



Multifunctional heterogeneous catalyst for one step transformation of lignocellulosic biomass into low oxygenated hydrocarbons



Cherif Larabi^{a,b,*}, Walid Al Maksoud^{a,b}, Kai C. Szeto^b, Anthony Garron^{a,b},
Philippe P. Arquilliere^{a,b}, Jean J. Walter^a, Catherine C. Santini^{b,**}

^a Synthopetrol, 37 Rue des Maruthins, 75008 Paris 8, France

^b 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

Mono and bimetallic nanoparticles based on ruthenium or copper–ruthenium with controlled size, supported on heteropolyanion were easily synthesized. The partial exchange of the kegg-in-type heteropolyacid protons by large monovalent cations such as Cs⁺ leads to the formation of salts with uniform microcavities and high surface area. Heteropolyanions with various amounts of cesium content were synthesized and their specific surface areas were measured. The solids with high surface area were used as supports and functionalized by copper and ruthenium nanoparticles. Cu_nRu_m@Cs_xPW catalysts thus obtained were characterized by various techniques including BET, TEM, XRD, solid state NMR and elemental analysis. Moreover, the effect of Ru loading and Cs content on the distribution of the particle size has been elucidated. Finally, the activities of the catalysts on the direct hydro-conversion of pine wood into liquids suitable for fuel application were evaluated and the influence of the experimental conditions such as temperature, hydrogen pressure, reaction time and the amount of the catalyst has been exemplified.

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1. Introduction

Conventional reserves of fossil sources including natural gas and oil are expected to decrease, while the need for energy is rising inexorably, resulting in energy supplies issue by the future. In addition, more drastic regulations are continuously introduced for the environment protection. As result, the need for sustainable sources of energy is emphasized, this implies immediate research to develop clean and renewable source of energy. It is believed that non-edible biomass such as lignocellulose could be a potential source for chemical platform and fuels as well as drop in fuels adaptable with current infrastructure and technology [1–6]. Fuels originated from biomass are carbon-neutral as the carbon dioxide produced during their combustions is recycled by plants through photosynthesis process. Due to the polymeric and complex structure of

lignocellulosic biomass, its deconstruction into simpler building block with the aim to produce value added bio-products and biofuel is necessary. Fisher–Tropsch process is a possible route to convert synthesis gas originated from the gasification of biomass into alkanes; this approach is a multistep process, it requires multiple gas conditioning and high operating pressures and temperatures [7]. Fast and slow pyrolysis are considered as promising strategies to convert biomass into chemicals including aromatic compounds and biofuel. Slow biomass pyrolysis leads to the formation of liquid phase and co-product up to 40 wt% of bio-char and more than 10 wt% of gas. Bio-oils produced from fast pyrolysis are characterized by their high oxygen and water contents, further stabilization and hydro-processing are required before being adaptable as bio-fuel [8–10]. Recent development in the field of heterogeneous catalyst with the aim of fast pyrolysis oil upgrading has been well reviewed by Ruddy et al. [11].

In fact, various heterogeneous catalysts are reported in the literature inter alia transition metal oxide or sulfide, supported noble metal nanoparticles and alternatives metal carbide, nitride and phosphide [11]. In the same optic, our group has reported a novel approach based on catalytic slow hydro-pyrolysis of solid lignocellulosic biomass. The process leads to a formation of 30 wt% of organics fraction containing less than 3 wt% of

* Corresponding author at: Université de Lyon, ICL, C2P2, UMR 5265 CNRS-ESCE Lyon, 43 bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France.
Tel.: +33 04 72 43 18 10; fax: +33 04 72 43 17 95.

** Corresponding author. Tel.: +33 04 72 43 18 10; fax: +33 04 72 43 17 95.

E-mail addresses: Cherif.larabi@univ-lyon1.fr (C. Larabi),
Catherine.santini@univ-lyon1.fr (C.C. Santini).

oxygen and 30 wt% of aqueous fraction with only 2 wt% of carbon [12]. The direct transformation process of lignocellulosic biomass into biofuel, involves first a controlled decomposition of the polymeric structure, followed by desoxygenation reactions through decarbonylation, decarboxylation, cracking or hydrocracking, hydrogenation and hydrodesoxygenation mechanisms [13]. Thus, a multifunctional catalyst that contains one or more transition metal dispersed on suitable supports is needed. To enable the catalytic activity of different species of a multifunctional catalyst in a synergistic way, the number, the distances, the physical and chemical environment have to be tuned [13]. Processes based on the use of multifunctional catalyst are largely overlooked in the field of bio-based chemistry. A direct conversion of furfural into butanediol over a multifunctional platinum nanoparticle supported on mixed oxide $\text{TiO}_2\text{-ZrO}_2$ is reported, the catalyst undergoes selective oxidation of furfural to furanones and their hydrogenation to butanediol [14]. Tungsten-based catalysts were found to be efficient in the transformation of cellulose to ethylene glycol through successively hydrolysis of cellulose, C–C bond cleavage of sugars and hydrogenation of glycolaldehyde [15]. Recently, Satsuma et al. reviewed the importance of the acid catalysis in the environmental friendly processes development [16]. Keggin heteropolyacids are strong Brønsted acids. Owing to their availability as well as their chemical and thermal stability, they are widely adopted in homogenous or supported for heterogeneous catalysis [17–19]. Due to very low surface area of heteropolyacid, to enable their use in heterogeneous catalysis, much efforts were dedicated to their loading on various carrier including silica, alumina and active carbon [20–22]. The insoluble heteropolyacid salt synthesized by proton exchange with large monovalent cations such as Cs^+ increases the acidity, thermal stability as well as the surface area [23]. Therefore, they are employed as heterogeneous catalyst [24] or support for multifunctional catalyst [25]. High catalytic activity for one-step conversion of biomass was found for multifunctional catalyst based on bimetallic nanoparticles supported on heteropolyacid salt ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) [12]. Herein, the shape and size of nanoparticles versus amount of heteropolyacid proton exchanged with cesium are studied, then their catalytic activities in the conversion of biomass are evaluated, finally the effect of experimental conditions (temperature, pressure, time and the amount of the catalyst) on the catalytic activity are optimized.

