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Amphiphilic magnetic composites based on layered vermiculite and fibrous chrysotile with carbon nanostructures: Application in catalysis

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ABSTRACT

This work describes the synthesis and catalytic applications of magnetic composites based on carbon nanotubes and nanofibers prepared by CVD (chemical vapor deposition) using two natural materials with special morphology, i.e. layered vermiculite clay and fibrous chrysotile. Extensive characterization by XRD, Mössbauer, Raman, SEM, TEM, TG/DTA, contact angle showed that the composites are made mainly of carbon nanotubes and nanofibers fixed on the surface of the layered or fibrous matrix containing also carbon coated iron or cobalt cores responsible for the magnetic properties of the composites. The combination of hydrophilic Si and Al oxides surface with the hydrophobic carbon nanostructure produced amphiphilic materials with remarkable effect on the interaction and separation of two phases system, e.g. oil and water. For example, immiscible oil/water mixtures can be easily emulsified in the presence of the amphiphilic composites producing a much more efficient interface. It is demonstrated that this emulsification is very important for the biodiesel synthesis and hydrolysis of soybean oil. After reaction, the emulsion can be easily broken by a simple magnetic separation process. This emulsion–demulsification process can be also used for biodiesel purification and wastewater treatment. The composites are also used to prepare a magnetically recoverable supported Pd catalyst for the hydrogenation of the model molecule 1,5-COD.

1. Introduction

Natural minerals based on silicates and aluminosilicates are very attractive materials for applications in catalysis and adsorption. These materials show good mechanical and thermal stability, acid and basic sites due to the Si and Al oxides and redox properties due to the presence of transition metals, especially Fe. Moreover, these minerals exist in different morphologies and textures that can be modified by mechanical and chemical controlled processing. Two of these materials are chrysotile and vermiculite.

Chrysotile [$Mg_3Si_2O_5(OH)_4$] is a magnesium silicate formed by hydrothermal alteration of olivines [$(Mg,Fe)_2SiO_4$)] and pyroxenes [$(Ca,Na,Fe)(Mn,Cr,Al)(Si,Al)_2O_6$)]. A special feature of chrysotile is the form of long thin microfibers/strings, which are able to orientate themselves in several different directions. Individual fibers tend to become entangled both within themselves and with adjacent fibers, forming an intricate mesh. Only few applications of chrysotille in catalysis have been found in the literature, such as support for metallocene [1], porphyrin [2,3], elimination of detergents [4] and generation of free radical [5]. The clay mineral vermiculite is a very interesting layered material with many potential industrial and environmental applications. Vermiculite can be modified by two processes, i.e. acid leaching and pillaring, to produce catalysts for different reactions. Some of these applications are in organic synthesis [6–9], removal of contaminants [10–17], hydrocarbon conversion [18,19], hydrogenation [20] and as support for ionic liquid [21].

In this work, a novel approach to use natural inorganic materials such as chrysotile and vermiculite in catalytic applications is developed. In this approach carbon nanofibers/nanotubes are produced by catalytic CVD on the surface of chrysotile and vermiculite to prepare magnetic amphiphilic composites. A schematic representation of the different composites preparation is shown in Fig. 1.

These composites have several special features. They are amphiphilic due to the simultaneous presence of hydrophobic

