HYDROGEN PRODUCTION VIA WATER GAS SHIFT REACTION ON A NICKEL BASED CATALYST

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In this paper the fundaments of the water gas shift reaction (WGSR) were described. An overview of the most commonly used catalysts for industrial applications as well as catalysts that are being developed are discussed. The main focus of this work was to perform catalytic activity tests for the WGSR in a laboratory apparatus. The tested catalyst was a nickel-based catalyst. Tests were performed using feed gas consisting of 50 mole % carbon dioxide and the balance nitrogen. Catalytic tests proved that the selected nickel-based catalyst was active for the WGSR. However, it was observed that methanation side reaction also took place.

Keywords: WGS; catalyst; hydrogen; carbon monoxide; nickel

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1. Introduction

The water gas shift reaction (WGSR) was discovered in 1780 by the Italian scientist Felice Fontana [1]. In the first published reports the process was described as a way of obtaining clean hydrogen from hydrogen containing gas contaminated with carbon monoxide and hydrocarbons. The gas mixture and excess steam were lead over pumice stone impregnated with nickel or cobalt at temperatures between 350 and 450 °C [2]. However, WGSR found its first industrial application only in 1913 as part of the Haber-Bosch process of ammonia manufacture. After several attempts to obtain clean H_2, including water electrolysis, it was soon realized that the most economically feasible process on such a large scale as ammonia production was the WGSR [3]. The process was perfected in 1915 by converting CO to CO_2 with steam over iron-chromium catalysts. Carbon dioxide was removed from the gas mixture via scrubbing [4].

Hydrogen demand is increasing and is expected to continue rising in its use as a fuel or as feedstock for the chemical and petrochemical industry. The most notable uses of hydrogen are ammonia production (and subsequent fertilizers production) and the processing of crude oil into fuels and high quality chemical products. Additionally, hydrogen is extensively used in metal and glass industry, electronic and food industry [5]. Nowadays hydrogen is becoming an interesting energy carrier as fuel and eventually as a possible substitute in the future to fossil fuels. Currently, can be observed increasing interest in the utilization of hydrogen for fuel cell applications. Moreover it is also anticipated that renewed interest in the Fischer-Tropsch technology will further enhance the demand for hydrogen. Therefore it is crucial to expand current hydrogen production capacity [6].

1.1. Fundaments of the water gas shift reaction

The WGSR is a reversible exothermic reaction between carbon monoxide and water steam to from carbon dioxide and hydrogen, as depicted in Eq. (1) [7].

$$H_2O(g) + CO(g) \leftrightarrow CO_2(g) + H_2(g) \qquad \Delta H_{298} = -40.6\ kJ/mol \qquad (1)$$

The WGS reaction is a catalytic, equilibrium controlled chemical reaction. Since WGSR proceeds without change in the number of moles, pressure does not affect equilibrium. However, up to the equilibrium moment total pressure can positively affect CO conversion since it increases the reaction rate [8].

Reaction equilibrium is mostly a function of temperature. Taking into consideration that WGSR is a mildly exothermic reaction, in order to increase H_2 production and reduce CO content the reaction should be conducted at lower temperatures. However, certain catalysts are not active at lower temperatures. Moreover, often to achieve the required reaction rate higher temperatures are required. Therefore, WGSR is conducted industrially in two stage catalytic converter. The first, high temperature (HT), stage operates at temperatures ranging from 320 to 450 °C. High temperatures favour fast CO conversion. The second stage, low temperature (LT), operates at temperatures ranging from 150 to 250 °C [8-11].

1.2. Catalysts for the water gas shift reaction

A variety of catalysts is capable to catalyse WGSR. The catalyst of choice can differ depending on reaction temperature. The WGSR is readily catalysed by both metal and metal oxides [11]. For industrial applications the WGSR catalysts are divided into two main classes: Fe-based and Cu-based used for HT and LT conversion, respectively [9].

