Research paper

Reactivity of platform molecules in pyrolysis oil and in water during hydrotreatment over nickel and ruthenium catalysts

Chiara Boscagli [a], Klaus Raffelt [a, *], Jan-Dierk Grunwaldt [a, b]

[a] Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany
[b] Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Engesserstr. 20, 76131, Karlsruhe, Germany

ABSTRACT

Hydrodeoxygenation (HDO) of fast pyrolysis oils for fuel and chemical production was investigated in a batch autoclave at 340 °C (8.0 MPa H_2 at room temperature) over nickel-based catalysts and Ru/C. The deoxygenation degree was similar over all catalysts, but different H/C ratios were observed in the upgraded oils, in line with the corresponding H_2 consumption. The highest values were found for Ru/C followed by NiCu/Al_2O_3. The composition of the upgraded oils produced over Ni-catalysts showed high ketone content, while the upgraded oil over Ru/C contained hydrocarbons and alcohols. Phenolic compounds exhibited low conversion over all catalysts. Subsequently the influence of the reaction medium (bio-oil or water) on the activity and selectivity of the catalyst was probed using phenol and D-glucose as model compounds representative for the cellulose and lignin fraction, respectively. Their reactivity in the bio-oil was tracked using isotopically-labelled phenol-d_6 and D-glucose-$^{13}C_6$. Phenol was HDO resistant, while D-glucose formed a complex product mixture recovered in the upgraded oil. In aqueous solution, phenol was converted mainly to methane over Ru/C and cyclohexane over NiCu/Al_2O_3, whereas both catalysts promoted hydrocracking of D-glucose to methane. Comprehensive analysis of the spent catalysts showed that inorganic deposits and further components in the bio-oil lead to different reactivity in the two media.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The increasing scarcity of crude-oil reserves is driving a transition in the future energy economy from fossil to renewable resources. As the main renewable source of carbon, biomass is an attractive prospect for production of transport fuels and chemicals [1]. The main challenge of the last decades has been the utilization and valorization of lignocellulosic materials that are not in competition with food supply [2]. From an economic and energetic point of view, fast pyrolysis followed by an upgrading method is considered to be an attractive strategy [3] for producing a substrate that could be further co-processed in a refinery or converted to fuels/chemicals in dedicated facilities [4]. Fast pyrolysis is a versatile process for different biomass feedstocks and an easy solution for energy densification in volume [5]. However, the bio-oils produced are not directly suitable as transportation fuel or for chemical

production and a subsequent upgrading process is therefore necessary [3,5–10].

Hydrodeoxygenation (HDO) is usually the preferred method among upgrading processes (e.g. zeolite cracking) since it can produce high quality fuels with high carbon efficiency [3]. Using an appropriate HDO catalyst and high hydrogen pressure, oxygen is eliminated from the organic molecules in bio-oil in the form of water, producing an upgraded oil that is more stable, with higher heating value and more similar to crude oil. A lot of progress regarding HDO has been achieved in the last years, using hydrodesulfurization and noble metals catalysts [3]. However, improving long-term stability of the catalyst is still a prerequisite for industrial applications [11–14]. Recent efforts in HDO have focused on alternative catalysts [15], which are preferably sulfur free, economically viable and environmentally friendly. Especially nickel-based catalysts, which are also studied in this work, have attracted considerable interest [15–27].

Until now, most studies on HDO catalysts concern model compounds (reviews of Ref. [12,28]) rather than pyrolysis oils [3,8,16–19,29] and only a few comparisons between these two

cases have been reported [17,30–32]. Testing a catalyst with model compounds presents the advantage of studying an easier system than bio-oils, which are difficult to compare with other literature studies due to their variable and complex composition. However, different factors that could affect the conversion and selectivity of a compound during HDO in pyrolysis oil, are generally not considered in studies with models compounds. For example, the polarity of the reaction medium [33], competitive adsorption of different species on the catalyst surface [32,34], parallel side-reactions [35] and catalyst deactivation [36–38] can lead to formation of different products, depending on whether the catalyst is tested in a pure solvent or in bio-oil.

The present work aimed to comprehend and compare the reactivity of phenol and D-glucose as platform molecules during HDO in pyrolysis oil and in a pure solvent. The light phase of a pyrolysis oil produced from wheat straw in the bioliq® pilot plant [39] was used, since it constitutes a simplified system for detecting reaction paths in comparison to the whole bio-oil. Firstly, the light phase was hydrotreated at 340 °C over different nickel-based catalysts (supported on different materials) and Ru/C (used as benchmark), and the catalyst performance and the reaction products were compared. Subsequently, the reactivity of isotopically-labelled compounds (phenol-d_6 and glucose-$^{13}C_6$) in pyrolysis oil was monitored over NiCu/Al$_2$O$_3$ (as representative of Ni-catalyst class) and Ru/C and compared to their reactivity in pure water to further understand the influence of the bio oil on the conversion and selectivity of the catalysts.

2. Materials and methods

2.1. Pyrolysis oil, reagents and catalysts

The deep HDO carried out in this study is the extension of a previous work done at milder conditions (250 °C) reported in Ref. [40]. The same feed and catalysts were used. The feed was the light phase of a pyrolysis oil produced by wheat straw at the bioliq® plant at the Karlsruhe Institute of Technology. The light phase was produced by a spontaneous phase separation of the whole bio-oil after the production and contained 56.7% water and low molecular weight compounds, mainly sugar derivatives (details on the solvent fractionation are given in Ref. [40]). The elemental composition C, H, N, O is reported in Section 3.1 and 3.3. In addition, the light phase contained 0.05% sulfur (wet basis) and 1.72% dissolved metals (mainly K).

