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Carbons from second generation biomass as sustainable supports for catalytic systems

Laura Prati^{a,*}, Davide Bergna^{b,c}, Alberto Villa^a, Paolo Spontoni^a, Claudia L. Bianchi^a, Tao Hu^b, Henrik Romar^{b,c}, Ulla Lassi^{b,c}

^a Università degli Studi di Milano, Dipartimento di Chimica, via C.Golgi 19, 20133 Milano, Italy

^b University of Oulu, Research Unit of Sustainable Chemistry, P.O. Box 3000, FI-90014 University of Oulu, Finland

^c Kokkola University Consortium Chydenius, University of Jyväskylä, Unit of Applied Chemistry, Talonpojankatu 2B, FI-67100 Kokkola, Finland

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ABSTRACT

In this study activated carbons were produced from the wood of three different wood species (pine, birch, spruce). The resulting activated carbons were characterized in bulk for ash content, carbon content (elemental analyses), specific surface area, and pore size distribution, and at the surface by measuring the autogenerated pH and studying their structure by XPS. All the samples presented high surface areas and appeared to be mesoporous materials (mesopores >80%). The carbons were then used as support for AuPt nanoparticles and tested in the liquid phase oxidation of glycerol (GLY) and in the hydrogenation of levulinic acid (LA), two important chemicals from cellulose-based biomass. The catalytic results showed that the catalyst activity depends on the structural features of carbons: in GLY oxidation the most active catalyst presents the lowest content of carboxylic acid (Birch derived carbon) whereas in LA hydrogenation a higher content of aliphatic structure seems to enhance the stability and therefore the activity of the catalyst (Spruce catalyst). The structure of the carbons does not affect greatly the selectivity of both selected model reactions.

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1. Introduction

Many recent reviews deal with the advantages of carbon supports for the preparation of highly dispersed metal catalysts [1–6]. Porous carbon materials like activated carbon have physical and chemical surface properties that can easily be tailored such as surface area, pore size distribution and surface acid–base characters that affect not only the metal dispersion but also the intrinsic activity of catalysts [3]. The metal–support interactions indeed can be tuned by varying the composition and the structural features of carbons [7,8]. Moreover, from a catalytic point of view the porous structure is of importance especially in the case of liquid phase reactions where diffusional limitation can be present when microporous materials are used [9].

Activated carbons can be generated starting from different C-containing precursors and normally the control on porous structure and composition is made by the careful control of the starting materials (hard or soft template syntheses) [10,11]. On the other hand an attractive feature of activated carbons is the cheapness due to

the natural, low cost, large availability of the starting materials. Therefore the present study explores the possibility to use second generation biomass materials for the preparation of activated carbon to be used as support for metal nanoparticles. In particular the aim of the study has been focused on the use of sawdust samples of birch (*Betula pendula*), pine (*Pinus sylvestris*) and spruce (*Picea abies*) which constitute waste fractions from the saw mill in Northern Finland, available in large quantities. These waste fractions are typically used for energy (heat) production having the heat values of 18.9, 19.0 and 19.3 MJ/kg for birch, pine and spruce, respectively.

The sawdust samples were dried at room temperature and sieved to a particle size smaller than 1.2 mm before being carbonized and activated in a one-step process. The obtained activated carbons are characterized by a large amount of mesopores thus promising supporting material for liquid phase catalysis. For the catalytic test we used two important reactions: the first related to the valorization of glycerol (oxidation) and the second to the transformation of levulinic acid into biofuels (reduction).

The catalysts were prepared by supporting pre-formed metal nanoparticles thus reducing as much as possible variation of size when supported. This approach allowed us to determine a correlation between the different composition of carbons and the activity of AuPt nanoparticle supported on them. Surprisingly we found

* Corresponding author.

E-mail address: laura.prati@unimi.it (L. Prati).

that different features should be considered in the two reactions in one case privileging the activity and in the other the resistance to poisoning in the other.

2. Experimental

Sawdust samples were supplied by sawmill located in Northern Finland. Before using the samples were room dried, and sieved to a particle size smaller than 1.2 mm.

2.1. Carbon synthesis and characterization

2.1.1. Carbonization and activation of sawdust

Carbonization and activation of the sawdust samples was performed in a single-step process using a rotating quartz reactor inserted in a Nabertherm oven. About 400 g of each sample was inserted to the reactor, during the carbonization step the temperature ramped from RT to 800 °C (10 °C/min). At 800 °C the temperature was kept for 2 h, during this period the reactor was flushed with 120 g/h of overheated steam (140 °C) produced by a steam generator using nitrogen as carrier. During the whole process the reactor was flushed with nitrogen in order to prevent oxidation of the samples. Oven was cooled down over night, continuously flushed with nitrogen. Finally carbons were taken out and dried at 105 °C for 8–12 h.

2.1.2. Total carbon content (TC) and elemental analysis

Elemental analysis was performed through PerkinElmer optical emission spectrometer Optima 5300 DV ICP–OES.

