



## Design of plurimetallc catalysts for solid biomass conversion: Batch versus continuous reactors



Cherif Larabi<sup>a,b,\*</sup>, Walid Al Maksoud<sup>a,b</sup>, Kai C. Szeto<sup>b</sup>, Anthony Garron<sup>a,b</sup>, Philippe P. Arquilliere<sup>a,b</sup>, Jean J. Walter<sup>a</sup>, Catherine C. Santini<sup>b,\*</sup>

<sup>a</sup> Synthopetrol, 37 Rue des Mathurins 75008 Paris 8, France

<sup>b</sup> Université de Lyon, ICL, C2P2, UMR 5265 CNRS-ESCE Lyon, 43 bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

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### ABSTRACT

Catalysts composed of plurimetallc particles (Cu, Ni and Ru) supported on Keggin type polyanion salts ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ) are synthesized and characterized by various physicochemical techniques. Several catalysts have been prepared in this view by varying the metal content. The organic yield obtained with  $\text{CuNi}_2\text{Ru}_1@$  CsPW catalyst (ca. 30 wt.%) is two times higher than the one found for the bimetallic  $\text{CuRu}_1@$  CsPW and close to the activity of  $\text{CuRu}_2@$  CsPW material. In the batch reactor, a high yield of good quality biofuel is obtained. However, the catalyst reusability is compromised due to high thermal treatment required for the charcoal removal from the surface of the material which causes catalyst degradation and particles sintering. Moreover, the accumulation of ashes on the catalyst surface decreases the active species accessibility. To avoid the contamination of the catalyst with ashes and charcoal, hydrotreatment process is combined with slow pyrolysis of biomass. Indeed, the pyrolysis oil resulted from thermal decomposition of biomass is treated in a fixed bed reactor containing  $\text{CuNi}_2\text{Ru}_1@$  CsPW. In this case, the catalytic activity is low, only 15 wt.% of biofuel is obtained, but the activity is stable even after four catalytic cycles.

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### 1. Introduction

In the past decade, nanomaterials, particularly metal nanoparticles (NPs) with controlled size, shape and composition gained a major interest and been a field of rapid research growth. There are two strategies to generate NPs, top-down and bottom-up. In the first approach, nano-objects are created from macro-materials, while in the second one, nanomaterials are built from molecular components [1]. Various physical and chemical methods are developed for metallic NP synthesis, including laser ablation, ion sputtering, gas–solid transformation, chemical reduction or precipitation, solvothermal reaction, sol–gel strategy in the presence of templates or micro-emulsion methods, and bio-inspired synthesis techniques [2,3]. Metallic NPs have a tendency to agglomerate, due to their small sizes and their high surface energies. Consequently, it is necessary to stabilize them as colloidal solutions [4–6] or their immobilization on various solid substrates, including silica, alumina, carbon, ceria, zeolite and polymers [7–9]. The physicochemical properties of NPs are composition, size and shape dependent, which distinguish them from corresponding bulk metal [10]. This makes them very attractive in various areas of applications, among others, medicine [11,12], electronic sensors [13], optical and magnetic nanomaterials [14,

15], as well as in catalysis [9]. Due to their small size, NPs have high surface to volume ratio, the concentration as well as the electronic environment of the atoms located in the corners, edges and surfaces are different, thus playing completely various roles in catalytic reactions [16].

As noble metals present low reserves and high cost, they have to be used in an efficient way. Rather than synthesizing unstable small NPs to increase their surface-to-volume ratios, alloy or core-shell NP structures of two or more metals are developed, where one type of metal or more can be found in core, and the other one on the surface. Thus, the activity, selectivity and stability of the nanocatalysts can be enhanced. Moreover, tuning the composition and geometry of the multimetallic NPs could result in multifunctional materials, where different elements work in a synergistic way. Among others, ruthenium is a noteworthy noble metal largely used in catalysis and have been associated with lots of other elements [17]. For example RuNi bimetallic NP (BNP) based catalysts are found to be effective in hydrogenation of levulinic acid [18], hydroreforming of the oils obtained by LDPE thermal cracking [19] and hydrogenolysis of lignocellulosic biomass [20].

