THE INFLUENCE OF SULPHUR DIOXIDE ON THE METHANATION ACTIVITY OF A NICKEL BASED CATALYST

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Abstract- Among the most promising applications of CO_2 is its catalytic fixation with hydrogen via the methanation reaction to form methane. In this work the theoretical foundations of the catalytic hydrogenation of carbon dioxide with hydrogen to methane, are described. The ability of a nickel based catalyst to catalyse methanation reaction in a laboratory apparatus was assessed. In order to test the effect of sulphur compounds a model gas mixture containing SO_2 at similar concentrations as flue gases from power plants was used.

Keywords- methanation, carbon dioxide, sulphur dioxide, catalyst

I. INTRODUCTION

Constant increase of carbon dioxide emissions from anthropogenic activities leads to the search of options for its recycling and utilization. A possible approach to the issue of CO_2 emissions from stationary sources such as power plants is carbon capture and sequestration (CCS) and its subsequent use as a feedstock material. Carbon dioxide is a nontoxic, non-flammable and abundant feedstock. For chemists, CO_2 is a very attractive C_1 building block in organic synthesis [1-3]. Recycled CO_2 as a carbon source for chemicals and fuels can be considered a sustainable feedstock. As a raw material its conversion into other products as a single reactant is difficult. Carbon dioxide reacts much easier when a co-reactant, such as H_2, is present. A very important catalytic process is the catalytic hydrogenation of CO_2 to methane, also known as the Sabatier reaction [1, 4].

Methanation of CO_2 has a variety of applications the two most notable being the purification of synthesis gas for ammonia production and the production of synthetic natural gas (SNG). NASA (The National Aeronautics and Space Administration) is also exceptionally interested in the application of CO_2 methanation for on-site production of life support consumables and propellants from Martian atmosphere [5]. Considering the increasing global fuel and energy demand, and the specifically recent global increase of natural gas demand [6, 7], methanation of CO_2 for SNG production is a very attractive application.

Methanation of CO_2, particularly when using as feedstock flue gas from power plants, faces a key issue since sulphur dioxide in the Czech Republic (depending on the) should not exceed levels of 400 - 2000 mg/m^3 [8]. Limit on sulphur content is not only an environmental issues but it can be a limitation during methanation since sulphur in the feed-gas acts as catalytic poison [9].

Given that the utilization of flue gas as feedstock for methanation can be a considered a sustainable use of resources this work is focused on the effect of SO_2 on the catalytic performance of a nickel based catalyst.

II. THEORY OF METHANATION

Catalytic methanation of CO and CO_2 to methane is an important catalytic process reported in 1902 by Sabatier and Sendersen. In equation (1) the reduction of CO_2 in the presence of H_2 is shown. Reportedly the reaction started at temperatures ranging from 190-230 ^oC and started to run smoothly at temperatures above 250 ^oC [4].

$$4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298\,K} = -165\ kJ\,mol^{-1} \quad (1)$$

The methanation reaction is reversible and exothermic ($\Delta H_{298\ K}$ = –165 kJ mol^{-1}). Even though the reaction is exothermic, some initial activation energy/heat is needed to start the reaction [11]. Given that a variety of metals and supports can be used as methanation catalysts the reaction temperatures vary. However it is established that CO_2 adsorbs dissociatively on nickel at temperatures from 25 ^oC and above [12].

Depending on the used catalyst methanation can be carried out at temperatures ranging from 100 to 450 ^oC [13-15].
Except reaction temperatures another factor that strongly influences methanation is H_2 to CO_2 ratio. Low ratio gives larger amount of high molecular mass products while when using a higher ratio more methane is produced. For better selectivity and higher methane yield is generally preferred to carry out the reaction at a H_2:CO_2 ratio of 3:1 up to 4:1 the latter being the stoichiometric ratio [16, 17].

