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Activity of Ni Catalysts for Hydrogen Production via Biomass Pyrolysis[1]

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Abstract—Ni catalysts were tested in the catalytic pyrolysis of biomass. The influence of Ni loading and various catalytic supports (ZrO_2, Al_2O_3, $ZrO_2 + Al_2O_3$, CeO_2, SiO_2) was studied. Although the gas phase was the main object of this study, solid and liquid residues were tested as well (mainly by TOC and GC-MS methods). Activity tests were performed in a batch reactor with mechanical stirring, equipped with on-line GC. Reaction was conducted at 700°C, with α-cellulose as a biomass model and with waste paper as an example of raw lignocellulosic material. Reactions in the presence of a catalyst gave a higher hydrogen yield. The most promising results were obtained with Ni/ZrO_2.

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The interest in using biomass for energy and hydrogen production is motivated largely by the increasing energy demand and global environmental requirements. The limited existing solutions for environmental problems like growing CO_2 emissions are pushing scientists to search for new ways of obtaining clean energy, with limited negative effects like the formation of harmful gases. Cellulose, being the largest fraction of lignocellulosic biomass, is the most abundant natural polymer with great potential to be used as a feedstock for alternative energy and fuels [1–3].

One of efficient and sustainable ways of providing hydrogen-rich gas as perspective source of clean fuel is cellulose pyrolysis. It is considered that via this way of cellulose valorization the future demands of hydrogen production can be fully satisfied [4, 5]. During the pyrolysis at high temperatures (700°C and above) due to complex processes which can occur (e.g. oligomerization and depolymerization) besides gaseous products (CO, CO_2, H_2 and CH_4) also unwanted unsaturated polymers, furanic species and tars can be formed [6, 7]. It has been proved in the literature that catalysts can have a beneficial effect on this process. Therefore, many catalytic systems based on Ni, Rh, Ru, Pt and Pd have been tested in this reaction [8–11].

Hydrogen-containing gas for industrial applications needs to have a sufficiently high concentration of H_2, and it requires the optimization of the pyrolysis reaction in which H_2 is produced. One of the ways to achieve this goal is the choice of an appropriate fine-tuned catalytic system. Nickel has been identified as one of the most efficient catalytic metals for this process, not only being economically attractive but also capable to increasing the hydrogen yield and limiting the tar formation by favouring the cleavage of C—C, C—H and O—H bonds [12–15]. However, despite a large number of studies concerning biomass pyrolysis, the influence of different supports on the ability of the catalyst to improve the hydrogen production has not been fully recognized.

The aim of our work was the further study of Ni catalysts potential and choice of the optimal systems based on this metal for highest hydrogen yield. We investigated the influence of metal loading and also the influence of different supports. In order to obtain a broader view on the reaction, we also analyzed the liquid and solid reaction products.

EXPERIMENTAL

The supported nickel catalysts (10–30% Ni) were prepared by the impregnation method. Nickel was introduced from $Ni(NO_3)_2 \cdot 6H_2O$ (Chempur, Piekary Śląskie; pure, p.a.) on Al_2O_3 (Merck, pure), SiO_2 (Merck, pure), ZrO_2 (Sigma-Aldrich, 99%) or CeO_2 (Sigma-Aldrich, 99.9%). The samples were aged for 24 h at room temperature. After evaporation of water, the catalysts were dried at 110°C for 2 h, then calcined in O_2 flow at 500°C for 4 h, and finally reduced in H_2 flow at 500°C in the same conditions. The binary supports were prepared the following way: Al_2O_3 was impregnated by $ZrO(NO_3)_2$ (Sigma-Aldrich, pure) for 24 h, then dried overnight at 120°C and calcined at 500°C for 4 h in O_2 flow. The prepared binary oxides were impregnated with Ni following the procedure described above.

