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Influence of trace substances on methanation catalysts in dynamic biogas upgrading

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Keywords

biogas, upgrading, Sabatier, surplus electricity, catalyst poisoning

Introduction

- Sabatier process-based biogas upgrading for utilization of surplus electricity produced from fluctuating renewable energy.
- 650 mostly farm scale biogas plants and a well-developed compressed natural gas (CNG) grid are located near wind farm sites [4].
- The Sabatier reaction is catalyzed by Nickel or Ruthenium catalyst and the equilibrium is far on the right hand site [5,7].:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H° = -165\ ^{kJ}/_{mol}.$$

- Carbon formation leads to deactivation by the considered reactions [1,2]:

$$2CO \rightarrow CO_2 + C \quad (1)$$
$$CH_4 \rightarrow 2H_2 + C \quad (2)$$
$$CO + H_2 \rightarrow H_2O + C \quad (3)$$
$$CO_2 + 2H_2 \rightarrow 2H_2O + C \quad (4)$$

- sulfur hydrogen as a trace component is well known as poison for Ni catalyst and can be easily removed by ZnO filters.
- There is a lag of studies about the influence of ammonia on the previously mentioned reactions and as a catalyst poison.
- This study investigate the influence of ammonia as a trace substances of biogas on the methanation catalyst

Materials and Methods

- Experimental setup as shown in Figure 1 was used to perform long lasting experiments (7 days).
- High loaded Ni catalyst was used to provoke coke formation in shorter time (66 %).
- 100 mg of pelleted and sieved (fraction between 425 μm and 250 μm) catalyst were used in a stainless steel reactor 4 mm in diameter.
- A stoichiometric feed was used at flow rates of 20 ml/min.
- A saturator containing a 100 mM NH_3 solution was used to introduce trace amounts of NH_3 into the feed stream.
- GC was used to determine product concentration during the whole experiment.
- Temperature programmed oxidation (TPO, 95 % O_2, 5 % Kr as internal standard) was used to determine carbon formed on the catalyst.
- The signal S of detected CO_2 was standardized using the Kr signal S_0 as internal standard.

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Results

- In all experiments deactivation due to carbon formation had been observed.
- The rate of deactivation and the properties of the decomposed coke were influenced by the feed gas composition.
- The presence of small amounts of ammonia caused lower deactivation rates and resulted in a more stable system.
- In summary, it can be observed that trace NH_3 concentrations could convey more positive effects than negative, with no pretreatment for NH_3 removal from biogas necessary when considering it as a feed gas for methanation processes using Ni catalysts.

Figures

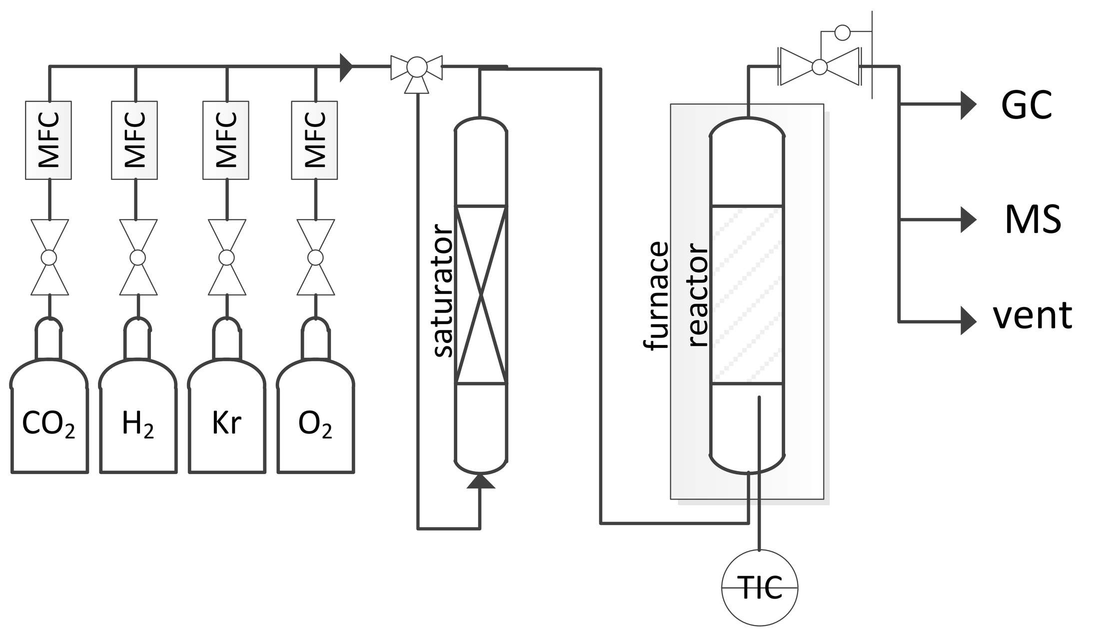

Fig. 1: Schematic representation of the experimental setup.

