

## Influence of trace substances on methanation catalysts in dynamic biogas upgrading

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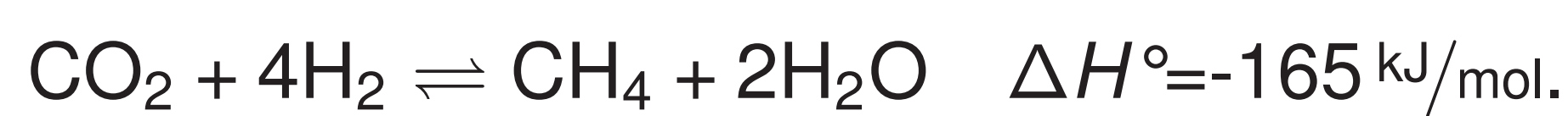


## Keywords

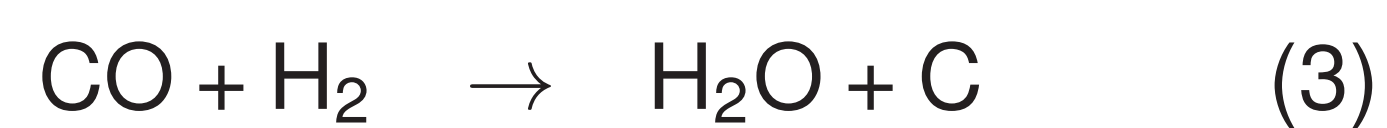
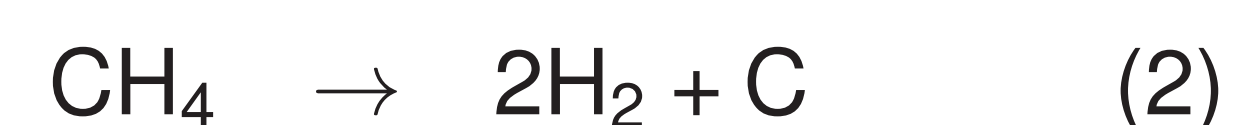
biogas, upgrading, Sabatier, surplus electricity, catalyst poisoning

## 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 side [5,7].:



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



- ▶ 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  $\mu\text{m}$  and 250  $\mu\text{m}$ ) 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  $\text{NH}_3$  solution was used to introduce trace amounts of  $\text{NH}_3$  into the feed stream.
- ▶ GC was used to determine product concentration during the whole experiment.
- ▶ Temperature programmed oxidation (TPO, 95 %  $\text{O}_2$ , 5 % Kr as internal standard) was used to determine carbon formed on the catalyst.
- ▶ The signal  $S$  of detected  $\text{CO}_2$  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  $\text{NH}_3$  concentrations could convey more positive effects than negative, with no pretreatment for  $\text{NH}_3$  removal from biogas necessary when considering it as a feed gas for methanation processes using Ni catalysts.