The activity tests were performed in a stirred batch reactor (Fig. 1) under atmospheric pressure at 700°C

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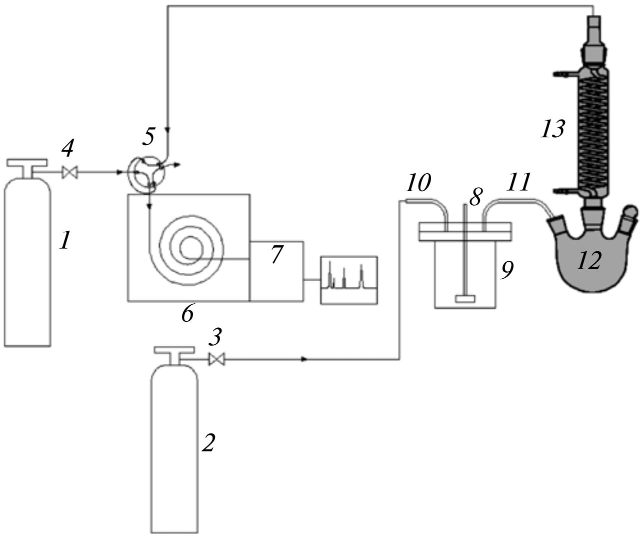

Fig. 1. Scheme of reaction system: *1*—GC flowing gas (Ar), *2*—reactor gas (Ar), *3* and *4*—flow meters, *5*—multi-way valve, *6*—GC, *7*—detector TCD, *8*—stirrer, *9*—batch stirred reactor, *10*—inlet of Ar, *11*—outlet of gases and liquid, *12*—round-bottom flask for liquid fraction, *13*—condenser.

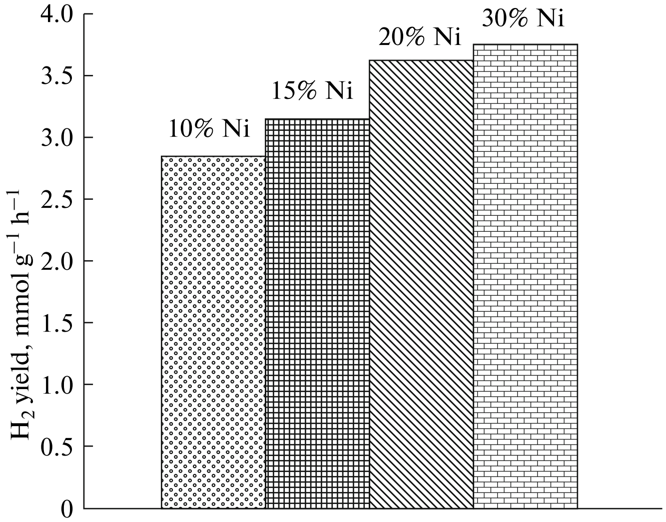

Fig. 2. Influence of Ni loading of Ni/Al_2O_3 catalyst on the H_2 production in biomass pyrolysis after 1 h reaction.

during 4 h. Reactor was loaded with the feedstock and heated to demanded temperature. α-Cellulose (Sigma-Aldrich, pure) was used for the pyrolysis. For a comparison, we also performed the pyrolysis tests of wastepaper, which besides cellulose and hemicellulose (90.3%) also contains lignin (9.7%). In every experiment 5 g of biomass and 0.2 g of nickel catalyst were used. Liquid products were condensed and trapped at −12°C. Gaseous products were analyzed by gas chromatography (GCHF 18.3, Chromosorb 102 column).

The gaseous products were determined on the basis of following equation:

$$N_g = \frac{c v_g}{v_m m},$$

where N_g—number of moles of gaseous products, c—percentage content of gas (on the base of chromatographic data), v_g—volume of gaseous products calculated on the basis of gases flow (dm^3), v_m—molar volume (22.4 mol/dm^3), m—mass of biomass sample (g). The amount of carbon in the solid residues remaining after the pyrolysis was measured by an automatic carbon analyzer TOC 5000 (Shimadzu) equipped with a solid sample module.

Temperature-programmed reduction (TPR) was performed on AMI1 system from Altamira Instruments (USA) equipped with a thermal conductivity detector and used for examining the reducibility of the catalysts calcined at 500°C. In the experiments, mixtures of 5 vol % H_2 and 95 vol % Ar or 2 vol % O_2 and 98 vol % Ar were used at space velocity 1.11×10^{-5} g h^{-1} cm^{-3} and linear temperature ramp of 10°C/min.

RESULTS AND DISCUSSION

As the aim of our research was to find the optimum catalytic system giving the highest H_2 yield, we concentrated first of all on the formation of gaseous reaction products (H_2, CO, CO_2 and CH_4).

