Advanced Catalysts for the Water Gas Shift Reaction

Erlisa Baraj, Karel Ciahotný and Tomáš Hlinčík *

Department of Gaseous and Solid Fuels and Air Protection, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic; erlisabaraj@gmail.com (E.B.); karel.ciahotny@vscht.cz (K.C.)

* Correspondence: tomas.hlinick@vscht.cz; Tel.: +420-220-444-073

Abstract: The WGS reaction is an exothermic reaction between carbon monoxide and steam to form carbon dioxide and hydrogen. This reaction, which has been used industrially for more than 100 years, has recently received a great deal of attention from researchers as one of the ways to produce environmentally acceptable hydrogen from fossil fuels in large quantities. For the application of this reaction on an industrial scale, the key is choosing the optimal catalysts that can ensure high CO conversion and have a long lifetime under industrial conditions. Therefore, new types of catalysts are being developed that meet these requirements better than the Fe- and Cu-based catalysts commonly used in the past. The WGSR on a commercial nickel-based catalyst and a laboratory-prepared copper- and cobalt-based catalyst was tested in a laboratory apparatus set up at the University of Chemistry and Technology Prague. The best performance of the laboratory-prepared catalyst was observed for the catalyst with a Cu content of 14.8 wt% and activated in a hydrogen atmosphere. The laboratory-prepared Co-based catalyst showed good WGSR activity in the temperature range of 200–450 °C, although this was always inferior to that of the Cu-based catalyst. When subjected to the feed gas containing 0.4 mole% \( \text{H}_2\text{S} \), the Co-based catalyst showed good resistance to sulphur poisoning. Therefore, Co-based catalysts can be considered good sulphur-tolerant intermediate temperature WGSR catalysts.

Keywords: WGSR; catalyst; carbon monoxide; hydrogen

1. Introduction

The WGS reaction is a moderately exothermic reaction between carbon monoxide and steam to form carbon dioxide and hydrogen and is often used to remove carbon monoxide from the synthesis gas to obtain high-purity hydrogen. The WGS reaction is shown in Equation (1) [1,2].

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ = -40.6 \text{ kJ mol}^{-1}
\]

(1)

In commercial applications, the process takes place in two steps to achieve the level of purity needed for various industrial applications. The first step, a high-temperature WGS (320–450 °C), takes place over iron-based catalysts. Higher temperatures increase the reaction rate favouring CO consumption and minimise the catalyst bed volume. The second step, a low-temperature WGS (150–280 °C), takes place over copper-based catalysts. Lower temperatures are necessary to achieve the minimum unconverted CO content, and hence the higher conversion [1,3–8]. It should be noted that the steam to carbon monoxide ratio (R) in the feed is a crucial factor that influences the WGS rate. For better performance, a steam to CO ratio of 3 to 4 is suggested [7,9].

A great deal of research is being conducted on the development of advanced catalysts. A detailed overview of research activities carried out in the field is given in our publication [9]. However, for large-scale applications, the metals present in classical industrial catalysts are to date the most efficient in terms of overall activity and costs [10–13]. Another important parameter of catalysts used in operational applications is their resistance to catalytic poisons, especially against sulphur compounds, which are often present as part of
converted gas mixtures. Monitoring the effect of catalytic poisons on individual catalysts is an important part of the experimental tests performed.

The study of catalysts for the low-temperature WGSR in a laboratory-built unit is described in this work. The main focus is to determine how different parameters such as catalyst preparation (calcination temperature, active metal content, activation) and reaction conditions (pressure, temperature, feed gas flow, feed gas composition) influence catalytic activity. Three types of catalysts were tested—a commercial Ni-based catalyst, laboratory-prepared Cu-based catalysts, and Co-based catalysts. The optimal catalyst preparation procedure in laboratory conditions was defined with the Cu-based catalyst and was subsequently applied during the preparation of the Co-based catalyst. These three catalysts were selected for experimental testing because the Ni-based catalyst is from the group of low-temperature catalysts, while the Cu- and Co-based catalysts are representatives of high-temperature catalysts. Most industrial WGS reactors use a combination of high-temperature and low-temperature types of catalysts. This ensures that a high degree of conversion of reactants to the desired products is achieved with acceptable catalyst reactor sizes. At high reaction temperatures, a high degree of conversion cannot be achieved for thermodynamic reasons, because with increasing temperature, the equilibrium shifts in favour of the reactants.

This work was created as part of a larger project aimed at developing precombustion technology of the coal used in H₂ production. The technological chain presupposes the gasification of coal, the purification of the produced gas, the conversion of CO using WGSR into gas containing hydrogen and CO₂, and its subsequent removal from the gas.

The aim of the research was to compare the efficiency of Cu and Co catalysts prepared in the laboratory with a commercially produced Ni-based catalyst, to compare the optimal working conditions and performance of all catalysts, and to determine their sensitivity to the presence of sulphur compounds in the gas.

2. Catalysts for the WGSR

Many materials are able to catalyse WGSR. For industrial applications, currently two classes of materials are mainly used: the HT iron-based catalyst and the LT copper-based catalyst. Most industrial HT Fe-based catalysts also contain Cr.

Attempts to decrease the cost of hydrogen purification through WGSR have led to the search for catalysts that are capable of performing WGSR in just one step at intermediate temperatures [10]. The broad utilisation of nickel in syngas-related reactions amongst which CO removal belongs possesses potential in its possible applications as a WGSR catalyst.

The utilisation of sulphur-containing syngas from coal and oil gasification processes has placed a great focus on the development of sulphur-tolerant WGS catalysts. The iron-based catalyst can tolerate small amounts of sulphur, but the high sulphur content found in syngas would quickly decrease the activity of the catalyst [4]. Moreover, Cu-based catalysts cannot tolerate even very low levels of sulphur. Therefore, a highly selective sulphur-tolerant catalyst for the WGS reaction would be desirable [10]. Since 1970, a series of patents on cobalt oxide/molybdenum oxide/caesium acetate supported on alumina has been filed. A major drawback of a sulphided CoMo catalyst for commercial applications is that the catalyst activity depends on hydrogen sulphide content. This means that most sulphided CoMo catalysts exhibit better catalytic performance in the presence of sulphur [4,14]. Cobalt-based catalysts have been investigated [14–16] as potential sulphur-tolerant but not sulphur-dependent WGS catalysts. A detailed description of the catalysts used for WGSR and the reaction mechanisms can be found in the work of Baraj et al. [9].

Sulphur-Resistant Catalysts for the WGS Reaction

Sulphur poisoning is one of the three main causes of WGSR catalyst deactivation [16]. For the industrial production of hydrogen through gasification of fossil fuels and the subsequent conversion of CO to CO₂ using WGSR, catalysts resistant to sulphur compounds are particularly suitable, since gas produced by gasification of fossil fuels usually also
contains H$_2$S. Therefore, our research activities focused on the development of new types of catalysts that would be able to tolerate a certain amount of sulphur compounds in the gas used for the WGSR in the long term.

Catalysts based on Cu and Co were prepared under laboratory conditions and tested along with an industrial Ni-based catalyst on a laboratory apparatus for the WGSR using three different gas mixtures, one of which also contained higher concentrations of H$_2$S. During the tests performed, the catalytic activity of the catalysts was monitored depending on the reaction conditions and the H$_2$S content in the gas.

3. Experiments

3.1. Laboratory Apparatus

All catalytic tests were carried out on a laboratory apparatus set up at the University of Chemistry and Technology (UCT) Prague, Figure 1. The apparatus was designed to work at temperatures up to 500 °C and pressures up to 8 MPa. All individual parts of the apparatus were connected by 6 mm stainless steel Swagelok tubes. Individual measuring and regulating elements were controlled by a digital programmable unit connected by RS 232 to a computer.

![Figure 1. Scheme of the laboratory apparatus used for catalytic testing of the WGSR.](image)

The gas feed pressure ranging from 0.5 to 8 MPa was controlled using an electronic pressure regulator (Bronkhorst High-Tech BV, Ruurlo, Netherlands). The gas feed flow, up to 10 L/min (100 kPa; 25 °C), measurement, and regulation were carried out using a thermal mass flow meter (Bronkhorst High-Tech BV, Ruurlo, Netherlands). To keep the pressure under control, two pressure gauges were placed before and after the regulating needle valve. At individual sections of the apparatus, ball valves that enabled rapid depressurisation were placed. The flow of the feed gas was regulated with the help of the needle valve located at the end. The gas flow produced that exited the apparatus was controlled by a G4 diaphragm flow meter supplied by the company Actaris.

To prepare for the WGSR, gas feed preheating was carried out in a tubular preheater placed in an oven equipped with a CLARE 4.0 temperature controller (Classic CZ, Ltd., Řevnice, Czech republic). The preheater was 80 cm long and had a diameter of 3.5 cm, making for a total volume of 77 mL. To obtain water vapour, distilled water was injected
into the preheater through a capillary connected to a KAPPA 10 piston pump (ECOM Ltd., Chrastany u Prahy, Czech republic). The preheated gas mixture was directed to the WGSR reactor, where the reaction took place. To monitor the apparatus temperature, thermocouples were placed before the preheater, in the preheater, between the preheater and the reactor, in the reactor, and in the water condenser vessel.

The reactor was a 15 cm long tubular reactor, with a diameter of 3 cm and a wall thickness of 4 mm, which makes a total volume of 106 mL. The reactor was located inside two protective stainless steel tubes. One of the tubes was 18.5 cm long, with a diameter of 10.8 cm and a wall thickness of 3 mm. The other protective tube was 18.5 cm long, with a diameter of 11.4 cm and a wall thickness of 3 mm. Additional reactor heating was possible with the help of a heat gun capable of heating up to 630 °C.

