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Influence of thermal treatment conditions on the characteristics of Cu-based metal oxides derived from hydrotalcite-like compounds and their performance in bio-ethanol dehydrogenation to acetaldehyde

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ABSTRACT

The influence of the copper presence on the active sites of catalysts derived from a hydrotalcite-like compound (HTLC) was investigated in bio-ethanol dehydrogenation. It was observed that the presence of copper lead to an inhibition of dehydration and coupling reactions that occurred on the mixed oxide ($MgAlO_x$) obtained by thermal decomposition of the HTCL, leading to selective formation of acetaldehyde. In situ X-ray absorption experiments revealed that the nature of the copper species depended on the nature of the atmosphere used to promote the HTCL decomposition: when the decomposition was conducted under helium atmosphere at 750 °C a mixture of Cu^0/Cu^{+1} species was formed, while when the decomposition was done under an oxygen/helium atmosphere there was only the presence of Cu^{+2} species. Because the mixed oxide formed after thermal decomposition of the HTCL presents activity for bio-ethanol dehydration, coupling and dehydrogenation reactions, on the studied systems the bio-ethanol conversion into acetaldehyde does not seem to be influenced by the different copper species, even though it is well known that Cu^0 and Cu^{+1} sites are necessary for the reaction.

1. Introduction

Hydrotalcite-like compounds (HTLCs) are layered double hydroxides (LDHs) with large use in adsorption and catalysis. These compounds are represented by the general formula $[M^{2+}{}_{1\text{-}x}M^{3+}{}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, x is the ratio $M^{2+}/(M^{2+}+M^{3+})$, and A^{n-} is the interlayer anion with charge n. The structure of these compounds consists of positively charged brucite-like layers alternated with negatively charged interlayers containing hydrated anions [1].

The evolution of the structure of HTLCs during thermal treatment has been reported in several studies and some of them have used in situ high temperature techniques such as high temperature X-ray diffraction (HTXRD) [2–5]. According to Kanezaki's studies [2–4], the predominant structure at room temperature (Phase I) is transformed into another phase (Phase II) at temperatures above 180 °C, which becomes a different phase at temperatures greater than 380 °C. On the other hand, Yang et al. [5] observed four temperature regions for the HTLCs thermal phase evolution. In the first temperature range, 70–190 °C, there were two different co-existing crystal phases (Phase I and Phase II, which differ in their basal spacing) and the structure remained intact. Above 190 °C Phase I began to be transformed into Phase II due to the release of OH— groups bonded to the Al^{3+} species. The authors also observed the degradation of the HTLC structure in temperatures above 280 °C with the OH^- groups bonded to Mg^{2+} being completely lost at 405 °C. Finally, the formation of an amorphous metastable mixed solid solution occurred in temperatures between 405 and 580 °C, and was associated to the decomposition of $CO_3{}^{2-}$ anions.

Mixed oxides containing transition metal cations can be precursors of redox and Lewis-type centers, showing an attractive catalytic activity. For instance, the copper-containing HTLCs can be used as a catalyst for the Baeyer-Villiger oxidation of ketones [6]. The mixed oxide catalysts obtained by thermal decomposition of Cu-Al or Cu-Mg-Al hydrotalcites have been used as catalysts in

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several reactions such as phenol alkylation [7,8], phenyl ethyne coupling [9], decomposition and reduction of nitrogen compounds [10–14], and NO_x and SO_x removal from flue gases [15,16].

The present work deals with the characterization of a copper-containing hydrotalcite-like precursor and its corresponding mixed oxide prepared by calcination under two different atmospheres. The aim was to couple two high temperature techniques (XRD and XANES) to obtain complementary information on the nature and transformation of the copper species during decomposition of a Cu-Mg-Al hydrotalcite either under oxidizing or inert atmosphere. The influence of the different copper species formed during decomposition over the activity in the bio-ethanol dehydrogenation reaction was evaluated.

2. Experimental

2.1. Synthesis of the hydrotalcite-like precursors

The Cu-Mg-Al hydrotalcite-like compound (with a $(M^{3+})/(M^{2+}+M^{3+})$ molar ratio equal to 0.25) was prepared at room temperature by co-precipitating an aqueous solution of the metallic cations with a highly basic carbonate solution under vigorous stirring. The synthesis gel produced had a composition of $0.375Cu(NO_3)_2$:$1.875Mg(NO_3)_2$:$0.75Al(NO_3)_3$:$2Na_2CO_3$:6.75NaOH.

The molar ratio (0.25) was selected in order to avoid segregation of $Mg(OH)_2$ or $Al(OH)_3$ [17]. The gel was aged under constant pH (13) for 18 h at 60 °C. Then, the obtained solid was filtered, washed with distilled water (90 °C) until the pH reached a value of 7, and finally dried in an oven kept at 80 °C during 12 h. The synthesized samples with and without copper were coded HT and Cu-HT, respectively. The Mg,Al-hydrotalcite (coded HT) was prepared using the same methodology without the addition of the copper nitrate salt and was used as reference. The synthesis gel of the HT sample had a composition of $2.25Mg(NO_3)_2$:$0.75Al(NO_3)_3$:$2Na_2CO_3$:6.75NaOH).