## Figures

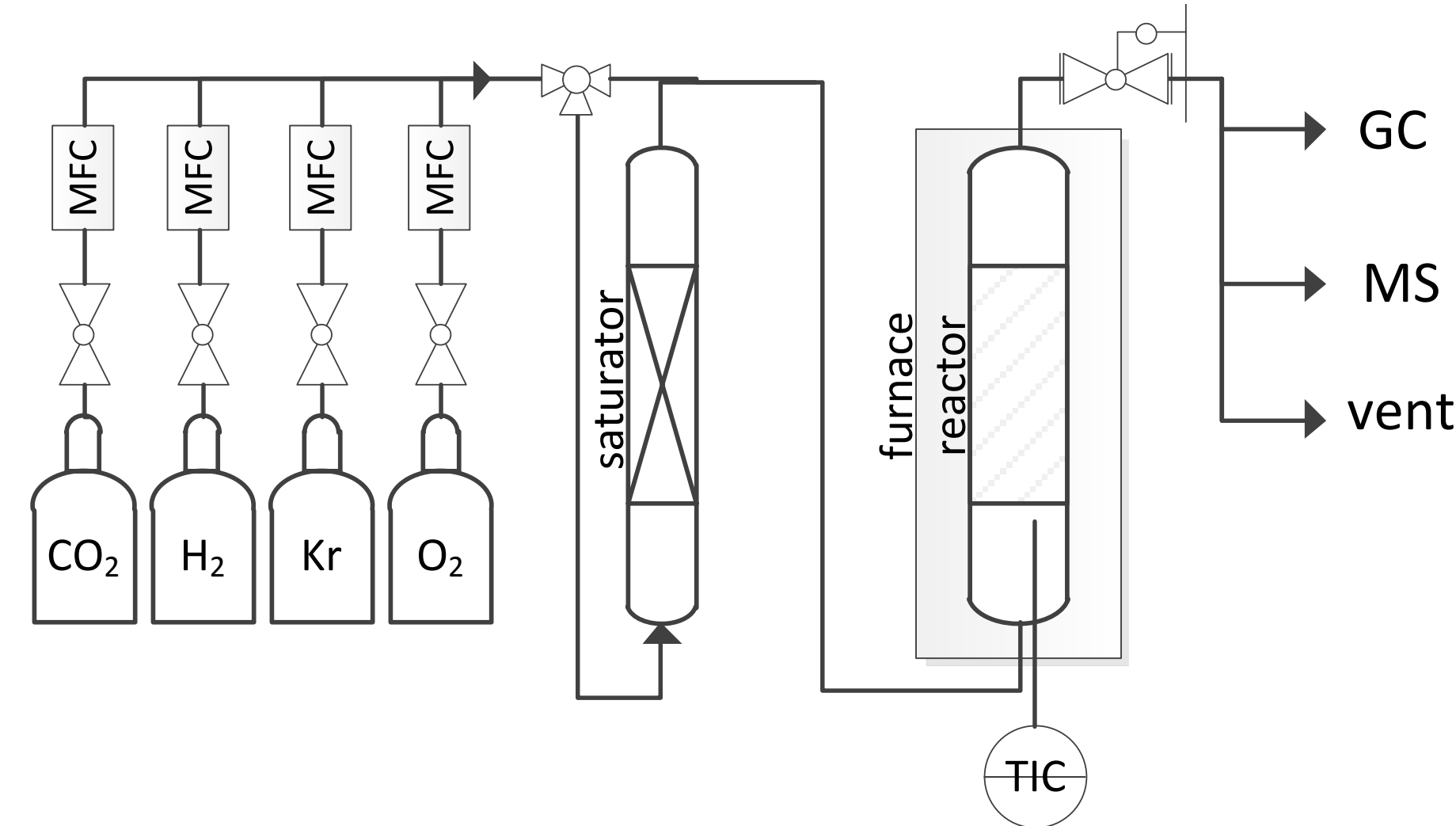


Fig. 1: Schematic representation of the experimental setup.

