Kinetic study for the methanation of CO_2 and CO mixed syngas on a Ni/Al_2O_3 catalyst

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Highlights
- A model of the experimental reactor has been developed for the methanation reaction.
- The kinetics of the CO_2 and CO methanation has been determined and validated.
- Competitive absorption of intermediates has been observed.

1. Introduction

In the last decades, the reduction of CO_2 emissions and the development of carbon-neutral technologies have been at the forefront of the research. Among these technologies, power-to-gas is a very promising way for re-using CO_2 and store renewable electric energy. Methane is indeed an efficient energy carrier, that can be stored and distributed using existing infrastructures. Our research work focuses on the development of a kinetic model of a new Ni/Al_2O_3 catalyst for converting both CO_2 and/or CO (syngas) into CH_4 using renewable H_2. The carbon sources are a biogas-to-biomethane upgrading plant coupled with a gasification plant of the digestate. In the literature, many researchers have studied different kinetic models of the methanation over Ni-based catalysts such as Xu and Froment (1984) [1], Koschany et al. (2016) [2], Schmider et al. (2021) [3], Quindimil et al. (2022) [4], Onrubia-Calvo et al. (2022) [5] etc. These existing kinetic models does not represent the reaction mechanism that occurs on the surface of our catalyst, so to design and optimize the reactor an in-depth study is required to reveal the mechanism.

2. Methods

On the one side, the catalytic tests were carried out in a quartz tube reactor (i.d. 4 mm) inserted in a stainless-steel tube to operate at high pressures (1 – 25 bar) and temperatures (20 – 500 °C). A mass of 75 mg of Ni/Al_2O_3 was mixed with 375 mg of SiC (particle size: 250 – 500 um) and inserted into the quartz tube between two layers of SiC to guarantee the continuity of the fluid-dynamics. Three different groups of gas mixtures were tested: CO_2, CO and syngas with both CO_2 and CO. Specific tests with CH_4 were also included for a total of 30 gas mixtures and they were designed to avoid the carbon deposition zone. Each gas mixture was tested at two pressures 5 bar and 15 bar and 6 temperatures from 250 °C to 400 °C. These 360 different operating conditions are statistically representative of the extremely complex reaction mechanism and could be elaborated to determine the kinetic parameters and validate the results. On the other side, we developed a model of the reactor to simulate the catalytic tests. In addition, we developed a fitting algorithm to obtain the kinetic parameters by minimizing the objective function (i.e., the residuals between the experimental and the modelled yields).

3. Results and discussion

For each gas mixture CO_2/CO conversion and CH_4 selectivity have been evaluated and compared graphically (as reported in **Fig.1**). The tests with only CO or CO_2 show a decreasing trend of methane yield as the CO_2/CO concentration increase in the gas mixture (**Fig. 1a-1b**), being constant the H_2 concentration, the H_2/CO and H_2/CO_2 ratio reduce. The tests with CO showed a higher deactivation suggesting a not negligible carbon deposition even though the gas mixtures were defined outside the carbon deposition region evaluated thermodynamically. Moreover, tests with both CO and CO_2 showed that the CO_2 conversion drastically drop as the CO concentration increases suggesting a strongly competitive adsorption between CO and CO_2. Also, the production of hydrocarbons from C_2H_6 to C_7H_{16} have been observed.
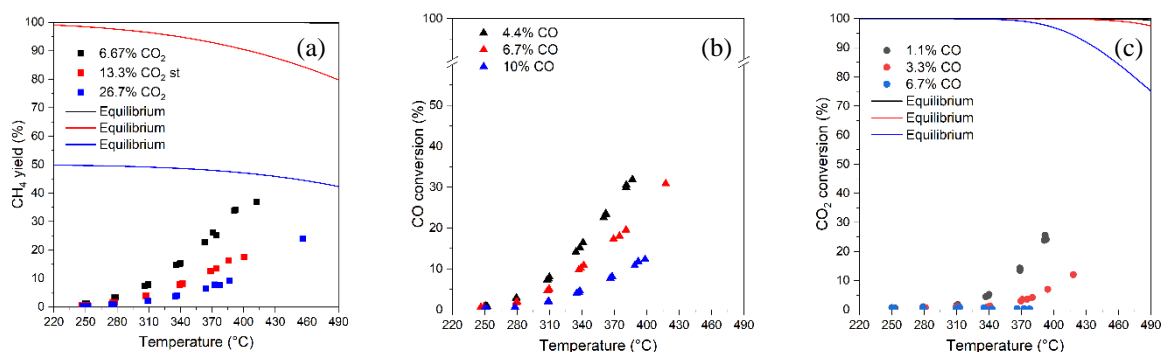
Figure 1. Results of the catalytic tests: (a) CH_4 yield at the variation of the CO_2 concentration, (b) CH_4 yield at the variation of the CO concentration and (c) CO_2 conversion at the variation of the CO concentration.

All the collected data were used with the mathematical model and the regression algorithm to find a suitable kinetic expression. Both Power-Law and LHHW expressions have been evaluated but only the latter describes the system of 3 reactions occurring at the same time. The mechanism proposed by Xu and Froment [1] was not suitable for describing our catalyst while the mechanism proposed by Koschany et al. [2] better describes the conversion of CO_2 to CH_4 and CO (**Fig. 2**)
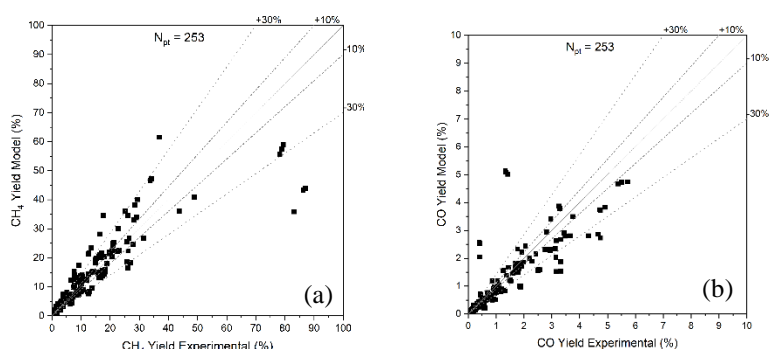
Figure 2. Parity plot of (a) CH_4 yield and (b) CO yield without outlier removal.

4. Conclusions

The Ni-based catalyst shows good activity and selectivity towards methane when exposed to the different gas mixtures. Moreover, the dissociative formyl mechanism seems to be the reaction mechanism that better fits our experimental results, whilst the dissociative carbon mechanism does not represent accurately the experimental results.

References

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