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Optimization of Ni/ZrO_2 catalytic performance in thermochemical cellulose conversion for enhanced hydrogen production

Agnieszka M. Ruppert[a,*], Michał Niewiadomski[a], Jacek Grams[a], Witold Kwapiński[b]

[a] Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology, ul. Żeromskiego 116, 90-924 Łódź, Poland
[b] Carbolea Research Group, Department of Chemical and Environmental Science, University of Limerick, Limerick, Ireland

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ABSTRACT

Hydrogen and syngas from cellulose or cellulosic biomass gasification are environmentally clean gaseous fuels used for power generation. In this work, we explored the potential of several Ni/ZrO_2 catalysts for the thermochemical conversion of cellulose to hydrogen. From the investigated catalysts the one consisting of tetragonal zirconia and containing the active phase with a small crystallite size and stable surface area, performed best in the cellulose conversion. Migration of zirconia on the nickel surface was found to be beneficial for catalytic performance. According to the XPS results, the highest Zr/Ni ratio was measured on the tetragonal phase of zirconia, followed by monoclinic ZrO_2, with amorphous zirconia showing the lowest migration tendency.

1. Introduction

Due to the increasing energy demand and climate changes there is a need to use alternative energy sources. It can be realized by developing new synthetic pathways of fuels and chemicals which would be based on lignocellulose as the most abundant second generation biofeedstock [1]. Hydrogen, which is currently mainly produced by natural gas steam reforming, in the future can also be obtained by cellulose valorization. Hydrogen is primarily used in methanol and ammonia syntheses, fuel cells, and hydrogenation reactions. One of the ways which can be applied to the production of gases of major importance in energy sector (H_2, CO) is a pyrolysis or gasification of lignocellulosic biomass [2].

In the biomass valorization, price of the catalytic materials is an important factor, therefore non-noble metal catalysts should be preferably used. Literature data show that nickel has a potential as an attractive, cheap metal catalyst for thermal conversion of biomass towards gases [3]. One of the major problems in gasification or pyrolysis of lignocellulosic feedstock is the formation of tars (condensable organic material) during the reaction. Condensed tar can cause the blocking and fouling of industrial turbines and engines.

Nickel is also considered as one of the best metals for tars elimination due to its ability to catalyze the C—C, C—H and O—H bond cleavage, which additionally confirms its choice as a metal catalyst [4–7]. However, due to severe conditions during the process (high temperature) catalysts based on Ni usually suffer from fast deactivation caused by rapid carbon deposition and sintering of Ni particles [8]. Their resistance to deactivation can be improved by the modification of surface properties of the used systems, i.e. by the development of a proper catalyst support. It is known that strong interactions between nickel oxide and some supports and high metal dispersion on a large surface area support can mitigate nickel sintering [9].

It is also known that ZrO_2, as a material with equilibrated amount of acidic and basic sites, limits the carbon deposition and possesses very good thermal stability and excellent redox properties [10,11], and the same may be considered an attractive support for Ni in thermal biomass conversion. The beneficial effect of Ni/zirconia was already shown in the literature, where the positive influence of ZrO_2 addition to Ni/Al_2O_3 catalysts was found in hydrogen production from glycerol [12]. Zheng et al. studied Ni/ZrO_2 catalysts in cyclic stepwise methane reforming towards hydrogen and found that by tuning the zirconia properties it is possible to considerably increase the catalytic activity, especially at high reaction temperatures. By application of zirconia nanocomposites they obtained comparably sized Ni and ZrO_2 nanocrystallites. Their sintering could be avoided due that fact they were able to change the nature of the carbon deposit which was a key to high stability of those materials [13]. Watanabe et al. found that zirconia catalysts can be very efficient in gasification of biomass in supercritical water, thanks to their acid-base properties [14]. It was also reported

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[*] Corresponding author. Tel.: +48 426313106; fax: +48 426313128.
E-mail address: aruppert@p.lodz.pl (A.M. Ruppert).

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that by tuning the size of ZrO_2 and Ni crystallites the hydrogen yield in methane reforming can be increased, and also catalyst stability can be improved at high temperatures [13]. On the other hand, low activity of ZrO_2 in some cases could be associated with its low surface area [12,15].

It was also shown in our earlier research [16,17], that from all tested oxides (Al_2O_3, SiO_2, CeO_2, TiO_2, MgO) ZrO_2 proved to be the most valuable support for Ni catalysts in the thermochemical biomass conversion, as the highest H_2 yield was obtained over commercial Ni/ZrO_2. Therefore in this work, we explored the potential of high surface area zirconia obtained by several different methods as an efficient support for nickel catalysts in thermochemical conversion of cellulose to hydrogen. To the best of our knowledge the subject was not investigated so far. Additionally we aim at understanding the nature of catalytic active sites and their influence on the activity enhancement.