III. METHANATION CATALYSTS

In the original work of Sabatier and Senderens was tested the hydrogenation of both CO and CO_2 over nickel at 250 ^oC. As a methanation catalyst nickel is preeminent; the metal is relatively cheap, it is very active having a high surface area and it is very selective to methane formation. Nickel is still one of the most widely used metals even though usually in supported form to prevent sintering. In addition the support can significantly influence the morphology of the active phase, its adsorption and its activity/selectivity, especially in well dispersed systems [18].

Among the most widely used support materials for nickel based catalysts are gamma-alumina (γ-Al_2O_3) and silicon dioxide (SiO_2) [12, 15, 19]. It should be noted that reportedly regardless of the support nickel has an increase on both CO_2 hydrogenation activity and CH_4 selectivity compared to unsupported nickel [18].

Cobalt, after nickel was the second successfully tested metal catalyst. Cobalt based catalysts have demonstrated good catalytic activity but always inferior to nickel based catalyst. Additionally the deposition of larger amounts of carbon on catalyst surface compared to when using nickel catalysts has been observed [20].

Deposition of surface carbon causes catalyst activity deactivation since it occupies some of the active sites required for reactant adsorption [21].

Certain noble metals such as ruthenium have been recognized even at the early stages of methanation as very active catalysts. However, initially the high cost of these materials mitigated against its wide use. Regardless of the high cost noble metals can compete with cheaper catalyst with qualities such as long catalytic life and high selectivity [21].

Among the most tested noble metals are ruthenium and rhodium based catalysts [22-25].

Ruthenium and its alloys show the highest activity, followed by rhodium. Platinum and palladium show considerably lower methanation activity [26]. The main drawback of almost all methanation catalysts including nickel based catalysts is that they are easily poisoned by sulphur compounds [9]. The only exception is molybdenum, which however reportedly forms at best only moderately active catalysts [27]. It is therefore important to investigate whether SO_2 in the concentration range present in flue gas from power plants deleterious for the activity of methanation catalysts.

IV. LABORATORY SETUP FOR METHANATION CATALYST TESTING

Catalysts test in a laboratory apparatus set up in UCT Prague designed to work at temperatures up to 500 ^oC and pressure up to 8 MPa, are carried out. The gas feed pressure ranging from 0.6 to 8 MPa flow up to 10 l/min (100 kPa; 25 ^oC), is regulated as needed. The manometers are placed before and after a control needle valve. At all individual sections of the apparatus are situated ball valves that enable rapid depressurization of the corresponding parts.

Gas flow is regulated by a needle valve, which is placed at the end of the gas flow train. Gas pressure regulation is carried out with a pressure regulator (Bronkhorst, High-Tech, B.V.). The gas feed is maintained at an overpressure of 2 MPa. Flow measurements are made via a Bronkhorst thermal mass flow meter, set to work at flows in the range of 0-10 l/min (100 kPa; 25 ^oC). Gas feed preheating, in order to prepare for the methanation reaction, is carried out in a tubular preheater placed in an oven. After being preheated the gas feed goes to a tubular reactor where methanation reaction takes place.

Gas produced from the methanation reactor is further cooled to condense out the water generated during the methanation reaction. The produced gas is cooled in a pressure vessel situated in a water bath set at -2 ^oC. In the final step, is determined the final concentration of methane, carbon dioxide and hydrogen sulphide, via GC-FID/TCD and GC-SCD. Laboratory apparatus scheme configuration is depicted in Figure 1.

In order to test the methanation activity of the catalysts test using a gas cylinder mixture consisting of 80 mole % H_2 and 20 mole % CO_2 gas feed on a commercially available nickel based catalyst, are performed. Catalyst composition was determined via X-ray fluorescence (XRF) analysis. Total catalyst quantity in the reactor was 100 g. Gas feed flow is set at 8 l/min (100 kPa; 25 ^oC) and the whole apparatus is under 2 MPa overpressure. Methanation at an initial temperature of 320 ^oC and subsequently at gradually lower temperatures until reaching 110 °C, was carried out. Produced gas samples are sampled and subsequently analysed every (approximately) 20 ^oC. Afterwards tests under the same operating conditions but with gas feed containing SO_2 were carried out. The gas feed containing SO_2 had the following composition: 20 mole % CO_2, 0.05 mole % SO_2 the rest H_2. The gas feed was chosen to be similar to flue gas from power stations after desulphurization. XRF analysis of the catalyst after sulfonating was performed.

