



Copper-supported pillared clay catalysts for the wet hydrogen peroxide catalytic oxidation of model pollutant tyrosol

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ARTICLE INFO

Article history:

Received 11 March 2008

Received in revised form 25 June 2008

Accepted 10 July 2008

Available online 25 July 2008

Keywords:

Copper

Pillared clay

Wet hydrogen peroxide catalytic oxidation

2-(4-Hydroxyphenyl)ethanol

ABSTRACT

The catalytic wet hydrogen peroxide oxidation of tyrosol, a major compound of the polyphenolic fraction present in olive oil mill wastewaters, was studied in batch and continuous reactors using copper-supported pillared clay catalysts under mild conditions. The catalysts were prepared by the solid-state reaction of Al-pillared clay synthesized with copper nitrate. The resultant materials were then calcined at 300 °C for 3 h under helium or oxygen. The catalytic activity of Cu-supported pillared clays was found to depend on the calcination method. The effects of several operating conditions were also studied. Our experimental results indicate that, under mild conditions and a stoichiometric amount of oxidant, the calcined material under helium (CuN_{He} catalyst) showed higher activity and stability (TOC abatement of roughly 80% and total elimination of tyrosol after 1 h reaction, without significant leaching of copper ions) than the calcined material under oxygen (CuN_{Oxy}). To better understand the catalytic behaviour of copper-supported pillared clay solids, fresh and used catalysts were characterized by X-ray diffraction, nitrogen adsorption, chemical analysis, temperature-programmed reduction (TPR), UV–visible diffuse reflectance spectroscopy, and transmission electron microscopy (TEM).

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1. Introduction

The Mediterranean countries are the main producers of olive oil. During olive oil extraction, large quantities (roughly 7 million tonnes per year) of strongly polluted water, known as olive oil mill wastewaters (OMW), are generated [1]. Because of its content (14–15%) of organic substances and phenols (up to 10 g L⁻¹), OMW is thought to be one of the most polluting effluents produced by the agrofood industries, which are characterized by high specific COD (chemical oxygen demand) [2–4]. The untreated release of OMW onto land is a danger for the environment. Several studies have shown that simple OMW phenolic compounds with low molecular weights are responsible for toxicity on seed germination [5], aquatic organisms [6–8], and bacteria [9]. Recovering these phenolic compounds, which have interesting antioxidant properties, could provide an interesting alternative source of biologically active polyphenols [10]. Several researchers have evaluated the feasibility and economic processes involved in the recovery of these phenolic compounds from OMW or solid wastes [11,12]. After these processes, however, further treatments are needed to

eliminate the toxicity of the effluents before they are discharged into the natural stream.

For these reasons, research has focused on developing efficient treatment technologies, including physical, chemical and biological processes [13]. Oxidation systems have often been used as pretreatments to decrease OMW toxicity and allow biological degradation. Since around 1980, attention has been paid to the development of an effective oxidation process called wet oxidation. In catalytic wet oxidation the reaction conditions are milder than in uncatalysed wet oxidation, but high temperature (over 150 °C) and high pressure (1–5 MPa) are still required. These severe operating conditions lead to high installation costs, which limit the practical applications of the process. Catalytic wet peroxide oxidation (CWPO) could be a more efficient process because the oxidizing properties of hydrogen peroxide are stronger than those of molecular oxygen. Moreover, the reaction conditions when hydrogen peroxide is involved as oxidant are close to the ambient ones (0.1 MPa, $T < 80$ °C). This enables a large amount of wastewater to be treated with the minimum consumption of energy. Heterogeneous catalysis would be preferred to homogeneous catalysis if a stable and active catalyst under operation conditions were found. Several materials have been proposed as catalysts for the oxidation of organic compounds in water [14,15]. However, deactivation was often observed with the solubilisation

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of the active phase. To get round this problem, stable catalysts have recently been developed. Transition-metal exchanged zeolites [16,17], Cu²⁺-containing pillared montmorillonite [18,19], and Fe³⁺- or Cu²⁺-pillared clays [20–24] have been proposed as active catalysts for the oxidation of organic compounds. These catalysts show a higher rate of conversion of the pollutants and a lower sensitivity to pH than iron ions in solution at the same reaction conditions. However, some of them exhibit partial leaching of the cations, probably because the metal is not bound efficiently in the solid, for example in the pillars for the clays [21,25,26]. Tatibouët and co-workers suggested that the high resistance to leaching and the good catalytic performance of the pillared clay catalysts could be attributed to a strong interaction between the metal species and the catalytic support [27].

