Preliminary study of a catalysts design for the MCFC/SOFC system for synthetic fuels production

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Highlights

- The highest CO conversion was obtained for the CoNiCeBa catalyst.
- Only for CoNiCeBa and BaFeNi/Al_2O_3 catalysts, at 300 °C, higher hydrocarbons (C_{3+}) were detected.
- Addition of Ni to the bulk CoCeBa catalyst is beneficial for the investigated process.

1. Introduction

Energy transition is central to the European Union's ambition to achieve climate neutrality by 2050. The European Union greenhouse gas emissions reduction targets have accelerated the move away from fossil fuels towards cleaner energy sources. Processing of captured CO_2 using H_2 from renewable sources is considered as an alternative route for obtaining chemicals and fuels. Currently, a promising approach involves adapting Molten Carbonate Fuel Cell technology to operate as an electrolyzer. Electrolysis based on MCFC allows the electrochemical conversion of H_2O and CO_2 into syngas free of contaminants such as S, Cl, and particles. Obtained syngas can be used either as a fuel in internal combustion engines or as a feedstock for chemical synthesis. The main advantage of this approach is the ability to adjust the CO:H_2 ratio in the produced syngas using a dedicated catalyst. In this research, two types of catalysts were investigated - bulk and supported catalysts.

2. Methods

The obtained catalysts were prepared by coprecipitation using K_2CO_3 as the precipitating agent. Bulk catalysts were labelled as CoCeBa and CoNiCeBa, while supported catalysts as BaCoFe/Al_2O_3 and BaNiFe/Al_2O_3. The commercial TZC-3/1 catalyst for the CO conversion process was also investigated. The obtained materials were studied using N_2 physisorption to determine the specific surface area and pore volume distribution, in situ X-Ray Powder Diffraction (XRPD) for phase composition analysis, and chemisorption of hydrogen and CO to investigate the bonding strength between the active phase and substrates. Catalyst morphology was studied using Scanning Transmission Electron Microscopy with Energy Dispersive X-Ray (STEM-EDX). Catalysts reduction process was examined using TPR. Before conducting activity tests, all catalysts were reduced in situ in the reactor under a hydrogen flow overnight at 600°C. Catalytic tests were conducted in a fixed bed flow reactor using different gas compositions (H_2/CO and H_2/CO/CO_2).

3. Results and discussion

The highest specific surface area was obtained for the bulk Co-Ni catalyst (CoNiCeBa). H_2-TPR analysis revealed that supported catalysts required much higher reduction temperature (up to 650°C). Based on the STEM-EDX analysis, it was concluded that the barium promoter was evenly distributed within the catalyst bodies. XRPD in situ analysis revealed that only for bulk Co-Ni catalyst, formation of $BaCeO_3$ phase during the reduction process was observed. Moreover, for supported catalysts, intermetallic CoFe and NiFe phases were identified after reduction. The most active catalyst, CoNiCeBa, achieved the highest CO conversion, independently of the flue gases composition (**Figure 1**). Moreover, the H_2/CO ratio was calculated for all investigated catalysts to determine which process predominates. For CoCeBa and BaNiFe/Al_2O_3 catalysts, CO usage is higher than H_2 usage, which suggests that Fischer Tropsch reaction dominates. For the bulk CoNiCeBa catalyst, the CO_x methanation process dominates, while for the supported BaCoFe/Al_2O_3 catalyst, RWGSR (Reverse Water Gas Shift Reaction) dominates.

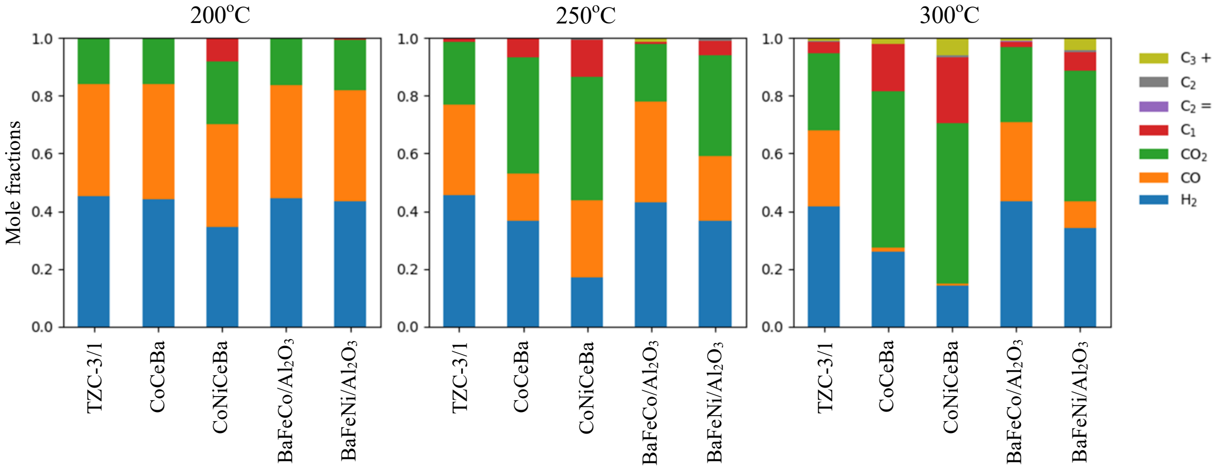

Figure 1. Preliminary catalytic test results for a gas composition of H_2:CO:CO_2 = 3:1.5:1.5.

4. Conclusions

Bulk catalysts are more active than supported catalysts. Bulk CoNiCeBa catalyst was the most active in the conducted catalytic tests. Moreover, for the CoNiCeBa catalyst, the highest concentration of C_{3+} hydrocarbons was observed. The addition of nickel to the CoCeBa catalyst is beneficial. Further research should be focused on studying the effect of Ni addition to the bulk CoCeBa catalyst and understanding the interactions between the intermetallic CoFe and NiFe phases in supported catalysts.

Acknowledgment

This work was supported by the NCN SHENG 4 program. Agr. No 2025/56/Q/ST4/00444.

References

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Keywords

Hydrogen; Catalyst; Fischer Tropsch; Hydrocarbons.