2. Experimental

2.1. Materials

Prior to use, the pine wood was grounded in a Retsch type RM100 mortar mill, sieved to give particle size less than 0.7 mm in diameter. In order to distinguish between the water formed during the decomposition process and the initially physisorbed water, the wood was pretreated and dried at 150 °C, 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), Cs_2CO_3 (99.9%, Alfa Aesar), $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$ (99.9%, Aldrich) and $(\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O})$ (99%, Aldrich) were purchased. The purity of the heteropolyacid was checked by ^{31}P liquid-state NMR, only the expected signal was observed. Keggin heteropolyacid ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$) was dried at 200 °C under vacuum (10^{-5} mbar) for 3 h in a glass reactor, dry oxygen was introduced to the reactor and heated at 200 °C for 2 h in order to oxidize the metals atoms that may have been reduced during the thermal treatment. The other metal compounds from the commercial sources were dried at 120 °C under vacuum (10^{-5} mbar) overnight and stored in the glove box.

2.2. Instrumentation

Prior the catalytic test, all the samples (neat support and the nanoparticles supported catalyst) were analyzed by: powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDX), elemental analysis (EA), magic angle spinning nuclear magnetic resonance (MAS NMR), N_2 adsorption–desorption, Fourier transform infrared spectroscopy (FTIRS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The liquids were analyzed with gas chromatography–mass spectrometry (GC–MS) and elemental analysis (EA).

X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker instrument, using a $\text{Cu K}\alpha_1$ radiation source in Bragg–Brentano reflecting geometry. The sample preparation was done by grinding the material until obtaining a fine powder, followed by addition of ethanol and in the end deposition of a suspension on a glass plate. TGA experiments were performed with a thermobalance, Mettler Toledo TGA/DSC1. Approximately 15 mg of material were placed in an Al_2O_3 crucible and heated under 30 ml min^{-1} of argon from room temperature to 1000 °C with a heating rate of 5 °C min^{-1} .

Scanning electron microscopy studies were conducted on an HITACHI S800 FEG scanning electron microscope (SEM). Transmission electron microscopy (TEM) observations were carried out on Philips CM120 instrument with an acceleration voltage up to 120 kV.

HRTEM analyses were done with a 200 kV analytical microscope JEM 2100 F from Jeol with an ultrahigh resolution a probe size under 0.5 nm and rapid data acquisition. The electronic microscopy analyses (SEM, TEM and HRTEM) were supported by energy-dispersive analysis of X-ray spectra (EDX) to probe the local composition of the particles as well as the composition of the surface of the support. The samples were suspended in toluene and ultrasonically treated for 2 min. Then, a drop of this suspension was disposed uniformly on a molybdenum grid and dried.

Elemental analyses (C, H and O) were 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, W) were carried out 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 were prepared by dissolving a corresponding metal salts with purity >99.99% in volumetric flasks with up to 5% nitric acid in water. Cs and P were measured at the CNRS central analysis department of the analytical science institute (Villeurbanne, France).

^{31}P (121.5 MHz), ^{133}Cs (39.36 MHz) magic angle spinning solid state NMR spectra were collected on a Bruker Avance 300 spectrometer. The impeller zirconia (ZrO_2) of 4 mm was filled with the desired product and sealed with a kel-f stopper, then transferred into the probe allowing rotation of the rotor at a speed of 10 kHz. The time between two acquisitions was always optimized to allow complete relaxation of the nucleus. Chemical shifts were measured relative to 85% H_3PO_4 aqueous solution for ^{31}P and 1 M of CsCl for ^{133}Cs .

Fourier transform infrared (FTIR) spectra were collected in transmission mode on Nicolet FT-5700. The solid samples were compressed into self-supporting wafers, by deposition of a suspension on a silicon wafer, or diluting the sample in KBr (typically 5 mg of the sample in 500 mg of the KBr). Afterwards, the pellet was placed in the sample holder when the spectra were recorded. The cell is equipped with KBr or CaF_2 windows. Typically, 16 scans were

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