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Dry reforming of methane over a Co-based catalyst: An experimental and microkinetics modeling study

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Highlights

- A Co-based catalyst is investigated under dry reforming conditions
- Feed gas composition and reactor pressure are varied
- A microkinetic reaction mechanism is proposed to simulate the experiments

1. Introduction

Dry reforming of methane (DRM) is one of the most promising technologies for the chemical valorization of carbon dioxide [1]. Compared to the well-established steam reforming process, H_2O as oxidant is replaced partially or completely by CO_2. As a result, syngas with a lower H_2/CO ratio is obtained, which presents a suitable feedstock for, among others, hydro formylation reactions or for synthetic fuels such as DME. As public awareness for man-made climate change rises and legal measures to mitigate green-house gas emissions are enacted, DRM is receiving increasing attention in the academic and industrial community. In order to be attractive on the commercial scale catalysts for DRM should be based on readily available active metals. One example is Nickel, which is commonly used for steam reforming of methane. Under the more severe reaction conditions of DRM, however, Ni tends to suffer from deactivation due to coke formation [2, 3]. Cobalt, in contrast, has shown higher coking resistance in experimental studies and is therefore investigated as another prospective candidate. In this work, a Co-based catalyst is studied under dry and combined reforming conditions at various pressures and feed compositions in order to develop an elementary step reaction mechanism.

2. Methods

A Co-based catalyst candidate was studied in a fixed bed reactor setup under dry and combined dry/steam reforming conditions. The molar ratio of methane and oxidant was varied in the range of 0.5 and 2.0 at pressures between 1 and 10 bar(a). Spent catalyst samples were characterized using XRD and CO chemisorption in order to determine the oxidation state of Co as well as the active surface area of the catalyst.

An elementary step reaction model has been developed based on a Langmuir-Hinshelwood mechanism. This model includes the activation of methane through step-wise cleavage of the C-H bond of the respective CH_x surface species. As observed on Nickel catalysts [4], adsorbed CO_2 can either dissociate directly into CO or assisted by hydrogen through reverse water-gas shift reaction via a COOH intermediate. Activation barriers for all reactions were calculated according to the semi-empirical UBI-QEP approach [5]. Pre-exponential factors were adjusted to match the experimental data with the results of steady state reactor simulations using the DETCHEM software package [6] while ensuring thermodynamic consistency of all parameters.

3. Results and discussion

The Co-based catalyst was activated under reforming conditions, i.e., no dedicated pretreatment was required. Methane conversion and product gas composition approached a steady state within about 40 hours of operation. The reaction rate for methane determined after 44 hours on stream is shown in Figure 1 as a function of the CH_4 to CO_2 ratio. In these experiments, at constant overall flow rate, the inlet concentration of one of the two reactants was held constant while the other one was lowered to give the desired CH_4/CO_2

ratio. As expected, the reaction rate decreases as the concentration of either reactant is lowered. However, there is a marked drop in reaction rate at low CH_4/CO_2 ratios, which is attributed to an oxidative deactivation of the Co catalyst due to the excess of CO_2. In case of strong metal-support interaction Co, can be oxidized by CO_2 or H_2O. In order to keep Co in the reduced and active state, a sufficiently high concentration of reductant must be provided. However, as pointed out recently, the higher oxidation tendency of Co may also be the reason for the higher coking resistance compared to Ni-based catalysts [7].

Measured and simulated mole fractions for all reactive species are compared in Figure 2. Good agreement between experiment and simulation is observed for CH_4/CO_2 ratios larger than or equal to 1.0 using a constant active surface area. CH_4/CO_2 ratios below 1.0, however, require the use of reduced active surface areas to achieve reasonable agreement. This finding further substantiates the notion of a correlation between catalyst activity and the ratio of oxidizing and reducing species in the gas phase.
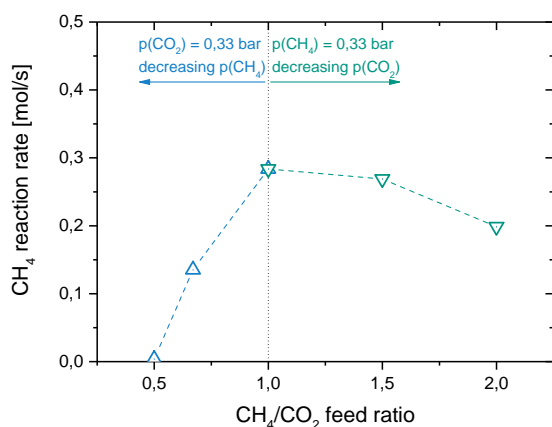
Figure 1. Experimentally observed reaction rate of methane during dry reforming at 820 °C as a function of CH_4/CO_2 ratio of the feed gas.
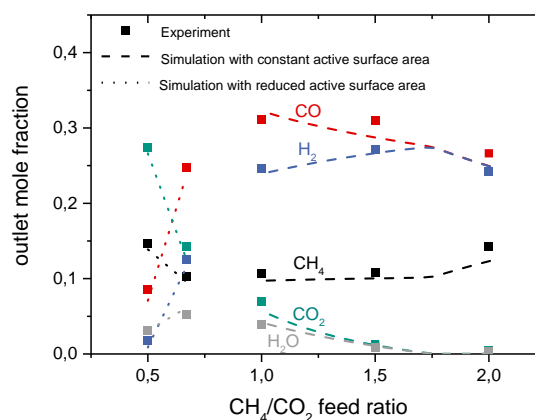
Figure 2. Comparison of outlet mole fractions of all reactive species determined experimentally and by steady state reactor simulations.

4. Conclusions

A Co-based catalyst was studied under various dry reforming conditions. No reductive pretreatment was necessary to activate the catalyst. While varying the CH_4/CO_2 ratio of the feed gas, a steep decline in activity was observed at CH_4/CO_2 ratios below 1.0, which is assumed to be caused by partial oxidation and deactivation of Co. Based on the UBI-QEP approach and experimental data, an elementary step reaction mechanism was developed. Good agreement between experiment and simulation is obtained at high CH_4/CO_2 ratios using a constant active surface area, while low CH_4/CO_2 ratios require the use of lower active surface area to account for the partial oxidation of the catalyst.

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