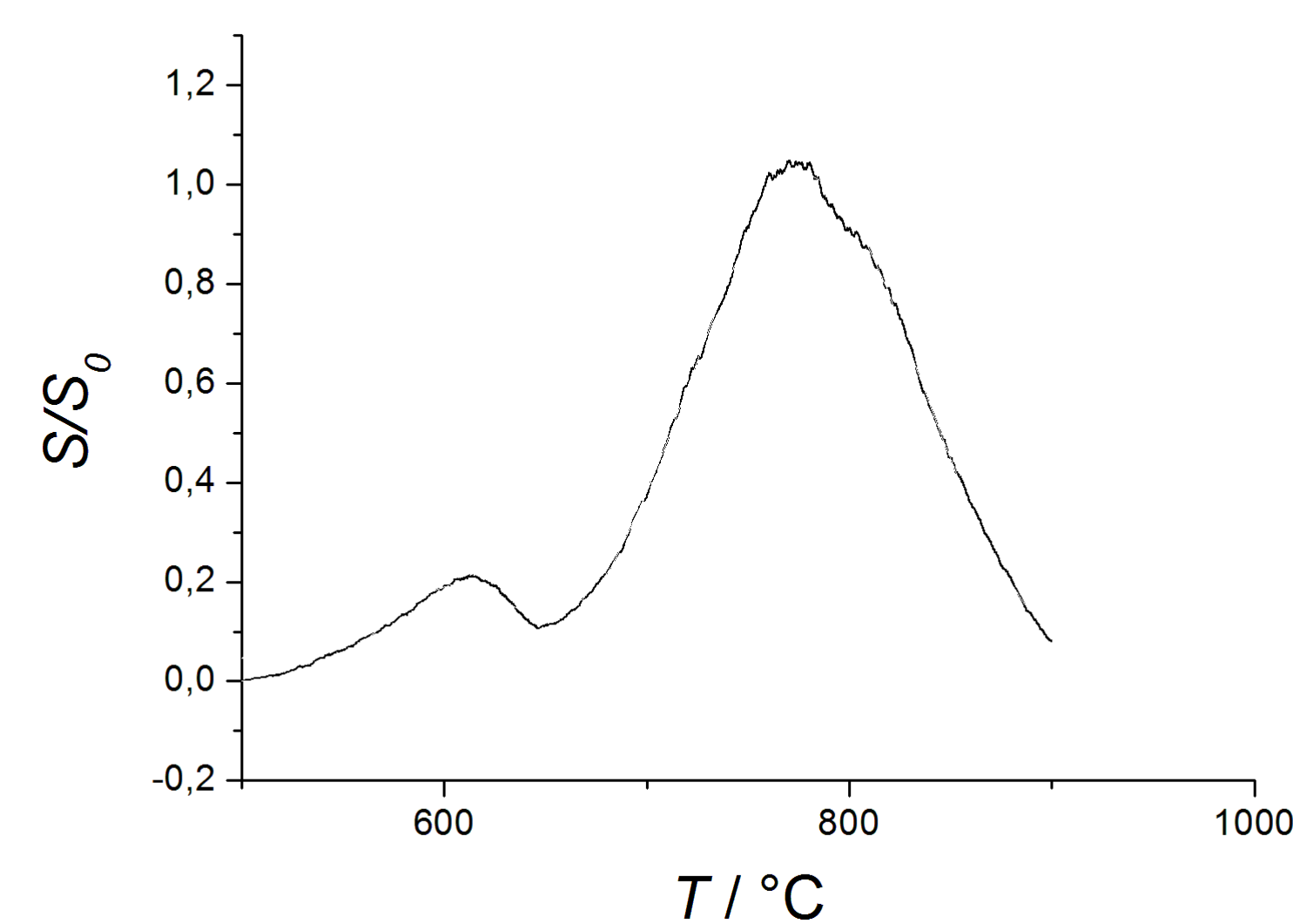


Fig. 2: Results of TPO for the methanation of "dry"  $\text{CO}_2$ : two different kind of formed carbon were observed.

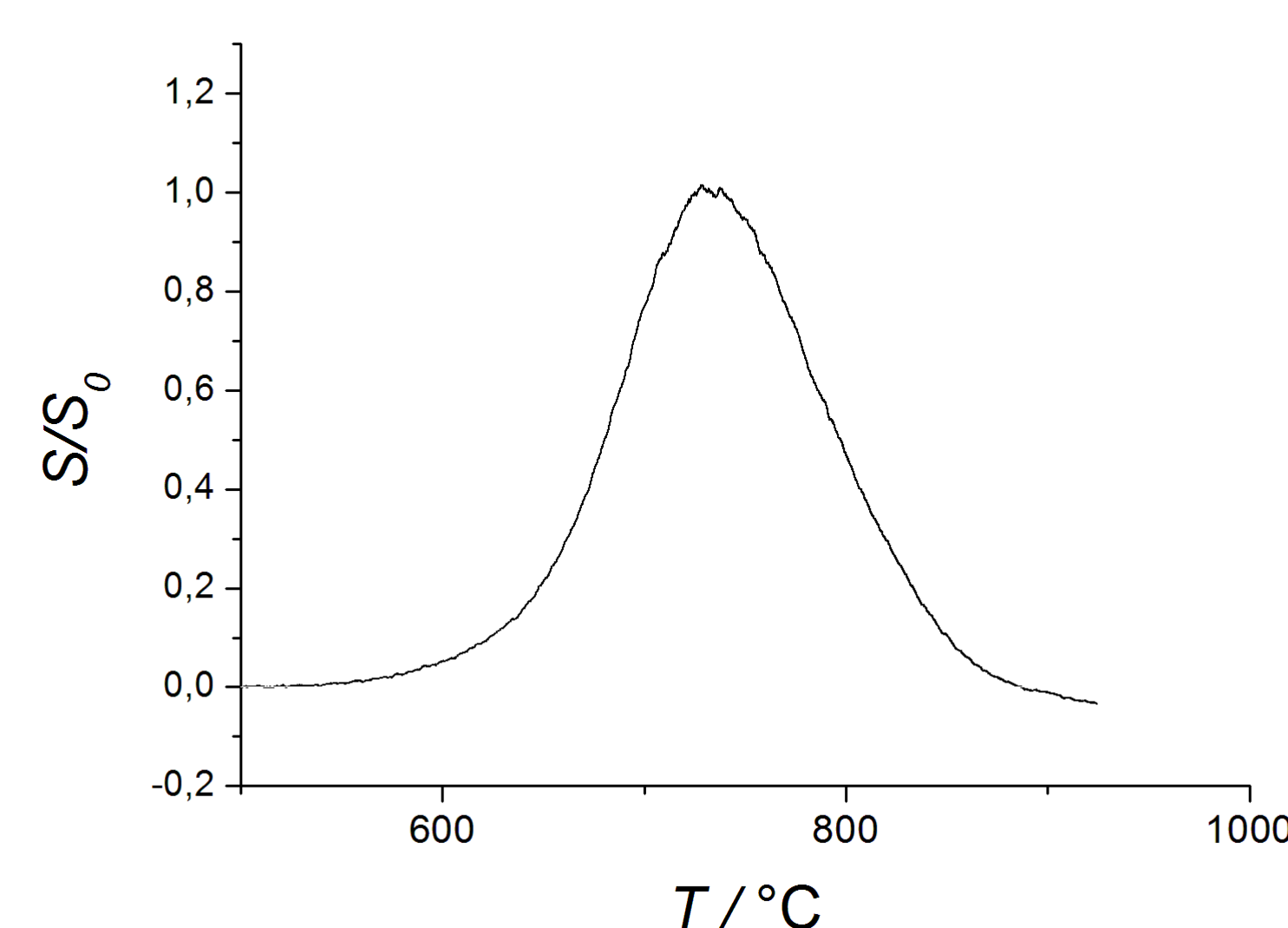


Fig. 3: Results of TPO for the methanation of  $\text{CO}_2$  containing small amounts of  $\text{H}_2\text{O}$ : the formation of "low temperature coke" is inhibited and the amount of "high temperature coke" is reduced.

