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Research paper

Sepiolite-carbon nanocomposites doped with Pd as improving catalysts for hydrodechlorination processes

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ABSTRACT

The present work introduces a new type of improved catalysts based on sepiolite-carbon nanocomposites anchoring Pd nanoparticles. The nanocomposites are prepared by assembly in aqueous media of graphene nanoplatelets (GNP) and the nanofibrous sepiolite under a sonomechanical treatment. The methodology allows the co-assembly of other nanomaterials such as multiwall carbon nanotubes (MWCNT) and Pd nanoparticles, these last ones in situ generated from $PdCl_2$ and further treatment with $NaBH_4$. The presence of silanol groups at the external surface of sepiolite favors the growth and assembly of Pd NP which exhibit a quite narrow size distribution independently of the composition of the prepared sepiolite-carbon nanocomposite. The electrical conductivity of the prepared sepiolite-carbon/Pd materials depends of the composition, being lower in materials with higher content in sepiolite. However, the presence of the clay mineral improves textural properties of the resulting materials. The prepared sepiolite-carbon/Pd nanocomposites were tested as catalysts in the hydrodechlorination (HDC) of 4-chlorophenol (4-CPh) under H_2 flux, showing all of them an exclusive selectivity towards phenol, though their catalytic activity depends on their composition. Sepiolite is able to neutralize the evolved HCl, favoring the catalytic process. In addition, the good balance between textural and electrical properties achieved in some of the prepared materials enhances the contact between the catalyst surface and the reagents and also favors the electronic transfer, making this new type of sepiolite-carbon/Pd systems very promising. In fact, the concept here reported could be extended to other catalytic applications where the supported metal acting as active center requires the presence of heat and water resistant conductive supports.

1. Introduction

Carbon and clay minerals are natural resources largely used by Humans since the prehistoric times in applications that in many of the cases are still maintained. Recently, the combination of both types of materials interacting at the micro- or nano-metric scale appears as a useful way to develop functional nanocomposites benefiting synergistic properties from both components (Darder et al., 2018).

Strictly speaking, graphene is an individual layer of carbon atoms in sp^2 hybridation arranged in a hexagonal lattice. Graphene is naturally present in graphite, whose structure is formed by stacking of these carbon layers connected by Van der Walls forces. Delamination by mechanical treatment or by chemical reactions is a relatively new process allowing the preparation of graphene–based materials provided with unique physico-chemical properties (Novoselov et al., 2004; Green and Hersam, 2009; Park and Ruoff, 2009). Carbon nanotubes are related compounds formed by the rolling of one (*single wall carbon nanotubes*, SWCNT) or various graphene layers (*multiwall carbon nanotubes*, MWCNT). Graphene could be also integrated in graphene- or graphite-nanoplatelets (GNP), which show a reduced number of stacked layers, below or up to 10 sheets, respectively (Chung, 2016).

On the other hand, clay minerals are typically phyllosilicates that usually exhibit a two-dimensional morphology. Sepiolite (Sep) shows a structural arrangement related to 2:1 magnesium clay minerals, such as talc but showing a regular inversion of the tetrahedral layers, leading to a fibrous morphology with structural channels and tunnels along the c* axis. Due to this special arrangement, this silicate exhibits a high density of silanol groups on its external surface as well as an elevated specific surface area value (ca. 300 $m^2 \cdot g^{-1}$) (Ruiz-Hitzky, 2001). The presence of those silanol groups allows the controlled chemical modification of the sepiolite surface giving rise to diverse hybrid functional materials by reaction with organosilanes (Barrios-Neira et al., 1974;

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Letaief et al., 2011), immobilization of nanoparticles (Aranda et al., 2008; Darder et al., 2014; Akkari et al., 2017; Aranda and Ruiz-Hitzky, 2018) and assembly of polymers (Fernandez-Saavedra et al., 2008; Ruiz-Hitzky et al., 2013; Alcantara et al., 2014).

Although carbons and clays are very different type of minerals (in terms of genesis, chemical composition, structural arrangement and properties), since more than one century they have been combined together for uses as pencil cores (Ruiz-Hitzky et al., 2016) and as electrical resistors (Longden, 1902). More recently, clay-carbon nanocomposites have been prepared as functional nanocomposites following two approaches: i) the template carbonization method, and ii) the direct assembly of components. In the first case clays are combined with diverse carbon precursors that are further submitted to thermal treatments above 500 °C in absence of oxygen to avoid combustion processes. Typical precursors have been polyacrylonitrile, polyfurfuryl alcohol and sucrose (Kyotani et al., 1988, 1994; Fernandez-Saavedra et al., 2004; Fernandez-Saavedra et al., 2009; Darder and Ruiz-Hitzky, 2005; Gomez-Aviles et al., 2007, 2010; Ruiz-Hitzky et al., 2011; Ruiz-Garcia et al., 2013, 2014), which results in carbonaceous materials showing sp^2 hybridization like in graphene-based materials and that combined with clays introduce electrical properties of interest in diverse applications (Darder et al., 2018). The second general procedure for the preparation of clay-carbon nanocomposites is considerably more simplistic, involving the direct assembly of carbonaceous materials and clay minerals. In this way, graphene-oxides can be reduced in the presence of montmorillonite nanolayers (Narayanan et al., 2017) and stable dispersions of carbon nanotubes (Fernandes and Ruiz-Hitzky, 2014) or graphene nanoplatelets (Ruiz-Hitzky et al., 2016) can be assembled to sepiolite fibers by sonomechanical treatments in aqueous dispersions. The preparation of these materials in a colloidal route facilitates their functionalization by incorporation in the same process of additional components, such as metal and metal-oxide nanoparticles, and the silanol groups at the surface of sepiolite assuring their immobilization (Pecharroman et al., 2006; Aranda et al., 2008; Pina-Zapardiel et al., 2011).

