

## Degradation of Basic Yellow 11 by Catalytic Wet Air Oxidation with Transition Metals Supported over Hydrotalcites

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Ni and Fe catalysts supported over hydrotalcites were prepared by incipient wetness impregnation and successfully employed in the catalytic wet air oxidation of a dye, Basic Yellow 11 (BY11). The influence of operational variables, compound concentration, catalyst loading as well as hydrotalcites calcination temperatures (350, 450, 550 and 650°C) was investigated. Also, the characterization of these materials (support and catalysts) was carried out by BET, XRD, SEM/TEM, TGA/DTG and XRF. During the CWAO of BY11, numerous partial oxidation products appeared and the knowledge of the kinetics that controls its oxidation process is fundamental to design, modelling and scale up of a CWAO pilot plant or industrial units. The reaction mechanisms in WAO and CWAO processes of BY11 were studied.

### 1. Introduction

Wastewater treatment and reutilization of industrial water is a critical issue for the suitable development of human activities. The need for effective water recycling has reinforced the research on tailored low cost pollution abatement since the existing solutions are not longer universal. In particular, the catalytic wet air oxidation (CWAO) process is one of the most promising technologies for the remediation of moderately concentrated and/or biotoxic water pollutants, when a stable and active catalyst can be provided (Garcia et al., 2005). To this purpose, the catalytic activity and stability of nickel and iron supported over hydrotalcite was tested in the CWAO of the target compound, Basic Yellow 11, at mild conditions of temperature and pressure.

The hydrotalcite type materials are layered double hydroxides (LDH) and their structure are very similar to the brucite  $[\text{Mg}(\text{OH})_2]$ . For LDHs an isomorphous substitution of  $\text{Mg}^{2+}$  by a trivalent element (generally aluminium) occurs in the brucite-like network and this replacing generates a positive charge in the brucite layer. The positively charged Mg-Al double hydroxide sheets are charge balanced by anions residing in the interlayer sections. During the synthesis of LDH both of magnesium and aluminium can be changed by many bivalent or trivalent cations respectively resulted in materials with different properties (Del Arco et al., 2010).

The range of metal cations incorporated in the layers of LDHs has been extended in recent years and LDHs containing three and four different metal ions, including a wide variety of transition metal ions, have been reported (Kovanda et al., 2003). Transition metal-containing LDH materials are of particular interest as catalysts in their own right and as precursors to other catalysts.

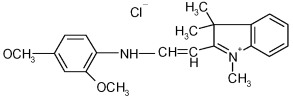
The objective of the present study was to clarify whether the degradation of organic pollutants, as exemplified by the Basic Yellow 11, might occur when iron or nickel catalysts supported over hydrotalcites are employed in CWAO.

## 2. Experimental Section

### 2.1 Materials

BY11 (Colour Index Number 48055), was kindly supplied by Sigma Aldrich (Spain) as a commercially available dye and used without further purification. Table 1 shows the main characteristics and structure of this dye. The other chemicals were obtained from Merck, Germany.

Table 1: Structural formula of BY11 compound and main characteristics

| Structure   | Formula and Molecular Weight                                     | Boiling Point | Melting Point | Vapor Density (Air=1) |
|---|--|---------------|---------------|-----------------------|
|  | $C_{21}H_{25}ClN_2O_2$<br>$372.89 \text{ g}\cdot\text{mol}^{-1}$ | Decomposes    | 100-110 °C    | 13                    |

### 2.2 Preparation and Characterization of Catalysts

The mass of the metallic precursor was calculated in order to obtain 2, 3, 5, 7, 10 wt% nickel or iron in the catalysts. After impregnation, the wet solid was dried overnight at 110°C and then activated under air at 550°C.

Textural characterization was carried out by  $N_2$  adsorption at 77 K. The BET surface areas ( $S_{BET}$ ) were calculated from the corresponding nitrogen adsorption isotherms. The morphology of the supports and catalysts was analyzed by scanning electron microscopy (SEM). Experiments were carried out with a JEOL JSM 6400 electron microscopy at 22 KeV. X-ray diffraction (XRD) was recorded by means of a diffractometer SIEMENS D-501 with a Ni-filtered  $Cu K\alpha$  radiation in order to check some structure data. Finally, X-ray Fluorescence (XRF) measurements were performed using a BRUKER S4 EXPLORER system, with software for data acquisition and analysis.

### 2.3 Catalytic Experiments

All experiments were conducted in a Hastelloy high-pressure microreactor C-276 Autoclave Engineers with a volume of 100 mL. The reactor (i.d. 50 mm) was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The temperature and the stirring speed were controlled by means of a PID controller.

