



Chromium and titanium/chromium-containing MCM-41 mesoporous silicates as promising catalysts for the photobleaching of azo dyes in aqueous suspensions. A multitechnique investigation

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ABSTRACT

Cr/MCM-41 and TiO₂/Cr/MCM-41 mesoporous silica were synthesized by the wet impregnation method. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and Electron Spin Resonance (ESR) techniques were employed for the nanocatalysts characterization and a comparison with previously reported results of UV–Vis diffuse reflectance spectroscopy (UV–vis DR), X-ray Diffraction (XRD) and N₂ adsorption/desorption analysis was carried out. It could be confirmed that the lower Cr loadings in the samples result in the increased presence of highly dispersed oxidized Cr species, which allows the desired heterojunction effect after the Ti loading and the high catalytic activity in the Acid Orange 7 (AO7) degradation. In this work, the analysis of the AO7 degradation progress by UV–vis and FT-IR spectroscopy has been made using the TiO₂/Cr/MCM-41(3.5) as photocatalyst, under visible and UV–vis radiation. Short irradiation times resulted in a high degradation of the azo and naphthalene groups present in the AO7 dye. At longer irradiation times, when total discoloration of AO7 solution is obtained (>97%), the biodegradability index (BOD₅/COD) reaches values greater than 0.40. This photocatalytic process could be used as a pre-treatment step before conventional biological treatment.

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1. Introduction

Due to the scarce freshwater resources, new tighter regulations concerning wastewater discharges have been established in many countries [1]. In this sense, the sustainable development became the main focus of the dialogue between the countries belonging to the United Nations (UN). Accordingly, there has been some progress on commitments to reconcile the economic activities with environmental protection [2]. On the other hand, industrial effluents of the textile industry are recognized as major pollutants due to the high amounts of water used during the dyeing operations [3–5]. Azo dyes represent the most significant group of dyes used in the industry today [5–7]. These compounds are widely

used not only in textiles but also in the leather, paints and printing industries. In fact, they are chosen as coloring products due to their unique properties such as high wet strength and relatively low cost [8,9]. Due to their resistant to biodegradation, effluents containing azo dyes are hardly degraded by conventional biological methods [1]. Thus, Advanced Oxidation Processes (AOPs), particularly heterogeneous photocatalysis, have emerged as promising technologies to remove refractory pollutants from water due to their ability to use highly reactive hydroxyl radicals [10]. The initial step in the photocatalytic process involves the absorption of photons of suitable energy by the catalyst particles and the consequent generation of electrons and holes. These species can migrate to the particle surface and take part in oxidation–reduction reactions that can finally lead to the mineralization of the pollutants [1]. However, while AOPs allow the degradation of most refractory compounds, they can be expensive when they are compared to conventional biological treatments. Therefore, their use is more suitable when the solution to be treated is not easily biodegradable or when the amount of organic matter is low. An economically

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viable option to treat wastewater containing nonbiodegradable pollutants consists in the combination of an AOP and a biological post-treatment. In this case, the chemical step is used to enhance the biodegradability of wastewater, so that it can be more easily treated biologically [11]. Besides, in order to design an efficient catalyst, it is very important to consider the properties that could affect the process development. Thus, it is of interest to synthesize materials with high surface area that can be used as a support of different photocatalytic species capable of working under visible light [12–14]. In this sense, the mesoporous molecular sieves MCM-41, have been extensively used as host porous structures [13,14]. Many transition metals oxides that absorb visible light could be loaded onto the surface of porous materials allowing a high dispersion of the active transition-metal species [12,13]. In previous work [15–17], we reported the modification of MCM-41 with different transition metals and their photocatalytic activity for the degradation of the azo-dye Acid Orange 7 (AO7). It was shown that using visible light, only the materials modified with Cr present high AO7 decolorization levels. Even though Cr modified mesoporous materials have been the subject of several literature reports [18–20], thorough and systematic investigations on the nature of the Cr species in terms of the Cr loading and its influence on the photocatalytic activity are scarce. A complete characterization of different Cr species requires the combination of spectroscopic techniques. In the present work, we investigated in detail the nature of the Cr species formed on these mesoporous silicates and their interaction with loaded Ti species. Additionally, the progress of the photocatalytic degradation of AO7 under visible and UV–vis light was analyzed by studying the time-dependent UV–vis and FT-IR spectral changes. Moreover, changes in the biodegradability of the reaction solution were also analyzed.