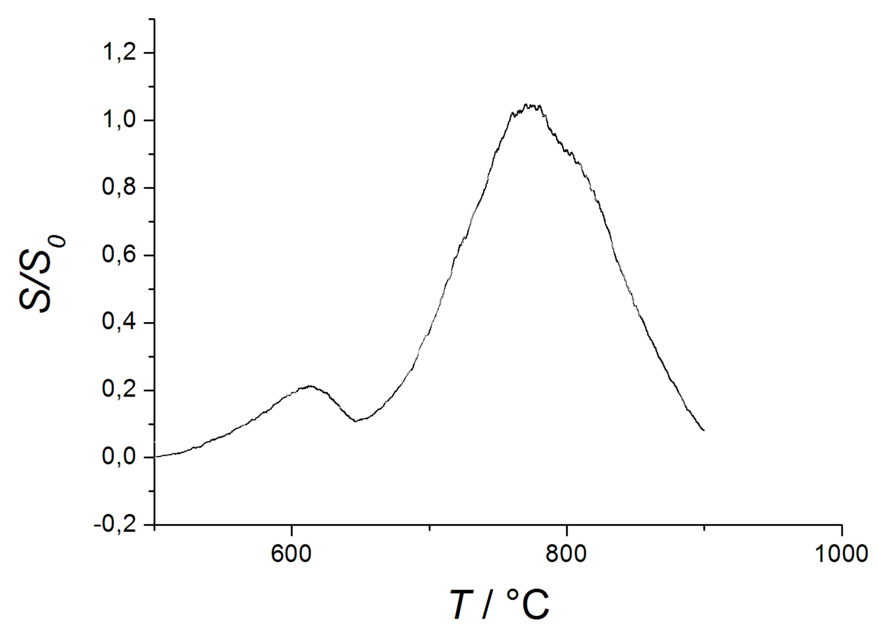

Fig. 2: Results of TPO for the methanation of "dry" CO_2: two different kind of formed carbon were observed.

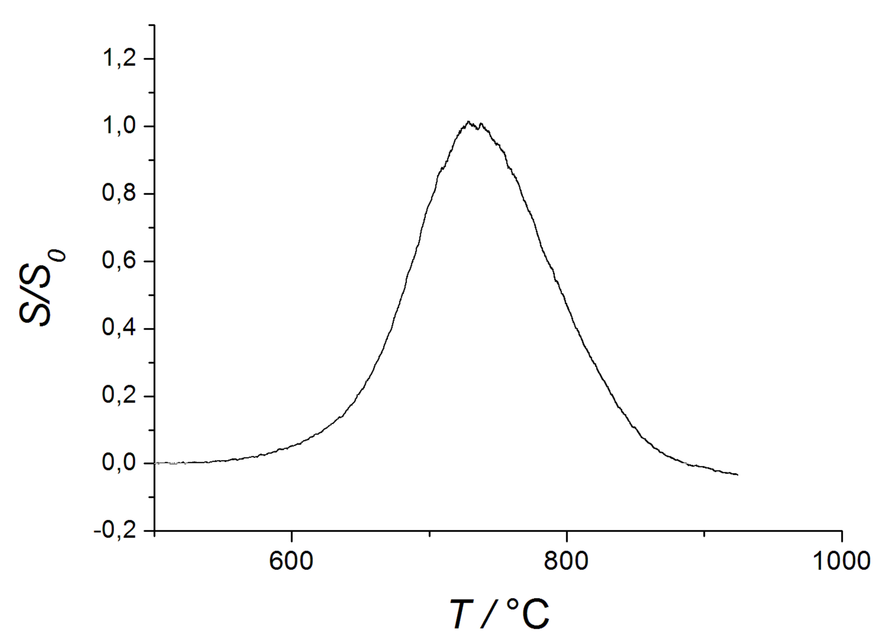

Fig. 3: Results of TPO for the methanation of CO_2 containing small amounts of H_2O: the formation of "low temperature coke" is inhibited and the amount of "high temperature coke" is reduced.

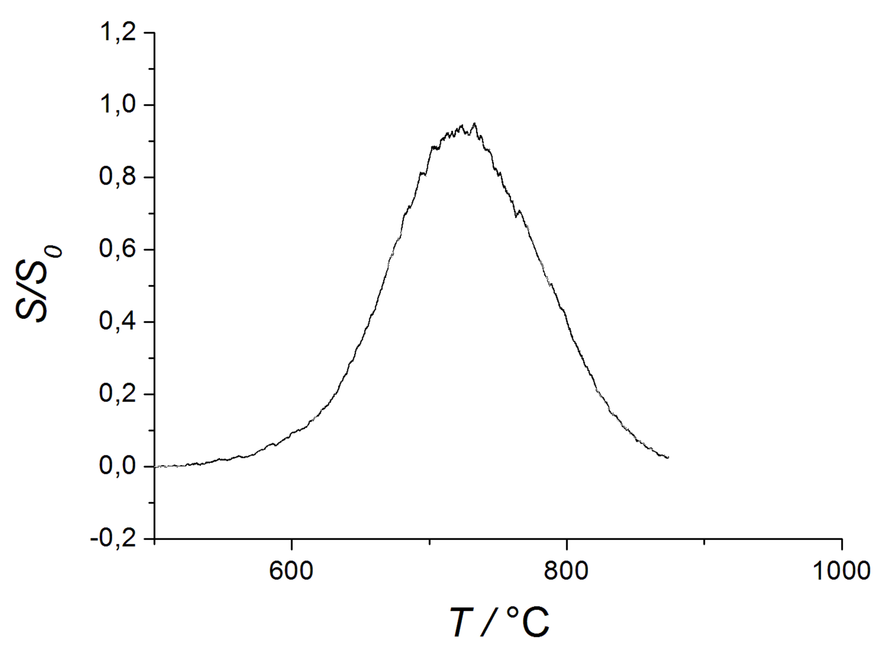

Fig. 4: Results of TPO for the methanation of CO_2 containing small amounts of ammonia and H_2O: the amount of carbon formed in the process is further reduced.

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