



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



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## HIGHLIGHTS

- Small amounts of ammonia cause lower deactivation rates of methanation catalysts.
- Ammonia lower the formation of carbon on methanation catalysts.
- Removal of ammonia is not necessary when biogas is used in methanation processes.
- Trace ammonia concentrations could convey more positive effects than negative.

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## ABSTRACT

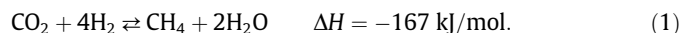
The aim of this work was to study the possible deactivation effects of biogas trace ammonia concentrations on methanation catalysts. It was found that small amounts of ammonia led to a slight decrease in the catalyst activity. A decrease in the catalyst deactivation by carbon formation was also observed, with ammonia absorbed on the active catalyst sites. This was via a suppression of the carbon formation and deposition on the catalyst, since it requires a higher number of active sites than for the methanation of carbon oxides. From the paper findings, no special pretreatment for ammonia removal from the biogas fed to a methanation process is required.

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## 1. Introduction

The Sabatier process has often been discussed as a storage option for the use of surplus electricity produced from fluctuating renewable energy sources like solar and wind. In Northern Germany, i.e. the state of Schleswig-Holstein, which has over 650 farm scale biogas plants and a well-developed compressed natural gas (CNG) grid located near wind farm sites (Jürgensen et al., 2014), provides a good case for the application of the Sabatier technology using biogas CO<sub>2</sub>.

The Sabatier reaction is catalyzed by nickel or ruthenium catalyst, with the equilibrium favoring CH<sub>4</sub> product formation (Müller et al., 2013; Twigg, 1989):



Anaerobically derived biogas (with high CO<sub>2</sub> content, approx. 40%) can thus be considered for use as suitable feed gas for the Sabatier reaction. In addition to the main components (i.e. approximately 60% of CH<sub>4</sub> and 40% of CO<sub>2</sub>), biogas contains small amount of hydrogen sulfide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>). H<sub>2</sub>S has been well described as a methanation catalyst poison, with several papers published on this topic since the 1970s (Dalla Betta et al., 1975). There is however a noticeable lack of research/studies on the possible influence of NH<sub>3</sub> on the methanation catalyst. With the decision to remove the biogas NH<sub>3</sub> prior to methanation being an important techno-economic one, this paper aims to provide some valued information on potential impacts that the NH<sub>3</sub> available in biogas could have on the catalyst activity and the overall progress of methanation process.

There are mainly six different mechanisms for catalyst deactivation reported in the literature: (i) poisoning, (ii) fouling, (iii) thermal

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degradation, (iv) vapor compound formation accompanied by transport, (v) vapor–solid and/or solid–solid reactions and (vi) attrition/crushing (Bartholomew, 2001). For the methanation processes only the first two mechanisms are considered to be applicable due to the low reaction temperature conditions used for the process.

Catalyst deactivation mechanisms by poisoning has been described to be via: (i) a strongly adsorbed atom blocking a few reactions sites, (ii) the atom modifying the electronic properties in neighbor atoms, (iii) possible changes in the surface structure, which in turn influences the activity of the surface sensitive reactions, (iv) the poison blocks access of absorbed reactants to each other, and (v) a prevention or slowing of the surface diffusion (Bartholomew, 2001).

Carbon deposition on Ni catalyst used in methanation or steam reforming takes place on the surface or in the pore mouths. Catalyst deactivation can be caused by the active site blockage, and/or a physical breakdown of the catalyst (Rostrup-Nielsen and Trimm, 1977).

The considered reactions for the production of carbon during the studied process are the Boudouard reaction and the methane thermolysis (Arkatova, 2010). These two reactions are considered to be the main source of carbon formation in the methanation of CO<sub>2</sub> and reforming of methane (Navarro et al., 2007). With methanation reaction temperatures of approx. 250 °C, the principal carbon source (and its deposition) during the methanation of CO<sub>2</sub>, is usually via the Boudouard reaction and not via the methane thermolysis (Arkatova, 2010). A full thermodynamic discussion of the assumed reactions was done by our research team and will be published soon. The reactions are catalyzed usually by nickel or ruthenium. High nickel concentrations are known to enhance carbon formation (Cunha et al., 2008).

