Catalysis Today 166 (2011) 194–200

Contents lists available at ScienceDirect

Catalysis Today

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

Modified electrode with hydrotalcite-like materials and their response during electrochemical oxidation of blue 69

M.A. Oliver-Tolentino[a], A. Guzmán-Vargas[a,*], A. Manzo-Robledo[b],
M.J. Martínez-Ortiz[a], J.L. Flores-Moreno[c]

[a] ESIQIE-IPN, Departamento de Ingeniería Química - Laboratorio de Investigación en Materiales Porosos, Catálisis Ambiental y Química Fina, UPALM Edif.7 P.B. Zacatenco, México, D.F. 07738, Mexico
[b] ESIQIE-IPN, Departamento de Ingeniería Química - Laboratorio de Electroquímica y Corrosión. Edif. Z-5 3er piso, UPALM, Zacatenco, México D.F. 07738, Mexico
[c] Universidad Autónoma Metropolitana-A, Area de Química de Materiales, Avenida San Pablo No. 180, 02200 México D.F., Mexico

ARTICLE INFO

Article history:
Available online 20 September 2010

Keywords:
Hydrotalcite-like materials (LDH)
Oxygen evolution reaction (OER)
Anodic processes
Electro-catalysis
Cation effect

ABSTRACT

In order to evaluate the electrocatalytic properties, Mg/Al and Mg/Ca/Al hydrotalcite-like materials (LDHs) and their corresponding mixed oxide were immersed in a carbon paste electrode matrix to obtain the so-called modified carbon paste electrode (MCPE). Previous to preparation of MCPE, LDH materials were characterized by different techniques, as XRD, FTIR and BET analysis. The electrochemical response of the electrodes was characterized in neutral conditions using reactive blue 69 dye as a probe molecule. Linear sweep voltammetry (LSV), cyclic voltammetry (CV), multi-sweep cyclic voltammetry (MSCV) and open circuit potential transient techniques were employed. Different current magnitudes in the oxygen evolution reaction (OER) were found as a function of thermal treatment and supporting electrolyte (pH). On the other hand, in a solution containing 250 ppm of the probe molecule at neutral pH, peaks attributed to blue 69 oxidation were found at ca. 0.65 and 0.95 V/SCE. The presence of calcium, as additional divalent cation, and the rehydration of the mixed oxide, due to memory effect, have a positive performance, increasing the magnitude of the electrocatalytic process.

1. Introduction

Layered double hydroxides (LDHs) belong to the anionic clay family or the hydrotalcite-like compounds. These materials have been discovered in Sweden in 1842 [1], but majority of LDHs actually used are obtained by synthesis. LDHs result of the association of divalent and trivalent metallic cations placed in the center of octahedral structures. On the edges, hydroxyl groups are placed. Those octahedral arrangements are joined to form a lamellar structure consisting of brucite-like layers and compensating anions situated in the interlayer space [2]. Hydrotalcite-like compounds can be represented by the general formula:

$$\left[\mathrm{M}^{\mathrm{II}}_{1-x}\mathrm{M}^{\mathrm{III}}_{x}(\mathrm{OH})_2\right]^{x+}\left[\mathrm{A}^{n-}_{x/n}\right]\bullet m\mathrm{H_2O}$$

where x varies from 0.1 to 0.34 [3].

Two of the most important properties of layered double hydroxides are memory effect and anion exchange. In the first one, lamellar structure of LDH is generally stable until 250 °C. Up to this temperature, water physisorbed in the interlayer space is eliminated and the dehydroxilation of the layers and compensation anions decomposition occurs [4]. Since LDH follows a thermal treatment up to 800 °C, periclase (MgO) and spinel ($MgAl_2O_4$) crystalline structures are identified. In the range of 450–600 °C, mixed oxide can be rehydrated to recover the original lamellar structure, as a function of the chemical composition [1]. This property is called "memory effect" and it is usually carried out in vapor phase or in aqueous solution [5]. In the second one, LDH materials present high anionic exchange capacity (2–5 meq/g) [2], which allows their application in different fields. For example, they can substitute anionic exchange resins for the water purification as trap of nitrates, chlorides or phosphates, but also as adsorbents of heavy metals and radioactive elements.

In catalysis, hydrotalcite-like compounds have been tested in several reactions such as epoxydation, aldol and Knoevenagel condensations, halide exchanges, Michael additions, reduction of aldehydes and ketones by hydrogen transfer from alcohols and transesterification reactions, among others [6–8]. After calcination of LDH, mixed oxide are obtained, which are basic solids. Moreover, the preparation of multi-metallic LDHs and their acid–base properties have been widely studied [5,9–11].

Apart from catalysis, LDHs have applications in the very varied domains such as adsorbents, medicaments (anti-acids), additives in the cosmetic and pneumatics industries, PVC stabilizers, corrosion inhibitors and flame retardants [1].

---

* Corresponding author. Tel.: +52 55 57296000; fax: +52 55 55862728.
E-mail address: aguzmanv@ipn.mx (A. Guzmán-Vargas).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.08.007

Table 1
Chemical composition in wt.%, formula, molar ratio and surface area of the solids.

Sample	Chemical composition (wt.%)					Formula	Molar ratio M^{II}/M^{III}		S_{BET}[a] (m^2/g)
	Mg	Ca	Al	N	C		Solution	Solid	
Mg/Al-HT	21.18	0	7.98	2.12	0.22	$Mg_{0.749}Al_{0.251}(OH)_2(NO_3)_{0.130}(CO_3)_{0.016}$	3	2.98	216
Mg/Ca/Al-HT	16.28	1.07	11.48	2.74	0.54	$Mg_{0.597}Ca_{0.024}Al_{0.379}(OH)_2(NO_3)_{0.174}(CO_3)_{0.040}$	3	1.64	155

[a] The surface areas were determined on the mixed oxide samples.

