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Carbon nanoparticles-Ru composites as an eco-friendly catalyst for the valorization of oleic acid

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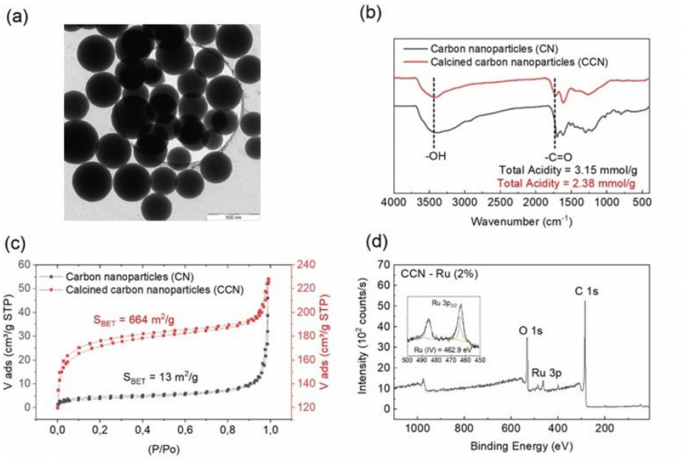
PURPOSE OF THE ABSTRACT

Nowadays unsaturated fatty acids (UFAs) have attracted the interest of various researches because of their abundance, low cost and versatility in terms of functional groups. Among them oleic acid is a renewable feedstock which can be used to produce pelargonic and azelaic acids through oxidative cleavage of the carbon-carbon double bond [1,2]. Mainly, this reaction can be addressed by ozonolysis or by transition metals in high oxidation states (homogeneous catalysis) involving hazardous solvents and oxidizing agents. Nevertheless, the difficulty of recovering homogeneous catalysts represents a problem at an industrial level. In addition, heterogeneous catalysts have not been much studied yet and most of them still present poor results in terms of conversion and selectivity. In this matter, carbon supports appear to be a promising solution. For instance, carbon black along with Ru and NaIO4 has demonstrated to be suitable in this reaction. However, it requires specific oxidation treatments or polymer deposition (e.g. polydopamine) to add extra functional groups for Ru ions chelation [3]. In order to address this issue, we report here on our synthesis of carbon nanospheres by hydrothermal treatment which allows obtaining directly nanometric carbon particles with high surface area and large amount of oxygenated groups ready to chelate Ru ions. Additionally, we propose to substitute the conventional oxidizing agent (NaIO4) by the eco-friendlier methylmorpholine N-oxide (NMO) in order to obtain a greener catalytic system for the valorization of oleic acid.

Methodology: Carbon nanoparticles (CNs) were prepared by heating a glucose aqueous solution in an autoclave at 180 °C for 24 hours. The obtained solid was washed thoroughly with distilled water and ethanol. Next, CNs were submitted to calcination under air atmosphere at 420 °C for 20 minutes. Then, RuCl3.H2O solution (10 mM) was used to impregnate Ru (2 wt%) on CNs and calcined carbon nanoparticles (CCNs) by wet impregnation method. CNs and CCNs were characterized by FTIR, N2 physisorption, Boehm's titration and XPS spectroscopy. Catalytic tests were performed in a biphasic system H2O/MeCN/AcOEt (4:2:1) at room temperature using NaIO4 and NMO as oxidizing agents. The reaction was monitored by Gas Chromatography and UV-Vis spectroscopy. Once a catalytic run ended, a catalytic test was performed with the hot-centrifugated aqueous medium to verify the activity of leached Ru species if any. Recycling tests were also performed using the same catalyst several runs successively.

Results: Particle size was verified by TEM analysis (Fig. 1a) while FTIR (Fig. 1b) and Boehm's Titration demonstrated that the number of oxygenated groups was higher than other carbonaceous materials even those having undergone oxidation treatments (e.g. with HNO3, KMnO4, etc.). The calcination step created microporosity in the carbon nanospheres (Fig. 1c). XPS spectroscopy showed that CN and CCN may use their functional groups to form complexes with Ru (Fig. 1c). As regards catalytic tests, it was possible to achieve a 95% conversion and selectivity towards azelaic acid (Fig 2a). Recycling tests demonstrated the stability of the synthesized composites whereas hot-centrifugation tests and UV-Vis spectroscopy confirmed that Ru(VIII)O4 performed the reaction mainly in the liquid phase, while the oxygenated groups of the support re-adsorb the reduced Ru species, maintaining the catalytic activity of the composite. NMO did not oxidize Ru(IV)O4 (Ru species on the support) to Ru(VIII)O4 (active species for oxidative cleavage) but it contributes with extra oxygen atoms to regenerate Ru(VI)O4 (reduced species in the reaction medium). By this mean, it was possible to combine NMO with NaIO4 in order to perform the oxidative cleavage. Therefore, carbon nanoparticles were easily synthesized with a large number of oxygenated groups necessary for the adsorption of Ru species throughout the reaction.

FIGURES



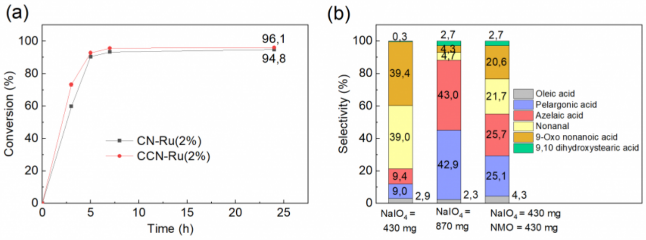


FIGURE 1

Fig 1.

a) TEM analysis; b); FTIR spectra; c) N2 physisorption isotherms; d) XPS spectra

FIGURE 2

Fig 2.

a) Catalytic activity b) Selectivity with CCN-Ru(2%)

KEYWORDS

Carbon nanoparticles | Oxidative cleavage | Oleic acid valorization | Hydrothermal treatment

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