Five nickel-based catalysts on various supports and in some cases including promoters were prepared by wet impregnation (details in Ref. [40]): NiCu/Al$_2$O$_3$ (17.8% Ni, 2.1% Cu, BET surface 66 m^2 g^{-1}), Ni/SiO$_2$ (22.0% Ni, BET surface 170 m^2 g^{-1}), Ni/ZrO$_2$ (5.8% Ni, BET surface 110 m^2 g^{-1}), NiW/AC (3.2% Ni, 7.8% W on Active Carbon, BET surface 1110 m^2 g^{-1}) and Ni/TiO$_2$ (5.8% Ni, BET surface 86 m^2 g^{-1}). The mean Waddel disk diameter of the catalyst particle size was less than 100 μm. A commercial Ni/Al$_2$O$_3$ (METH 134 C&CS, nominal loading Ni 20%, Ca 3%, BET surface 76 m^2 g^{-1}) and Ru/C(Sigma Aldrich, 206180, nominal loading 5%, BET surface 870 m^2 g^{-1}) were also tested as benchmark.

For the studies with model compounds in water (milliQ), phenol (Merck, 8.22296.1000) and D-glucose monohydrate (Merck, 1.08342.2500) were used. Phenol-d_6 (Aldrich, 176060) and D-glucose-$^{13}C_6$ (Deutero GmbH, 50302) were added to the pyrolysis oil for studies about the reactivity in this medium.

2.2. Hydrodeoxygenation experiments

The experiments were carried out in an Inconel alloy 625 autoclave designed for pressures up to 36 MPa and temperatures up to 400 °C (manufactured at IKFT-KIT, Fig. S1 of Supporting Information). It was equipped with a magnetically-coupled stirrer (torque 80 N cm, Premex reactor AG) and a gas injection stirrer was employed to facilitate mass transfer of hydrogen in the liquid medium. Heating cartridges inserted in a brass mantle were used for heating and the power supply was controlled by Labview software.

Three kinds of experiment were carried out:

- HDO of the light phase of pyrolysis oil over different nickel-based catalysts or Ru/C: 2.5 g catalyst and circa 50 g light phase were inserted in the autoclave;
- HDO of the light phase of the pyrolysis oil with isotopically labelled molecules over NiCu/Al$_2$O$_3$ or Ru/C: 2.5 g catalyst, circa 50 g light phase, 200 μg phenol-d_6 and 200 μg D-glucose-$^{13}C_6$ were inserted in the autoclave. Additional experiments with 10% D-glucose monohydrate in the light phase over NiCu/Al$_2$O$_3$ and Ru/C were carried out to gain more information about its reactivity;
- HDO of platform molecules in milliQ water over NiCu/Al$_2$O$_3$ or Ru/C: 2.5 g catalyst, 50 g of 10% phenol or D-glucose monohydrate solution were inserted in the autoclave.

A blank test (without catalyst) was carried out for each type of experiment. The results are reported as the average of two experiment replicates. The percentage values indicating concentrations or yields presented in this paper are reported as mass fraction, if not else specified.

Once the reagents were inserted in the autoclave, the autoclave was purged with nitrogen and then pressurized with hydrogen (purity 99.9999%) until 8.0 MPa at room temperature. The stirrer was set at 16.7 Hz and a heating ramp rate of 15 K min^{-1} was used to reach 340 °C. In this case, the stabilisation of the bio-oil (to avoid polymerization and excessive coke production) was performed during the heating ramp, as reported previously in literature [10,40]. For the sake of comparison, similar reaction conditions to previous literature studies [17,18,41,42] were used. Mass transfer between gas-liquid and liquid-solid phase were minimized using a good mixing (16.7 Hz, gas injection stirrer) and small size of the catalysts grains. The global reaction time including the heating ramp was 100 min. Afterwards the reaction was quenched, first with a flow of compressed air and then with a bath of ice/water. A gas aliquot was sampled and the autoclave was evacuated. The hydrogen consumption was calculated by subtracting the partial pressure of hydrogen at the beginning and end of the reaction (at room temperature) using the Soave-Redlich-Kwong equation as described previously in Ref. [40]. The product mixture was collected and centrifuged at 7240 RCF for 30 min (Thermo Scientific Heraus Biofuge Stratos, fixed angle rotor 26 n.75003014) to separate the two liquid phases (an aqueous phase and an upgraded oil) and the spent catalyst. The solid was washed with acetone and then dried. To overcome excessive losses in the mass balance, the liquid product yields were calculated using the elemental composition of each phase and the principle that the mass of carbon and oxygen should be conserved during the reaction (equation system below):

$$\begin{cases} Tot\ C = (\%wp * C_w + \%oil * C_{oil})/100 \\ Tot\ O = (\%wp * O_w + \%oil * O_{oil})/100 \end{cases}$$

Tot C and *Tot O* are the quantity of carbon and oxygen theoretically recovered from the liquid products. These were calculated by subtracting the respective quantities in gas and solids (oxygen in the solids was considered negligible) from those contained in the original feed. *%wp* and *%oil* are the yields (mass fraction expressed as percentage) of aqueous phase and upgraded oil respectively, produced during the reaction. C_w and C_{oil} are the carbon contents