## 2. Methods

### 2.1. Catalyst

Commercially available Ni catalyst on silica-alumina support delivered by ALFA AESAR was used as the methanation catalyst. The Ni used was 66% (w/w) to provoke carbon formation in shorter time. The catalyst was pelleted and sieved with two sieves (mesh opening sizes of 425 μm and 250 μm). The fraction obtained on the 250 μm sieve was chosen for the experiments.

### 2.2. Experimental setup

Simulated feed gases controlled by mass flow controllers were used in this study. The experimental setup is shown in Fig. 1. A

stoichiometric feed comprising 20% CO<sub>2</sub> and 80% H<sub>2</sub> was used at flow rates of 20 ml/min. To focus on the carbon formation from Boudouard reaction the natural CH<sub>4</sub> fraction of anaerobic derived biogas was neglected. The software Aspen plus was used to determine the necessary concentration of NH<sub>3</sub> in the saturator: since biogas is produced in aqueous phase it is delivered with 100% humidity from the digester and NH<sub>3</sub> concentrations of 200 ppm. It is state of the art in biogas facilities that the main water content is removed by cooling to ground temperature, i.e. the biogas is in equilibrium with liquid phase. It was found that an ammonia solution of 100 ppm in the hydrogen feed stream is suitable to reach the same concentrations as they appear under real biogas conditions after cooling to ground temperature. The H<sub>2</sub> stream was bypassed the saturator to avoid the solution of CO<sub>2</sub> in the liquid phase. In experiments where NH<sub>3</sub> was introduced into the feed stream the saturator was installed in the H<sub>2</sub> feed containing the NH<sub>3</sub> solution. The NH<sub>3</sub> solution was refreshed every 48 h to avoid appreciable changes in the concentration.

The experiments were carried out in a stainless steel reactor 4 mm in diameter. The reactor was heated by an electrical furnace and filled with 100 mg catalyst. The catalyst was held in place using glass wool, with a thermocouple affixed to the catalyst bed. The products were analyzed by GC using a HySep D column in combination with a FID and TC sensor. The catalyst was reduced under pure hydrogen atmosphere at 600 °C for 6 h. The conversion of hydrogen which was used to monitor the extent of catalyst deactivation, is defined as

$$x = 1 - \frac{\dot{n}_{\text{out}}^{\text{H}_2}}{\dot{n}_{\text{in}}^{\text{H}_2}} \quad (2)$$

To determine the amount of formed coke during the experiments temperature programmed oxidation (TPO) was used. For the TPO, a mixture of 5% O<sub>2</sub> in argon (Ar) was used with 5% of krypton (Kr) as internal standard at flow rates of 20 ml/min, and with a heating rate of 1 °C/min. The products were analyzed via mass spectroscopy. The signal *S* of detected CO<sub>2</sub> were standardized using the Kr signal *S*<sub>0</sub> as internal standard.

## 3. Results and discussion

### 3.1. Conversion and deactivation

In the control experimental “dry” case (i.e. with the feed stream devoid of any H<sub>2</sub>O or NH<sub>3</sub>), a continuous decrease in the conversion of H<sub>2</sub> from 6.5% to 5% was observed during the

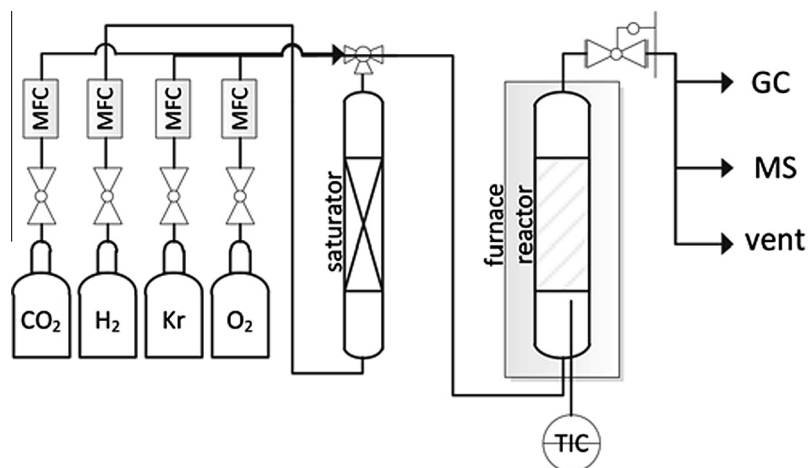


Fig. 1. Schematic representation of the experimental setup.

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