The HT – WGSR is typically carried out using an iron oxide catalyst structurally promoted with chromium oxide. Typical catalyst used in industrial applications contain about 8 wt % Cr_2O_3 (chromia). The active phase of the catalyst is Fe_3O_4 (magnetite). The presence of chromia prolongs the catalysts effective lifetime by stabilizing the material and preventing sintering

[12, 13]. Except catalyst stabilization it is believed that chromia, to a lower extent than magnetite, can also catalyse the reaction [14].

The LT – WGSR enhances the process by allowing a higher CO conversion and yields in H_2 production. Industrially the catalyst used in this phase is a mixture of copper and zinc oxide. Quite often Al_2O_3 (alumina) serves as a support. The catalysts are unstable at high temperature conditions due to Cu sintering. Thus operation temperatures should not exceed 300 °C [15, 16].

Conventionally used catalysts have their advantages and disadvantages. For instance Fe-based catalysts have the advantage of being cheap and stable but the need of high temperatures is their major limitation. On the other hand, Cu-based catalysts have good activity at lower temperatures but are more susceptible to poisoning (due to the presence of sulphur and chlorine compounds) and operate in a limited temperature range due to sintering [6, 8]. Therefore research on catalysts that have higher activity at lower temperatures and improved stability is crucial. Various metals such as cobalt, molybdenum, gold, platinum, rhodium and palladium are being tested [17-22].

In recent years, Au and Pt-based catalysts have received extended attention since they show very high activity at low temperatures and potential stability in oxidizing atmospheres [9]. It is still difficult to establish which metal shows better catalytic activity since most available data are presented for very specific experimental conditions. Platinum based catalysts have received much attention and have been applied for single stage WGS reaction. The support plays an important role especially in single stage WGS. Some of the most commonly used supports for Pt-based catalysts are ceria and zirconia [21, 23]. However it has been pointed out that a well prepared and properly activated Au based catalyst can be at least as active as a Pt-based catalyst [24].

Except having good activity catalysts should also be financially feasible. Nickel is one of the most widely used metals as catalyst since it has a high surface area and is relatively cheap [25]. Taking into account costs and also the need to develop new catalysts that operate at intermediate temperatures nickel based catalysts have been receiving attention [26, 27]. Moreover in bimetallic catalysts the presence of nickel has positively affected catalyst activity in the temperature range 100 to 240 °C [28].

2. Experimental

2.1. Laboratory apparatus for catalytic activity measurements

A commercial nickel based catalyst was tested in a laboratory apparatus set up in UCT Prague designed to work at temperatures up to 500 ºC, pressure up to 8 MPa. For WGSR catalyst testing a model gas mixture containing 50 mole % CO and 50 mole % N_2. The gas feed pressure ranging from 0.6 to 8 MPa was controlled via an electronic pressure regulator (Bronkhorst High-Tech B.V., Netherlands). Flow measurements and regulation up to 10 $l \cdot min^{-1}$ (100 kPa; 25 ºC), were performed via a thermal mass flowmeter (Bronkhorst High-Tech B.V., Netherlands). Manometers were placed upstream and downstream a control needle valve. At all individual sections of the apparatus ball valves were situated that enabled rapid depressurization of the corresponding parts.

Gas feed preheating, in order to prepare for the WGSR, was carried out in a tubular preheater placed in an oven equipped with a temperature regulator CLARE 4.0 (Clasic CZ s.r.o., Czech Republic). The preheater was 80 cm long and had a diameter of 3.5 cm making for a total volume of 0.77 dm^3. Distilled water, in order to obtain water vapour, was injected via a capillary in the preheater. The preheated gas mixture afterwards flowed to the WGSR reactor. The reactor was a 15 cm long tubular reactor, with a diameter of 3 cm, wall thickness of 4 mm making for a total volume of 106 ml. The reactor was wrapped with a heating wire and was situated inside two stainless steel protective tubes. One of the protective tubes was 18.5 cm long, had a diameter of 10.8 cm and wall thickness of 3 mm. The other protective tube was 18.5 cm long, had a diameter of 11.4 cm and wall thickness of 3 mm.

