On the development of highly-efficient Ni catalysts for CO2 hydrogenation

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Highlights
- Nickel-based catalysts over various supports were tested in the CO2 hydrogenation reaction.
- Good catalytic performances were yielded by Ni/Zr and Ni/Al solids at 400 ºC 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 CO2 emissions in the atmosphere in the last century. There are technologies to reduce these emissions, such as CO2 capture and sequestration (CCS), enabling future CO2 uses. Among these, CH4 production via the CO2 hydrogenation process can be highlighted, because this way not only CO2 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 CO2 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.

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. 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 CH4 production.

The aim of the present work is the development of highly-efficient supported Ni-based catalysts for methane production through CO2 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 CO2 conversion and CH4 yield.

2. Methods
A series of Ni supported catalysts, using different solids as supports (two commercial γ-Al2O3 materials: Axens Spheralite (Sp) and Alfa Aesar (AA), as well as CeO2, ZrO2, TiO2, SiO2 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 ºC 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 N2 adsorption, hydrogen temperature-programmed-reduction (H2-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 ºC, using different CO2 gas hourly space velocities (GHSV ranging from 6 to 24 N L CO2/gcat·h). High purity H2 and CO2 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 H2/CO2 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 CO₂ space velocity on the evolution of the CO₂ 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 CH₄ 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 Al₂O₃ as a support, and Ni-ZrO₂). Different CO₂ space velocities (6, 12 and 24 N L CO₂/gcat·h) were also studied using the Ni catalyst supported on Spherical Al₂O₃ (Ni-sp).

![Figure 1. A. CO₂ conversion; B. CH₄ yield evolution over the reaction time.](image)

All the catalysts showed good catalytic performance during the reaction time studied although Ni-ZrO₂ stood out by the high CO₂ conversion and CH₄ yield provided (around 80 %). As expected, the conversion decreased by increasing the space velocity, though showing a remarkable stability on the conversion and CH₄ yields throughout. As concerns the selectivity to CH₄, although a suitable comparison requires data at very similar conversion, the results suggest that Ni-ZrO₂ is more selective than the Ni/Al₂O₃ catalysts.

For the catalysts prepared over Al₂O₃ supports, notable differences could be observed in CO₂ conversion and CH₄ 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 CO₂ 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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References


Keywords

CO₂ valorization, Hydrogenation Nickel Catalysts, Metal-Support interaction.