The gas produced was cooled in a condenser pressure vessel with a total volume of 0.55 dm$^3$ located in a F32ME water bath (Julabo GmbH, Seelbach, Germany) set at −2 °C. The water bath contained water mixed with antifreeze. The pressure vessel had a draining valve whose opening allowed condensate water to drain when the apparatus was under pressure. In the water draining apparatus, pressure was carefully controlled and never decreased to more than 50% of the initial pressure value. In the final part of the apparatus, sampling of the produced gas was performed.

### 3.2. Selected Catalyst and Catalyst Preparation

The first tested catalyst was a commercial nickel-based catalyst (BASF, Ludwigshafen, Germany). Later on, using the impregnation method, two types of catalysts, copper- and cobalt-based catalysts, were prepared and tested. Wet impregnation, a well-known procedure, was chosen for catalyst preparation.

All laboratory-prepared catalysts were impregnated over $\gamma$-Al$_2$O$_3$. This transition alumina is usually obtained by the calcination of aluminium hydroxides and oxyhydroxides. Depending on the calcination temperature, different metastable phases of Al$_2$O$_3$ can be obtained, as shown in Equation (2). Gamma alumina is reportedly formed from boehmite at temperatures between 350 and 800 °C [17,18]. At higher temperatures, the surface area decreases significantly due to the phase transformation from $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ [19].

$$\text{boehmite} \rightarrow \gamma\text{-Al}_2\text{O}_3 \rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$$

(2)

As a raw material for the preparation of support for all catalysts, boehmite (AlO(OH)) was chosen. Boehmite was in the form of pellets with dimensions $6 \times 4$ mm. The specific surface area was around 280 m$^2$/g and the total pore volume was 0.43 mL/g. The pores distribution was 85% of the total pore volume below 6 nm. The most important step was to determine the optimal support calcination temperature without causing great loss of specific surface area. Different calcination temperature ranges were tested to obtain a support that would not have a decrease in surface area of more than 20% and loss of pores below 6 nm. The tested supports included the non-calcined support (labelled support “1”) and supports calcined at 400, 500, 600, 700, and 800 °C (labelled supports “2–6”). Calcination at all temperatures was performed for 4 h in a muffle furnace in air atmosphere.

For comparative purposes, the Cu-based catalyst was impregnated on not-calcined and calcined boehmite. The Co-based catalysts were prepared using only calcined boehmite based on the experimental results acquired with Cu-based catalysts prepared with calcined and non-calcined support.

### 3.2.1. Copper-Based Catalyst

Calcined boehmite (that is transformed in the active $\gamma$-Al$_2$O$_3$ form) was used for the preparation of Cu/$\gamma$-Al$_2$O$_3$ catalysts. The Cu/$\gamma$-Al$_2$O$_3$ catalysts were prepared using a 20 wt% solution of copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O). The solution was heated to 70 °C with continuous mixing at a speed of 400 rpm. Once the temperature was stabilised, the support was submerged into the solution and continuous mixing was reduced at 350 rpm. The support was left in the heated solution for 90 min. Subsequently,
the catalyst was filtered with the help of a Büchner funnel at atmospheric pressure. After filtration, the catalyst was left to dry overnight at 105 °C. Finally, the catalyst was calcined at 500 °C. The applied temperature gradient was 15 °C/min. The calcination temperature was then kept constant for a total calcination time of 4 h. Afterwards, the catalyst was cooled in a desiccator. The same impregnation procedure was applied when using both the calcined and non-calcined support.

3.2.2. Cobalt-Based Catalyst

For the preparation of Co/γ-Al₂O₃ catalysts, only calcined boehmite was used, that is, transformed in the active γ-Al₂O₃ form. Only single impregnation catalysts were prepared using a 20 wt% solution of cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O). The preparation procedure was the same as described for the copper catalyst.

3.3. Catalyst Characterisation

All commercial and laboratory-prepared supports and catalysts were characterised in terms of elemental composition, surface area, and pore distribution before and after catalytic tests.

3.3.1. X-ray Fluorescence Spectroscopy

The chemical composition of the catalyst was determined via X-ray fluorescence (XRF) using an ARL 9400 XP spectrometer (Thermo Fischer Scientific, Inc., Waltham, USA). Data analysis was processed using Winxrf software, version 3. All results presented in this work from XRF analysis are not normalised.

3.3.2. Specific Surface Area and Pore Volume

Surface area and total pore volume were measured by N₂ adsorption and desorption isotherms using a COULTER SA3100 instrument (Beckman Coulter, Inc., Brea, CA, USA). Both isotherms were determined at relative pressure in the range of 0–0.99 and with liquid nitrogen at temperature –196 °C. The measurements were evaluated on the basis of the shapes of the adsorption and desorption isotherms. For the region corresponding to the relative pressure 0.1–0.35, the amount of adsorbed nitrogen was evaluated based on the Brunauer–Emmet–Teller (BET) equation. From the obtained coefficient, the BET surface area of each catalyst was determined. The total pore volume was determined based on the quantity of adsorbed nitrogen at relative pressure near 1. The pores’ size distribution was calculated from the desorption isotherms based on the Barrett–Joyner–Halenda (BJH) model.

3.4. Catalytic Activity Tests

The experimental conditions applied in this work were designed to simplify laboratory apparatus testing in order to perform the maximum possible number of catalytic tests. In the reactor, 50 g of catalyst was always placed in a pellet or cylinder shape, which represents a bulk density ranging from 1.1 to 2.6 g/mL. To verify the influence of catalyst activation, selected catalysts were activated in a hydrogen flow for 3 h at 400 °C. During the course of each individual experiment, the apparatus was always pressurised. Catalyst activity tests were performed at pressures of 0.5, 2, 4, and 6 MPa. These pressure values were selected to assess the influence of pressure on selectivity toward the WGSR, and hence, hydrogen production. Initially, the apparatus was heated to just over 100 °C using ultraclean N₂. Once the desired temperature was reached, the feed gas was switched to the model gas mixture. The feed gas flow was established in the range of 1.5–6.0 L/min (100 kPa; 25 °C), which corresponded to a space velocity of approximately 3000–15,000 h⁻¹. Specific feed gas flow values will be given when discussing each individual experiment. The composition of the used model gas mixtures is depicted in Table 1. Model gas mixture 1 was chosen to determine catalyst behaviour under variable thermodynamic conditions regardless of the feed gas composition. Model gas mixture 2 was selected to determine the resistance of the
catalyst to sulphur poisoning once the optimal testing parameters were identified. Model gas mixture 3 was chosen to simulate the composition and sulphur content in real synthesis gases to assess how the catalyst behaves under real conditions. Due to safety concerns, up to 50 mole% N\textsubscript{2}, as an inert gas, was always present in the gaseous feed mixture. The use of N\textsubscript{2} feed gas is a common practice in research works to mitigate safety risks in laboratory environments [9,20]. Additionally, it is not uncommon in industrial applications for the feed gas to contain inert gases [21,22]. The hydrogen sulphide content in both gas mixtures 2 and 3 of 0.4 mole%, the equivalent of 5576 mg/m\textsuperscript{3}, is similar to the syngas produced from the gasification of brown coal.

Table 1. Model gas mixtures used during the catalytic tests.

| Compound | Model Gas Mixture 1 (mole%) | Model Gas Mixture 2 (mole%) | Model Gas Mixture 3 (mole%) |
|----------|-----------------------------|-----------------------------|-----------------------------|
| CO       | 50.0                        | 50.0                        | 50.0                        |
| CO\textsubscript{2} | -                           | -                           | 8                           |
| H\textsubscript{2}  | -                           | -                           | 34.0                        |
| H\textsubscript{2}S| -                           | 0.4                         | 0.4                         |
| N\textsubscript{2} | balance                     | balance                     | balance                     |

After switching to the model gas mixture, the apparatus pressure was regulated to the desired value (0.5, 2, 4, or 6 MPa). Once the pressure was reached, water was pumped into the preheater. The volume flow of water was calculated for a gas flow containing 50 mole% CO.

The water volume was calculated based on the highest feed gas flow of 6 L/min, making the CO flow 3 L/min (25 °C; 100 kPa). In the calculations, the value of the water density was 997.04 g/cm\textsuperscript{3} at 25 °C. The calculated water volume was 2.18 cm\textsuperscript{3}/min. As previously mentioned, gas flow fluctuations were quite normal because it was relatively difficult to regulate a constant selected flow value; thus, the calculations were made with an optimal average flow value. Although the calculated water volume was 2.18 mL/min, the actual pumped water volume during all experiments was 1.2 mL/min. This reduction in water volume was necessary because in the preparatory stages it was observed that water condensation was very elevated. This value corresponds to the highest possible water flow that did not cause problems during the experimental tests.

After water injection, the apparatus temperature was gradually increased by increasing the preheater temperature with the help of the heat gun. Catalytic tests were carried out in the temperature range of 120–470 °C. The gas produced was sampled when the temperature was stable, which corresponded to approximately every 20 °C. Gas samples were collected in 3 L sampling bags that were analysed by gas chromatography (GC). After gas sampling was performed, the water condensate was always drained off. During the course of the catalytic tests, produced gas online analysis, to have the reaction progress under control, was performed with the analyser Multitec 540 (Herman Sewerin GmbH, Gütersloh, Germany). Once sampling was performed and water condensate was removed, the whole apparatus had to be repressurised to the selected experimental pressure.

