Cu-based nanoparticle - graphene-oxide aerogels as potential solid state catalysts

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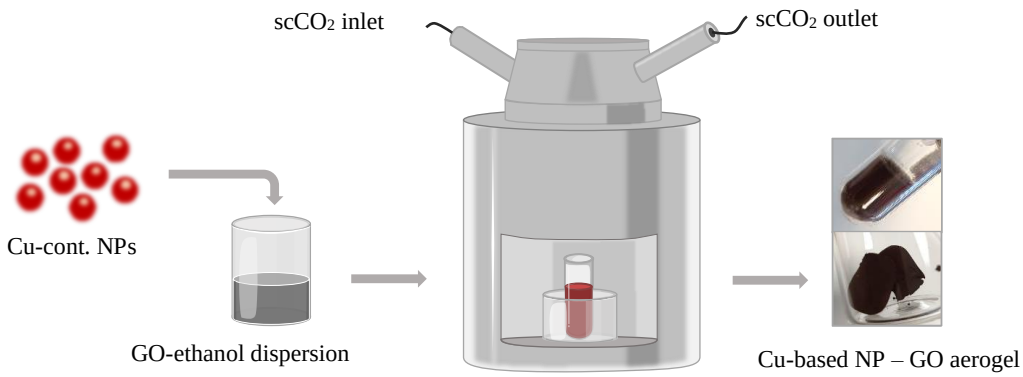
The preparation of 3D graphene oxide (GO) macrostructures was carried out using an environmental friendly supercritical carbon dioxide ($scCO_2$) method. This approach has the advantage that most of the oxygenated groups on the surface are preserved [1]. These maintained functional groups make the sponges suitable for attaching organic or inorganic entities to the surface of the GO sheets and thus making this material a natural candidate for catalytic support (e.g. CO_2 hydrogenation to methanol). This kind of support, apart from giving great stability to the catalyst, provides large surface area and high electron mobility, thus assisting the reaction through the charge transfer process. A further beneficial property of the $scCO_2$ as a reaction media through the preparation is its ability to penetrate into the pores with small sizes, thus the functionalization of the internal surface of the matrix and the homogenous distribution of entities, like metal-containing nanoparticles can be ensured. The well-dispersed nanoparticles act as active centers, capable of catalyzing specific reactions. The unique structural advantages along with the rich surface chemistry make the metal-containing NP–GO aerogels an excellent solid-state platform for catalytic applications. The main objective of this work is synthetizing and characterizing graphene-oxide sponges doped with copper-containing nanoparticles (Cu-based NPs), as a potential catalyst for heterogeneous catalytic systems.

Cu-based NPs in the form of Cu, CuO and CuO/ZnO bimetallic were synthetized by conventional precipitation methods. The composite aerogel monoliths were formed during the treatment with $scCO_2$ at 200 bar and 45 ˚C, by direct self-assembly starting from the ethanol dispersion of a Cu-based NP-GO mixture.



Preparation of Cu-cont. NPs - GO monolith using supercritical CO_2

The structure and the morphology of the Cu-based NPs and the composite aerogels were investigated by solid-state characterization technics. With X-ray diffraction and electron diffraction measurements the presence of the metal-containing particles are demonstrated. Scanning electron microscopy and transmission electron microscopy images were used to confirm the nanometric size of the particles and how they are homogenously attached to the GO sheets. Attenuated reflectance Fourier transformed infrared spectroscopy was used to demonstrate the presence of the remained functional groups of the GO sheets. The successfully obtained composite aerogels will be evaluated as a solid-state catalyst for CO_2 hydrogenation to methanol.

[1]Borrás et al., Preparation and characterization of graphene oxide aerogels: Exploring the limits of supercritical CO_2 fabrication methods, Chemistry - A European Journal, 24 (59) (2018), pp. 15903-15911, 10.1002/chem.201803368

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