Journal of Hazardous Materials 244–245 (2013) 46–53

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Ni/MgAlO regeneration for catalytic wet air oxidation of an azo-dye in trickle-bed reaction

Ana Vallet[a], Gabriel Ovejero[a], Araceli Rodríguez[a], José A. Peres[b], Juan García[a,*]

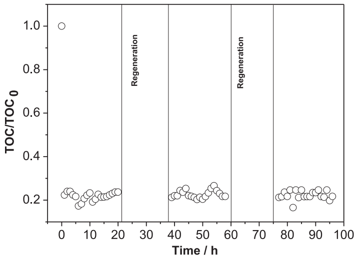
[a] *Grupo de Catálisis y Procesos de Separación (CyPS), Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain*

[b] *Centro de Química de Vila Real, Universidade de Trás-os-Montes e Alto Douro, Apartado 1013, 5001-801 Vila Real, Portugal*

HIGHLIGHTS

- Ni supported over hydrotalcite calcined precursors as catalyst.
- Catalytic wet air oxidation in trickle bed reactor for Chromotrope 2R removal.
- Dye removal depends on temperature, initial dye concentration and flow rate.
- The catalyst proved to bare-usable after in situ regeneration.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 August 2012
Received in revised form 15 October 2012
Accepted 8 November 2012
Available online 19 November 2012

Keywords:
Catalytic wet air oxidation
Chromotrope 2R
Nickel
Trickle-bed reactor
Catalyst regeneration

ABSTRACT

Active nickel catalysts (7 wt%) supported over Mg–Al mixed oxides have been recently developed and it has also been demonstrated that they are also highly selective in Catalytic Wet air Oxidation (CWAO) of dyes. CWAO of Chromotrope 2R (C2R) has been studied using a trickle bed reactor employing temperatures from 100 to 180 °C, liquid flow rates from 0.1 to 0.7 mL min^{-1} and initial dye concentration from 10 to 50 ppm. Total pressure and air flow were 25 bar and 300 mL min^{-1}, respectively. The catalyst showed a very stable activity up to 24 h on stream with an average TOC conversion of 82% at 150 °C and $T_r = 0.098\,g_{Ni}$ min mL^{-1}. After the reaction, a 1.1 wt% C of carbonaceous deposit is formed onto the catalyst and a diminution of 30% of the surface area with respect of the fresh catalyst was observed. An increase in the space time gave higher TOC conversions up to $T_r = 0.098\,g_{Ni}$ min mL^{-1}, attaining values of 80% at 180 °C. The performance of TOC and dye removal does not decrease after two regeneration cycles. In total, a 57 h effective reaction has been carried out with no loss of catalytic activity.

1. Introduction

Large amounts of wastewater containing products hazardous to the environment are produced each year. Among these products, dyes are of a great importance due to its presence in textile, dyeing, printing and fertilizing industries, among others. The color and high COD of these effluents may cause serious environmental problems. An effective decolorization and detoxification method is therefore needed to remove the toxic or carcinogenic dye residues and their by-products, which is an important issue in the field of wastewater treatment.

Advanced oxidation processes (AOPs) have been previously described as promising technologies to remove persistent pollutants from contaminated water when conventional water treatment processes are not efficient enough. AOPs are based on physico-chemical processes that enable to oxidize the pollutants by means of highly oxidizing agents, mainly hydroxyl radicals [1]. The

---

[*] Corresponding author. Tel.: +34 91 394 4111; fax: +34 91 394 4114.
E-mail addresses: govejero@quim.ucm.es (G. Ovejero), juangcia@quim.ucm.es (J. García).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.11.019

oxidation process leads ideally to a complete mineralization into CO_2, N_2, water and mineral acids such as sulfuric and hydrochloric [2–6].

Among AOPs, Wet Air Oxidation (WAO) has been proved to be an effective technology for the treatment of dye-containing solutions [7]. However, the application of traditional WAO is limited because of the high temperature, pressure and long operation time [8]. Catalytic Wet Air Oxidation (CWAO) was a technology developed on the basis of WAO in the 1970s. The presence of the catalyst can lower the reaction time, temperature and pressure. It is an available method employed for the treatment of high-concentration effluents, as well as poisonous, detrimental and hardly degradable wastewater. Copper ion is the most effective catalyst when homogeneous reactions are considered and has been successfully employed for the treatment of wastewaters discharged from petrochemical industries [9]. Heterogeneous catalysts are less effective but present the advantage of being easily separated from the reaction medium and are preferred to soluble catalysts, which have to be recovered by an additional separation process [10–12] which makes the process more expensive.