The WGS activity of each catalyst was expressed in terms of percentage of CO converted (X\textsubscript{CO} (%)), CO\textsubscript{2} yield (Y\textsubscript{CO\textsubscript{2}} (%)), and, if applicable, selectivity towards CO\textsubscript{2} formation (S\textsubscript{CO\textsubscript{2}} (%)). Furthermore, for a better overview of the experimental results, the molar fraction of hydrogen in the gas produced will always be given.

3.5. Product Analysis

The gas produced was analysed online and offline. As mentioned above, an online analysis was performed for orientation purposes to establish whether the reaction was taking place. Offline analysis was performed to obtain a quantitative result of the produced gas composition. Condensed water was also analysed when using feed gas containing H\textsubscript{2}S to determine the total sulphur content.
3.5.1. Online Produced Gas Analysis

The gas produced from the apparatus was analysed using Multitec 540 (Herman Sewerin GmbH, Gütersloh, German). The analyser used had the ability to simultaneously measure CH\textsubscript{4}, CO\textsubscript{2}, and O\textsubscript{2}. Multitec 540 (Herman Sewerin GmbH, Gütersloh, German) is equipped with selective infrared sensors for CH\textsubscript{4} and CO\textsubscript{2} and with electrochemical sensors for O\textsubscript{2}. The working temperature range of the analyser is from \(-10\) to \(40\) °C. Depending on whether or not CO\textsubscript{2} was detected, it was possible to determine if the WGSR was taking place and adjust the apparatus temperature accordingly.

3.5.2. Offline Determination of Hydrocarbons, Permanent Gases, and Sulphur Compounds

The content of hydrocarbons and permanent gases in the produced gas was determined using Agilent HP 7890 gas chromatography (GC) model (Agilent Technologies, Santa Clara, USA) coupled with a thermal conductivity detector (TCD) and a flame ionisation detector (FID). The GC was fitted with two independent channels in order to allow for the analysis of both organic and inorganic compounds in the produced gas. Helium was used as carrier gas for both channels to allow analysis of the H\textsubscript{2} content in the gas produced.

The sulphur compounds in the gas produced were analysed by Agilent 7890 GC coupled with Agilent 355 sulphur chemiluminescence detector (SCD) (both from Agilent Technologies, Santa Clara, USA). The carrier gas for this chromatographic configuration was N\textsubscript{2}.

3.5.3. Analysis of Sulphur in Condensed Water

The determination of total sulphur content in condensed water samples was performed via an ion-coupled plasma ion-emission spectrometer (ICP-OES). The ICP-OES was the model iCap 7400 Duo equipped with the CETAC ASX-520 autosamples (both from Thermo Fisher Scientific, Inc., Waltham, MA, USA).

4. Results and Discussion

Catalytic tests were performed using three different catalysts: the commercial Ni-based catalyst, laboratory-made Cu-based catalysts, and Co-based catalysts. Catalyst selection was based on good availability and low financial cost of the metal components. The commercial Ni-based catalyst was chosen as an example of an available industrial catalyst. The Cu-based catalyst was selected as a typical industrial LT-WGSR catalyst. The Co-based catalyst was selected to represent an active LT-WGSR catalyst with good tolerance to the presence of sulphur compounds in the feed gas.

Catalytic tests were performed in the temperature range of 120–480 °C. This temperature range covers the temperature ranges commonly applied for testing low- to mid-temperature WGSR catalysts [3,4,21,22]. To assess the influence of pressure on catalyst activity and selectivity toward the WGSR, experiments were carried out in a broad pressure range of 0.5–6 MPa. It should be noted that 0.5 MPa was the base pressure applied to test all catalyst samples. The feed gas flow was in the range of 1.5 to 6 L/min (which corresponds to 0.03 to 0.12 mol/min of CO). Water flow volume was 1.2 mL/min. In addition, it should be noted that after analysing the produced gas, it was confirmed that N\textsubscript{2} in no way participated in the reaction. No nitrogen compounds were present in the gas produced.

4.1. Catalytic Tests of Nickel-Based Catalyst

Catalytic activity tests of the Ni-based catalyst were performed in the temperature range of 120–480 °C. In order to test the influence of pressure on catalyst activity and selectivity toward the WGSR, tests at 0.5, 2, 4, and 6 MPa were performed. For the experiments at different pressure values, the feed gas was model gas mixture 1 consisting of 50 mole% CO and 50 mole% N\textsubscript{2}. In a consecutive step, the resistance to sulphur poisoning was tested at 0.5 MPa pressure using a model gas mixture consisting of 50 mole% CO,
0.4 mole% H₂S, and balance N₂. The average gas feed flow was 4.8 L/min (25 °C; 100 kPa), corresponding to a molar ratio of CO to H₂O of 1.45.

4.1.1. Nickel-Based Catalyst Characterisation
X-ray Fluorescence, BET Surface Area, Pore Volume, and Pore Distribution

X-ray fluorescence analysis of the nickel-based catalyst before the catalytic tests showed that its main component was Ni, and other major compounds were Si and Mg. The description and composition are summarised, and BET surface area of the fresh catalyst, the total pore volume, and the pore distribution are presented in Table 2.

| Parameter               | Value            |
|------------------------|------------------|
| Catalyst shape         | Pellet           |
| Catalyst dimensions [mm]: height × diameter | 3.8 × 4.0         |
| Ni content [wt%]       | 72.17            |
| Si content [wt%]       | 13.89            |
| Mg content [wt%]       | 11.94            |
| BET surface area [m²·g⁻¹] | 195.24         |
| Total pore volume [mL·g⁻¹] | 0.326           |
| Pores below 6 nm [%]   | 33.55            |

After catalytic tests using a feed gas containing 50 mole% Co and 50 mole% N₂, no substantial differences in catalyst composition were observed. The catalyst XRF analysis after using the model gas mixture containing 0.4 mole% H₂S showed that the catalyst contained 13.6 wt% S. As a result of the presence of sulphur nickel, the silicon and manganese content were reduced to 64.8, 10.3, and 8.6 wt%, respectively.

4.1.2. Effect of Temperature and Pressure on Catalyst Activity

After GC-FID/TCD analysis of the produced gas was performed, it was established that the WGSR took place in the presence of the nickel-based catalyst using a feed gas containing 50 mole% CO and 50 mole% N₂. The catalyst proved to be active for the WGSR under all described experimental conditions. The WGS reaction started to run at temperatures above 155 °C. Once the reaction started, a fast temperature increase of about 20 °C was observed, due to the mildly exothermic nature of the reaction.

The catalyst behaved in a similar way at all pressures of 2 MPa and higher. In fact, the CO conversion for pressures of 2, 4, and 6 MPa was above 95% in the temperature range of 220–480 °C. The highest CO conversion was 99.9% at pressure 4 MPa and temperature 318 °C, as shown in Figure 2. The highest CO₂ yield was 82.6% at pressure 4 MPa and temperature 433 °C, as shown in Figure 3. Selectivity towards CO₂ formation, at all pressures, was at its highest value always at lower temperatures. A rapid drop in selectivity was always observed at about 50 °C after the start of the reaction, of at least 20%. The highest hydrogen content in the range of 10.6–12.1 mole% was reached at 0.5 MPa in the temperature range of 260–480 °C. At reaction pressure 4 and 6 MPa the hydrogen content was at its lowest values, never exceeding 3.3 mole%. Therefore, from a research point of view, pressure 0.5 MPa is the most suitable for the highest hydrogen yield over the commercial Ni-based catalyst. The results of the catalytic tests under different pressure conditions are summarised in Figures 4 and 5.

In addition to hydrogen and carbon dioxide, it was observed that a major component present in the gas produced at all applied pressures was methane. The presence of methane indicated that the chosen nickel-based catalyst was also active for the methanation reaction. At pressures 2, 4, and 6 MPa at temperatures above 220 °C, the methane content was above 10 mole%. The highest CH₄ content in the gas produced of more than 12 mole% was observed at 4 MPa in the temperature range of 210 to 360 °C. Meanwhile, at pressure 0.5 MPa, the side methanation reaction was suppressed. In addition to methane, other hydrocarbons,
such as ethane, propane, and butane, were also present at trace concentrations in the gas produced at pressures 2–6 MPa.

From the acquired data, it was confirmed that the elevated pressure neatly influenced the WGS reaction, shown by low hydrogen content along with high methane content. Higher pressure had a negative effect on selectivity towards the WGSR since it positively affected the side methanation reaction. In the presence of the nickel-based catalyst under the described experimental conditions, the formed H\textsubscript{2} reacted with the formed CO\textsubscript{2} and/or CO in the feed to produce CH\textsubscript{4}. Moreover, the fact that the gas composition produced at 4 and 6 MPa was quite similar indicated that after certain values, pressure does not play a substantial role for either the WGSR or the methanation reaction. The results obtained from this set of experimental tests indicate that indeed nickel-based catalysts are active for

---

**Figure 2.** Catalytic tests with feed gas mixture 1 (50 mole\% CO and 50 mole\% N\textsubscript{2}) at pressure 0.5 MPa over a commercial Ni-based catalyst: (A)—CO conversion, CO\textsubscript{2} yield, and CO\textsubscript{2} selectivity; (B)—composition of the gas produced.
the WGSR, but it is imperative to find the right catalyst composition in order to suppress the side methanation reaction.

Figure 3. Catalytic tests with feed gas mixture 1 (50 mole% CO and 50 mole% N₂) at pressure 2 MPa over a commercial Ni-based catalyst: (A)—CO conversion, CO₂ yield, and CO₂ selectivity; (B)—composition of produced gas.

