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

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Significance and Relevance

This study presents a detailed kinetic analysis of a 24 wt. % Ni/Al_2O_3 catalyst for the hydrogenation of CO_2 and CO to CH_4, focusing the attention on CO_2 and CO co-methanation. From the experimental results obtained, an LHHW kinetic model was developed that can simultaneously describe the two methanation reactions and the phenomenon of competitive adsorption in co-methanation tests, with preference of CO adsorption on the catalytic surface. The obtained results help to understand and clarify the preferential pathways of methanation reactions.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent decades, reducing greenhouse gas emissions and developing carbon-neutral technologies have been key research priorities. Among these technologies, Power-to-Gas is a highly promising method for reusing CO_2 and storing renewable electrical energy. Methane is an efficient energy carrier that can be stored and distributed using the existing infrastructure[1]. Supported Ni catalysts are the most widely used industrial catalysts for methanation reactions as they are highly efficient and significantly less expensive than noble metals[2]. Despite the fruitful studies conducted on methanation catalysts, there are still debates regarding the reaction pathways, the reaction mechanism and rate-determining steps on Ni-based catalyst. Recent studies indicate that CO_2 methanation could occur via either dissociative[3] or H-assisted associative[4] CO_2 adsorption forming CO* and COOH* species, respectively. CO methanation, instead, appears to proceed via a dissociative carbon pathway on supported Ni catalysts[5], while following a dissociative formyl pathway on co-precipitated Ni/Al catalyst[6]. The aim of this work is to derive a unique kinetic model capable of describing all the reaction pathways (CO_2, CO and CO_2+CO methanation) on a 24 wt. % Ni/Al_2O_3, analyze the main mechanisms of deactivation and the non-linear effect of CO_2 and CO on thermal profiles for reactor scale-up.

Materials and Methods

For the kinetic tests, a fixed-bed reactor configuration consisting of 75 mg of 24 wt. % Ni/Al_2O_3 catalyst diluted with 375 mg of SiC was adopted. The different CO-CO_2-H_2 reactant syngas mixtures were tested at two pressures, 5 bar and 15 bar and six temperatures from 250 °C to 400 °C, for a total of 360 different operating conditions. In parallel, a model of the experimental reactor was created to simulate the tests, along with a minimization algorithm for determining the kinetic parameters.

Results and Discussion

The competitive adsorption phenomenon observed in CO_2 and CO co-methanation tests is described in Figure 1. The catalyst has proven to have stronger affinity for CO, which preferentially adsorbs and converts onto the catalytic sites, even at low molar fractions (around 1.1 mol.%). Despite the fact that equilibrium conditions are not reached, CO conversion decreased at low CO molar fraction because CO started to be produced from CO_2 by RWGS reaction, which is favored at high temperatures. Both CH_4 formation rate (from CO methanation) and CO formation rate (from RWGS reaction) increased above 360 °C. The derived three-reaction kinetic model is the best one in order to describe this phenomenon, as observed from the Parity Plot reported in Figure 2. Based on experimental results, and in accordance with literature, CO_2 methanation could occur via either dissociative or H-assisted associative CO_2 adsorption, with the latter slightly favored because it requires only one active site. During CO_2 methanation, no hydrocarbons formation was detected, suggesting that CH_4 formation occurs through hydrogenated species as reaction intermediates. On the other hand, if the partial pressure of CO is higher (such as during CO methanation) the dissociative carbon pathway is prevalent leading to the formation of C* species that can lead to the formation of solid carbon on surface catalyst, thus causing coking or diffusing into the Ni structure forming Ni carbides which are active sites for Fischer-Tropsch synthesis reaction. This may be the explanation for the formation of hydrocarbons in the C_2-C_5 range detected in CO methanation.

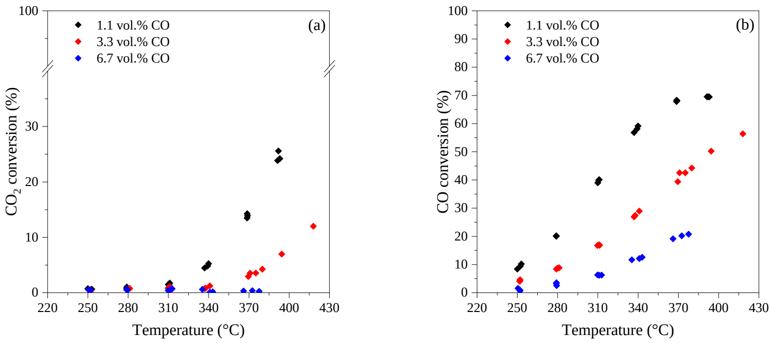

Figure 1. CO_2 (a) and CO (b) conversion varying the CO partial pressure and the temperature. Reaction conditions: 1200 $Nl/h/g_{cat}$, 5 bar, 40.0 vol.% H_2 and 3.3 vol.% CO_2 in N_2, 75 mg Ni/Al_2O_3.

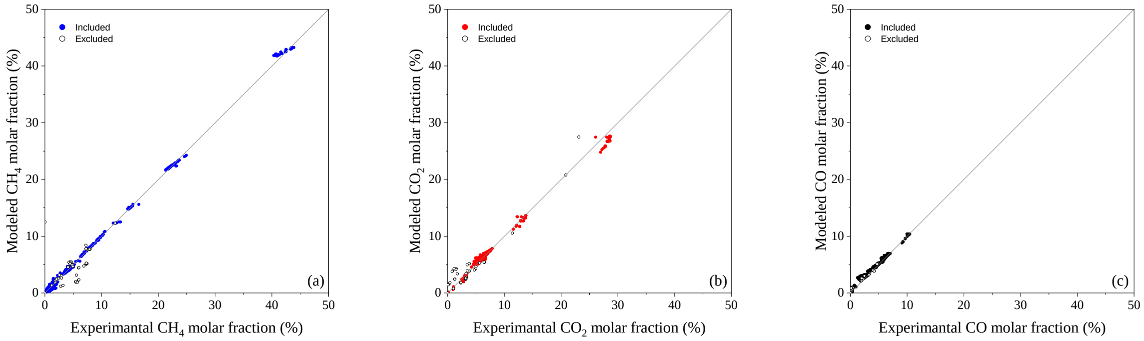

Figure 2. Parity plots comparing the experimental and the modeled molar fractions at the reactor outlet for the following gas species: (a) CH_4, (b) CO_2 and (c) CO. Tests near equilibrium and that did not meet Weisz-Prater transport criteria and statistical Cook were excluded from the simulation.

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