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Comment

Architectured mesoporous materials modified with nickel for alternative energy and environmental applications: Hydrogen storage and photo-Fenton contaminant degradation

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HIGHLIGHTS

- The synthesis time influences on the textural and chemical properties of Ni-MCM-41.
- Ni incorporation into mesoporous walls decreases the accessibility to the active sites.
- The low Ni loading favor the H_2 adsorption of Ni-MCM-41 materials at 77 K.
- Ni-MCM-41 materials provided an interest alternative in Atrazine degradation.

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ABSTRACT

Ni-MCM-41 nanocomposites were prepared by direct hydrothermal synthesis with different Ni contents. Various characterization techniques were conducted in order to study the properties of the materials. H_2 storage capacity and degradation of atrazine by heterogeneous photo-Fenton-like process were studied. The results indicated that the structural, chemical, adsorption and catalytic properties of the resulting materials strongly depend on the hydrothermal treatment days and the nickel content. The increase in the Si/Ni molar ratio leads to higher presence of nickel oxide and increment in hydrothermal treatment days favours the Ni incorporation inside mesoporous walls, decreasing the accessibility to the active sites.

1. Introduction

Environmental pollution is one of the greatest problems that the human civilization is facing today. Industrial and agricultural activities generate serious environmental pollution in air, water and soil, deteriorating the ecological balance of ecosystems and the human health. On the one hand, the massive energy demand of the world is mainly satisfied by the nonrenewable fossil fuels, which produce environmental pollution problems and undesired alterations in the weather patterns arising from global warming effect. The decrease of fossil fuel supply and global warming require the search of new alternative and renewable energy sources [1]. Hydrogen is regarded as a future energy carrier due to its high energy density per unit as long as it is produced from renewable sources. However, the on-board vehicular hydrogen storage is the main barrier for the implementation of hydrogen economy. Therefore, many studies are focused on nanoporous materials as hydrogen storage systems, which must meet the requirements established by D.O.E (United States Department of the Energy) [2–5].

On the other hand, the water pollution by toxic pollutants is other major concern today. Among different agrochemicals, atrazine is one of the most widely used herbicides in sugarcane, corn and sorghum cultures [6,7]. Due to the direct application of atrazine to crops, there is the opportunity for the substance to contaminate soil and, consequently, water sources via runoff. This pollutant, not readily biodegradable presents relatively high persistence [8]. Current research shows that atrazine exposure may pose a threat to human health, with drinking water providing the most widespread route of exposure [9]. In this sense, the called advanced oxidation processes (AOPs) are being investigated exhaustively for the removal of contaminants from the environment [10]. Among them, the photo-Fenton process appears as an effective alternative method to treat recalcitrant organic pollutants like most agrochemicals [11,12]. Besides Fe (conventional Fenton process), other transition metals can also catalyze the reaction mentioned above. In fact, the reaction system using Ni as the photo-Fenton

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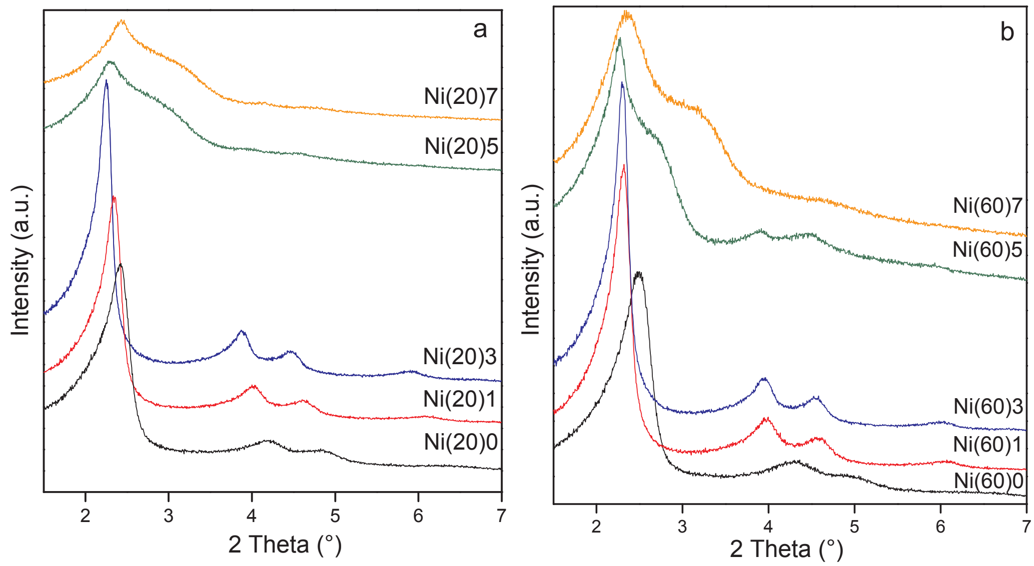