V. RESULTS AND DISCUSSION

X-ray fluorescence analysis of the nickel based catalyst showed that its major components were 63.5 wt. % NiO and 20 wt. % SiO_2 and no sulphur content. Methane and carbon dioxide concentrations in the gas produced during methanation of the gas feed 80 mole % H_2 and 20 mole % CO_2 on the nickel based catalysts are depicted in Fig 2.

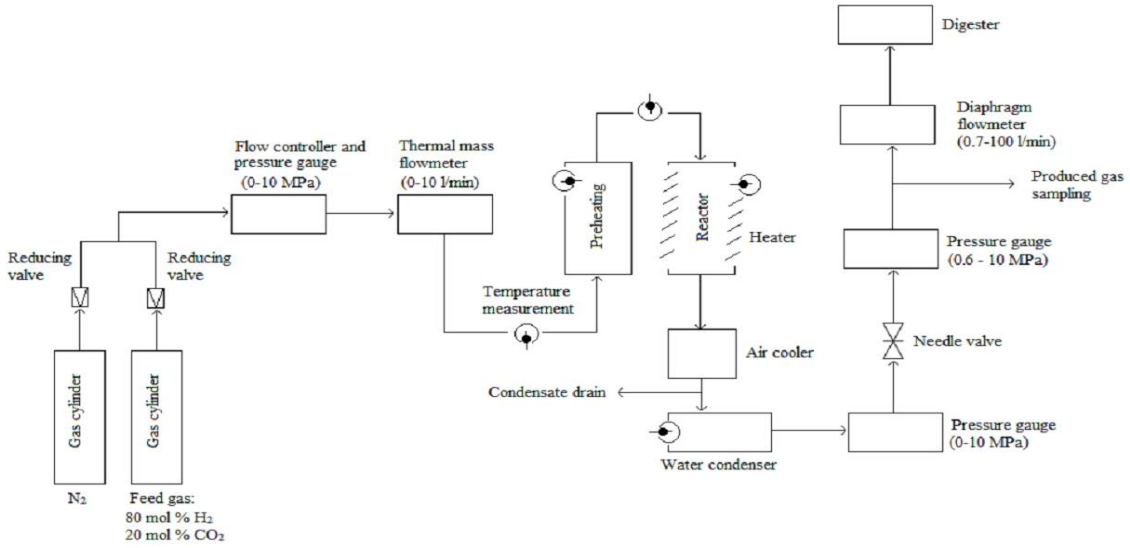


Figure 1. Laboratory apparatus for CO_2 and H_2 methanation

Under similar reaction conditions the same analysis when using the model mixture of flue gases consisting of 20 mole % CO_2, 0.05 mole % SO_2 was performed. As it can be observed the methanation rates strongly decreases reaching very quickly catalyst deactivation and therefore zero methane production. In this case the measurement continued until it was confirmed that CH_4 levels were indeed zero i.e. until 200 ^oC. Except methane and carbon dioxide in the produced gas hydrogen sulphide content was as well determined. Hydrogen sulphide was present in the produced gas since SO_2 in the presence of H_2 reacts to form it. In equation (2) the reaction is depicted.