The gas inlet, gas release valve, cooling water feed, line pressure gauge and rupture disk were situated on the top of the reaction vessel. The liquid sample line and the thermocouple were immersed in the reaction mixture.

The reactor was first charged with 100 mL of the BY11 solution and the catalyst (if necessary), and initially pressurized with nitrogen to ensure inert atmosphere. Afterwards, the system was heated to the desired temperature and a sample was withdrawn. This was considered zero time for the reaction, and TOC conversion during this time can be neglected while calculating initial rates. Oxygen from the cylinder was then sparged into the liquid phase and samples were withdrawn periodically after sufficient flushing of the sample line. Pressure drop was monitored and additional oxygen was charged in order to maintain a constant total pressure.

#### 2.4 Product Analysis

At the desired reaction time, aliquots of the solution were collected and analyzed for total organic carbon (TOC) using a combustion/non-dispersive infrared gas analyzer (Shimadzu TOC analyzer). The residual BY11 concentration was determined by an UV-vis spectrophotometer using a Shimadzu spectrophotometer at 413 nm. Toxicity was determined by means of a Microtox analyzer (model 500). Finally, the intermediates were identified by GC-MS (Agilent 5973 N MSD) and HPLC with a C18 column.

### 3. Results and Discussion

#### 3.1 Characterization of Catalyst Metal Supported on Hydrotalcite

Fig. 1a shows the XRD powder patterns of hydrotalcite dried at 100°C, where all samples presented the characteristic reflections corresponding to layered double hydroxide structure, and no different crystalline phases were detected. Fig. 1b exhibits the XRD patterns of the samples of Ni catalysts calcined at several temperatures for 5 h. The surface areas increased as calcination temperatures increased up to 550°C due to the release of H<sub>2</sub>O and CO<sub>2</sub> from the dissociation of hydroxyl and carbonate groups in the interlayers of hydrotalcite (Tichit et al., 1995). Results obtained for Fe catalysts were similar. It is well known that when an LDH is calcined below 700 °C, only the metal oxide of the metallic cation present in major amount will be detected (Olsbye et al., 2002). Accordingly, in all samples only a poorly crystallized MgO phase was obtained. No significant agglomeration of nickel or iron particles based on TEM analysis was observed when the calcination temperatures were below 550 °C. On the other hand, thermogravimetric analysis (Figs. not shown) showed the typical thermal transformation of hydrotalcites with loss of adsorbed water until 250°C, followed by almost complete decarbonation and dehydroxylation at 500°C. It was also observed that the increase of the nickel or iron content led to a decrease in thermal stability of the original hydrotalcite phase. A further weight loss at 600°C is due to the loss of carbon dioxide associated to a mixed nickel or iron-magnesium solid structure already reported by other authors (Chmielarz et al., 2002). The higher BET surface areas ( $S_{\text{BET}}$ ) were obtained for the samples calcined at 550°C, reaching values of 156.5 and 150.0 m<sup>2</sup>.g<sup>-1</sup> for Ni (5)/HT

and Fe(5)/HT, respectively. This was the calcination temperature employed in the preparation of the catalysts used in further experiments.

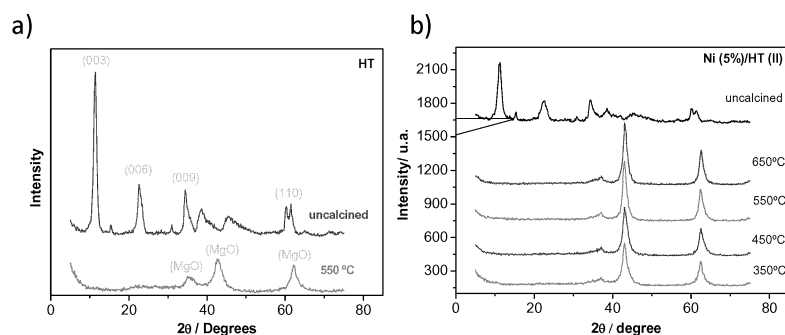


Figure 1: a) Powder X-ray diffraction patterns of the layered double hydroxide compound, b) Powder X-ray diffraction patterns of nickel supported on hydrotalcite obtained after thermal treatment of the LDHs

### 3.2 Catalytic Activity: Catalytic Wet Air Oxidation Process

The influence of metal content on the BY11 removal using Ni and Fe catalysts prepared by incipient wetness impregnation was studied by varying the metal content from 2 to 10 %. The reductions in TOC and color (concentration dye) for the different contents are shown in Figure 2. It can be seen that the nickel catalyst, gave higher removal of TOC and color at different metal contents than iron catalyst. In general, when metal content increases from 2-10%, TOC and colour removal is improved with both catalysts. Also, a positive effect was observed when catalyst concentration was increased (Figs. not shown). The catalytic results show that the activity for oxidation was increased. TOC and color removal is improved in the catalytic reaction.