In this context, mesoporous materials [12], and layered double hydroxides prepared by different synthesis methods, as well as various chemical compositions [13], have been employed in the preparation of modified electrodes. These last materials have been also applied as electrochemical sensors, owing to their anionic exchange capacity to oxidize organic molecules by metallic complexes or surfactants inside the lamellar structure [14,15]. Idemura et al. [16] achieved the reduction of ferrate(III) ions and ligand-exchange during an intercalation process on Mg–Al hydrotalcite-like materials.

Furthermore, it was found that current observed in a clay-modified electrode depends on the porosity, nature, number and activity of the reactive sites [17]. Scavetta et al. [18–20] showed that the electronic conductivity in Ni/Al HDT-like materials can occur due to a complex mechanism involving an “electron hopping” along the layers, which can be attributed to: (i) an inner redox reaction between oxidized and reduced forms of the M^{II}/M^{III} couple and (ii) a migration of anions inside the interlayers to compensate the positive extra-charge. This mechanism depends only on the OH^- desolvation and the adsorption process onto the electrode surface.

In this context, the treatment of wastewater-containing dye compounds is a technological challenge because their catalytic oxidation (treatment more commonly employed) presents some disadvantages. It is well known that the main pollution problem by dyes is their capacity of assimilation–adsorption in water, using ordinary process, causing photosynthesis modification for flora. On the other hand, dye compounds used in textile industry are highly soluble in water, and they show high resistance to the action of chemical agents.

Therefore, an alternative environmental method for the elimination of these pollutants is the so-called advanced oxidation processes (AOPs). AOP is a promising method for the treatment of water contaminated with organic non-biodegradable compounds [21–25].

Azo-dye blue 69 is a synthetic colorant used and wasted by textile industry. This compound shows two main absorbance peaks in the UV–vis region: (i) aromatic ring at 320 nm and (ii) color absorption at 605 nm [26,27]. The main conjugated structures in the blue 69 molecule are the azo group, the benzene and the naphthalene rings; due to the presence of the anion SO_3^- linked to the naphthalene rings, it can be used as a supporting electrolyte. The structure of the molecule is presented in Fig. 1.

In this study, the electrocatalytic response on MCPE with Mg/Al and Mg/Ca/Al hydrotalcite-like materials was evaluated during the electrochemical oxidation of azo-dye blue 69. Electro- and physico-chemical techniques were used to correlate the obtained results.

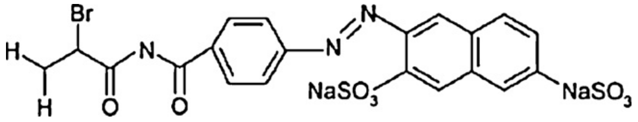

Fig. 1. Chemical structure of dye blue 69.

2. Experimental

2.1. Material preparation

Layered double hydroxides (LDHs), with different M^{II}/M^{III} molar ratios were prepared by coprecipitation method at pH 10 of suitable amounts of $Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 6H_2O$ and $Ca(NO_3)_2\cdot 4H_2O$ (Aldrich, 99.99%, USA) with a 2.0 M solution of NaOH (Aldrich, 99%). The addition of the alkaline solution and pH were controlled by a pH-STAT Tritando apparatus (Metrohm, Switzerland). The suspension was stirred overnight at 80 °C, and then the solid was separated by centrifugation, rinsed thoroughly with distilled water (Na < 100 ppm), and dried overnight at 80 °C. The LDHs were heat-activated in air flow at 450 °C for 4 h (heating rate: 2 °C/min) to yield the $M^{II}(M^{III})O$ mixed oxide. Samples were labeled as Mg/Al-HT, Mg/Ca/Al-HT, for the layered double hydroxides and Mg/Al-Ox and Mg/Ca/Al-Ox, for the corresponding mixed oxide solids.

2.2. Electrode preparation

Modified carbon paste electrodes (MCPEs) were prepared mixing graphite powder (Alfa Aesar, 99.9995%, USA), silicon oil (Aldrich) and the corresponding LDH at 20 wt.%. Then, the mixture was mechanically homogenized and inserted in a 2 mm diameter cylinder (0.0314 cm^2). The surface contact on the MCPE was made with a platinum wire.

2.3. XRD, IR and BET analyses

Chemical analysis of the samples as prepared was performed at the Service Central d’Analyse du CNRS (Solaize, France). XRD patterns of the samples, as prepared or calcined at 450 °C, were recorded on a D8 Focus Bruker AXS instrument using Cu-Kα1 radiation ($\lambda = 1.542$ Å, 35 kV, and 25 mA). N_2 sorption experiments at 77 K were carried out on samples previously calcined at 450 °C and outgassed at 280 °C (10 – 4 Pa), with a Micromeritics ASAP 2000 instrument. Specific surface areas were calculated using the BET method. Absorption/transmission IR spectra were run at RT on a Magna-IR Nicolet 750 spectrophotometer, working in the range of wavenumbers 4000–400 cm^{-1} at a resolution of 4 cm^{-1} (number of scans 64).

2.4. Electrochemical measurements

Electrochemical characterization was performed in a conventional three-electrode cell. Carbon rod and saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. Electrochemical techniques, such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), multi-sweep cyclic voltammetry (MSCV) and transient open circuit potential, were employed using a Potentiostat–Galvanostat (Autolab PGSTAT30-2, Switzerland). Distilled water-solution of blue 69 was used as supporting electrolyte and probe molecule. The electrode was immersed into the solution until the open circuit potential (E_{OCP}) was stable. Prior to use, the solution was purged with argon for at least 15 min.