2. Experimental procedures

2.1. Synthesis

The metal-free MCM-41 mesoporous molecular sieve was synthesized as previously reported [21], using cetyltrimethylammonium bromide (Merck 99%) as template and tetraethoxysilane (Aldrich 98%) as silicon source (method B in reference [21]). The synthesis mixture (pH 11.25) was stirred at room temperature for 4 h. Then, this gel was heated at 343 K under stirring in a closed flask. The Cr modified MCM-41 materials were prepared by the wet impregnation method as reported in our earlier work [15] using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Anedra 98%) as Cr precursor. The used amount of this salt was the corresponding one to achieve a loading of 10.00, 5.00, 3.50, 1.50 and 0.75 wt.%. The resulting powder was dried at 333 K and calcined for 9 h at 773 K. Then, these solids were also modified by TiO_2 loading using a 3.2 wt.% of titanium *n*-butoxide (Fluka 97%) solution in isopropanol (Cicarelli 99.5%). The materials were named: Cr/MCM-41(x) or $\text{TiO}_2/\text{Cr}/\text{MCM-41(x)}$, where x indicates the theoretical loading of Cr.

2.2. Characterization

The materials were characterized by XRD, UV–vis DR and N_2 adsorption according to [17]. Here, X-ray photoelectron spectra were collected using a physical electronics PHI 5700 spectrometer with non-monochromatic $\text{MgK}\alpha$ radiation (300 W, 15 kV, 1253.6 eV) for the analysis of photo-electronic signals of C 1s, O 1s, Si 2p, Ti 2p and Cr 2p and multichannel detector. Spectra of powdered samples were recorded with the constant pass energy values at 29.35 eV, using a 720 μm diameter analysis area. During data processing of the XPS spectra, binding energy values were referenced to the C 1s peak (284.8 eV) from the adventitious

contamination layer. The PHI ACCeSS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves, in order to determine the binding energy of the different element core levels more accurately. The error in the binding energy (BE) was estimated to be ca. ± 0.1 eV. ESR spectra of calcined samples at 773 K were recorded with a Bruker ESP 300 spectrometer at 9.5 GHz in the 110–300 K temperature range. SEM micrographs were obtained in a JEOL model JSM 6380 LV, working voltage: 20 kV. Lower resolution TEM images were obtained in a JEOL Model JEM-1200 EXII System, working voltage: 120 kV.

2.3. Catalytic experiments

The degradation experiments were performed with a photoreactor as it was described elsewhere [15–17] using four UV–vis lamps (Actinic BL 20 W, Philips) as a source of light. The concentration (C) of AO7 was monitored using Jasco V 650 spectrophotometer by measuring the absorbance at $\lambda = 485$ nm assigned to the hydrazone form of the dye. The cleavage of the $-\text{N}=\text{N}-$ bond leads to decolorization of the solution. Therefore the decolorization percentage was calculated as $X = (C_0 - C) \times 100/C_0$ [16,17]. The progress of the photocatalytic process was made by FT-IR spectroscopy using a Jasco 5300. Samples for FT-IR analyses were prepared evaporating the solution at 50 °C under reduced pressure in presence of KBr used as a solid support. The mineralization degree of AO7 was measured from the Total Organic Carbon (TOC) concentration changes using a TOC/TNB Analyzer Vario TOC cube. The mineralization efficiency was defined by the following equation: $(\text{TOC}_0 - \text{TOC}) \times 100/\text{TOC}_0$, where TOC is the value of TOC obtained at time *t* and TOC_0 correspond to the initial value of TOC. The chemical oxygen demand (COD) measurements were obtained by following the closed reflux, colorimetric method [22]. The 5-days biochemical oxygen demand assay (BOD_5) was employed to evaluate changes in the biodegradability of the samples, employing the respirometric method [22] with a BOD System (Velp Scientifica) and PolySeed[®] inoculum (Interlab[®]).

3. Results and discussion

3.1. Structural characterization

The characterization results by XRD and N_2 adsorption of the synthesized catalysts were presented by us elsewhere [17]. Here, measurements of transmission electron microscopy of the calcined materials were made in order to examine their structural regularity. TEM images of the pure siliceous MCM-41 and $\text{TiO}_2/\text{MCM-41}$ samples are shown in Fig. 1. MCM-41 sample presents a well-defined mesoporous structure (Fig. 1(a)), exhibiting well ordered parallel straight mesochannels characteristic of the hexagonal pore arrangement of MCM-41 type materials [23], which was also observed by us in the XRD patterns [17]. The average mesopore size estimated by TEM is around 2.5 nm which is in agreement with the values determined from adsorption data [17]. It should be noted that in Fig. 1(a) the image is viewed perpendicularly to the direction of the hexagonal pore arrangement [24], clearly showing the presence of straight mesochannels arraying along the long axis [25]. Then, the image corresponding to $\text{TiO}_2/\text{MCM-41}$ is similar to MCM-41 sample (Fig. 1(c)), in the periodicity of the hexagonal mesopore arrangement. Nevertheless, after the loading with titanium, it is noteworthy that there were segregated TiO_2 particles on the external surface of silicate. This result is expected for materials modified with transition metals prepared via wet impregnation [26–31]. In fact, Fig. 1(b) and (c) show small TiO_2 particles which

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