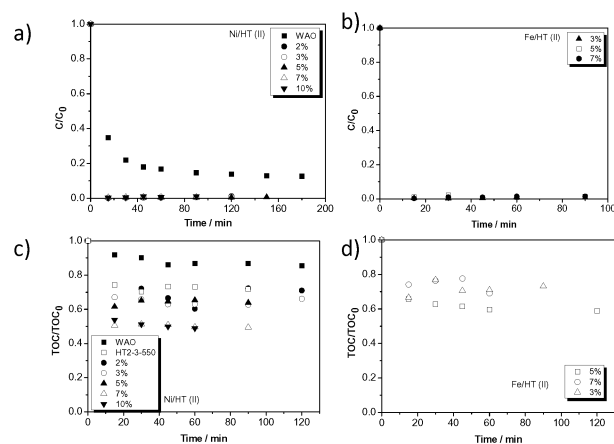


Figure 2: Influence of metal content: Color removal with a) Ni and b) Fe catalysts, and TOC removal with c) Ni and d) Fe catalysts in CWAO

To investigate the leaching of prepared Ni (5%) and Fe (5%) supported over hydrotalcite by incipient wetness impregnation, the content of Ni or Fe in the reaction effluents was determined by AAS. A membrane filter (0.2  $\mu\text{m}$ ) was used to separate the solution from the catalyst. Low Ni leaching (less than 3%) was detected whereas 10% of the initial Fe was found in the solution. As Ni catalyst was the most efficient, reutilization experiments were carried only with this catalyst. The Ni catalyst could be reused with the retention of its catalytic activity and selectivity, as shown in Fig. 3. This experiment proves again that the prepared Ni catalyst is an effective and reusable catalyst. However, the Fe catalyst was less effective for the oxidization of basic yellow 11, leaching was observed in this catalyst.

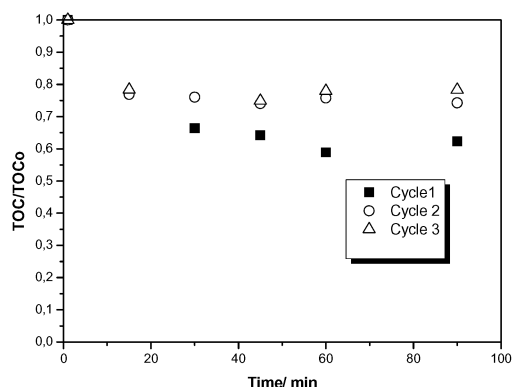


Figure 3: Reuse experiment of Basic Yellow 11 oxidation with Ni supported on hydrotalcite catalyst in CWAO

To measure intermediates formed during the oxidation, a concentration of 50  $\text{mg}\cdot\text{L}^{-1}$  was used for reaction at 120  $^{\circ}\text{C}$  and 8.8 bar partial pressure over Ni/HT catalysts. The oxidized solution was taken for GC-MS analysis. Several intermediates were identified in the oxidized solution: Acetaldehyde, (1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene, acetaldehyde, benzenamine-2,4-dimethoxy, 1H-indole-2,3-dihydro-1,3,3-trimethyl-2-methylene, ethanol, acetone, 2-methylidoline. Some studies on oxidative degradation of organic dyes have been reported previously (Garcia et al., 2005; Thompson et al., 1994). Several species are believed to be responsible for the decoloration, which include free radical species (Thompson et al., 1994). However, the exact mechanism for dye destruction is still in question. Most probably, the degradation proceeds by an adsorption-oxidation-desorption mechanism. Firstly, the BY11 molecules are adsorbed onto surface of the hydrotalcite. Secondly, the nascent free radical species have high oxidizing ability and cause destructive oxidation of the organic dye. Thirdly, the small molecules from dye degradation are desorbed off the hydrotalcite surface and the catalyst is, thus, recovered. Finally, the measured BY11  $\text{EC}_{50}$  (not shown) based on the Microtox procedure was better in toxicity reduction for the Ni than Fe catalyst.

#### 4. Conclusions

Nickel or iron supported on hydrotalcite by incipient wetness impregnation can be used as catalysts for selective oxidation of basic yellow 11 in aqueous media. The catalytic activity of these catalysts when the reaction is carried out in metal content range 2-10% and catalyst concentration 4 g.L<sup>-1</sup> is moderate in TOC removal, but high in color elimination, Ni(5)/HT being the catalysts that showed the highest catalytic performance at 120 °C. In addition, the catalyst can be recycled without any loss in its capacity and efficiency.

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