Firstly we focused on finding the optimal Ni loading, and screened Ni/Al_2O_3 catalysts with the nickel load in the 10–30 wt % range. Their catalytic activities are shown in Fig. 2. We noticed that the activity increased with Ni loading, reaching the maximum value for 30% Ni/Al_2O_3, although the results for 30% and 20% nickel were comparable. Therefore, having in mind the economical reasons and still very promising results of 20% Ni, we decided to choose that catalyst.

In the next step, nickel was supported on various oxides. The activities of those catalysts are shown in Fig. 3. On each of catalysts, the amount of hydrogen produced in cellulose pyrolysis was considerably higher and the amount of CO_2 was lower in comparison with noncatalytic biomass pyrolysis. In contrast, the changes in the amount of CH_4 and CO obtained in catalytic and noncatalytic reactions were not so significant, in the agreement with the literature data [16]. The highest amount of hydrogen was found in the case of 20% Ni/ZrO_2 (Fig. 3), while for the other catalysts those amounts remained comparable. The mole fractions of gaseous products obtained on the most active system were the following: H_2—0.51, CO—0.20, CH_4—0.06, CO_2—0.23.

Due to the variety of applied conditions described in the literature in which this reaction was conducted it is very difficult to compare the results directly. However, it was often shown that Ni supported on Al_2O_3 is one of the most effective catalytic systems [17]. In our

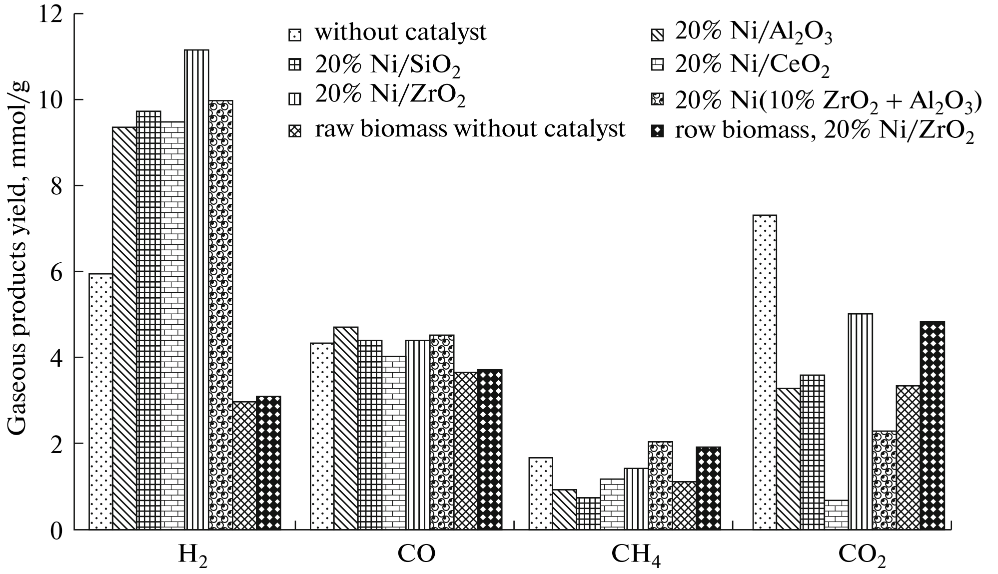

Fig. 3. Influence of support nature of 20% nickel catalyst on the amount of gaseous products of biomass pyrolysis.

