Influence of trace substances on methanation catalysts in dynamic biogas upgrading

Jurgensen, Lars; Ehimen, Ehiazesebhor Augustine; Born, Jens; Holm-Nielsen, Jens Bo; Rooney, David

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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]:

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H^\circ=-165 \text{kJ/mol}
\]
▶ Carbon formation leads to deactivation by the considered reactions [1,2]:

\[
\begin{align*}
2\text{CO} & \rightarrow \text{CO}_2 + \text{C} \\
\text{CH}_4 & \rightarrow 2\text{H}_2 + \text{C} \\
\text{CO} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{C} \\
\text{CO}_2 + 2\text{H}_2 & \rightarrow 2\text{H}_2\text{O} + \text{C}
\end{align*}
\]
▶ 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 NH₃ solution was used to introduce trace amounts of NH₃ into the feed stream.
▶ GC was used to determine product concentration during the whole experiment.
▶ Temperature programmed oxidation (TPO, 95% O₂, 5% Kr as internal standard) was used to determine carbon formed on the catalyst.
▶ The signal S of detected CO₂ was standardized using the Kr signal S₀ as internal standard.

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 NH₃ concentrations could convey more positive effects than negative, with no pretreatment for NH₃ 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” CO₂: two different kind of formed carbon were observed.
Fig. 3: Results of TPO for the methanation of CO₂ containing small amounts of H₂O: 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 CO₂ containing small amounts of ammonia and H₂O: the amount of carbon formed in the process is further reduced.

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References