2. Experimental

2.1. Catalyst preparation

Zirconium oxides were prepared using several methods described below. The following abbreviations are used in the text:

- ZR-1 was a commercial ZrO_2 material which was used as delivered (Aldrich, 99%).
- ZR-2 was prepared by calcination in air of $ZrO(NO_3)_2\cdot H_2O$ (Aldrich, 99% purity) at 400 °C for 4 h.
- ZR-3 was prepared by precipitation with Pluronic® P123 (PEG-PPG-PEG) (Aldrich, average Mn ~ 5800) polymer template from $ZrO(NO_3)_2$ [18]. First, aqueous solution of P123 and zirconium precursor ($ZrO(NO_3)_2\cdot xH_2O$ (Aldrich, 99% purity)) was prepared, with 0.03 M concentration of $ZrO(NO_3)_2$ and 0.03 molar ratio of P123 to ZrO_2. Ammonia (Chempur, 25% concentration, pure for analysis) was then added dropwise to pH = 11 and the mixture was heated to 88 °C and stirred for 24 h. The precipitate was filtered on a Büchner funnel and washed with acetone (StanLab, pure for analysis) to remove template polymer residues, and then with water. It was then dried at 110 °C in air for 24 h and calcined in air at 500 °C for 3 h.
- ZR-4 was prepared by similar precipitation method as described above, only without a polymer template.
- ZR-5 was prepared from $ZrOCl_2$ (Sigma–Aldrich, pure for analysis ($\geq$99.5%)) by precipitation with NaOH followed by calcination at 700 °C in air [19]. First, 200 ml of 0.4 M $ZrOCl_2$ was added dropwise to 60 ml of 5 M NaOH (StanLab, pure for analysis). Then the mixture was heated to 104 °C and stirred for 24 h. The precipitate was filtered on a Büchner funnel and washed with 0.05 M solution of NH_4NO_3 (Chempur, pure (min. 99%)) and then with water until neutral pH. It was then dried in air at 110 °C overnight and calcined in air at 700 °C for 3 h.
- The catalysts were obtained by impregnating the oxides with 1 M $Ni(NO_3)_2$ ($Ni(NO_3)_2\cdot 6H_2O$ (Chempur, pure for analysis (min. 99%)) aqueous solution to obtain 20 wt.% Ni content calculated for the catalyst amount. Before the reaction the catalysts were calcined in air at 500 °C for 4 h, except Ni-ZR-6, which was prepared by high temperature treatment of Ni-ZR-1 at 900 °C for 4 h.
- Ni-ZR-X (X = 1–6) are used for the nickel-impregnated catalysts.

Samples which were subjected to characterization ‘after reaction’ were prepared in the same conditions as during reaction but without the presence of cellulose, in order to avoid the influence of other factors like carbon deposit and tar formation.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) was performed on AMI1 system from Altamira Instruments 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 3.1×10^{-9} g s^{-1} cm^{-3} and linear temperature ramp of 10 °C min^{-1}. The surface area was measured by the BET method.

X-ray photoelectron spectroscopy (XPS) surface analysis of the investigated catalysts was performed on Kratos AXIS 165 spectrometer using Al mono Kα X-ray. The samples were fixed onto the sample holder by double-sided adhesive tape.

Powder X-ray diffractograms were collected using a PANalytical X’Pert Pro MPD diffractometer. The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40 kV and 30 mA. Data were collected in the 5–90° 2θ range with 0.0167° step. Crystalline phases were identified by references to ICDD PDF-2 (ver. 2004) database. All calculations were performed with X’Pert HighScore Plus computer program.

Transmission electron micrcoscope (TEM) – JEM-2100F, JEOL – was used for the measurement of the metal particle size on the surface of the different supports. Prior to TEM analysis, all catalysts were reduced for 1 h at 500 °C under hydrogen flow.

2.3. Catalytic activity

The activity tests were performed in a 250 cm^3 stirred batch reactor under atmospheric pressure and 15 cm^3 min^{-1} flow of Ar at 700 °C during 4 h. Pyrolysis of α-cellulose (Sigma–Aldrich, pure) as a biomass model (5 g) was conducted both without a catalyst and in the presence of a nickel catalyst (0.2 g). In the case of NiO only 0.04 g of the catalyst was used, which is equivalent of the NiO quantity in the supported systems. Gaseous products were analyzed by gas chromatography (GCHF 18.3, Chromosorb 102 column) equipped with the TCD detector. Besides the gas fraction, the liquid one was also collected. It appeared that the presence of catalysts decreased the amount of condensables in comparison to a reaction without catalyst. For all investigated Ni/zirconia catalysts the composition of liquid phase was similar. Liquid fraction was analyzed by GC–MS.

3. Results

3.1. Catalytic performance

As the aim of our research was to find the optimum Ni/zirconia system which provides the highest hydrogen yield, the focus was on a formation of light gaseous reaction products (H_2, CO, CH_4 and CO_2).

The activity results are presented in Fig. 1. It appeared that among tested Ni/zirconia catalysts the highest H_2 yield was achieved in the case of Ni-ZR-5 and just slightly lower yield was obtained for Ni-ZR-2, whereas the lowest yield was observed for Ni-ZR-3. In every case the hydrogen yield was higher in the presence of a catalyst. The amount of CO_2 was lower in most cases when a catalyst was used, compared to the non-catalytic reaction. In contrast, the changes in the amount of CH_4 and CO obtained in catalytic and non-catalytic reactions were insignificant. The highest CH_4 yield was achieved over Ni-ZR-4.

The exact mechanism of thermal decomposition of cellulose is unknown. The depolymerized sugar unit intermediates are probably adsorbed on the metal surface, where they undergo dehydrogenation, hence the increasing hydrogen yield in the presence of a catalyst. Subsequently, the cleavage of C—O and C—C bonds can occur to form various carbonaceous products. Without external