Demonstration Study of CO_2 Methanation using NiO/Al_2O_3 catalysts

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1. Introduction

Acting towards the global effort to eliminate greenhouse gas emissions, the EIZ Energy Storage and Conversion Lab is at the forefront of advancing hydrogen-based energy storage and converter technologies, targeting CO_2-neutral energy systems in the kW to MW range. This endeavor involves the establishment of a specialized laboratory, integrating material research and component development for Power-to-X-to-Power (P2X2P) applications. The primary objectives of the Chair of Applied Physics and Semiconductor Spectroscopy entail the fabrication of novel and efficient catalysts for CO_2 hydrogenation, in order to achieve milder and more economical methane and methanol synthesis conditions for efficient integration in power plant concepts. Current investigations focus on nickel as the active phase for CO_2 methanation, since it has been proven to be highly active, selective towards methane, thermally stable, and cost-effective [1]. In the long term, the project aims to combine nickel with a plethora of supports/promoters, with a particular focus on ceria, which is proven to exhibit a high oxygen storage capacity, allowing it to promote the activation and transfer of oxygen during methanation [2,3].

2. Materials and Methods

A laboratory-scale tubular reactor is used to extensively evaluate catalyst properties for CO_2 methanation. The reactor is placed vertically inside an oven and filled with the catalyst, forming a 10 cm long fixed catalyst bed. Experimental conditions, including oven temperature, pressure, and reactant concentration, are systematically varied to understand their impact on the catalyst behavior. The temperature distribution is measured along the length of the catalyst bed, providing valuable insights into the reaction kinetics and heat transfer. The gaseous products are analyzed using a nondispersive infrared spectrometer (NDIR), coupled with a Fourier-transform infrared spectrometer (FTIR). The latter allows the creation of user-defined reference spectra, which will facilitate the identification of unknown reaction products when testing self-prepared catalysts of different properties. As a reference, 5 g of a commercial NiO catalyst on 2 mm Al_2O_3 spheres with a Ni content of 20% wt. has been examined and then compared to self-prepared 1 mm NiO/Al_2O_3 spheres and powders to assess their catalytic performance and respective efficiency. The home-made catalysts were prepared by the wetness impregnation method using $Ni(NO_3)_2$ targeting a similar nickel content as the reference sample.

3. Results and Discussion

The experiments shown in Fig. 1 have been performed with a set oven temperature of 350°C and a variation of the CO_2 volumetric flow rate (Q_{CO2}) from 10 to 25 ml/min while maintaining a H_2/CO_2 ratio of 4:1 and a constant inlet flow of 125 ml/min with N_2 as balance. The left diagram shows the temperature distributions along the methanation reactor, shifting towards higher temperatures as the flow rate of the reactants increases. The profiles reach a maximum temperature within 0.5 cm after the beginning of the catalyst bed (i.e., at about 2.5 cm behind the oven inlet), which indicates where most of the exothermic reactions take place. The diagram on the right-hand side shows that the resulting CO_2 conversion reaches a maximum for a CO_2 flow of Q_{CO2} = 15 ml/min. The respective H_2 conversion and CH_4 yield improve with increasing Q_{CO2}. It is argued that the changes observed in conversion and yield are the result of dilution with N_2, slight changes in residence time, and, more importantly, an increase in reactor temperature accelerating the reaction rate towards thermodynamic equilibrium. The activity of this reference sample is compared to the home-made catalysts. E.g., the temperature dependent conversion and yield highlight possible kinetic limitations in the reaction rates and allow for a direct comparison of the temperature at which thermodynamic equilibrium conditions are reached.

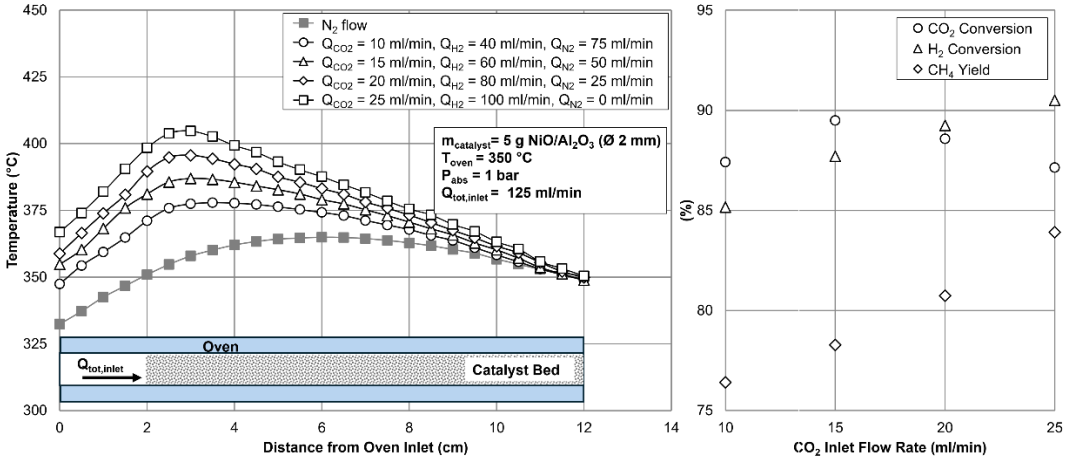

Figure 1. (left) Temperature distribution along the methanation reactor tube length and (right) CO_2 conversion, H_2 conversion, and CH_4 yield depending on CO_2 inlet volumetric flow rate at an oven temperature of 350 °C, an absolute pressure of 1 bar, a constant total volumetric flow rate of 125 ml/min and 5 g of NiO/Al_2O_3 spheres with a diameter of 2 mm.

References

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