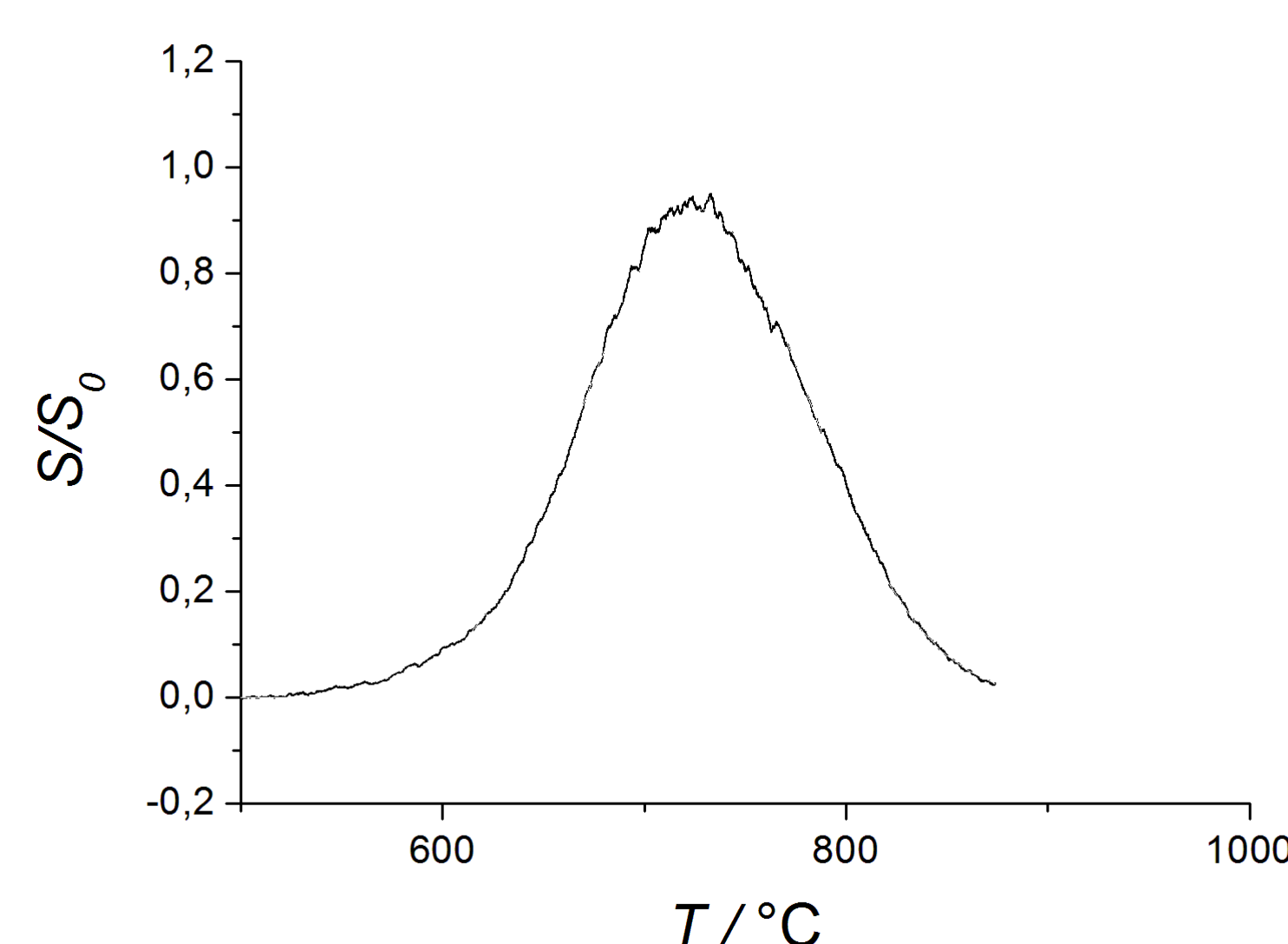


Fig. 4: Results of TPO for the methanation of  $\text{CO}_2$  containing small amounts of ammonia and  $\text{H}_2\text{O}$ : the amount of carbon formed in the process is further reduced.

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