The produced gas was cooled in a pressure vessel of a total volume of 0.55 dm^3 situated in a water bath F32ME (Julabo GmbH, Germany) set at -2 °C. Excess material condensed in the pressure vessel. In the final part of the apparatus, sampling of produced gas was performed. The scheme of laboratory apparatus is depicted in **Fig. 1**.

2.2. Catalytic activity measurement

In the reactor was placed 100 g of nickel based catalyst. Feed gas flow was set at approximately 8 $l \cdot min^{-1}$ (100 kPa; 25 ºC). During all experiments the whole apparatus was at pressure. Catalyst activity tests were performed for pressure 0.5, 2, 4 and 6 MPa. Initially the apparatus was heated at 470 °C using ultra clean N_2. Once the desired temperature was reached feed gas was switched to the model gas mixture consisting of 50 mole % CO and 50 mole % N_2. At this point apparatus pressure was regulated to the desired pressure (0.5, 2, 4 or 6 MPa). Once pressure was reached water was pumped into the preheater. Water flow was maintained constant at 3.5 $l \cdot min^{-1}$. The WGSR took place at an initial temperature of 470 °C. Subsequently the reaction took place at gradually lower temperature until reaching 150 °C or zero CO conversion. Produced gas was sampled and analysed approximately every 20 °C. During every sampling interval, excess water condensate was pumped out from the pressure vessel.

2.3. Catalyst characterization

Elemental analysis was performed via X-ray fluorescence (XRF) on a Spectrometer ARL 9400 XP (Thermo Fischer Scientific Inc., USA). Data analysis via the software Winxrf, was carried out.

