

## On the development of highly-efficient Ni catalysts for CO<sub>2</sub> hydrogenation

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### Highlights

- Nickel-based catalysts over various supports were tested in the CO<sub>2</sub> hydrogenation reaction.
- Good catalytic performances were yielded by Ni/Zr and Ni/Al solids at 400 °C throughout.
- Different metal-support interactions can be observed for the Ni catalysts prepared.

### 1. Introduction

Currently, some of the biggest challenges are the environmentally sustainable development and supply of renewable energy resources, in view of the massive consumption of fossil fuels, which has dramatically increased the CO<sub>2</sub> emissions in the atmosphere in the last century<sup>1</sup>. There are technologies to reduce these emissions, such as CO<sub>2</sub> capture and sequestration (CCS), enabling future CO<sub>2</sub> uses. Among these, CH<sub>4</sub> production via the CO<sub>2</sub> hydrogenation process can be highlighted, because this way not only CO<sub>2</sub> can be valorized, but also high-purity methane is produced, which can be further injected into the natural gas distribution grid or destined to other uses such as the transport sector. Hydrogenation of CO<sub>2</sub> has received renewed interest in recent years owing to the relatively abundant availability of high purity hydrogen that can potentially provide mature technologies such as water electrolysis with surplus renewable power generation<sup>2</sup>.

Methanation is an exothermic and reversible reaction; hence, the reactor design, focusing on the heat transfer and temperature control strategies, is key to manage the existing thermodynamic limitations. This process is usually carried out in a fixed-bed reactor using metal catalysts, being nickel the usual choice due to its high activity, selectivity and moderate cost. However, conventional Ni catalysts are easily deactivated by sintering, coke deposition and/or poisoning<sup>3</sup>. A convenient formulation of the catalyst support and suitable preparation and activation procedures of the supported Ni catalyst can improve the performance by increasing the metallic dispersion, stabilizing the active metal phase and enhancing the selectivity toward CH<sub>4</sub> production.

The aim of the present work is the development of highly-efficient supported Ni-based catalysts for methane production through CO<sub>2</sub> hydrogenation. The specific objectives were the study of the effects of the catalysts preparation, the characteristics of the catalyst support and the reaction conditions on the catalytic activity and stability, especially the influence on CO<sub>2</sub> conversion and CH<sub>4</sub> yield.

### 2. Methods

A series of Ni supported catalysts, using different solids as supports (two commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> materials: Axens Spheralite (Sp) and Alfa Aesar (AA), as well as CeO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and mixed oxides of them), were prepared following a wetness impregnation method, in order to obtain a Ni metal loading of 15 % (m/m) final content. All supports were calcined before impregnation (500 °C for 4 h in a muffle furnace) and after the impregnation step, the catalysts were calcined again at the same conditions. The catalysts were characterized by N<sub>2</sub> adsorption, hydrogen temperature-programmed-reduction (H<sub>2</sub>-TPR), X-ray diffraction (XRD) and CO pulse chemisorption. The catalytic tests were conducted in a microscale fixed-bed quartz reactor under atmospheric pressure. The reaction temperature was varied between 250 and 400 °C, using different CO<sub>2</sub> gas hourly space velocities (GSHV ranging from 6 to 24 N L CO<sub>2</sub>/g<sub>cat</sub>·h). High purity H<sub>2</sub> and CO<sub>2</sub> gases were fed into the reaction system by means of Bronkhorst mass flow controllers, so as to have a stoichiometric gas feeding mixture with a H<sub>2</sub>/CO<sub>2</sub> molar ratio of 4. The composition of the dry outlet gas was analyzed on-line by means of a micro gas chromatograph equipped with a thermal conductivity detector (TCD).

### 3. Results and discussion

A selection of the results showing the effects of the catalyst support and that of the CO<sub>2</sub> space velocity on the evolution of the CO<sub>2</sub> conversion over time at 400 °C and 1 atm are depicted in Fig. 1A. On the other hand, Fig. 1B shows the evolution of the CH<sub>4</sub> yield during these experiments. In these figures, the catalytic performance of three different catalysts is presented under the same reaction conditions (Ni-sp, and Ni-AA using Al<sub>2</sub>O<sub>3</sub> as a support, and Ni-ZrO<sub>2</sub>). Different CO<sub>2</sub> space velocities (6, 12 and 24 N L CO<sub>2</sub>/g<sub>cat</sub>·h) were also studied using the Ni catalyst supported on Spheralite γ-Al<sub>2</sub>O<sub>3</sub> (Ni-sp).

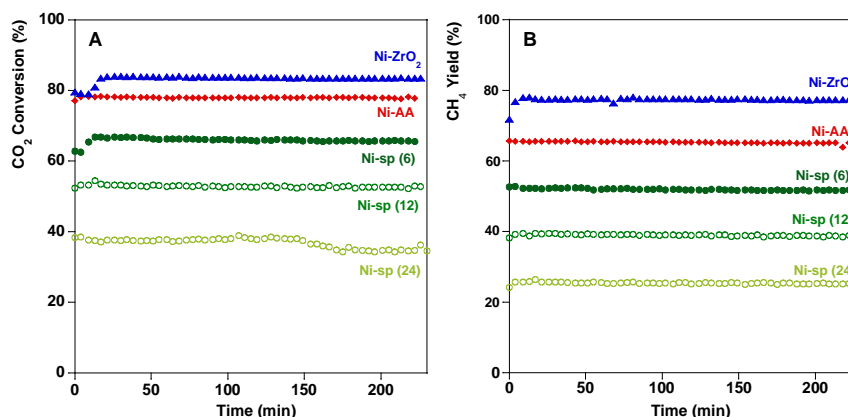


Figure 1. A. CO<sub>2</sub> conversion; B. CH<sub>4</sub> yield evolution over the reaction time.

All the catalysts showed good catalytic performance during the reaction time studied although Ni-ZrO<sub>2</sub> stood out by the high CO<sub>2</sub> conversion and CH<sub>4</sub> yield provided (around 80 %). As expected, the conversion decreased by increasing the space velocity, though showing a remarkable stability on the conversion and CH<sub>4</sub> yields throughout. As concerns the selectivity to CH<sub>4</sub>, although a suitable comparison requires data at very similar conversion, the results suggest that Ni-ZrO<sub>2</sub> is more selective than the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

For the catalysts prepared over Al<sub>2</sub>O<sub>3</sub> supports, notable differences could be observed in CO<sub>2</sub> conversion and CH<sub>4</sub> yield. These distinct results could be attributed to differences found in the Ni-support interactions of the samples, according to the TPR analyses, where the Alfa Aesar sample (Ni-AA) showed better reducibility.

### 4. Conclusions

All studied Ni-based catalysts showed good performance in the CO<sub>2</sub> hydrogenation, and a remarkable stability at the high reaction temperature considered. The nature the catalyst support has proven to play a key role in the catalytic performance. Among the possible reasons, the metal-support interactions seem to be of great relevance. Further work is underway with the rest of the Ni catalysts prepared.

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### Keywords

CO<sub>2</sub> valorization, Hydrogenation Nickel Catalysts, Metal-Support interaction.