4.1.3. Effect of Hydrogen Sulphide on Catalyst Activity

Resistance against sulphur poisoning was tested using a model gas mixture as feed gas containing 50 mole% CO, 0.4 mole% H₂S, and balance N₂. Based on the results obtained during the catalytic tests using model gas mixture 1, pressure 0.5 MPa was selected as the most suitable for higher H₂ production. The temperature was kept constant at 426 °C, which was within the temperature range that corresponded to high CO conversion, CO₂ yield, CO₂ selectivity, and H₂ production during the tests with model gas mixture 1. The
total feed volume of 1056 L corresponds to a catalytic test that lasted 3.7 h. In Figure 6, changes in CO conversion, CO$_2$ yield, selectivity, and product contents in the produced gas are depicted depending on the total feed gas volume passing through the catalyst bed.

**Figure 4.** Catalytic tests with feed gas mixture 1 (50 mole% CO and 50 mole% N$_2$) at pressure 4 MPa over a commercial Ni-based catalyst: (A)—CO conversion, CO$_2$ yield, and CO$_2$ selectivity; (B)—composition of the produced gas.

In Figure 7, the changes of the H$_2$S and carbonyl sulphide (COS) content in produced gas during the course of the catalytic test are depicted compared to the H$_2$S content in the feed gas. The hydrogen sulphide content in the produced gas and the feed gas is represented by the surface area below the curves, “H$_2$S output” and “H$_2$S feed”, respectively. Therefore, it is clear that over 90% of the H$_2$S present in the feed gas is adsorbed in the catalyst. Both
H$_2$S and COS peaked roughly at the same time, reaching 297.7 mg/m$^3$ and 64.7 mg/m$^3$, respectively. Subsequently, the content of both compounds decreased again. The presence of COS can be explained by Equation (3) [23].

$$\text{H}_2\text{S} + \text{CO} \rightarrow \text{H}_2 + \text{COS}$$

It should be noted that during the course of the catalytic test, catalyst deactivation was not reached. This can also be observed by the results in Figure 6, where it is clear that the catalyst remained active throughout the course of the experiment. However, a certain decrease in CO conversion, CO$_2$ yield, and CO$_2$ selectivity can be observed, reaching
average values of 86, 61, and 76%, respectively. Although after XRF analysis 13.6 wt% of S (the equivalent of 6.8 g of S) was detected, the catalyst was not significantly deactivated in terms of CO conversion. The adsorption of sulphur in the catalyst is probably responsible for the slight decrease in catalytic activity. The hydrogen sulphide present in the water condensate was also determined. There were not very significant fluctuations for each sampling. The average H$_2$S content in the water condensate was 8.17 µg/L.

**Figure 6.** Catalytic tests with feed gas mixture 2 (50 mole% CO, 0.4 mole% H$_2$S, balance N$_2$) at 0.5 MPa pressure over a commercial Ni-based catalyst: (A)—CO conversion, CO$_2$ yield, and CO$_2$ selectivity; (B)—composition of produced gas.

### 4.2. Catalytic Tests of Copper-Based Catalyst

The results depicted are for catalytic activity tests of Cu-based catalysts prepared by different methods. All experiments were carried out in the temperature range of 120–480 °C. The specific temperature range will be given in the comments of each individual set of
experiments. The influence of catalyst activation was first tested in a hydrogen atmosphere. Catalytic activity was tested at 0.5 MPa. Subsequently, the influence of support calcination was examined, again at 0.5 MPa. Once the effect of both hydrogen activation and support calcination on catalyst activity was established, catalytic tests were performed at higher pressures, 2 and 6 MPa. The consecutive step was to compare the catalytic activity of catalyst prepared with multiple impregnation (10 times with a 20 wt% solution) and impregnation in a 10 wt% solution. All these experiments were carried out in the presence of model gas mixture 1. The feed gas flow was in the range of 1.5–6 L/min (25 °C; 100 kPa). In a consecutive step, resistance to sulphur poisoning was performed at pressure 0.5 MPa using model gas mixture 2.

![Figure 7. Catalytic tests with feed gas mixture 2 (50 mole% CO, 0.4 mole% H₂S, balance N₂) at pressure 0.5 MPa over a Ni-based catalyst. H₂S and COS content in the produced gas (output) compared to the H₂S content in the feed gas.](image)

4.2.1. Support Characterisation

The results of X-ray analysis of non-calcined boehmite (sample 1) and calcined boehmite at temperatures 400, 500, 600, 700, and 800 °C (samples 2–6) are summarised in Table 3. From the results it can be seen that at the calcination temperature of 500 °C all AlO(OH) was converted to the desired γ-Al₂O₃ phase.

![Table 3. Composition of the support after different calcination temperatures.](table)

| Calcination (°C) | 400 (2) | 500 (3) | 600 (4) | 700 (5) | 800 (6) |
|-----------------|---------|---------|---------|---------|---------|
| γ-Al₂O₃ (wt%)    | 83      | 100     | 100     | 100     | 100     |
| AlO(OH) (wt%)   | 17      | 0       | 0       | 0       | 0       |

The results of the BET specific surface area and total pore volume are summarised in Figure 8. At the calcination temperature, 500 °C, the loss of specific surface area was not that prominent and the total pore volume remained at a high value. The specific surface area was 255.5 m²/g and the total pore volume was 0.45 mL/g. Furthermore, the pore distribution was suitable for further catalyst preparation, since 77.4% of the total pore
volume remained below 6 nm. At higher calcination temperatures, a considerable drop in pores below 6 nm was observed. For example, even at 600 °C, pores below 6 nm made up only 50% of the total pore volume, and at 800 °C it was reduced to just about 16%.

**Figure 8.** Specific surface area and pore volume of supports 1–6.

Except for maintaining structural properties, 500 °C was a sufficiently high calcination temperature for the transition of all AlO(OH) to γ-Al₂O₃ phase. Based on the results acquired, the support calcination temperature 500 °C was selected as the most suitable, as expected based on research in the literature.

### 4.2.2. Copper-Based Catalyst Characterisation

The two major components for all catalysts were Cu and Al. The catalyst prepared with non-calcined boehmite contained 11.4 wt% Cu and 47.5 wt% Al. The catalyst prepared with a calcined support impregnated in the 20 wt% solution contained 18 wt% Cu and 49.0 wt% Al.

Using a calcined support, a catalyst impregnated only once in a 10 wt% solution of (Cu(NO₃)₂·3 H₂O was also prepared. In Tables 4–6, the description and characterisation based on XRF and BET analysis for every tested Cu-based catalyst are summarised.

**Table 4.** Fresh Cu-based catalyst prepared with non-calcined support impregnated in a 20 wt% solution description, XRF analysis and BET analysis results.

| Parameter                        | Value          |
|----------------------------------|----------------|
| Catalyst shape                   | Cylinder       |
| Catalyst dimensions [mm]; height x diameter; internal diameter | 6.2 x 4.9; 1.9 |
| Cu content [wt%]                 | 11.4           |
| Al content [wt%]                 | 47.5           |
| BET surface area [m²/g]          | 215.4          |
| Total pore volume [mL/g]         | 0.403          |
| Pores below 6 nm [%]             | 64.88          |
Table 5. Fresh Cu-based catalyst prepared with calcined support impregnated in a 20 wt% solution description, XRF analysis and BET analysis results.

| Parameter                                      | Value       |
|------------------------------------------------|-------------|
| Catalyst shape                                 | Cylinder    |
| Catalyst dimensions [mm]: height × diameter;  | 6.2 × 4.9; 1.9 |
| internal diameter                              |             |
| Cu content [wt%]                               | 14.8        |
| Al content [wt%]                               | 49.0        |
| BET surface area [m²/g]                        | 198.07      |
| Total pore volume [mL/g]                       | 0.407       |
| Pores below 6 nm [%]                           | 48.62       |

Table 6. Fresh Cu-based catalyst prepared with calcined support impregnated in a 10 wt% solution description, XRF analysis and BET analysis results.

| Parameter                                      | Value       |
|------------------------------------------------|-------------|
| Catalyst shape                                 | Cylinder    |
| Catalyst dimensions [mm]: height × diameter;  | 6.2 × 4.9; 1.9 |
| internal diameter                              |             |
| Cu content [wt%]                               | 8.1         |
| Al content [wt%]                               | 47.8        |
| BET surface area [m²/g]                        | 213.6       |
| Total pore volume [mL/g]                       | 0.417       |
| Pores below 6 nm [%]                           | 55.13       |

The composition of the catalyst was also determined after catalytic tests with model gas mixtures containing H₂S. The catalyst that underwent tests using model gas mixture 1 did not exhibit changes in composition. The catalyst prepared from calcined support and impregnated once in a 20 wt% solution was the only one to undergo the test using a model gas mixture containing H₂S. XRF analysis showed that the amount of Cu and Al remained. However, 2.5 wt% S in the catalyst was detected. It can be assumed that sulphur bonds with copper to form copper sulphide. On the basis of XRF results, not all copper was transformed into its sulphuric form.

The results of XRD analyses of all three tested catalysts are given in Table 7.

Table 7. The results of XRD analyses of all three tested catalysts.

| Catalyst       | Metal Crystallite Size (nm, XRD) | Alumina Crystallite Size (nm, XRD) |
|----------------|----------------------------------|-----------------------------------|
| Ni/γ-Al₂O₃     | 8                                | 5                                 |
| Cu/γ-Al₂O₃     | 37                               | 5                                 |
| Co/γ-Al₂O₃     | 20                               | 5                                 |

4.2.3. Effect of Hydrogen Activation on Catalyst Activity

A comparison of catalyst activity after activation in a hydrogen atmosphere for 3 h at 500 °C was made and no activation was performed. Catalyst was prepared using non-calcined boehmite as support impregnated in a 20% solution of (Cu(NO₃)₂·3 H₂O. The influence of hydrogen activation was tested in only one catalyst, specifically, the one with the least time-consuming preparation under the assumption that the activation effect would be the same for all laboratory-prepared catalysts. Experiments were carried out in the temperature range of 120–450 °C under 0.5 MPa pressure. The feed gas was model gas mixture 1, and the flow rate was 1.5 L/min, corresponding to a molar ratio of CO to H₂O of 0.45.