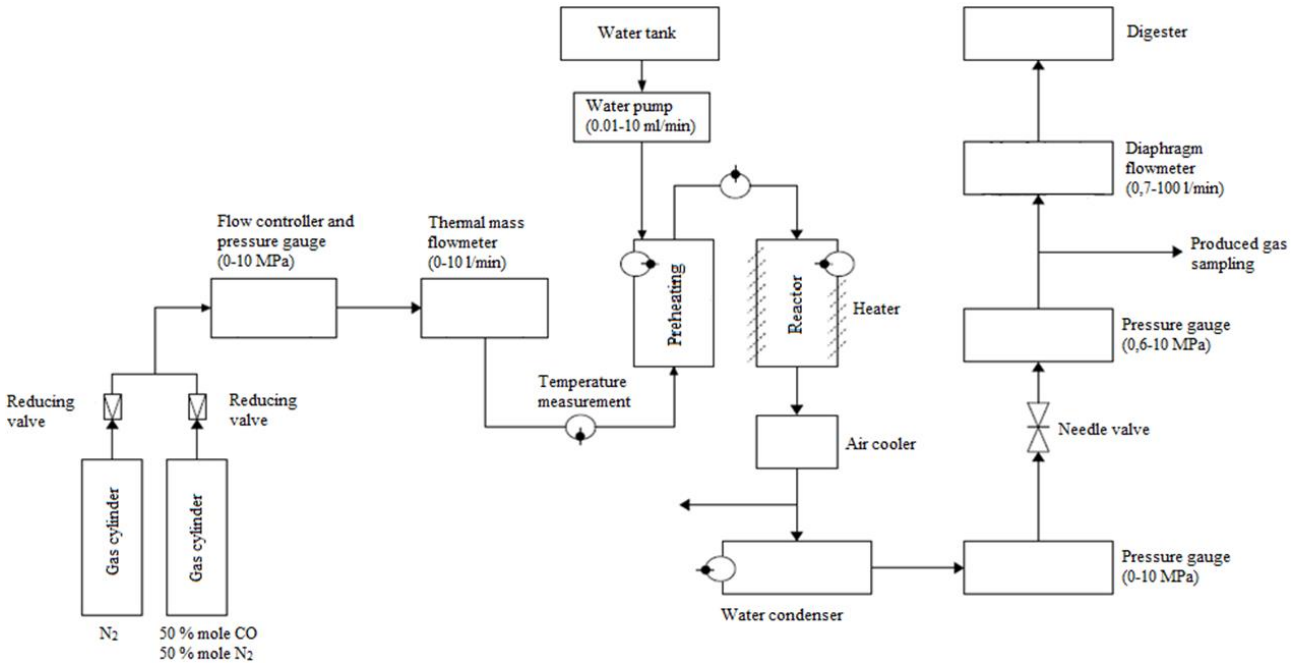

Fig. 1 Laboratory apparatus for the WGSR

Surface area and total pore volume were measured by N_2 adsorption and desorption isotherms at -196 °C using a COULTER SA3100 instrument (Beckman Coulter Inc. USA). Samples were degassed at 13 Pa and 150 °C. Surface area was determined based on BET (Brunauer–Emmett–Teller) isotherm measurement. Pore size distribution was calculated based on the BJH (Barrett-Joyner-Halenda) model.

2.4. Product analysis

Gaseous products were analysed via a gas chromatograph (GC) Agilent HP 6890 (Agilent Technologies, USA) coupled with a standard flame ionization detector (FID) and a standard thermal conductivity detector (TCD). The GC was fitted with two independent channels in order to make possible the analysis of both organic and inorganic gaseous products in the produced gas. The FID channel permitted the determination of the organic products while the TCD channel permitted the determination of the inorganic products. Since H_2 was one of the compounds of interest, He was chosen as mobile phase.

3. Results and discusions

3.1. Catalyst characterization

X-ray fluorescence

X-ray fluorescence analysis of the nickel based catalyst before tests showed that its major component was Ni. Catalyst support was SiO_2. Nickel content in the catalyst was 74.07 wt % while SiO_2 content was 25.93 wt. %.

BET analysis and pore size distribution

Catalyst surface area based on BET analysis was 195.24 $m^2 \cdot g^{-1}$. Catalyst total pore volume was 0.3256 $ml \cdot g^{-1}$. Acording to BET theory the adsorption isotherm was type II [29].

Gaseous product analysis

After GC-FID/TCD analysis of produced gas was established that the WGSR reaction took place in the presence of the nickel based catalyst. Thus the catalyst proved to be active for the WGSR under the described experimental conditions. However except hydrogen and carbon dioxide it was observed that a major component of the produced gas was methane at all applied pressures. The presence of methane indicated that the chosen nickel based catalyst had catalytic activity also for the methanation reaction. In **Fig. 2** - **Fig. 5** the produced gas compositions for each individual pressure are depicted.

The highest CO_2 content in produced gas, indicating the highest CO conversion rate, was 41.33 mole %. This CO_2 content was achieved under 4MPa pressure and temperature 433 °C experimental conditions. However, the highest hydrogen content in the produced gas of 12.1 mole % was observed at 0.5 MPa pressure and temperature 485 °C. The highest methane content in the produced gas of over 12 mole % was observed at 4 MPa pressure and in the temperature range from 210 to 360 °C. Similar results were also observed for 6 MPa pressure in the temperature range from 260 to 360 °C.

From the acquired data it was confirmed that elevated pressure does not positively influence the WGSR.

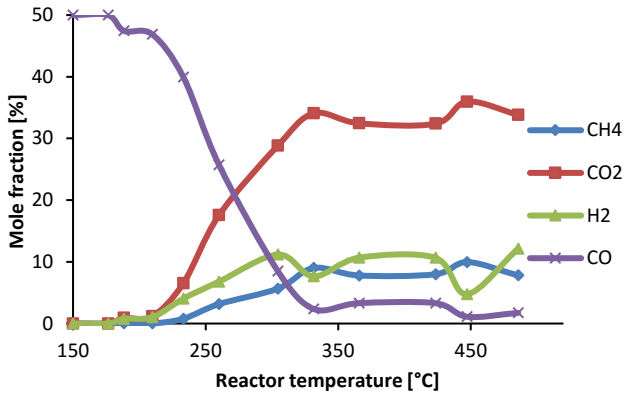

Fig. 2 Produced gas composition at pressure 0.5 MPa.