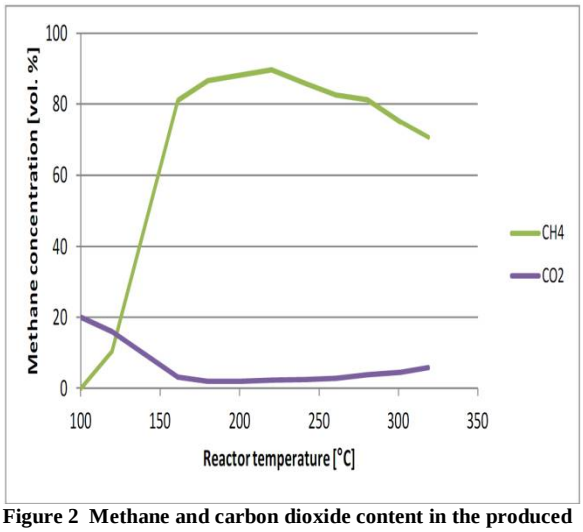


Figure 2 Methane and carbon dioxide content in the produced gas at different reaction temperatures for feed gas 20 vol. % CO_2 and 80 vol. % H_2.

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \qquad (2)$$

In figure 3 methane and carbon dioxide content are depicted. In figure 4 H_2S concentration in the temperature range 200 to 320 ^oC is depicted.

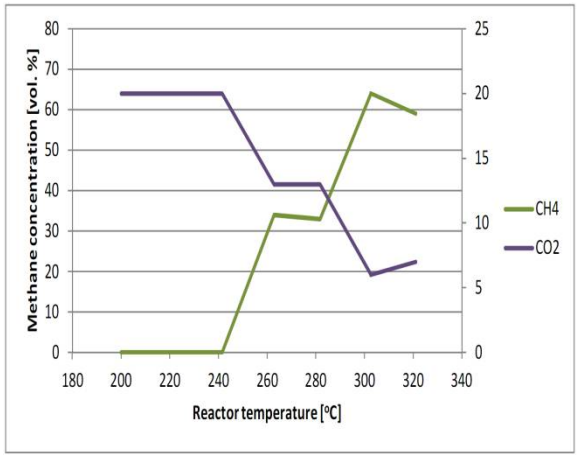


Figure 3 Methane and carbon dioxide content in the produced gas at different reaction temperatures for feed gas 20 vol. % CO_2, 0.05 vol. % SO_2 the rest H_2.Figure 4 Hydrogen sulphide content in the produced gas

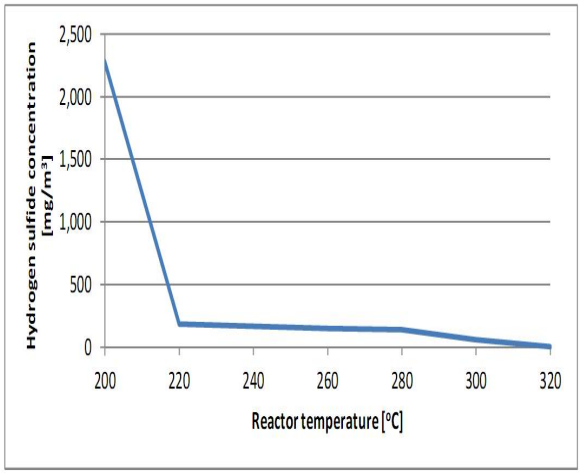


Figure 4 Hydrogen sulphide content in the produced gas

After measurements with feed gas containing SO_2 XRF analysis of the catalyst was again carried out. It was observed a substantial increase of the sulphur content reaching 15.5 wt. %.

CONCLUSIONS

Carbon dioxide and hydrogen methanation on a nickel based catalyst under laboratory conditions were performed. The gas feed consisted of 80 mole % H_2 and 20 mole % CO_2. The reaction was carried out at 2 MPa overpressure, and temperature ranging from 110 °C to 320 °C. The highest CO_2 conversion rate producing 90 vol. % CH_4 was reached at 220 ^oC. A notable decrease on catalytic activity was observed when using flue gas model mixture consisting of 20 mole % CO_2, 0.05 mole % SO_2 the rest H_2. The highest methane content in the produced gas was 64 vol. % at 300 ^oC. Afterward a rapid decrease on CH_4 formation was observed reaching zero conversion at 240 ^oC. Hydrogen sulphide in the produce gas increased during the experiment reaching its maximum of 2 277 mg/m^3 at 200 ^oC.

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