The influence on CO conversion and CO₂ yield of catalyst activation in hydrogen flow is depicted for non-activated and activated catalysts in Figures 9A and 10A, respectively. In
both cases, the WGSR started to take place at about 128 °C. Catalyst activation positively influenced both conversion and yield. The highest CO conversion of 94.8% and the CO$_2$ yield of 59.2% were reached at 333 °C when the reaction was carried out on an activated catalyst. The CO$_2$ leaving the catalytic reactor was partially dissolved in the aqueous condensate. Therefore, the CO$_2$ yield balance was incomplete. The hydrogen-activated catalyst had some WGSR activity even in the temperature range of 128–240 °C. Meanwhile, the activity of the non-activated catalyst in the same temperature range was negligible. However, for both catalysts, a considerable increase in catalytic activity was observed at temperatures above 250 °C. At temperatures above 420 °C, the catalytic activity started to decrease.

Figure 9. Catalytic tests with feed gas mixture 1 (50 mole% CO, 50 mole% N$_2$) at pressure 0.5 MPa over a Cu-based (11.4 wt%) catalyst prepared with non-calcined support: (A)—CO conversion and CO$_2$ yield over a non-activated catalyst; (B)—all product over a non-activated catalyst.
At catalyst bed temperatures above 450 °C, the conversion of CO to CO₂ decreases, because the thermodynamic equilibrium of a given reaction is already significantly shifted in favour of the reactants at this temperature.

In Figures 9B and 10B, the composition of the gas produced when the reaction was running over a non-activated and activated catalyst, respectively, is depicted. In addition to higher conversion and yield, catalyst activation also had a positive effect on H₂ production. The highest H₂ content of 30.6% was recorded at 366 °C. Selectivity towards CO₂ is not addressed since the only carbon-containing product was indeed CO₂. Therefore, CO₂ selectivity was constantly close to 100%. The Cu-based catalyst exhibited high selectivity for CO₂ formation since products of the side methanation reaction were not detected. On the basis of the acquired results, catalyst activation has a significantly positive effect on
the overall catalytic performance. Therefore, hydrogen activation plays a crucial role in catalyst utilisation.

4.2.4. Effect of Support Calcination Temperature on Catalyst Activity

The catalyst was prepared using non-calcined boehmite as support and calcined support at 500 °C. Both catalysts were prepared by impregnation in a 20 wt% solution of (Cu(NO$_3$)$_2$·3H$_2$O). Before the WGS reaction tests, both catalysts were activated in a hydrogen atmosphere for 3 h at 400 °C. Catalytic tests were carried out under pressure 0.5 MPa and in the temperature range of 120–450 °C. The feed gas was model gas mixture 1 and the flow was set at 1.5 L/min. The conversion of CO, the CO$_2$ yield, and the composition of the gas produced when using an activated catalyst prepared with calcined support are depicted in Figure 10. In Figure 11, CO conversion, the CO$_2$ yield, and the composition of gas produced over an activated catalyst prepared with calcined support are depicted. Selectivity toward CO$_2$ formation is not presented since CO$_2$ was the only relevant carbon-containing product. Trace amounts of methane were detected at about 140 °C when the support was not calcined. Nevertheless, the quantity was not relevant to the overall catalyst WGSR performance.

The performance of the catalyst prepared with calcined and non-calcined support was comparable. However, the catalyst prepared with calcined support exhibited slightly better performance compared to the catalyst prepared with non-calcined support. The WGSR over the catalyst with calcined support started to run at about 125 °C. The highest catalytic activity was in the temperature range of 250–400 °C. At 334 °C the highest CO conversion and CO$_2$ yield of 97.7 and 64.2% were reached, respectively. The CO$_2$ leaving the catalytic reactor was partially dissolved in the aqueous condensate. Therefore, the CO$_2$ yield balance was incomplete. More or less the same reaction temperature was recorded when the highest conversion and yield of the catalyst with the non-calcined support were achieved. The highest H$_2$ content in the produced gas of 32.6 mol% was reached, also when the reaction was run over the catalyst with calcined support, at about 360 °C. Both catalyst peak performances were achieved at approximately the same reaction temperatures. In the temperature range 400–450 °C, for the WGSR running over the catalyst prepared with calcined support and activated, a decrease in catalytic activity can be observed. This is a behaviour similar to the one observed also when the WGSR was running over an activated catalyst with non-calcined support. The higher activity of the catalyst prepared with calcined support can be related to the higher Cu content. It should be noted that support calcined at 500 °C showed the highest increase in total pore volume. Most likely the increase in pore volume made possible the impregnation of a greater quantity of copper.

4.2.5. Effect of Temperature and Pressure on Catalyst Activity

Taking into account the effect of hydrogen activation and support calcination, the effect of pressure on catalyst activity was tested using a catalyst prepared with calcined support impregnated in a 20% solution of (Cu(NO$_3$)$_2$·3H$_2$O) and activated for 3 h at 500 °C in a hydrogen stream. In addition to the previously presented results obtained at 0.5 MPa pressure, catalytic tests were performed at 6 MPa pressure. On the basis of the acquired results when the WGSR was running over the Ni-based catalyst, only the lowest applied pressure and highest applied pressure were selected. The feed gas was model gas mixture 1. The feed gas flow was set at 6 L/min (25 °C; 100 kPa) corresponding to a molar ratio of CO to H$_2$O of 1.8. The reaction temperature range was 120 °C to 450 °C. For a better comparison of the acquired results, graphs obtained from data at different pressures will be displayed next to each other. Selectivity toward CO$_2$ formation will not be addressed since the presence of hydrocarbons was negligible. The reaction started to run at 125.2 °C when the apparatus pressure was 0.5 MPa. When the apparatus pressure was 6 MPa, the reaction started to run at a slightly higher temperature of 133 °C.
Figure 11. Catalytic tests on a Cu-based (14.8 wt%) activated catalyst prepared with calcined support with feed gas mixture 1 (50 mole% CO, 50 mole% N\textsubscript{2}) at pressure 0.5 MPa: (A)—CO conversion and CO\textsubscript{2} yield; (B)—composition of produced gas.

In Figure 12A, CO conversion, CO\textsubscript{2} yield, and composition of the gas produced under experimental pressures of 0.5 MPa are depicted. In Figure 13A, CO conversion, CO\textsubscript{2} yield, and composition of produced gas under experimental pressures of 6 MPa are depicted. Interestingly, the highest CO conversion and CO\textsubscript{2} yield of 88.7 and 54.9%, respectively, were reached when the tests were carried out under 6 MPa pressure at 284 °C. The highest CO conversion and CO\textsubscript{2} yield under 0.5 MPa pressure of 77.5 and 49.8%, respectively, were
reached at 331 °C. However, it should be noted that catalytic activity when performing the tests at 0.5 MPa was relatively constant and greater in a wider temperature range. Higher conversion and yield values at pressure 6 MPa and temperature 284 °C can be attributed to the fact that the increased pressure positively affects the WGSR up to the equilibrium point [12,18]. The flow rate was probably too high to reach equilibrium.

Figure 12. Catalytic tests on a Cu-based (14.8 wt%) activated catalyst, prepared with calcined support, with feed gas mixture 1 (50 mole% CO, 50 mole% N₂) at pressure 0.5 MPa; flow rate 6 L min⁻¹: (A)—CO conversion and CO₂ yield; (B)—composition of produced gas.
Figure 13. Catalytic tests on a Cu-based (14.8 wt\%) activated catalyst, prepared with calcined support, with feed gas mixture 1 (50 mole\% CO, 50 mole\% N$_2$) at pressure 6 MPa; flow rate 6 L min$^{-1}$: (A)—CO conversion and CO$_2$ yield; (B)—composition of the gas produced.

4.2.6. Effect of Flow Rate on Catalyst Activity

To assess the effect of flow rate on catalyst activity, the results obtained from the catalytic tests performed under pressure 0.5 MPa, in the temperature range of 120–450 °C, and at flow rates 1.5 and 6.0 L/min will be compared in this section. The feed gas was model mixture 1. The results obtained from catalytic tests with flow rate 1.5 L/min are depicted in the previously mentioned Figure 11. The results obtained from catalytic tests with flow rate 6 L/min are depicted in the previously mentioned Figure 12. In both cases,
the reaction started running at about 125 °C. In both cases, the highest conversion and yield were reached at around 330 °C. The highest hydrogen content in the gas produced was also reached in both cases at around 360 °C. However, when the catalyst was subjected to a lower flow rate CO conversion, the CO₂ yield and hydrogen content were higher. Nevertheless, it should be noted that with respect to hydrogen production, the differences are not very significant. Therefore, for industrial applications, the feed flow rate of 6 L/min is interesting when taking into account the absolute hydrogen production per unit of time.