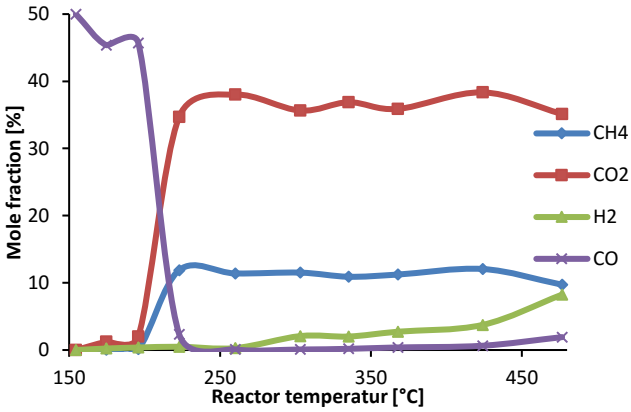

Fig. 3 Produced gas composition at pressure 2 MPa.

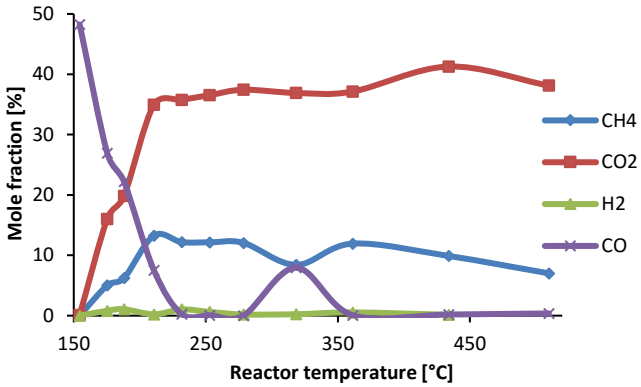

Fig. 4 Produced gas composition at pressure 4 MPa.

On the contrary low hydrogen content along with high methane content at elevated pressure indicated that higher pressure had a positive effect on the methanation reaction. The fact that produced gas composition at 4 and 6 MPa was quite similar indicates that after certain values pressure does no longer play a substantial role for neither WGSR nor methanation reaction.

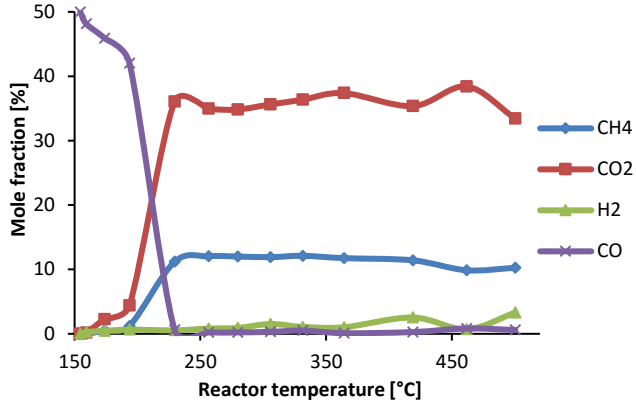

Fig. 5 Produced gas composition at pressure 6 MPa.

4. Conclusions

The selected commercial nickel based catalyst proved to be active for the WGSR reaction under the applied laboratory experimental conditions. Experiments were performed using a model gas mixture consisting of 50 mole % CO and 50 mole % N_2. Tests were performed at 0.5, 2, 4 and 5 MPa pressure and in the temperature range 150 - 470 °C. During the course of the experiments it was observed that in the produced gas was also present methane indicating that the catalyst was active also for the methanation reaction.

The highest conversion rate of CO to CO_2 was 83 % and was reached at 4 MPa pressure and temperature 433 °C. The highest H_2 content of 12.1 mole % was at 0.5 MPa pressure and temperature 485 °C. The highest methane content in the produced gas of over 12 mole % was observed at 4 MPa pressure and in the temperature range from 210 to 360 °C. Similar results were also observed for 6 MPa pressure in the temperature range from 260 to 360 °C.

The acquired data indicated that the produced hydrogen via WGSR immediately reacts with either carbon monoxide or carbon dioxide to form methane. Taking into consideration that elevated pressure positively affects methanation it is only natural that the highest methane content in the produced gas was observed at pressure 4 and 6 MPa.

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