Different Behavior of Commercial Nickel and Ruthenium Catalysts on Biogas Upgrading

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Abstract

This study investigates the behavior of five commercial catalysts based on Ni or Ru oxides as active phases for CO_2 methanation at atmospheric pressure. The research evaluates the influence of both temperature and the partial pressure of the reactants on the performance of the different catalysts studied.

Introduction

Power-to-Methane (P2M) technology has proven to be a promising option in the energy transition. P2M enables the conversion of renewable hydrogen - produced via water electrolysis using surplus electricity - into methane. The hydrogenation of CO_2 is carried out through the Sabatier reaction (r.1), in which CO_2 reacts with H_2 to produce methane as the main product. The resulting methane behaves as an energy carrier characterized by its stability and ease of transport, and that can be injected into the already existing natural gas grid.

$$CO_2 + 4H_2 \rightleftharpoons CO_2 + H_2O \qquad \text{(r.1)}$$
$$\Delta H_{r,\,298\text{ K}}=-165.1\text{ kJ/kmol}$$

To drive the methanation reaction, catalytic solids are required to reduce the activation energy, thereby increasing CO_2 conversion while maintaining high selectivity toward CH_4. Commonly used catalysts for this purpose include those with active phases based on nickel oxides (Ni), ruthenium oxides (Ru), or cobalt oxides (Co) [1]. Ru exhibits high catalytic activity, but its high market price limits the scalability of the process [2]. In contrast, Ni offers good activity and selectivity toward methane but may suffer from gradual deactivation due to coke deposition on the active sites. However, these limitations can be mitigated by incorporating other metals into the formulation, such as cerium (Ce) or iron (Fe) [3].

In this study, four different commercial methanation catalysts are evaluated—two Ni-based and two Ru-based. Their performance is analyzed at various reaction temperatures and different reactant partial pressures, using a conventional fixed-bed reactor.

Experimental

The experiments were carried out in a conventional fixed-bed reactor made of quartz. The reactor is equipped with five thermocouples axialy positioned at heights of 1, 3, 6, 9, and 12 cm to measure the temperature profile within the catalytic bed. The different catalysts used are described in **Table 1**.

The reaction tests included 0.5 g of catalyst and 19 g of SiC as a filler solid to enhance thermal diffusion within the fixed bed, thus preventing the formation of "*hot spots*". For each reaction test, the molar ratio of reactants (H_2:CO_2) was set between 2:1 and 6:1. Once the reactant ratio in the feed was fixed, the temperature was varied from 400 °C down to 250 °C in 25 °C increments.The feed to the reactor consisted of $10\%^{v}$ inert gases ($5\%^{v}$ de N_2 y $5\%^{v}$ de Ar) and $90\%^{v}$ of the reactive mixture at the required proportion.

Results

Figure 1 shows the performance of each catalyst with a feed stoichiometry of 4:1. The ruthenium-based catalysts exhibited unexpected behavior, showing significant deactivation at temperatures between 350 and 400 °C. Within this same range, the maximum CO_2 conversion was observed. This behavior has been linked, through stability tests, to a thermal-induced change in the crystal structure of the active Ru phase. This undesirable loss of activity in the ruthenium catalysts (C and D) reduces their competitiveness for industrial scale-up.

Regarding catalysts A and B, they displayed similar behavior; however, catalyst A showed higher methane yield at lower temperatures, whereas both reached thermodynamic equilibrium at higher temperatures. This effect is explained by the higher active phase loading in catalyst A, allowing operation under less favorable kinetic conditions.

Figure 2 presents the CO_2 conversions using catalyst A at different temperatures and H_2:CO_2 ratios. The expected effect can be observed, with CO_2 conversion maximizing as the hydrogen ratio increases, since CO_2 is the limiting reactant. Conversely, for sub-stoichiometric ratios (2:1), lower CO_2 conversions are obtained since H_2 becomes the limiting reactant and is insufficient to react with all the CO_2.

Conclusions

The nickel-based catalysts (A and B) exhibited the highest activity, CO_2 conversion, and CH_4 yield. In contrast, the ruthenium-based catalysts (C and D) showed a significant deactivation, negatively affecting both conversion and methane yield. A positive effect on methane yields was observed when operating with an over-stoichiometric H_2:CO_2 ratio.

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Table 1. Catalysts used throughout this work

Catalyst	Main active phase	ϕp (µm)
A	25 %^{w} Nickel	100-200
B	20 %^{w} Nickel	100-200
C	2 %^{w} Ruthenium	2000
D	1.97 %^{w} Ruthenium	2000

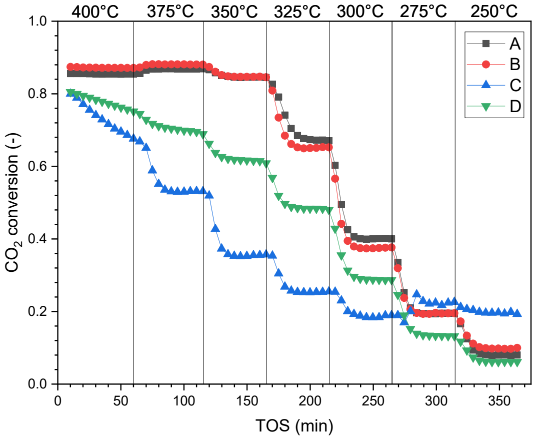

Figure 1. CO_2 conversion vs time on stream (TOS) for the different catatalyst included in this study at different operating temperatures.

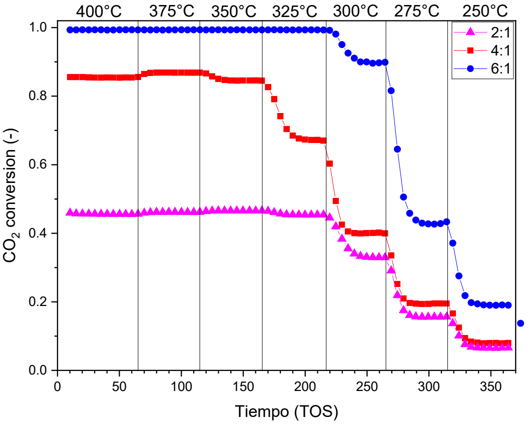

Figure 2. CO_2 conversion vs time on stream (TOS) for catalyst A at different H_2:CO_2 ratios