Fig. 1. Low-angle XRD patterns of samples with Si/Ni molar ratios (a) 20 and (b) 60.

catalyst can follow a similar "mechanism of reaction" as that of Fe and is referred as a photo-Fenton-like reaction [13–15]. Recently, much attention has been paid to the photo-Fenton and photo-Fenton-like processes, mainly focusing on the heterogeneous process [16]. Thus, the use of heterogeneous catalysts, such as mesoporous materials, provides an easy separation and recovery of the catalyst from the treated wastewater, not causing secondary metal ion pollution [17].

The discovery of the new family of mesoporous molecular sieves M41S in 1992 by Mobil scientists [18], opened a new area of inorganic nanoporous materials with very promising applications [18]. One of the members of this family, the MCM-41 materials have attracted much interest, mostly due to their large specific area (> 900 m^2/g) and controlled pore dimensions with uniform pore size distribution (2–10 nm). Mesoporous materials modified with various heteroatoms into the framework, such as Fe, Ni, Pt, Pd, Cu, have received considerable attention in catalytic processes [19–22] as well as in adsorption processes. A number of synthesis methods have been studied to modify the MCM-41 support with an appropriate metallic cation, achieving a proper metal dispersion and improving the number of active sites per unit area [23–25]. Thus, in order to improve the hydrogen storage of these materials, it is well known that the metal incorporation into the pure siliceous MCM-41 structure increases the hydrogen adsorption capacity [25–27]. Incorporation of metals into the pores of mesoporous materials can be achieved by direct synthesis or by post-synthesis. The addition of the metal ions during the synthesis of the mesoporous materials can preferably lead to stabilization of highly dispersed metal species into the mesoporous framework. Meanwhile, post-synthesis methods such as wet impregnation, favor the formation of bigger metal oxides over the surface of support. In previous studies [26,28], we have reported that low Ni loadings favoured the hydrogen adsorption of MCM-41 materials modified with Ni by wet impregnation method. On the other hand, Parasanth et al. (2010), reported that metal incorporation into the mesoporous materials in situ during hydrothermal synthesis enhanced of hydrogen adsorption.

In this sense, MCM-41 modified with nickel by direct incorporation method, constitutes a very attractive solid in order to investigate the hydrogen adsorption as well as the degradation of pollutants in aqueous solution using Fenton and photo-Fenton systems.

In this work, we present the preparation of nickel modified mesoporous silica by a direct synthesis method based on a sol-gel process. The influence of the Si/Ni molar ratio in the synthesis gel and the hydrothermal treatment days on the physico-chemical properties has been studied. We focus on the study of the effect of nickel over the structural order, textural and chemical properties. Thus, mesoporous materials were exhaustively characterized to determine their potential utilization as materials for hydrogen storage and degradation of a model agrochemical (atrazine, ATZ) by a heterogeneous photo-Fenton process.

2. Materials and methods

2.1. Synthesis and characterization

The nickel-containing mesoporous materials were prepared by hydrothermal synthesis and the samples were named as Ni(*x*)y, where "*x*" is the Si/Ni initial molar ratio and "*y*" is the hydrothermal treatment days. See Supporting Information for details on synthesis procedure and different characterization techniques employed.

2.2. Hydrogen storage measurement

Hydrogen (99.999%) physisorption experiments at 77 K and pressures up to 10 bar were performed using an automated nanometric system ASAP 2050 (Micromeritics Instrument Corporation). Previous to all the adsorption experiments, the samples were degassed at 573 K during 12 h under vacuum conditions (5×10^{-3} mmHg).

2.3. Atrazine degradation

Photo-Fenton-like reactions for atrazine (ATZ, 2-chloro-4-ethylamino-6-isopropylamino-striazine, $C_8H_{14}ClN_5$, ≥90%, SYNGENTA) degradation were carried out in an isothermal, well mixed, batch annular reactor. See Supporting Information for details on the experimental reaction and atrazine concentration measured [29].

Supplementary information about the device, procedures and the degradation processes of this herbicide under photo-Fenton system can be found in Benzaquén et al. [30].

3. Results and discussion

3.1. Characterization of the solids

Fig. 1a and b show the XRD patterns obtained for all the calcined materials with initial Si/Ni molar ratios = 20 and 60 in the initial gel and synthesis days of 0, 1, 3, 5 and 7 days. All of the patterns exhibit a main (1 0 0) peak and three weak reflections ascribed to (1 1 0), (2 0 0) and (2 1 0) planes, which are typical of highly ordered MCM-41