Supplementary Materials

C-Heterogenized Re Nanoparticles as Effective Catalysts for the Reduction of 4-Nitrophenol and Oxidation of 1-Phenylethanol

Ana P. C. Ribeiro [1,*], Beatriz M. Santos [1], Rute F. C. Faustino [1], Armando J. L. Pombeiro [1,2] and Luísa M. D. R. S. Martins [1,*]

[1] Departamento de Engenharia Química, Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal
[2] Research Institute of Chemistry, Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya Street, 117198 Moscow, Russia
* Correspondence: apribeiro@tecnico.ulisboa.pt (A.P.C.R.); luisammartins@tecnico.ulisboa.pt (L.M.D.R.S.M.)

Abstract: Rhenium nanoparticles (Re NPs) supported on Norit (activated carbon—C) and graphene (G) were prepared by a solvothermal method under microwave irradiation (MW). The synthesised heterogeneous catalysts were characterised and tested as reduction and oxidation catalysts, highlighting their dual catalytic behaviour. In the first case, they were used, for the first time, to reduce 4-nitrophenol, in aqueous medium, under MW irradiation. Re catalysts were easily recovered by centrifugation and recycled up to six times without significant activity loss. However, the same Re catalysts in MW-assisted oxidation of 1-phenylethanol with no added solvent experienced a significant loss of activity when recycled. The higher activity of the rhenium nanoparticles supported on graphene (Re/G) catalyst in both reactions was assigned to the higher dispersion and smaller particle size of Re NPs when graphene is the support.

Keywords: microwaves; rhenium; catalysis; oxidation; nanoparticle; graphene; activated carbon; 1-phenylethanol; reduction; 4-nitrophenol

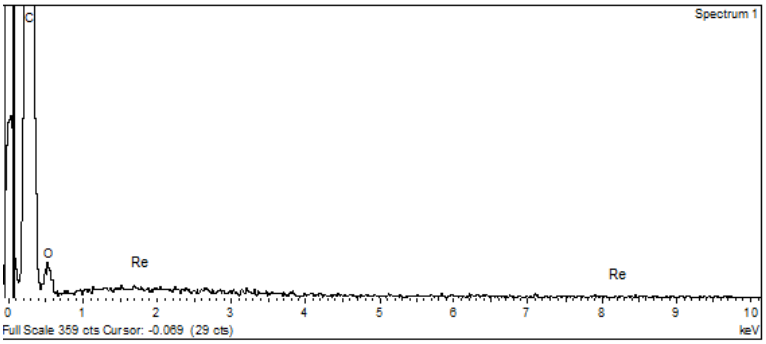

Figure S1. EDS spectrum of Re/G.

Table S1. - Catalytic performances[a] of Re/C and Re/G as a function of catalyst load and temperature.

Entry	Catalyst	Amount (μmol)	T (°C)	k_{app} x10^{-3} (s^{-1})
1	Norit			----
2	G	0.2	50	----
3	$[Re_2(CO)_{10}]$			NR

[a]Conditions:15 W, reaction time up to 30 min. [4-NP] = 7.5 × 10^{-3} M; [$NaBH_4$] = 0.169 M; NR – No reaction.

Table S2. – Oxidation of 1-phenylethanol in heterogeneous conditions[a].

Entry	Catalyst	Amount (μmol)	Temp. (°C)	Time (min)	Yield[b] (%)	TON[c]	TOF[d]
1	G	20	50	60	1.4	---	---
2	C	20	50	60	1.3	---	---

[a]General reaction conditions: 15 W power, TBHP (10 mmol), 1-phenylethanol (5 mmol). [b] Yield (%) = moles of product(s) per 100 moles of substrate. [c] Turnover number (TON) = moles of product(s) per mole of catalyst. [d] Turnover frequency (TOF) (h^{-1}) = TON/reaction time.

Reference:

[1] F. Iskandar., U. Hikmah, E. Stavilab and A. H. Aimona, Microwave-assisted reduction method under nitrogen atmosphere for synthesis and electrical conductivity improvement of reduced graphene oxide (rGO), *RSC Adv*., **2017**, 7, 52391