evaluated, as shown in Figure 2. At low temperatures, increasing the pressure increases the yield, whereas above 300 °C, the effect of pressure in the range of 5 to 7 bar is minimal, confirming that the relevant variable is temperature. In any case, increasing the pressure allows yields higher than those obtained at atmospheric pressure, validating the high synthetic natural gas production activity of catalyst B. In these tests, replicates were repeated out at pressures of 5 and 6 bar to ensure reproducibility.

Finally, given that the industrial process associated with this study has indicated the possible presence of H_2S in the feed stream at concentrations of around 5 ppm, it is important to evaluate the effect of this compound on the performance of the catalysts. Figure 3 shows the evolution of activity over 24 hours of operation (TOS). For the first 30 minutes, the loss of activity is exponential, being followed by a progressive linear loss of activity. This trend is similar for all the solids studied, but at different times and intensities. This behaviour highlights the influence of H_2S as a poisoning agent, which causes a decrease in active sites that reduces the activity of all the catalysts.

Conclusions

Catalyst B exhibited the best overall performance in terms of CH_4 yield and availability. Increasing the pressure in the reaction system intensifies the methanation reaction, resulting in higher yields and greater CO_2 conversion.

The long-term experiments show a loss of activity for all the catalysts tested, in the presence of moderate concentrations of H_2S, indicating their sensitivity to sulphur poisoning. Deactivation phenomenon was more pronounced during the first few minutes of TOS, decreasing almost linearly subsequently.

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Figures

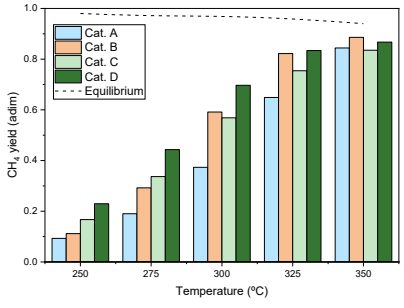

Figure 1. Comparison of CH_4 yield versus temperature at atmospheric pressure for various catalysts tested. CO_2:H_2 ratio of 4:1.

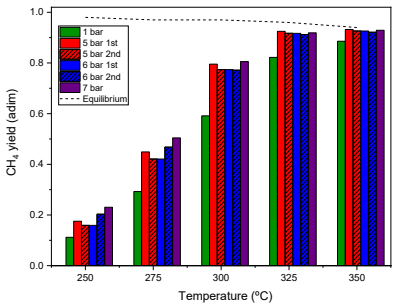

Figure 2. CH_4 yield with catalyst B versus temperature for different operation pressures.

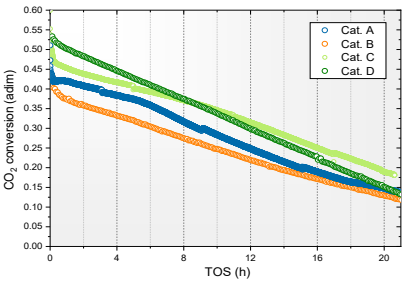

Figure 3. Loss of CO_2 conversion in catalysts exposed to 5 ppm H_2S during long-term tests with an H_2:CO_2 ratio of 4:1, 300 ºC and 1 bar.