Co-precipitated Ni–Mg–Al hydrotalcite (HT) has been found to be active for the liquid phase oxidation of alcohols with molecular oxygen [13], while supported iron oxide catalyst prepared from Mg–Al HT revealed the high activity for ethylbenzene dehydrogenation [14] and for dyes treatments [15]. HT, or layered double hydroxides (LDHs), are anionic clays. The structure of the HT is very similar to brucite $Mg(OH)_2$, where an isomorphous substitution of Mg^{2+} by a trivalent element M^{3+} occurs. When Mg^{2+} ions are replaced by a trivalent ion, a net positive charge is compensated by anions in the interlayer. The hydrotalcite-like compounds are generally described by the general formula: $[Mg_{1-x}Al_x(OH)_2]^{x+}[\,A^{n-}_{x/n} \cdot MH_2O]^{x-}$, where M is the metal and A the anion. Anionic clays based on HT have arisen considerable interest because of the diversity of their chemical compositions and its uncountable applications such as catalysts, catalysts supports, ion exchangers, stabilizers and adsorbents [16]. A large number of hydrotalcite-like compounds have been extensively studied as precursors, since they permit a rather suitable dispersion for the metal catalyst. Ni/MgAlO mixed oxides have shown remarkable properties as catalysts precursors such as high metal dispersion and stability against sintering, even under extreme conditions [17].

The high activities of all these catalysts are undeniable due to the stable and highly dispersed active metal species [18]. Moreover, hydrotalcites possess an interesting property, i.e. a “memory effect,” by which hydrotalcite structure is reconstituted when the mixed oxide obtained after hydrotalcite calcination is dipped in aqueous solution [18].

Chromotrope 2R (C2R) is a monoazo dye with several applications in textile industry. Azo dyes represent about one-half of dyes actually used in the textile industry and, as a consequence, a relevant problem is related to the release of these products in the environment [19,20]. In this work, we aimed at preparing nickel catalysts supported over Mg–Al mixed oxides (Ni/MgAlO), obtained from the calcination of HT, by incipient wetness impregnation of $Ni(NO_3)_2{\cdot}6H_2O$ for the CWAO of C2R to study the catalyst effect on the process efficiency. The effect of operational conditions such as temperature and initial dye concentration will also be tested, as well as the catalyst stability and its regeneration.

2. Experimental

2.1. Materials and catalyst preparation

C2R was selected as the model pollutant because it is hardly biodegradable by the conventional biological processes, but widely employed in the textile, colour solvent, ink, paint, paper, pharmaceutical and plastic industries. The dye was purchased from Sigma–Aldrich (Steinheim, Germany) and used without further purification (Table 1).

2.2. Preparation of the catalyst

HT precursor, with Mg/Al = 5, was employed as support in the preparation of nickel catalysts. It was prepared by the co-precipitation method proposed by Yamaguchi et al. [21]. $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_2{\cdot}9H_2O$ (Sigma–Aldrich, Steinheim, Germany) in desired amounts were dissolved in 600 mL of water to form solution A. Besides, Na_2CO_3 and NaOH were mixed in 300 mL of water to form solution B. Solution B was stirred for 1 h at constant temperature of 65 °C. Then, solution A was slowly dropped forming a precipitate [22]. The resulting solution was aged at 60 °C for 18 h. Then, it was filtered and washed with distilled water at 40 °C for 2 h. The resulting precipitates were dried at 100 °C for 12 h.

Nickel catalyst was prepared by incipient wetness impregnation technique employing $Ni(NO_3)_2{\cdot}6H_2O$ purchased from Panreac (Barcelona, Spain) in aqueous solution as precursor and impregnated over the prepared HT support. The precursor amount was calculated to obtain a catalyst load of 7 wt% of nickel in the final analysis. The resulting solid was calcined at 550 °C for 5 h.

2.3. Characterization

The support and the nickel catalyst were characterized by physical adsorption of nitrogen at −196 °C in a Micromeritics ASAP 2010 apparatus. XRD patterns were recorded using a SIEMENS D-501 diffractometer. The metal loading was determined by mean of ICP-AES. More detailed characterization procedures can be found in previous work [23].

2.4. CWAO reactions

Continuous experiments were carried out in a Microactivity-Reference unit (PID Eng & Tech, model MA-Ref), which is an automated and computer-controlled continuous-flow trickle-bed laboratory reactor. Concentrations of the fed aqueous solutions ranged from 10 to 50 ppm. A fixed-bed tubular reactor in Hastelloy C-276 was heated with a reactor furnace and integrated within the hot box. Liquid and gaseous flows were introduced into the hot box system, which includes an electric forced convection heater which permits the process route to be preheated and kept at temperatures up to 190 °C. The liquid reactant was introduced into the unit using a HPLC positive alternative displacement pump (Gilson, model 307). The oxygen source in these experiments was air, which was fed to the system through an electronic mass-flow controller. The preheated gas and liquid streams merge in a T-joint and are then introduced to the top of the reactor through a 10 mm sintered 316 stainless-steel filter (another is located at the outlet of the reactor, which protected the arrangement from possible catalyst fines). A porous (2 mm) plate made of Hastelloy C-276, supported on a 316 stainless-steel pipe, was placed inside and near the middle of the reactor tube to support the fixed bed composed of 0.7 g of Ni/MgAlO catalyst placed over inert spherical glass beads. The reaction temperature was measured by a thermocouple, which was inserted through the upper end of reactor and was in contact with the catalyst bed. The thermocouple was regulated from the pre-set temperature by a PID temperature controller (TOHO, model TTM-005). The gas and liquid phases, which passed the catalytic bed in a co-current down flow mode and flowed out at the bottom of the reactor, were separated in a high-pressure liquid–gas (L/G) separator cooled with a Peltier cell. The L/G separator equipped with