2.1.3. Specific surface areas and pore size distributions

Specific surface areas and pore distributions were determined from the adsorption–desorption isotherms using nitrogen as adsorbate. Determinations were performed with a Micromeritics ASAP 2020 instrument. Portions of each catalyst (100–200 mg) were degassed at low pressure (2 μ m Hg) and high temperature (140 °C) in order to clean their surfaces. Adsorption isotherms were obtained by immersing sample tubes in liquid nitrogen (–196 °C) to obtain isothermal conditions. Nitrogen was added to the samples in small steps and the resulting isotherms were obtained. Specific surface areas were calculated from adsorption isotherms according to the BET [12] method, while nitrogen adsorption and desorption isotherms were used to calculate the pore size distribution using the BJH method [13] With the used instrument setup μ -pores down to 1.5 nm in diameter could be measured.

2.1.4. Autogenerated pH

pH was measured by suspending a carbon sample (50 mg) in a degassed 10^{–1} M KCl solution (50 mL) overnight.

2.1.5. XPS analyses and TEM images

The X-ray photoelectron spectroscopy (XPS) were acquired with an ESCALAB 250Xi (Thermo Fisher Scientific) spectrometer using monochromatic Al K α radiation source (1486.7 eV) operated at 20 mA and 15 kV. The catalyst samples were pressed on an Indium film and the spot size of 900 μ m was used. The C, O, N and In were measured for all samples. The spectral analysis was carried out with Avantage V5 processing software. Charge compensation was used to determine the presented spectra and the calibration of the binding energies (BE) was performed by applying the C1s line at 284.6 eV as reference.

A Energy filtered transmission electron microscope (EFTEM) LEO 912 OMEGA EFTEM was used to study the microstructure of the catalysts in the Center of Microscopy and Nanotechnology (CMNT) University of Oulu. The catalyst samples were dispersed in acetone

and pretreated in ultrasonic bath. A small drop of microemulsion was deposited on a copper grid pre-coated with carbon.

2.1.6. Atomic Absorption Spectroscopy

The initial metal content and metal leaching were checked by Atomic Absorption Spectroscopy (AAS) analysis of the filtrate, on a PerkinElmer 3100 instrument.

2.2. Preparation of AuPt supported catalysts

NaAuCl₄•2H₂O (Au: 0.031 mmol) was dissolved in 60 mL of H₂O, and PVA (1%, wt%) was added (Au/PVA = 1:0.5 wt/wt). The yellow solution was stirred for 3 min, after which 0.1 M NaBH₄ (Au/NaBH₄ = 1:4 mol/mol) was added under vigorous magnetic stirring. The ruby-red Au(0) sol was formed immediately. Within a few minutes of sol generation, the gold sol was immobilized by adding the support (acidified to pH 2 by sulphuric acid in order to maximize the electrostatic interaction between the carbon surface and the MNPs) under vigorous stirring. The amount of support was calculated as having a gold loading of 0.60 wt%. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors). The Au/support was dispersed in 40 mL of water, with K₂PtCl₄ (Pt: 0.021 mmol) and PVA solution (Pt/PVA = 1:0.5 wt/wt) added. H₂ was bubbled (50 mL/min) under atmospheric pressure and room temperature for 2 h. The slurry was filtered and the catalyst washed thoroughly with distilled water. The total metal loading was 1 wt%.

2.3. Catalytic tests

2.3.1. Glycerol oxidation

Reactions were carried out in a thermostated glass reactor (30 mL) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 mL) containing oxygen at 3 bar. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow time diagram. The glycerol was dissolved in 10 mL of water, mixed the catalyst (0.3 M the final concentration of glycerol, glycerol/metal = 500 mol/mol). The reactor was pressurized at 3 bar of O₂ and thermostated at the appropriate temperature. Once the required temperature was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. The reaction was initiated by stirring.

2.3.2. Levulinic acid hydrogenation

Levulinic acid (LA) hydrogenation was performed at 70 °C, using a stainless steel reactor (50 mL capacity), equipped with heater, magnetic stirrer, gas supply system and thermometer. The LA solution (30 mL; 0.3 M) was added into the reactor and the desired amount of catalyst (LA/metal ratio = 1000 mol/mol) was suspended in the solution. The autoclave was then purged three times with nitrogen before charging 7 bar of H₂. The mixture was heated to the reaction temperature, 70 °C, and stirred (1250 rpm).

In the case of AuPt on Spruce carbon the catalyst was tested in a recycling experiment: after each run the catalyst was recovered by centrifugation and used in another experiment without any further treatment with a fresh LA solution.

2.3.3. Analysis of products

The reaction mixture, after separation from the catalysts by filtration, was analyzed using high performance liquid chromatography (HPLC). Samples were removed periodically (0.5 mL) under stirring and analyzed by high-performance liquid chromatography (HPLC) using a column (Alltech OA-10308, 300 mm \times 7.8 mm) with UV and refractive index (RI) detection in order to analyze the product mixtures. H₃PO₄ 0.1 wt% solution was used as the eluent. The

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