N°16 / OC

TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Carbon black-Polydopamine-Ruthenium composite as a recyclable boomerang catalyst for the oxidative cleavage of oleic acid

AUTHORS

Sebastian GAMEZ / UNIVERSITÉ CATHOLIQUE DE LOUVAIN, PLACE LOUIS PASTEUR, 1 BTE L4.01.06, LOUVAIN-LA-NEUVE
Ernesto DE LA TORRE / ESCUELA POLITECNICA NACIONAL, AV. LADRÓN DE GUEVARA 253, QUITO
Eric GAIGNEAUX / UNIVERSITÉ CATHOLIQUE DE LOUVAIN, PLACE LOUIS PASTEUR, 1 BTE L4.01.06, LOUVAIN-LA-NEUVE

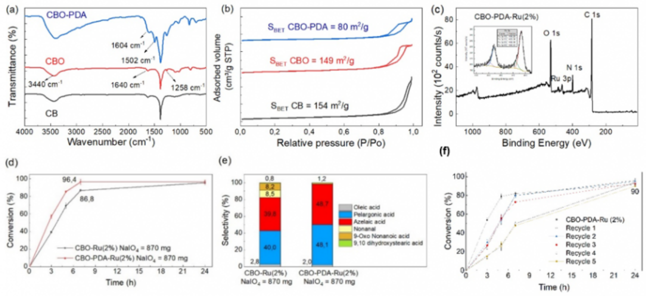
PURPOSE OF THE ABSTRACT

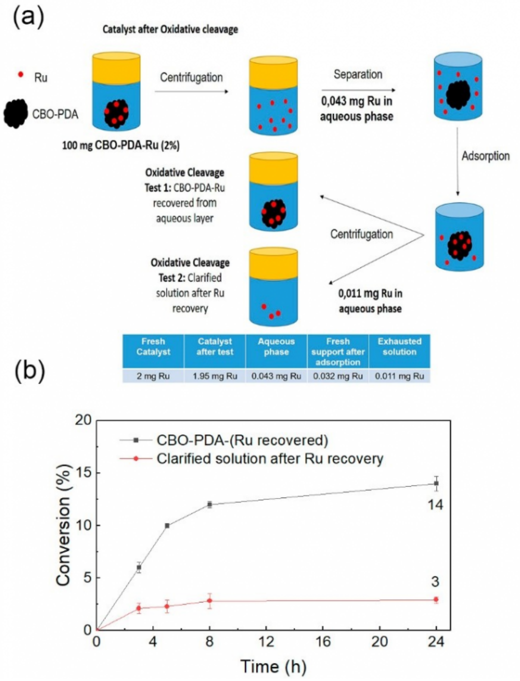
Unsaturated fatty acids (UFAs) have become an interesting source of chemical base materials for several industries due to the shortage in petroleum deposits and pollution issues [1]. For instance, oleic acid can be transformed into pelargonic and azelaic acids through the oxidative cleavage of the carbon-carbon double bond. These two acids are very useful for herbicides and cosmetics synthesis respectively [2]. Oxidative cleavage of UFAs can be achieved mainly by homogeneous catalysts [3]. On the other hand, heterogeneous catalysts have been less documented explaining their currently poor results. Therefore, we developed a suitable heterogeneous catalyst benefiting from polydopamine (PDA) functional groups grafted on oxidized carbon black (CBO) to anchor active Ru ions. Actually taking the example of the cleavage of oleic acid we demonstrate that while Ru(VIII)O4 as oxidized by NaIO4 is the active species in the homogeneous phase, a boomerang catalytic mechanism is engaged with Ru species moving back to the solid phase when the reaction ends [4].

Methodology: Carbon black (CB) was oxidized to CBO with a 5.0 M HNO3 solution at 90 °C for 24 h under reflux. The solid was removed by centrifugation, washed with warm distilled water and dried at 110 °C overnight. Then, 200 mg of dopamine hydrochloride was dissolved in a 10 mM buffer solution of tris(hydroxymethyl)aminomethane. When the solution passed from colorless to pale brown, 1 g of dried CBO was added to the solution and magnetic stirred for 24 h at room temperature. Next, the CBO-PDA composite was removed by centrifugation, washed with distilled water and dried overnight at room temperature. Afterwards, Ru ions (10 mM RuCl3.H2O solution) were incorporated at a nominal loading of 2wt% by wet impregnation on CBO-PDA composite. CBO and CBO-PDA were characterized by FTIR, N2 physisorption, Boehm's titration and XPS spectroscopy. Catalytic tests were performed in a biphasic system of H2O/MeCN/AcOEt (4/2/1) at room temperature and the reaction was monitored by GC, UV-Vis and NMR spectroscopies. CBO-PDA-Ru catalyst was characterized before and after catalytic runs by ICP, FTIR and XPS spectroscopy. Additionally, catalytic tests were performed with the aqueous media to verify the activity of leached Ru species.

Results (see our reference [4] for more details): The presence of OH (3400 cm-1), C=O (1640 cm-1) and lactones (1258 cm-1) was found in CBO FTIR spectrum confirming the oxidation of CB. The presence of PDA on the composite was confirmed by its characteristic peaks at 1604 and 1502 cm-1 on FTIR spectra. These peaks correspond to the N-H and C-N vibrations respectively (Figure 1a). As compared to pristine CB, specific surface area and pore volume decreased by a factor of 2 after PDA deposition due to the filling of the gaps in between CBO particles (Figure 1b). For CBO-PDA-Ru, the Ru 3p doublet at 463.0 eV and 485.2 eV on XPS spectra is interpreted as Ru(IV), which means that PDA is forming a complex with Ru (Figure 1c). Catalytic tests confirmed that 7 h is sufficient to reach conversions and selectivities around 95%. Advanced hot-filtration and recyclability tests compared the Ru catalysts with and without PDA (Figure 1d) confirmed that Ru ions leached towards the reaction medium during oxidative cleavage. But the catalyst remained active after 5 recycles (Figure 1f). The explanation for these results is the occurrence of a boomerang behavior where Ru dissolves, performs the oxidative cleavage and returns to the support once the reaction ends. To probe this hypothesis a specific complex protocol was designed in which the solid and the organic layer were removed after a catalytic test; next the support (CBO-PDA) was added to the aqueous layer along with a fresh layer of ethyl acetate with oleic acid; finally, 8 equivalents of NaIO4 was added to re-oxidize the residual Ru if any. Only a 14% of conversion was achieved, demonstrating that most of Ru returned to the support.

FIGURES





Fresh Catalyst	Catalyst after test	Aqueous phase	Fresh support after adsorption	Exhausted solution
2 mg Ru	1.95 mg Ru	0.043 mg Ru	0.032 mg Ru	0.011 mg Ru

FIGURE 1

Figure 1

a) FTIR spectra; b) N2 physisorption isotherms; c) XPS spectra; d) Catalytic activity; e) Selectivity; f) Recycle tests

FIGURE 2

Figure 2

Boomerang catalysis a) protocol; b) confirmation

KEYWORDS

Boomerang catalysis | oxidative cleavage | oleic acid | Heterogeneous catalysis

---

BIBLIOGRAPHY

[1] S. Mecking, Angew. Chem., Int. Ed., 2004, 43, 1078–1085.
[2] K. Hill, In Pure and Applied Chemistry, 200, 72, 1255–1264.
[3] S. Rup et al., Ultrasonics Sonochemistry, 2009, 16, 266–272.
[4] S. Gamez et al., Chemical Engineering Journal, 2022, 427, 131820