Thus, clay-carbon nanocomposites involving sepiolite would facilitate the preparation of materials decorated with metal nanoparticles allowing their application in heterogeneous catalysis. The remarkable electrical conductivity of the carbon component can play an important role in different catalytic processes: for instance, in the Fenton-like reaction, the conductivity of the carbon fraction is a useful property that plays a key role in the electronic transfer from zerovalent to oxidized metal nanoparticles acting as catalysts (Lemos et al., 2016). Regarding other catalytic reactions, such as hydrogenation processes, Feng et al. (2015) described the influence of the conductivity properties in terms of more efficient hydrogen chemisorption and spill-over, though the possible mechanism is still unclear. In fact, the adsorption features provided by the silicate backbone and the improved conductivity properties given by the assembled graphene-based materials could enhance the catalytic activity of these type of systems (Anadao et al., 2011; Nie et al., 2011; Behrouz and Rad, 2015; Rad et al., 2015). However, there are few works in literature where clay-carbon nanocomposites were combined with metal nanoparticles in order to obtain more efficient catalysts. In this context, chrysotile has been recently used as support of carbon produced by chemical vapor deposition of EtOH in presence of Co and utilized as catalyst in oxidation by Fenton-like reaction (Lemos et al., 2016). Also chrysotile can be directly combined with MWCNT and used to catalyze the hydrolysis of soybean oil and for the synthesis of biodiesel (Teixeira et al., 2012). On the other hand, montmorillonite mixed with graphene-oxide has been reported as catalyst in the Biginelli reaction, with partial reduction of graphene oxide by the clay in the process, (Narayanan et al., 2017).

In this general context, the aim of the present work has been to develop new catalysts based on the anchoring of Pd nanoparticles on sepiolite-carbon nanocomposites prepared by assembly in aqueous media of GNP and the fibrous clay under a sonomechanical treatment. The catalytic activity of the resulting sepiolite-carbon/Pd nanocomposites in the hydrodechlorination (HDC) of 4-chlorophenol (4-CPh) has been studied and evaluated this new type of catalysts. Hydrodechlorination is a promising remediation process consisting in the removal of chlorine using a hydrogen source (Keane, 2011). In fact, it enables the removal of organic chlorinated compounds converting them into less harmful products. This is the case of chlorophenols, which are often components in herbicides, pharmaceuticals, water disinfection products, bleaching by-products, etc. Metals such as Pd, Pt and Ru are the most common metals used in catalytic HDC processes (Díaz et al., 2008), but their activity is strongly influenced by the nature of the support, with carbonaceous solids leading to the most active catalysts (Diaz et al., 2009; Meng et al., 2010; Zhou et al., 2012). Although the clay-carbon materials here prepared do not offer better electrical conductivity than other carbon supports, their specific surface area and the presence of surface silanol groups, facilitating the immobilization of metallic NP, constitute a way to develop new catalysts. Moreover, by proving it, this concept could be extended to other catalytic applications where the supported metal acting as active center requires the presence of heat and water resistant conductive supports.

2. Experimental

2.1. Materials

Graphene nanoplatelets (GNP) were supplied by KNANO as KNG-150, with > 10 packed graphene sheets, 5–15 nm of thickness and 1–20 μm diameter. Sepiolite (Sep) from Vallecas-Vicálvaro deposits in Madrid (Spain) was supplied as a rheological grade product by Tolsa, under Pangel S9 commercial trademark (> 95% of pure sepiolite). Multiwall carbon nanotubes (MWCNT) were obtained from Dropsen (95% of purity). The average diameter of the nanotubes was 10 nm and the average length 1.5 μm.

2.2. Preparation of the sepiolite-carbon/Pd nanocomposites

The sepiolite-carbon/Pd nanocomposites materials were prepared according to the original procedure described in a previous work (Ruiz-Hitzky et al., 2016). The individual components of the nanocomposites materials were sepiolite, graphene nanoplatelets, multiwall carbon nanotubes and $PdCl_2$. The procedure is based on a simple dispersion assisted with ultrasound irradiation (on/off periods of 10 s) of the selected amounts of individual components in 150 mL of ultra pure water (R > 18.2 MX, Elga Maxima Ultra Pure Water). Firstly, sepiolite was dispersed in water and 2 kJ of ultrasound energy were applied. Secondly, the carbon materials, GNP and/or MWCNT, were also dispersed and 10 kJ were applied. Then, 1.5 mL of a stock solution containing 15 mg of $PdCl_2$ in 10 mL of 0.1 M HCl 0.1 M were added to the dispersion and an additional ultrasound energy of 15 kJ was applied. All the resulting dispersions were homogeneous and stable. Finally, 1 mL of 0.3 mM $NaBH_4$, was added to the dispersion and kept under magnetic stirring for 1 h. The sepiolite-carbon nanocomposite was separated by filtration. Table 1 shows the different nanocomposites prepared and the

Table 1
Labels and composition of the sepiolite-carbon/Pd nanocomposite materials prepared in this work.

Sample label	Weight proportion (sepiolite basis)		
	Sep	GNP	MWCNT
Sep/Pd	1	–	–
Sep/0.02MWCNT/Pd	1	–	0.02
Sep/0.2GNP/0.02MWCNT/Pd	1	0.2	0.02
Sep/2GNP/Pd	1	2	–
Sep/2GNP/0.02MWCNT/Pd	1	2	0.02

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