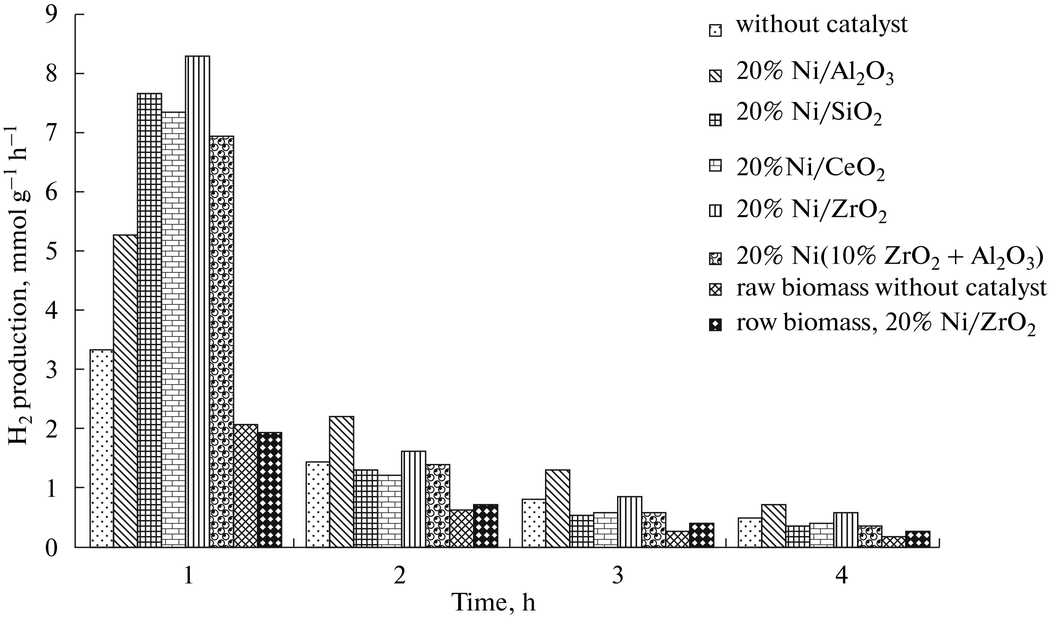

Fig. 4. Production of hydrogen in the subsequent time periods of biomass pyrolysis process on different 20% nickel catalysts.

work, despite the good performance of Ni/Al_2O_3, better H_2 yield was obtained on Ni/ZrO_2.

We also performed the analysis of gaseous products of biomass pyrolysis after each hour of reaction time on different samples of 20% nickel catalysts (Fig. 4). The formation of hydrogen was the highest in the first hour of the reaction. After this a sharp decrease of H_2 formation was initially noticed, which then became less significant. This trend was similar for all tested catalysts. Despite the highest overall activity of Ni/ZrO_2, the smallest drop in the hydrogen amount was noticed in the case of nickel supported on Al_2O_3. Probably the alumina-supported catalyst is the most stable in the reaction conditions. That is why, in the next part of our research we decided to synthesize a catalyst which would combine the best features of investigated systems (high activity and good stability). Taking the above into account we prepared catalysts with 20% Ni supported on binary oxides (10–30% ZrO_2–Al_2O_3). The activity of those binary oxide-sup-

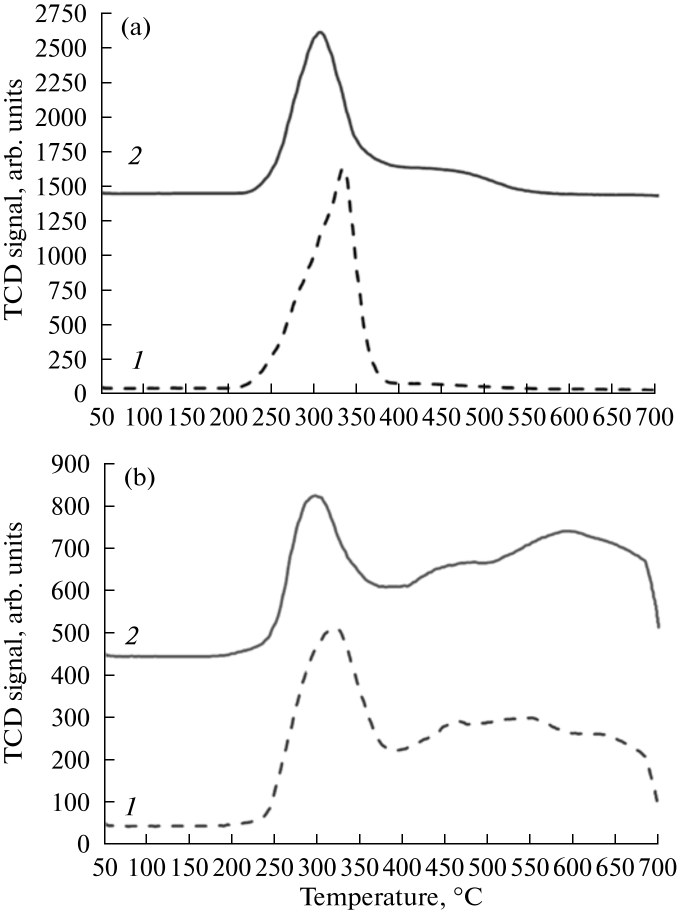

Fig. 5. TPR profiles of 20% Ni/ZrO_2 (a) and 20% Ni/Al_2O_3 (b) catalysts: *1*—fresh sample, *2*—reoxidized catalyst.