Lignocellulosic biomass is a worldwide abundant and sustainable source for the production of value-added chemicals, such as aromatics and biofuels [21–23]. Carbon dioxide is admitted to be responsible for the global warming. Unlike fossil fuels, burning biofuels does not contribute to increase the amount of  $\text{CO}_2$  in the atmosphere, since the amount produced during the combustion is recycled through the photosynthesis process [23]. Thermochemical process for conversion of

\* Corresponding authors.

E-mail addresses: [cherif.larabi@univ-lyon1.fr](mailto:cherif.larabi@univ-lyon1.fr) (C. Larabi), [catherine.santini@univ-lyon1.fr](mailto:catherine.santini@univ-lyon1.fr) (C.C. Santini).

biomass including gasification, fast and slow pyrolysis as well as catalytically assisted pyrolysis has received tremendous research interest and activity over last decades. The latter one is admitted to be the most promising process to convert biomass to biofuel.

Recently, a catalyst based on Cu–Ru BNP supported on heteropolyanion is reported to be effective in direct conversion of sawdust into biofuel [24–26]. Due to the fact that the deoxygenation reactions involved in such process occur on the surface of the particles, more accessible ruthenium and copper are needed. Ni is introduced to develop trimetallic particles (Ni cores and Cu–Ru shells) as demonstrated for Ni–Ru [27]. In addition, it is observed that Ni can spill over hydrogen to Cu. Furthermore, it is reported that copper improved the control of the ruthenium NP dispersion, enhanced the hydrogenation as well as the hydrodeoxygenation catalytic activity [24,28]. Herein, the synthesis and the characterization of multifunctional trimetallic CuRuNi NPs supported on heteropolyanion with the aim to increase surface to volume ratio of CuRu alloy are described. Catalytic activities of the synthesized materials in a direct conversion of sawdust pine wood in the presence of various catalysts which contain different amount of CuRu and Ni are provided.

Moreover, the performances of two different catalytic systems, batch and continuous reactors are described. In fact, in the batch reactor, the catalyst and the solid biomass are in contact. In the second one, two continuous reactors are connected in series, the first one is dedicated to the pyrolysis and the second one to the hydrotreatment of the volatiles produced in the first reactor.

## 2. Experimental

### 2.1. Materials

The lignocellulosic biomass (sawdust) used is originated from pine wood. It is grounded in a Retsch type RM100 mortar mill, and then sieved to give particles with size lower than 1 mm. In order to distinguish between physisorbed water and water formed during the decomposition process, the sawdust is dried at 150 °C and then stored in the glove box.

Phosphotungstic acid;  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$  (99.9%, Aldrich), cesium carbonates;  $\text{Cs}_2\text{CO}_3$  (99.9%, Alfa Aesar), ruthenium chloride hydrate;  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (99.9%, Aldrich), copper nitrate hemipentahydrate;  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (98%, Aldrich), nickel acetylacetonate;  $\text{Ni}(\text{acac})_2$ ,  $(\text{NiC}_{10}\text{H}_{14}\text{O}_4, 95\%$ , Strem) are used as received without further purification. The purity of the heteropolyacid is checked by  $^{31}\text{P}$  liquid-state NMR. Only, the expected signal is observed. Keggin heteropolyacid ( $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ ) is dried at 200 °C under vacuum ( $10^{-5}$  mbar) during 3 h in a glass reactor. Dry oxygen is introduced to the reactor and heated at 200 °C during 2 h, in order to oxidize the metallic atoms that may have been reduced after the aforementioned dehydration process. The other metal compounds from the commercial sources are dried at 120 °C under vacuum ( $10^{-5}$  mbar) overnight and stored in the glove box.

### 2.2. Instrumentation

Prior to the catalytic test, all the samples are analyzed by: powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectrometry (XPS), elemental analysis (EA), magic angle spinning nuclear magnetic resonance (MAS NMR),  $\text{N}_2$  adsorption-desorption, Fourier transform infrared spectroscopy (FTIRS). The liquids are analyzed with gas chromatography–mass spectrometry (GC-MS) and elemental analysis (EA).

X-ray powder diffraction (XRD) patterns are recorded on a D8 Advance Bruker instrument, using a  $\text{Cu K}\alpha_1$  radiation source in Bragg–Brentano reflecting geometry. The sample preparation is done by grinding

the material until obtaining a fine powder, followed by addition of ethanol, and at the end, deposition of a suspension on a glass plate.