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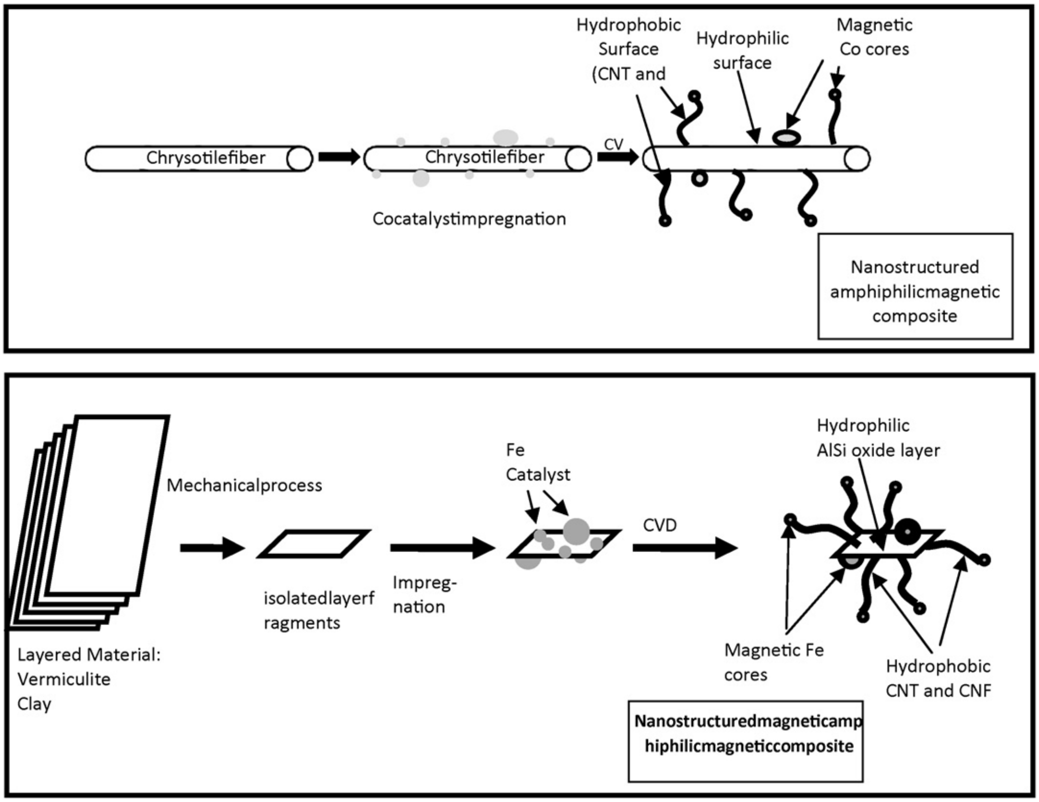

Fig. 1. Schematic representation of the production of the amphiphilic magnetic composites from chrysotile and vermiculite.

carbon nanotubes (CNT) and nanofibers (CNF) and hydrophilic Si and Si–Al oxide surface. This amphiphilic character allows the composites to interact well with aqueous and different organic phases. Also, the composites are magnetic and can be removed from different media by a simple magnetic separation process.

An important application of these magnetic amphiphilic composites is in the emulsification and demulsification of oil–water systems. These processes are used in different areas such as fine chemical industry, pesticides, essential oils, flavors, pharmaceutical, laundries, and wastewater treatment [22–25].

Hereon, it is described the use of these magnetic amphiphilic composites to promote catalytic reactions involving oil interfaces. The first application is for the biodiesel process in three different steps: synthesis, washing/purification and wastewater treatment. It is also demonstrated the effect on the catalytic hydrolysis of vegetable oil. Finally, the composites were used to produce a magnetic reusable Pd supported catalyst for hydrogenation reactions.

2. Experimental

Chrysotile was obtained from SAMA (Brazil). Initially, the mineral (5 g) was impregnated with cobalt nitrate dissolved in distilled water (100 mL) followed by slow evaporation and then dried at 80 °C for 12 h. Special care, such as use of mask and exhaustion,

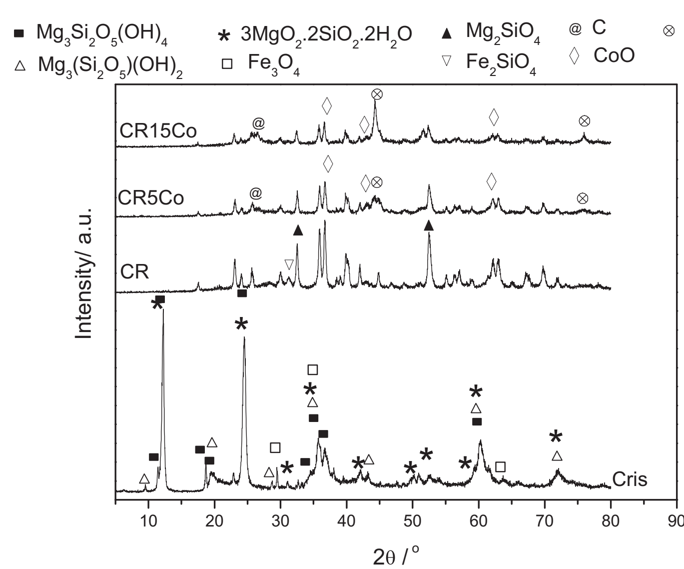

Fig. 2. XRD patterns for chrysotile before and after CVD with 5 and 15%Co obtained by CVD with ethanol at 800 °C.