4.2.7. Effect of Copper Content on Catalyst Activity

The effect of different Cu content on catalyst activity is discussed in this section. The results previously presented were obtained with a catalyst impregnated once in a 20 wt% solution and will be compared with two additional catalytic tests. The additional results discussed here are those obtained: (1) using a catalyst impregnated 10 times with a solution of 20% by weight, which resulted in Cu content of 47.6 wt%; (2) using a catalyst impregnated once in a solution of 10% by weight, which resulted in Cu content of 8.1% by weight. All catalytic tests were carried out under pressure 0.5 MPa, in the temperature range of 120–450 °C and at feed flow rate 1.5 L/min. The conversion of CO and the yield of CO₂ for the catalyst with copper content of 47.6 and 8.1% by weight are depicted in Figures 14A and 15A, respectively. Selectivity is not addressed because no other carbon-containing compounds, except CO₂, were formed during the course of the catalytic tests. The composition of gas produced for the catalyst with 47.6 and 8.1 wt% copper content is depicted in Figures 14B and 15B, respectively.

The reaction started at 124 °C on a catalyst containing 8.1 wt% Cu and at 130 °C on a catalyst containing 47.6 wt% Cu, see Figure 15. When using the catalyst with a 47.6 wt% Cu content, an increasing trend in both conversion and yield in the whole temperature range can be observed. This behaviour can be attributed to the fact that when a catalyst has high Cu content, the active centres start to gradually activate with increasing temperature. Therefore, the behaviour of the catalyst with 47.6 wt% copper is different from that of the other catalysts. The maximum CO conversion of 93.5% and CO₂ yield of 61.2% were reached at 443 °C. When the WGS reaction was carried out on the catalyst containing 8.1 wt% Cu, the maximum CO conversion of 87.7% and a CO₂ yield of 56.9% were reached at 255 °C. The highest H₂ content in the gas produced, 30.9 mole% at 443 °C, was also observed for the catalyst with higher Cu content.

Although the catalyst with 47.6 wt% copper in the temperature range of 375–450 °C shows better activity, the overall performance is inferior. On the basis of the obtained results, it seems that the Cu content positively influences catalyst activity. However, the question posed is to what extent? When the results are compared with those obtained using a catalyst with 14.8 wt% Cu content, it can be observed that the catalyst with the highest Cu content is not the most active one. In fact, better CO conversion, CO₂ yield, and H₂ content in the gas produced are obtained from the catalyst containing 14.8 wt%. For the temperature range of 250–400 °C, catalyst activity grows in the following order: Cu 47.6 wt% < Cu 8.1 wt% < Cu 14.8 wt%. Therefore, for Cu-based catalysts it can be stated that there is a certain optimal combination of the Cu content and surface area, which can be a matter of further research.

This order of activity can be explained by differences in surface area. The catalyst containing 8.1 wt% Cu had the largest surface area of 213.60 m²/g, followed by 198.07 m²/g for the catalyst containing 14.8 wt% Cu. A slight loss in surface area with the increasing Cu content can be observed. However, the surface area loss was much greater for the catalyst containing 47.6 wt% Cu, reaching a value of only 93.69 m²/g. The catalyst with the highest Cu content showed an almost 53% loss in surface area compared to the most active catalyst. This indicates that the Cu content has a positive effect on catalyst activity until the point when surface area losses are not too great. Loss in total surface area, often attributed to catalyst deactivation, has been reported to have a negative effect on the catalyst performance [15,24]. In the case of Cu-based WGSR catalysts, the reaction rate
has even been reported to be proportional to the metal surface area [25]. In the case of the
catalyst with the highest Cu content, it is evident that a portion of the Cu atoms remain
“trapped” inside the catalyst pores and as a result they do not take an active part in the
catalytic reaction.

Figure 14. Catalytic tests on a Cu-based activated catalyst (47.6 wt%) prepared with calcined support
with feed gas mixture 1 (50 mole% CO, 50 mole% N₂) at pressure 0.5 MPa: (A)—CO conversion and
CO₂ yield; (B)—composition of the produced gas.

4.2.8. Effect of Hydrogen Sulphide on Catalyst Activity

The resistance against sulphur poisoning was tested using model gas mixture 2 as
feed gas. Based on the results obtained during the catalytic tests using model gas mixture 1,
a catalyst with 14.8 wt% Cu content was the one tested. Before the catalytic test, the catalyst
was activated in a hydrogen flow for 3 h at 500 °C. The catalytic test was carried out under
the following experimental conditions: pressure 0.5 MPa, feed gas flow rate 1.5 L/min,
and constant temperature set at 330 °C (temperature at which the highest conversion and
yield were reached). Sampling was performed in relatively long intervals. In Figure 16, CO conversion, CO$_2$ yield, and produced gas composition are depicted. After about 745 L of feed gas, which corresponds to over 8 h, the catalyst was totally deactivated. The first sampling was performed 40 min after the apparatus was switched to feed gas mixture 2. At this point, the catalyst still had quite good activity, reaching 74.2% conversion, 43.4% yield, and 20.5 mole% hydrogen content in produced gas. However, the analysis of the second sample showed a decrease of at least 30% in all values. Eventually, after 745 L of feed gas, the catalyst was deactivated.

Figure 15. Catalytic tests on a Cu-based activated catalyst (8.1 wt%) prepared with calcined support with feed gas mixture 1 (50 mole% CO, 50 mole% N$_2$) at pressure 0.5 MPa: (A)—CO conversion and CO$_2$ yield; (B)—composition of the produced gas.
Figure 16. Catalytic tests on a Cu-based (14.8 wt%) activated catalyst, prepared with calcined support, with feed gas mixture 2 (50 mole% CO, 0.4 mole% H₂S, balance N₂) at pressure 6 MPa: (A)—CO conversion and CO₂ yield; (B)—composition of the produced gas.

In Figure 17, the hydrogen sulphide and carbonyl sulphide content in the gas produced is depicted. The highest H₂S concentration was 988.8 mg/m³, while the highest COS concentration was 57 mg/m³. The presence of COS is explained by Equation (3). The total sulphur content in the condensate water was determined. During the course of the catalytic test, the sulphur content gradually increased and the highest concentration of 308.7 mg/L was determined in the last sample.
To confirm catalyst deactivation, a catalytic test was performed on the utilised catalyst using model gas mixture 1. As expected, no catalytic activity was observed. XRF analysis of the catalyst after the tests showed 2.5 wt% S content. The content of Cu and Al had not changed. The relatively fast deactivation of the laboratory-prepared Cu-based catalyst confirms the reported high sensitivity of this class of catalyst towards sulphur compounds present in the feed gas [26].

4.3. Catalytic Tests of Cobalt-Based Catalyst

In this section, results of Co-based catalyst characterisation are presented. Catalyst preparation and reaction conditions were set on the basis of the results presented for the Cu-based catalyst. Therefore: (1) the catalyst was prepared using calcined support impregnated in a 20% by weight solution; (2) prior to each catalytic test, activation in hydrogen stream at 400 °C for 3 h was performed; (3) catalytic tests were carried out under pressure of 0.5 MPa; (4) The feed gas flow rate was set at 1.5 L/min. Activity tests were carried out using all three model gas mixtures.

4.3.1. Cobalt-Based Catalyst Characterisation

The catalyst had a very dark greyish-brown colour. X-ray fluorescence analysis of the nickel-based catalyst before the catalytic tests showed that its major components were Co and Al.

In Table 8, the catalyst description and characterisation results are depicted. After catalytic tests using feed gas containing 50 mole% Co and 50 mole% N₂, no substantial differences in catalyst composition were observed. XRF analysis of the catalyst after using the model gas mixture containing 0.4 mole% H₂S showed that the catalyst contained approximately 3.5 wt% S.

The catalyst surface area based on the BET analysis was 205.07 m²/g. The total pore volume of the catalyst was 0.4033 mL/g. Regarding the distribution of the pores, pores below 6 nm made up 54.81% of the total volume of pores.
Table 8. Fresh Co-based catalyst prepared with non-calcined support impregnated in a 20 wt% solution description, XRF analysis and BET analysis results.

| Parameter                        | Value         |
|----------------------------------|---------------|
| Catalyst shape                   | Cylinder      |
| Catalyst dimensions [mm]: height × diameter; | 6.2 × 4.9; 1.9|
| internal diameter                |               |
| Co content [wt%]                 | 9.6           |
| Al content [wt%]                 | 44.5          |
| BET surface area [m²/g]          | 205.1         |
| Total pore volume [mL/g]         | 0.403         |
| Pores below 6 nm [%]             | 54.81         |

4.3.2. Water-Gas Shift Reaction over Cobalt-Based Catalyst

The first catalytic test was performed using model gas mixture 1. The catalytic test was carried out in the temperature range of 200–450 °C. The WGS reaction started to run at temperatures slightly below 230 °C. Once the reaction started, a relatively faster increase in temperature was observed. The temperature of the reaction beginning indicates that the Co-based catalyst can be considered an “intermediate temperature catalyst”. The results acquired at up to 450 °C show that the catalyst exhibited a stable activity increase. Due to the limitation of the experimental apparatus construction, the reaction was conducted only until 450 °C. Therefore, the maximum activity for the Co-based catalyst was not reached. However, the laboratory-prepared Co-based catalyst proved to be active for the WGSR under the experimental conditions applied in this work. In Figure 18, CO conversion, CO₂ yield, CO₂ selectivity, and produced gas composition are depicted.

At temperature 450 °C, the highest CO conversion and CO₂ yield of 66.5 and 47.4%, respectively, were reached. Selectivity towards CO₂ formation was at its highest, over 99%, in the lower temperature range. With increasing temperature, the catalyst started to become more active, producing more CO₂ but also forming methane, thus causing a decrease in selectivity of CO₂. Therefore, the laboratory-produced catalyst also exhibits activity for the methanation reaction. Formation of methane for the WGSR taking place over a Co-based catalyst has also been reported by Batista et al. [27]. The highest content of all products in the gas produced was observed at the highest reaction temperature, i.e., 450 °C. The hydrogen content was 13.1 mole% and the methane content was 3.2 mole%.