SEM studies are conducted on an FEI Quanta 250 FEG scanning electron microscope, TEM and HRTEM observations are carried out with a 200 kV analytical microscope JEM 2100 F from Jeol with an ultrahigh resolution probe size under 0.5 nm and rapid data acquisition. The electronic microscopy analyses (SEM, TEM and HRTEM) are supported by EDX to prove the local composition of the particles as well as the composition of the surface of the support. For TEM, samples are suspended in toluene and ultrasonically treated for 2 min. Then, a drop of this suspension is disposed uniformly on a molybdenum grid and dried. O.

For SEM, powder is linked to an alumina holder coated with carbon double face tape.

Kratos Analytical Axis Ultra DLD X-ray Photoelectron Spectrometer with an Al K alpha source ( $h\nu = 1486.6$  eV) at the detection angle of 90° is used to conduct XPS studies. The samples are placed on a metallic indium surface and transferred from a glove box to the device without air break. The spectra are collected over a range of 0–1200 eV and high-resolution spectra of Ni, Cs, W, Cu, and Ru regions are provided. The atomic concentrations of the elements are determined by peak area ratios. X-Ray Auger electron spectroscopy is performed in the same equipment.

Elemental analyses (C, H and O) are performed at the Welience – Pôle Chimie Moléculaire Faculté des Sciences Mirande (Dijon, France), using CHNS/O thermo electron flash 1112 Series elemental analyzer. Metal concentrations (Cu, Ru, Ni and W) are measured using inductively coupled plasma atomic emission spectrometry (ICP-AES) apparatus (JOBIN YVON 38 Type III) in the “Laboratoire des Sciences Analytiques, Laboratoire d’Analyse Industrielle Unité CPE Lyon (LSA)” in CPE Lyon (Villeurbanne, France). ICP standards are prepared by dissolving a corresponding metal salt with purity >99.99% in volumetric flasks with up to 5% nitric acid in water. Cs and P are measured at the CNRS central analysis department of the analytical science institute (Villeurbanne, France).

$^{31}\text{P}$  (121.5 MHz),  $^{133}\text{Cs}$  (39.36 MHz) magic angle spinning solid state NMR spectra are collected on a Bruker Avance 300 spectrometer. The impeller zirconia ( $\text{ZrO}_2$ ) of 4 mm is filled with the desired product and sealed with a kel-f stopper, then transferred into the probe Bruker spectrometer allowing rotation of the rotor at a speed of 10 kHz. The time between two acquisitions is always optimized to allow complete relaxation of the nuclei. Chemical shifts are measured relative to 85%  $\text{H}_3\text{PO}_4$  aqueous solution for  $^{31}\text{P}$  and 0.01 M of CsCl for  $^{133}\text{Cs}$ .

FTIR infrared transmission (IR) spectra are collected in transmission mode on Nicolet FT-5700. The solid samples are mixed with KBr powder, compressed into self-supporting wafers then placed in the sample holder and the spectra are recorded. The cell is equipped with  $\text{CaF}_2$  windows. Typically, 32 scans are recorded for each spectrum with a resolution of  $2\text{ cm}^{-1}$ .

Adsorption–desorption isotherms of nitrogen at 77 K are measured for all the materials with a ASAP 2020 (Micromeritics) surface and porosity analyzer. Cumulative pore volume is calculated using BJH model for adsorption isotherm. Before the adsorption analysis, the samples are degassed for 4 h at 180 °C.

Light hydrocarbons analyses and quantifications are performed on a HP 5890 gas chromatograph, equipped with a flame ionization detector (FID) and a  $\text{KCl}/\text{Al}_2\text{O}_3$  on fused silica column ( $50\text{ m} \times 0.32\text{ mm}$ ). Heavier organic hydrocarbons formed are separated by a MS compatible HP5 column ( $30\text{ m} \times 0.25\text{ mm}$ ) and analyzed by GCMS (Agilent GC 6850 MS 5975C) (Electron energy 70 eV; Emission 300 V; Helium flow rate:  $0.7\text{ cm}^3 \cdot \text{min}^{-1}$ ).

### 2.3. Catalytic materials synthesis and testing

First of all, 0.4 M solution of cesium carbonate and 1 M solution of heteropolyacid are prepared by dissolving 13 g of dry  $\text{Cs}_2\text{CO}_3$

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