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International Symposium on Air and Water Pollution Abatement Catalysis (AWPAC) – Catalysis for renewable energy

Catalytic performance of a Ni catalyst supported on CeO₂, ZrO₂ and CeO₂–ZrO₂ in the upgrading of cellulose fast pyrolysis vapors



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ARTICLE INFO

Article history:

Received 29 December 2014

Accepted after revision 2 March 2015

Available online 2 November 2015

Keywords:

Heterogeneous catalysis

Supported catalysts

Nickel

Cerium

Zirconium

Sustainable chemistry

ABSTRACT

This work was devoted to the investigation of the catalytic performance of a Ni catalyst supported on CeO₂, ZrO₂ and CeO₂–ZrO₂ in the upgrading of cellulose fast-pyrolysis vapors. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and temperature-programmed reduction (TPR) were used for the surface characterization of the prepared materials. The activity of the catalysts was evaluated by analytical pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). It was demonstrated that the use of 20%Ni/15%CeO₂–ZrO₂ allowed one to obtain the highest olefin and paraffin contents, while owing to the application of 20%Ni/ZrO₂ catalyst the largest amount of aromatics was produced and a considerable decrease in the amount of carboxylic acid fraction was noticed.

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1. Introduction

Biomass is considered to be one of the most abundant alternative energy sources. Its great potential results from its low price and wide availability and from the fact that it does not contribute to the increase in the emission of carbon dioxide [1,2]. Moreover, lignocellulosic biomass, consisting mainly of cellulose, hemicelluloses and lignin, does not compete with the production of food. Among the most popular methods for its conversion are pyrolysis and gasification [3–5]. Both of them allow one to obtain liquid fraction, permanent gases and solid residue (char). However, the contribution of each one of these phases

can be different depending on the type of process and reaction conditions. Fast pyrolysis consists of the thermal decomposition of feedstock in the absence of reactive gas (oxygen or steam), leading to the maximization of the liquid products [6]. This can be achieved by very high heating rates of the biomass and fast separation of the arising products, which limits secondary cracking reactions resulting in the formation of a larger amount of gases [7].

In spite of the optimization of the reaction conditions, the produced bio-oil is usually a mixture of hundreds of organic compounds that can be divided into several groups: hydrocarbons, acids, ketones, aldehydes, alcohols, sugars, esters, ethers, epoxides and others. Moreover, the presence of water is also observed. Water and a wide group of oxygen-containing compounds are responsible for most of the bio-oil disadvantages, including low heating value,

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corrosiveness, chemical and thermal instability and immiscibility with petroleum fuels. It is therefore impossible to supply such a product directly to automotive engines. One of the most popular processes leading to the improvement of bio-oil quality is the reduction of the oxygen content by converting undesirable compounds (acids, aldehydes, etc.) into desirable ones (hydrocarbons). This can be achieved by the upgrading of biomass fast pyrolysis vapors. The upgrading process is usually carried out in the presence of a catalyst, which allows one to increase the yield of less oxygenated compounds.

The literature data show that among the most popular catalysts used in this process are zeolites and mesoporous materials [8–10]; however the studies concerning the application of metal oxides have also been presented [11]. It appears that the introduction of nickel onto their surface results in a further increase in the yield of hydrocarbons [12]. Lu et al. [13] compared in their studies the surface properties of mesoporous supports (i.e. MCM-41 or SBA-15) with TiO_2 , ZrO_2 and $\text{TiO}_2\text{-ZrO}_2$ oxides. They reported that the second group of materials possessed better hydrothermal stability, and their lower production cost makes them more suitable to be applied as supports for catalysts of the upgrading of biomass pyrolysis vapors. Therefore, in the next step of those investigations, two noble metals – ruthenium and palladium – were introduced on their surface using the impregnation method. In order to achieve a better dispersion of the metals, the supports were firstly impregnated by cerium nitrate and calcined in air as the presence of cerium oxide is believed to promote the metal dispersion on the catalyst's surface. The obtained results revealed that such catalysts can significantly reduce the amount of acids, phenols and sugars, simultaneously increasing the content of hydrocarbons, linear ketones, and cyclopentanones. The advantages of cerium oxide used as a catalyst support are not only associated with the ability to stabilize metal dispersion, but also to enhance oxygen storage/transport in the structure of the catalyst and to improve the oxidation and reduction of the introduced metal [14]. Cerium oxide was successfully applied as a catalyst support in many industrial processes, such as methane reforming [15] or water–gas shift reaction [16], among others. It has been however reported that the surface properties of CeO_2 may be strongly influenced by thermal treatment. One of the methods for improving its thermal stability and redox properties is the addition of zirconium oxide.

