Influence of the Cr loading in Cr/MCM-41 and TiO$_2$/Cr/MCM-41 molecular sieves for the photodegradation of Acid Orange 7

Verónica Elías [a,c], Ema Sabre [a], Karim Sapag [b,c], Sandra Casuscelli [a,c], Griselda Eimer [a,c,*]

[a] Centro de Investigación y Tecnología Química (CITeQ), Universidad Tecnológica Nacional, Facultad Regional Córdoba, Maestro López esq. Cruz Roja Arg. Ciudad Universitaria, 5016, Córdoba Capital, Argentina
[b] INFAP-Universidad Nacional de San Luis, Chacabuco 917 (5700) San Luis, Argentina
[c] CONICET, Argentina

ABSTRACT

MCM-41 materials were modified with different Cr contents and then loaded with Ti by the wet impregnation method. The samples were characterized by XRD, XRF, N$_2$ adsorption, UV–vis DR and TPR. Their photocatalytic activity was evaluated for the degradation of an Acid Orange 7 (AO7) aqueous solution irradiated by UV–vis and only visible light. The presence of Cr^{6+} species highly dispersed on the MCM-41 structure had a significant influence on the photoactivity. With respect to the samples only loaded with Cr, a theoretical loading of 3.5 wt.% allowed an AO7 degradation percentage of around 70%. Higher loadings result in the incremented presence of Cr^{3+} inactive species, as clusters or α-Cr$_2$O$_3$ nano-particles, producing no notable increase in the photoactivity. For its part, the presence of Ti in the samples with lower Cr loadings causes an increase in the AO7 degradation which could be associated to a heterojunction effect between active Cr^{6+} species and the titania. For the samples with higher Cr loadings, the lack of synergism could be due to the increased presence of inactive Cr^{3+} species that avoid this expected interaction.

1. Introduction

Industrial dyestuffs including textile dyes are recognized as being an important environmental threat because they consume considerable amounts of water during the dyeing and finishing operations. Due to the scarce freshwater resources, new tighter regulations concerning wastewater discharges have been established in many countries [1]. The most used dyes on the textile and printing industries are the azo-compounds which are suspected to be human carcinogens as they form toxic aromatic amines [2–4]. Taking into account that they cannot be adequately treated by conventional biological process, intensive investigations on new treatment techniques of these wastewaters have been conducted. In this sense, the called advanced oxidation processes (AOPs) have emerged. Among them, the heterogeneous photocatalysis is one of the highly effective methods used on the remediation and treatment of a wide variety of organic pollutants and microbial substances due to their ability to produce a complete degradation

of them. A photocatalytic degradation reaction is usually conducted for dissolved compounds in water, at mild temperature and pressure condition, using UV-illuminated semiconductors powder without the requirements of expensive oxidants. A semiconductor is commonly characterized by the energy gap between its electronically populated valence band and its largely vacant conduction band [5]. This band gap determines the wavelength required for excitation of an electron from the valence band to the conduction band. The most studied photocatalyst due to the important results obtained with their use is the TiO$_2$ [6–8] whose band gap is around 3.2 eV. Thus, TiO$_2$ requires UV light to be excited and become capable of photo-oxidation [9]. Moreover, with the use of TiO$_2$ some limitations in the performance of a conventional photocatalytic reactor should be taken into account since they affect the process development. The main limitations are: (1) the low surface area of TiO$_2$ particles (50 ± 15 m^2/g) that besides, when they are used in aqueous suspensions tends to form aggregates which provokes a higher decrease in the surface area affecting the process efficiency and (2) the small size ($\sim$0.5 μm) of the TiO$_2$ particles that does not facilitate their recovery from the effluent wastewater [10]. On the other hand, taking into account that the UV light is not only expensive but also harmful to aquatic life, it emerges the need to develop photocatalysts capable of working in visible light. Thus, the possibility to use solar radiation as a source of energy allows classifying heterogeneous photocatalysis as a sustainable technology.

* Corresponding author at: Centro de Investigación y Tecnología Química (CITeQ), Universidad Tecnológica Nacional, Facultad Regional Córdoba, Maestro López esq. Cruz Roja Arg. Ciudad Universitaria, 5016, Córdoba Capital, Argentina. Tel.: +54 0351 4690585; fax: +54 0351 4690585.
E-mail address: geimer@scdt.frc.utn.edu.ar (G. Eimer).

Many transition metals oxides absorb part of the spectrum of visible light. Nevertheless, their catalytic performance is limited by the low surface areas. In order to overcome this limitation, the incorporation or the loading of transition metals onto the surface of porous materials could result a good strategy to reach a high dispersion of the active transition-metal species. The mesoporous molecular sieves belonging to the M41S family, particularly, the one having an hexagonal packed array of unidirectional large channels, MCM-41, offers unique opportunities to be used as 'host porous structure'; this allows the preparation of new nanostructured composite materials that could result in photocatalysts active under visible light [10,11]. In this context, photocatalytic procedure seems to be an interesting technology for remediation of textile wastewater. In previous studies [12,13], 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) used as a probe molecule. It was shown that using visible light, only the materials modified with Cr present high AO7 decolorization. In this work, we study the influence of the Cr content on the photocatalytic performance of the TiO$_2$ loaded Cr/MCM-41 composites, paying special attention to the presence of some heterojunction effect between the Ti and Cr species.