Figure 18. Cont.
Figure 18. Catalytic tests on Co-based (9.6 wt%) activated catalyst prepared with calcined support with feed gas mixture 1 (50 mole% CO, 50 mole% N₂) at pressure 0.5 MPa: (A)—CO conversion and CO₂ yield; (B)—composition of the produced gas.

4.3.3. Effect of Hydrogen Sulphide on Catalyst Activity

The effect of hydrogen sulphide on the feed gas was tested using model gas mixture 2. During the catalytic test, the temperature was kept constant at about 440 °C, which is close to the temperature when the highest activity was reached. In Figure 19, CO conversion and CO₂ yield, CO₂ selectivity, and produced gas composition are depicted. The catalyst was subjected to a total volume of 6997 L of model gas mixture 2, which corresponds to almost 78 h of catalytic tests.

The presence of H₂S influenced catalyst activity since a decrease in both CO conversion and CO₂ yield was observed. The average CO conversion was 32.4% and the average CO₂ yield was 20.9%. Selectivity towards CO₂ formation is not addressed since, except for the presence of 6.7 mole% methane in the first sample (20 L of feed gas over the catalyst), no additional methane was detected. Regarding the H₂ content in the gas, a decrease was observed to an average of 9.5 mole%. It should be noted that despite suppression of catalyst activity, the presence of H₂S did not cause full catalyst deactivation. Catalyst activity remained relatively constant during the whole catalytic test. The experimental results demonstrate that the catalyst has good tolerance to hydrogen sulphide in the feed gas. Therefore, we indicate that Co-based catalysts are indeed more sulphur-resistant than Cu-based catalysts.

In Figure 20, the hydrogen sulphide and carbonyl sulphide content in the gas produced is depicted. The highest H₂S concentration was 992.8 mg/m³, while the highest COS concentration was 521 mg/m³. The total sulphur content in the condensate water was determined. During the course of the catalytic test, the sulphur content gradually increased to a relatively stable value. The highest total sulphur content was 699.3 mg/L.

In a subsequent step, the activity of the sulphided catalyst was tested by feeding model gas mixture 1. Catalytic tests were carried out in the temperature range of 200–450 °C. In Figure 21, CO conversion and the CO₂ yield (A) and composition of produced gas (B) are depicted.
The WGS reaction started at 241 °C, a slightly higher temperature compared to the non-sulphur catalysts. Although H$_2$S was no longer present in the feed gas, a considerable decrease in CO conversion, CO$_2$ yield, and H$_2$ content was observed. At 449 °C, the highest CO conversion and CO$_2$ yield of 22.1 and 13.5%, respectively, were reached. The highest H$_2$ content of 7.6 mole% was also determined at the same reaction temperature. The trace concentration of CH$_4$ was detected at 449 °C. Therefore, selectivity of CO$_2$ is not addressed. On the basis of the XRF analysis, the catalyst contained 3.5 wt% S after the catalytic tests. The laboratory-prepared Co-based catalyst seems to have a higher tolerance to sulphur content compared to that of Cu-based catalysts. However, H$_2$S in the feed gas significantly decreases the catalytic performance.
Figure 20. Catalytic tests with feed gas mixture 2 (50 mole% CO, 0.4 mole% H\textsubscript{2}S, balance N\textsubscript{2}) at a pressure of 0.5 MPa on Co-based catalyst (9.6 wt%). Content of H\textsubscript{2}S and COS in the gas produced.

4.3.4. Effect of Feed Composition

The final catalytic test was performed by feeding model gas mixture 3 over a fresh laboratory-prepared Co-based catalyst. Model gas mixture 3 had a composition and sulphur content similar to real syngas. The reaction started at about 230 °C. In Figure 22, CO conversion, CO\textsubscript{2} yield, CO\textsubscript{2} selectivity, and produced gas composition are depicted. An increase in CO conversion and CO\textsubscript{2} yield can be observed with increasing temperature. This is a similar behaviour trend to the one observed when using feed gas mixture 1, Figure 18. However, the absolute values of CO conversion and CO\textsubscript{2} yield when using model gas mixture 3 were much lower. At 471 °C, the highest CO conversion and CO\textsubscript{2} yield of 27.2 and 17.6%, respectively, were reached. Selectivity toward CO\textsubscript{2} formation was virtually 100% during the entire catalytic test. Only a minor methane content of a maximum of 0.1 mole% was detected at temperatures above 450 °C.

The highest H\textsubscript{2} content of 44.8 mole% in the gas produced, which corresponds to the production of an additional 10.8 mole%, was also observed at 471 °C. In addition to loss of catalytic activity due to H\textsubscript{2}S deactivation, H\textsubscript{2} concentration in the feed gas also influences performance. Wang et al. [28] report visible declines in CO conversion at different reaction temperatures, since the catalytic performance deteriorated due to the increase in H\textsubscript{2} concentration in the feed gas. Furthermore, they state that the influence of H\textsubscript{2} concentration in the feed gas on CO conversion decreases with increasing temperature. This behaviour can also be observed in the results depicted in the present work, since the highest H\textsubscript{2} content in the gas produced was observed at the highest reaction temperature.

In Figure 23, hydrogen sulphide and carbonyl sulphide content in produced gas is depicted. The highest H\textsubscript{2}S concentration was 962 mg/m\textsuperscript{3}, while the highest COS concentration was 188 mg/m\textsuperscript{3}. The presence of COS is explained by Equation (3). In the entire temperature range, some fluctuations in the content of both compounds could be observed. However, except for the initial low content in the first sample, H\textsubscript{2}S and COS were present at relatively stable concentrations. The total sulphur content in the condensate water was determined. During the course of the catalytic test, the sulphur content gradually increased and the highest concentration of 55.7 mg/L was determined in the last sample sampled at 332 °C.
Figure 21. Catalytic tests with feed gas mixture 1 (50 mole\% CO, 50 mole\% N\textsubscript{2}) at pressure 0.5 MPa over sulphided Co-based (9.6 wt\%) catalyst. (A)—CO conversion and CO\textsubscript{2} yield; (B)—composition of the gas produced.

4.4. Comparison of Tested Catalyst

Of the tested catalysts, the Ni-based catalyst showed the greatest catalytic activity. The required reaction temperature of this catalyst to achieve a CO to CO\textsubscript{2} conversion of more than 90\% is 200 °C for this catalyst at a pressure of 2 MPa and higher. However, this catalyst produces high methane yields (above 10\%) at temperatures above 225 °C. The Ni-based catalyst is only slightly sensitive to the presence of sulphur in the gas. During its long-term operation, the efficiency of the catalyst for the conversion of CO to CO\textsubscript{2} gradually decreases.
Figure 22. Catalytic tests with feed gas mixture 3 (50 mole% CO, 34 mole% H\textsubscript{2}, 8 mole% CO\textsubscript{2}, 0.4 mole% H\textsubscript{2}S, balance N\textsubscript{2}) at pressure 0.5 MPa over a Co-based catalyst (9.6 wt%): (A)—CO conversion, CO\textsubscript{2} yield, and CO\textsubscript{2} selectivity; (B)—produced gas composition.

The laboratory-based Cu catalyst has lower catalytic activity in the WGS reaction compared to the Ni-based catalyst. A reaction temperature of at least 250 °C is required to achieve a CO to CO\textsubscript{2} conversion of more than 90%. The advantage of this catalyst is that it does not produce any methane as a byproduct. However, the Cu-based catalyst is extremely sensitive to the presence of sulphur compounds in the gas, which causes its very rapid deactivation.

The laboratory-prepared Co-based catalyst showed the lowest catalytic activity of all the catalysts tested. In the catalyst reactor used, this catalyst failed to achieve a CO
to CO₂ conversion efficiency of more than 90% under any experimental conditions. This catalyst produces methane as a byproduct at temperatures above 375 °C in concentrations exceeding 10%. The Co-based catalyst is able to withstand the sulphur compounds present in the gas for a long time. There will only be a decrease in its catalytic efficiency for the WGS reaction due to the conversion of the catalytically active element to the sulphide form.

![Graph showing H₂S and COS concentration vs. Reactor temperature](image)

**Figure 23.** Catalytic tests with feed gas mixture 3 (50 mole% CO, 34 mole% H₂, 8 mole% CO₂, 0.4 mole% H₂S, balance N₂) at pressure 0.5 MPa over a Co-based catalyst (9.6 wt%). Content of H₂S and COS in the gas produced.

### 5. Conclusions

A commercial Ni-based catalyst, laboratory-prepared Cu-based catalysts, and a laboratory-prepared Co-based catalyst were tested in a laboratory apparatus constructed at UCT Prague. Compared to published work, a considerably higher feed flow rate was applied, which made it possible to accelerate the performed experiments while maintaining an acceptable WGSR activity and in general good selectivity.

The commercial Ni-based catalyst (72.2 wt% Ni) was found to be active for the WGSR.

- During WGSR catalytic tests at pressures 2, 4, and 6 MPa, the Ni-base catalyst behaved in a similar way. More than 95% carbon monoxide conversion was reached in the temperature range of 220–480 °C.

- The use of calcined support (Al₂O₃) at 500 °C and activation in a hydrogen atmosphere had a positive effect on the performance of Cu-based catalysts prepared in the laboratory.

- The activated catalyst prepared with calcined support (Cu content 14.8 wt%) exhibited the best activity in the temperature range of 250–400 °C and pressure 0.5 MPa, achieving the highest CO conversion, CO₂ yield, and H₂ content.