2.2. Synthesis of the mixed oxides

Mixed oxides were obtained by calcining the HT or Cu-HT samples under two different atmospheres: 5%(v/v) O_2/He or pure He. The HT or Cu-HT samples were heated from room temperature up to 750 °C at a 10 °C min^{-1} heating rate, and the final temperature was held for 2 h. The samples obtained after the calcining step of HT and Cu-HT were coded MO and Cu-MO, respectively.

2.3. Catalyst characterization

2.3.1. X-Ray fluorescence (XRF)

The chemical composition of the synthesized samples was determined by XRF using a Rigaku Rix 3100 instrument. Before the analysis, HT and Cu-HT samples were pressed (4000 Kgf) using a Carver Laboratory Press (Model C), and the waffles were analyzed for Mg, Al and Cu contents. The obtained results were expressed as weight percentages of MgO, Al_2O_3 and CuO.

2.3.2. N_2 physisorption

Specific surface area and mesoporous volume were measured at −196 °C using an ASAP 2000 Micromeritcs automatic analyzer. The samples were outgassed at 200 °C for 12 h before measuring the isotherm. The specific surface area values were determined using the B.E.T. and the total pore volume was derived from the amount of gas absorbed at a relative pressure of $P/P_0 = 0.95$.

2.3.3. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

Thermogravimetric analysis was performed in order to follow and identify the thermal decomposition processes taking place between room temperature and 800 °C. A Rigaku thermobalance (TAS-100) was used and the experiments were done using a flow of synthetic air atmosphere and a heating rate of 10 °C min^{-1} during the heating.

2.3.4. In situ X-Ray diffraction (XRD)

The in situ X-ray diffraction measurements were carried out at the XPD beamline at the Brazilian Synchrotron Light Laboratory (LNLS) in Campinas, Brazil. The wavelength used was 1.5333 Å and the X-ray had energy of 8.17 keV. Samples in powder form were placed in a homemade furnace (Arara) installed in the Huber goniometer and the measurements were made in reflection mode (Bragg-Brentano geometry). The XRD patterns were obtained by one-dimensional Mythen – 1 K detector (Dectris) installed 1 m from the furnace. The thermal decomposition was performed using a total flow of 100 mL min^{-1} of pure He or a 5%(v/v) O_2/He gas mixture and a heating rate of the 10 °C min^{-1} up to 750 °C. XRD patterns were collect for 2θ values ranging from 31 to 51° with a scan-step of 0.05°. XRD patterns of HT, Cu-HT, OM and Cu-OM before and after the thermal decomposition were recorded with a 2θ scanning from 25 to 80°, scan-step of 0.025 º using a Cyberstar scintillation detector.

2.3.5. In situ X-ray absorption near-edge structure (XANES) at Cu K-edge

The in situ XANES measurements at the Cu K-edge (8979 eV) were performed at the DXAS beamline of the LNLS. The DXAS is a dispersive beamline equipped with a focusing curved Si(111) monochromator operating in Bragg mode that selects radiation from a bending magnet source in X-ray range from 4 keV up to 14 keV and focuses it at the sample position. The detection is made by an 1152 × 1242 (500 × 900) pixel CCD solid-state detector, with conversion of X-rays into visible light for spectral analysis. The samples were prepared as self-supporting pellets containing ~100 mg of sample and placed into a tubular quartz reactor (diameter = 20 mm and X-ray path length = 440 mm), which was sealed with Kapton windows for transmission measurements. The thermal decomposition of samples was performed using a total flow of 50 mL min^{-1} of He or 5 % (v/v) O_2/He gas mixture and a heating rate of the 10 °C min^{-1} up to 750 °C. After thermal treatment, the samples were cooled to 300 °C under the same treatment atmosphere, and then ethanol (4.2 mL min^{-1}) was admitted under flow of helium (50 mL min^{-1}) in order to characterize the changes in copper oxidation state and local coordination during the reaction. XANES spectra of the reference materials Cu, Cu_2O and CuO were recorded at room temperature.

2.3.6. High resolution transmission electron microscopy (HR-TEM)

Before analysis the MO and Cu-MO samples were mechanically crushed with a mortar and pestle and the obtained powder was then dispersed in a copper grid coated with a holey carbon film. This type of grid makes it possible to image copper particles on areas not overlapping the carbon film. Electron micrographs were recorded with a Philips CM-200 FEG instrument. The operating voltage was 200 kV. The microscope is equipped with an UltraTwin lens giving a resolution of ~0.12 nm. Image processing, i.e. automatic crystal identification and measurements, were carried out using Digital Micrograph software.

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