2. Experimental procedures

2.1. Synthesis

The metal-free MCM-41 mesoporous molecular sieve was synthesized as previously reported [14] following the method B, using cetyltrimethylammonium bromide (Merck 99%) as template and tetraethoxysilane (Aldrich 98%) as silicon source. The synthesis mixture (pH 11.25) was stirred at room temperature for 4 h. Then, this gel was heated at 70 °C 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 [12] using Cr(NO$_3$)$_3$·9H$_2$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 60 °C and calcined for 9 h at 500 °C. Then, these catalysts 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 TiO$_2$/Cr/MCM-41(x), where x indicates the theoretical loading of Cr.

2.2. Characterization

The (XRD) x-ray diffraction patterns were recorded in a Philips PW 3830 diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the range of 2θ from 1.5° to 7° and from 20° to 80°. A profile fitting was made to each maximum in the high angle range, and the mean crystallite size $\langle D \rangle$ of the corresponding phase was estimated using the Scherrer formulae: $\langle D \rangle$ = 0.9λ/β cos θ, where β (in radians) is the peak intrinsic breadth after subtraction of the instrumental contribution, λ is the x-ray wavelength and θ is the Bragg angle [15]. It is worth to note that the Scherrer equation was used in order to perform a rough estimation of the crystallite size. Lower resolution TEM images were obtained in a JEOL Model JEM-1200 EXII System, working voltage: 120 kV. SEM images were obtained in a SEM Σigma-ZEISS. Energy-dispersive x-ray (EDX) analyses were conducted in a microprobe Jeol JXA 8230.

UV–vis diffuse reflectance spectra (UV–vis DRS) in absorbance mode were recorded using an Optronics OL 750-427 spectrometer in the wavelength range of 200–900 nm. The Cr and Ti content was determined by x-ray fluorescence (XRF) using an Innov-X System model ALPHA-4000. After the reaction, total Cr leaching into the reaction mixture was measured by ICP. The specific surface area, the pore size distribution and the total pore volume were determined from N$_2$ adsorption–desorption isotherms obtained at −196 °C using a Micromeritics ASAP 2010. The surface area was determined by the Brunauer–Emmett–Teller (BET) method in the pressure range of P/P_0: 0.01–0.25. The pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) method, based on the Kelvin equation [16]. The reducibility of the catalysts was measured by temperature-programmed reduction (TPR) experiments in a Quantachrome Chembet 3000. In these experiments, the samples were heated at a rate of 10 °C/min in the presence of H$_2$ (5% H$_2$/N$_2$ flow, 20 mL/min STP), and the reduction reaction was monitored by the H$_2$ consumption.

2.3. Catalytic experiments

The degradation experiments were performed with a photoreactor, as it was described in a previous report [12,13] using four UV–vis lamps (Actinic BL 20W, Philips) as a source of light. These lamps emit a continuum spectrum in the wavelength range between 350 and 400 nm and two bands at 404 and 438 nm. In order to exclude UV radiation (λ < 380 nm) in the experiments carried out under visible radiation, an acrylic filter of 4 mm thick was placed between the lamps and the reactor. The suspension volume employed in the experiments was 0.5 L with an initial concentration of the AO7 (Aldrich >85%) and the catalyst of 20 ppm and 1 g/L, respectively. Prior to each reaction, the catalyst was calcined at 500 °C. To ensure the adequate suspension of the catalyst, air bubbling was used by injection of compressed air through the sintered glass at the bottom of the reactor, adjusting the air flow rate to 1 L/min. With this flow, around 90% percentage of oxygen saturation was reached. All of the experiments were performed under natural pH condition (around 5). Prior to irradiation, the suspension was stirred in the dark under air flow for 45 min in order to reach the adsorption/desorption equilibrium. After the adsorption period, an initial sample was extracted to calculate the initial concentration (C_0) and then, the experimental run starts. Samples were collected each 1 h and filtered. The concentration (C) of AO7 was monitored by measuring the absorbance at λ = 485 nm using Jasco 7800 spectrophotometer. The degradation percentage was calculated as X = (C_0 − C) × 100/C_0.

3. Results and discussion

3.1. Material characterization

Table 1 shows the chemical composition and the textural and structural properties of the calcined catalysts. Fig. 1A and B shows the XRD patterns obtained for all of the synthesized materials. The well-resolved diffraction lines observed for Cr/MCM-41(x) samples (Fig. 1A) in the 2θ range of 1–7° are indexed to the (1 0 0), (1 1 0) and (2 0 0) reflections, characteristic for hexagonal mesostructures. The results indicate that the well-ordered pore structure of MCM-41 was retained even for the sample Cr/MCM-41(10) with the higher Cr content. Some modifications in the diffraction pattern were observed when TiO$_2$ was also loaded in the Cr-modified materials (Fig. 1B). Nevertheless, the three diffractions lines are still observed indicating that the structure was not strongly affected by the loading of the both metals: Cr and Ti. The second part of the XRD analysis was performed in the range of 20–80° in order to assess the crystallinity of the Cr and Ti oxides loaded onto the MCM-41 support. No peaks corresponding to Cr oxides were observed on the wide-angle XRD patterns (Fig. 2A(a–d)) corresponding to the lower Cr-content samples. This fact could indicate that these particles, if exists, are in amorphous state or are