- A comparison of the catalytic activity of Cu-based catalysts was performed at pressures 0.5 and 6 MPa. The highest CO conversion and CO₂ yield of 88.7 and 54.9%, respectively, were reached at pressure 6 MPa and temperature 284 °C.

- The hydrogen content was the highest (26.6 mole%) at temperature 360 °C and pressure 0.5 MPa.

- No hydrocarbons were present when carrying out the WGSR at pressure 0.5 MPa, while at pressure 6 MPa methane (up to 0.12% at 449 °C) and ethane were found at temperatures above 308 °C.
A lower flow rate positively influences catalytic activity since it increases the residence time of the reactant species, leading to better conversion.

The WGSR reaction over a laboratory-prepared Co-based catalyst (9.6 wt%) started to run at temperatures around 230 °C.

The catalyst exhibited a stable increase in activity in the temperature range of 200–450 °C. At 450 °C, the highest CO conversion of 66.5% was reached. Due to construction limitations, the reaction could not be carried out at higher temperatures.

Selectivity towards CO$_2$ formation was at its highest, over 99%, in the lower temperature range. With increasing temperature, the catalyst started to become more active, producing more CO$_2$ but also forming methane, thus causing a decrease in selectivity of CO$_2$. At 450 °C, the highest hydrogen and methane content of 13.1 and 3.2 mole%, respectively, was achieved.

The effect of H$_2$S in the feed gas varies for different catalysts. The commercial Ni-based catalyst showed a decrease in catalytic activity, but was not fully deactivated. The laboratory-prepared Cu-based catalyst was fully deactivated after being subjected to only 745 L of feed gas. The activity of the laboratory-prepared Co-based catalyst activity initially decreased, but remained relatively stable even after being subjected to 6997 L of feed gas.

The Co-based catalyst was tested using feed gas similar to syngas containing H$_2$S. The highest H$_2$ content in the gas produced corresponded to the production of an additional 10.8 mole%. It should be noted that, except for loss of catalytic activity due to H$_2$S deactivation, the presence of H$_2$ in the feed gas further deteriorates the catalytic performance.

The laboratory-prepared Co-based catalyst can be considered a good “intermediate temperature” WGSR catalyst that is tolerant to the sulphur content in the feed gas. It can be used for WGSR in the case of gaseous mixtures with high sulphur content, produced for example by coal gasification.

**Author Contributions:** E.B. performed experiments and analyses, prepared catalysts, and wrote the article; K.C. was responsible for conceptualisation, methodology, and supervision; T.H. was responsible for original draft preparation, performed construction of the laboratory apparatus, and also provided valuable information for the use of catalysts. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** All relevant data are included in the article.

**Conflicts of Interest:** The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper. There are no conflicts to declare.

**References**

1. Smirniotis, P.G.; Gunugunuri, K.R. *Water Gas Shift Reaction: Research Developments and Applications*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2015. [CrossRef]
2. Chen, E. History. In *Fuel Cell Technology Handbook*, 1st ed.; Hoogers, G., Ed.; CRC Press: Boca Raton, FL, USA, 2003. [CrossRef]
3. Newsome, D.S. The Water-Gas Shift Reaction. *Catal. Rev.* 1980, 21, 275–318. [CrossRef]
4. Mendes, D.; Mendes, A.; Madeira, L.M.; Iulianelli, A.; Sousa, J.M.; Basile, A. The water-gas shift reaction: From conventional catalytic systems to Pd-based membrane reactors—A review. *Asia-Pac. J. Chem. Eng.* 2010, 5, 111–137. [CrossRef]
5. Alamolhoda, S.; Vitale, G.; Hassan, A.; Nassar, N.N.; Almao, P.P. Synergetic effects of cerium and nickel in Ce-Ni-MFI catalysts on low-temperature water-gas shift reaction. *Fuel* 2019, 237, 361–372. [CrossRef]
6. Pal, D.B.; Chand, R.; Upadhyay, S.N.; Mishra, P.K. Performance of water gas shift reaction catalysts: A review. *Renew. Sustain. Energy Rev.* 2018, 93, 549–565. [CrossRef]
7. Chen, W.H.; Jheng, J.G. Characterization of water gas shift reaction in association with carbon dioxide sequestration. *J. Power Sources* 2007, 172, 368–375. [CrossRef]
8. Grenoble, D.C.; Estadt, M.M.; Ollis, D.F. The chemistry and catalysis of the water gas shift reaction: 1. The kinetics over supported metal catalysts. *J. Catal.* 1981, 67, 90–102. [CrossRef]
9. Baraj, E.; Ciahotný, K.; Hlinčík, T. The water gas shift reaction: Catalysts and reaction mechanism. *Fuel* 2021, 288, 119817. [CrossRef]
10. Fuentes, E.M.; da Costa Faro Júnior, A.; de Freitas Silva, T.; Assaf, J.M.; do Carmo Rangel, M. A comparison between copper and nickel-based catalysts obtained from hydrotalcite-like precursors for WGSR. *Catal. Today* **2011**, *171*, 290–296. [CrossRef]

11. Han, N.; Race, M.; Zhang, W.; Marotta, R.; Zhang, C.; Bokhari, A.; Klemeš, J.J. Perovskite and related oxide based electrodes for water splitting. *J. Clean. Prod.* **2021**, *318*, 128544. [CrossRef]

12. Han, N.; Yao, Z.; Ye, H.; Zhang, C.; Liang, P.; Sun, H.; Wang, S.; Liu, S. Efficient removal of organic pollutants by ceramic hollow fibre supported composite catalyst. *Sustain. Mater. Technol.* **2019**, *20*, e00108. [CrossRef]

13. Han, N.; Wang, S.; Yao, Z.; Zhang, W.; Zhang, X.; Zeng, L.; Chen, R. Superior three-dimensional perovskite catalyst for catalytic oxidation. *EcoMat* **2020**, *2*, e12044. [CrossRef]

14. Mellor, J.R.; Copperthwaite, R.G.; Coville, N.J. The selective influence of sulfur on the performance of novel cobalt-based water-gas shift catalysts. *Appl. Catal. A* **1997**, *164*, 69–79. [CrossRef]

15. Hutchings, G.J.; Copperthwaite, R.G.; Gottschalk, F.M.; Hunter, R.; Mellor, J.; Orchard, S.W.; Sangiorgio, T. A comparative evaluation of cobalt chromium oxide, cobalt manganese oxide, and copper manganese oxide as catalysts for the water-gas shift reaction. *J. Catal.* **1992**, *137*, 408–422. [CrossRef]

16. Copperthwaite, R.G.; Gottschalk, F.M.; Sangiorgio, T.; Hutchings, G.J. Cobalt Chromium Oxide: A Novel Sulphur Tolerant Water-Gas Shift Catalyst. *Appl. Catal.* **1990**, *63*, L11–L16. [CrossRef]

17. Bartholomew, C.H. Sintering kinetics of supported metals: Perspectives from a generalized power law approach. *Stud. Surf. Sci. Catal.* **1994**, *88*, 1–18. [CrossRef]

18. Bartholomew, C.H. Mechanisms of catalyst deactivation. *Appl. Catal. A* **2001**, *212*, 17–60. [CrossRef]

19. Hou, P.; Meeker, D.; Wise, H. Kinetic studies with a sulfur-tolerant water gas shift catalyst. *J. Catal.* **1983**, *80*, 280–285. [CrossRef]

20. Ratnasamy, C.; Wagner, J.P. Water Gas Shift Catalysis. *Catal. Rev.* **2009**, *51*(3), 325–440. [CrossRef]

21. Maciel, C.G.; Silva, T.F.; Assaf, E.M.; Assaf, J.M. Hydrogen production and purification from the water–gas shift reaction on CuO/CoO–TiO2 catalysts. *Appl. Energy* **2013**, *112*, 52–59. [CrossRef]

22. Aliabadi, H.Z. Thermodynamic modeling of the high temperature shift converter reactor using minimization of Gibbs free energy. *Int. J. Chem. Mol. Eng.* **2009**, *49*, 189–193. [CrossRef]

23. Babita, K.; Sridhar, S.; Raghavan, K.V. Membrane reactors for fuel cell quality hydrogen through WGS—Review of their status, challenges and opportunities. *Int. J. Hydrogen Energy* **2011**, *36*, 6671–6688. [CrossRef]

24. Popa, T.; Guoqing, X.; Barton, T.F.; Argyle, M.D. High temperature water gas shift catalysts with alumina. *Appl. Catal. A* **2010**, *379*, 15–23. [CrossRef]

25. Giné, M.J.L.; Amadeo, N.; Laborde, M.; Apesteguia, C.R. Activity and structure-sensitivity of the water-gas shift reaction over CuZnAl mixed oxide catalysts. *Appl. Catal. A* **1995**, *131*, 283–296. [CrossRef]

26. Twigg, M.V.; Spencer, M.S. Deactivation of supported copper metal catalysts for hydrogenation reactions. *Appl. Catal. A* **2001**, *212*, 161–174. [CrossRef]

27. Batista, M.S.; Santos, R.K.; Assaf, E.M.; Assaf, J.M.; Ticianelli, E.A. High efficiency steam reforming of ethanol by cobalt-based catalysts. *J. Power Sources* **2004**, *134*, 27–32. [CrossRef]

28. Wang, C.; Liu, C.; Fu, W.; Bao, Z.; Zhang, J.; Ding, W.; Chou, K.; Li, Q. The water-gas shift reaction for hydrogen production from coke oven gas over Cu/ZnO/Al2O3 catalyst. *Catal. Today* **2016**, *263*, 46–51. [CrossRef]