ported catalysts was higher than Ni/Al_2O_3 alone, and in that case the addition of zirconium dioxide was beneficial. This can be in agreement with the literature, where it was mentioned that the addition of ZrO_2 can additionally improve the coking resistance of this catalyst and therefore result in higher its activity in the reaction [18]. However, the activity of the best binary oxide system 20% $Ni/(10\% ZrO_2–Al_2O_3)$ was still lower in comparison with 20% Ni/ZrO_2.

Amounts of liquid fraction and solid residue after cellulose pyrolysis at 700°C

Sample	Liquid fraction, g	Solid residue, g
No catalyst	1.02	1.06
20% $Ni/(10\% ZrO_2 + Al_2O_3)$	0.71	1.18
20% Ni/Al_2O_3	0.63	0.97
20% Ni/SiO_2	0.43	0.88
20% Ni/CeO_2	0.86	1.04
20% Ni/ZrO_2	0.78	0.95

We also performed pyrolysis tests with waste paper samples as an example of raw biomass, however it appeared that the observed hydrogen yield was much lower than in the case of the reactions with α-cellulose.

In order to observe the behavior of the catalysts at the reaction temperature we performed the TPR measurements. Here we present the most stable (Ni/Al_2O_3) and the most active (Ni/ZrO_2) catalysts as examples. The TPR profiles of the catalyst which shows the highest selectivity towards hydrogen formation are shown in Fig. 5a. During the first reduction only effects from the reduction of NiO were visible and the temperature of maximum hydrogen consumption was 330°C. After recalcination this peak diminished and its maximum was shifted to 305°C. Additionally, slight effects of the interaction of active phase with the zirconia surface were observed at temperatures up to 540°C. In contrast, for Ni/Al_2O_3 (Fig. 5b) during the first reduction treatment, besides the effects connected with the reduction of the Ni phase, we could also notice the hydrogen consumption in the high temperature region (390–700°C). Those effects were still present after another calcination-reduction treatment. This difference in the interaction of Ni phase with the support could be a reason of the differences of catalytic activity of the analyzed samples.

The analysis of liquid fraction and solid residue of cellulose pyrolysis was performed also (table). It appeared that the amount of liquid fraction formed during the reaction was lower in the catalytic process than in the pyrolysis without a catalyst. There was also a tendency visible that the amount of liquid was the highest in the case of Ni/ZrO_2, followed by the catalyst supported on binary oxide ZrO_2 + Al_2O_3 and then on Al_2O_3 only. The GC-MS analysis of liquid fraction was also performed. The results revealed the presence of a large number of organic compounds in the investigated liquids. They contained mainly anhydro sugars, furanic species, and some other unsaturated and cyclic components, in agreement with the literature [19].

In order to examine the cellulose conversion we also performed the Total Organic Carbon (TOC) analysis of solid residue. In general the conversion of cellulose was higher in the presence of a catalyst. TOC analysis showed that C content in the solid residue was in the range of 83–97 wt %.

So, it has been demonstrated that Ni/ZrO_2 is the most efficient catalyst among the tested materials, even in comparison with Ni/Al_2O_3, which had previously been considered one of the most efficient gasification catalysts. The amount of hydrogen was almost twice as high in the presence of Ni/ZrO_2 in comparison with the reaction without a catalyst. The addition of ZrO_2 to Ni/Al_2O_3 improved the hydrogen yield. However, the activity of the best binary oxide system 20% $Ni/(10\%ZrO_2 + Al_2O_3)$ is still lower in comparison to 20% Ni/ZrO_2. The differences in activity of the investigated materials can be related to various interactions of Ni phase with the support.

We are currently performing further investigations of the systems based on the most promising material—Ni/ZrO_2—with raw biomass samples.

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