Taking this into account, we decided to apply $\text{CeO}_2\text{-ZrO}_2$ as a support of the catalysts for biomass fast pyrolysis vapors upgrading. Due to its promising catalytic performance and relatively low cost, nickel was used as the active metal. Similar materials consisting of Ni introduced on $\text{CeO}_2\text{-ZrO}_2$ surface have been earlier applied in the steam reforming of ethanol and bio-oil, reforming of methane and gasification of model tar (benzene, toluene), among other processes [17–22]. In our work, the influence of the composition of the Ni catalyst support on the distribution of the products arising in the upgrading process of biomass fast pyrolysis vapors has been investigated. Commercial cellulose was applied as a reference material. The activity of the catalysts was

evaluated by analytical pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). The surface properties of the synthesized catalysts were also characterized.

2. Experimental

2.1. Preparation of the catalyst

Zirconium oxide was prepared from ZrOCl_2 (Sigma-Aldrich, pure for analysis ($\geq 99.5\%$)) by precipitation with NaOH followed by calcination at $700\text{ }^\circ\text{C}$ in air. First, 200 mL of 0.4 M ZrOCl_2 were added dropwise to 60 mL of 5 M NaOH (StanLab, pure for analysis). Then the mixture was heated to $104\text{ }^\circ\text{C}$ and stirred for 24 h. The precipitate was filtered on a Büchner funnel and washed with a 0.05 M solution of NH_4NO_3 (Chempur, pure (min. 99%)) and then with water until a neutral pH is obtained. It was then dried in air at $110\text{ }^\circ\text{C}$ overnight and calcined in air at $700\text{ }^\circ\text{C}$ for 3 h. In the case of a monoxide support consisting of cerium oxide, the commercial material (Sigma-Aldrich, 99.9%) was used as delivered.

The 15% $\text{CeO}_2\text{-ZrO}_2$ support was prepared by the impregnation of ZrO_2 obtained as described above with an aqueous solution of $\text{Ce}(\text{NO}_3)_3$ (Sigma-Aldrich). The mixture was left for 24 h and then evaporated. The resulting powder was dried at $120\text{ }^\circ\text{C}$ for 2 h. Then it was calcined at $500\text{ }^\circ\text{C}$ for 4 h.

The 20% Ni catalysts were prepared by the impregnation method. Nickel was introduced from $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Chempur, pure) on CeO_2 , ZrO_2 and $\text{CeO}_2\text{-ZrO}_2$ surfaces. The samples were aged for 24 h at room temperature. After water evaporation, the catalysts were dried at $110\text{ }^\circ\text{C}$ for 2 h, then calcined in an O_2 flow at $500\text{ }^\circ\text{C}$ for 4 h.

2.2. Characterization of the catalyst

The surface area measurements were carried out on an ASAP2010 Micromeritics device using N_2 as an adsorbent at $-196\text{ }^\circ\text{C}$, with prior outgassing at $200\text{ }^\circ\text{C}$ for 3 h in order to desorb the impurities or the moisture. The Brunauer–Emmett–Teller (BET) specific surface area was calculated from the N_2 adsorption isotherm.

The acidity of the measured samples was determined by temperature-programmed desorption of ammonia (TPD- NH_3). Prior to the measurements, each sample was heated at $500\text{ }^\circ\text{C}$ for 1 h under an argon atmosphere. After cooling the samples to $100\text{ }^\circ\text{C}$, the adsorption of ammonia was performed for 15 min. Afterwards, flushing of the samples with argon was carried out for 15 min. The measurement was performed by heating the samples to $500\text{ }^\circ\text{C}$ with a ramp of $27\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and registering the amount of desorbed ammonia using a thermal conductivity detector (TCD).

Temperature-programmed reduction (TPR) was performed on an AMI1 system (Altamira Instruments) equipped with a thermal conductivity detector and used for examining the reducibility of the catalysts calcined at $500\text{ }^\circ\text{C}$. In the experiments, a mixture of 5 vol.% H_2 and 95 vol.% Ar was used at the space velocity of $3.1 \times 10^{-9}\text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-3}$ and a linear temperature ramp of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

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