In this context we have developed a simple, new protocol for Al–Cu-pillared clay preparation and studied the activity and stability of the catalysts obtained for the catalytic wet peroxide oxidation (CWPO) of tyrosol. *p*-Hydroxyphenylethanol (tyrosol) was chosen as the model compound because, like hydroxytyrosol, which can be produced during the oxidation of tyrosol, it is one of the most significant phenols in OMW. Also, fewer studies in the literature are related to the oxidation of tyrosol than to the oxidation of phenol, *p*-coumaric acid or *p*-hydroxybenzoic acid.

2. Experimental

2.1. Materials

Tyrosol, 2-(*p*-Hydroxyphenyl)-ethanol 98% from Aldrich Co. was used in this study. Commercial Wyoming montmorillonite from Comptoir des Minéraux (France) was used as starting clay. Al and Cu nitrate (Aldrich Co.) were used as precursors for the pillaring solution and solid reaction, respectively.

2.2. Catalysts preparation

2.2.1. Starting material

The Wyoming montmorillonite was sieved to obtain an extracted fraction with a particle size of less than 2 μm. Its cation exchange capacity, determined by the adsorption of copper ethylenediamine complex, was 100 mequiv./100 g (ignited) clay, and its BET surface area was 29 m²/g. The starting material for the pillaring procedure was the sodium form of this montmorillonite, which was obtained by treatment with 1 mol L⁻¹ NaCl solution (three times exchanged), followed by washing and dialysis until the result of the reaction for the presence of Cl⁻ was negative. The product was then air dried at 60 °C.

2.2.2. Catalysts synthesis

Alumina-pillared clay was prepared by slowly adding Al-pillaring solution into an aqueous suspension of montmorillonite. The pillaring solution was prepared by dissolving 0.2 mol L⁻¹ Al-nitrate in 0.45 mol L⁻¹ NaOH solution. The hydrolysis molar ratio OH/Al was kept at 2.25. The pH of the solution was about 3.8 and the solution remained clear. The diluted montmorillonite suspension (10 g L⁻¹) was prepared by adding the montmorillonite powder into the distilled water. The pillaring reaction was carried out under continuous vigorous stirring by dropwise adding the pillaring solution into the montmorillonite suspension. After centrifugation, the solid fraction was washed by dialysis in distilled water and dried at room temperature. The sample was then calcined for 5 h at 500 °C under airflow. The temperature was raised to 500 °C at a rate of 1 °C/min and this temperature was maintained for 5 h.

The copper-supported Al-pillared clays were prepared by the solid ion exchange method. Typically, 5 g of the already synthesized Al-pillared clay were intimately mixed with the desired percentage of copper nitrate [Cu(NO₃)₃·9H₂O] in an agate mortar for 10 min. This was followed by heating at 300 °C for 3 h under helium. The solid was then cooled to ambient temperature, washed six times with distilled water, dried at 80 °C for 24 h, and then calcined at 300 °C for 3 h under helium flow for the first (referenced as CuN_{H₂O}) and under oxygen flow for the second (referenced as CuN_{Oxy}). CuN stands for copper nitrate precursor.

2.3. Characterizations

The X-ray powder diffraction (XRD) patterns were measured on a Philips PW 1730/10 diffractometer CuK_α (λ = 1.54184 Å) radiation. The position of the *d*₀₀₁ ray in the XRD is related to the interlayer distance and, therefore, to the pillar height.

Quantitative chemical analysis of the copper in the modified clays was determined by X-ray fluorescence using SFX Siemens SRS 330, and the amount of leached metal was determined by atomic absorption spectrometry using a PerkinElmer 400 spectrophotometer.

Nitrogen adsorption experiments, for samples previously degassed at 120 °C for 12 h, were performed at –196 °C using a Micromeritics ASAP 2000 instrument. Specific surface area was calculated by the BET method.

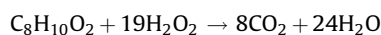
Temperature-programmed reduction (TPR) measurements were performed using a Thermofinnigan TPDRO 1100 system. A mixture of H₂ (5%) in argon with a flow rate of 20 mL min⁻¹ was used to reduce the samples (0.12 g), which were placed in an oven heated from 40 to 990 °C at a heating rate of 10 °C min⁻¹ and maintained at 990 °C for 20 min. The reduction of CuO to metallic copper was used to calibrate the TPR apparatus for H₂ consumption.

UV–vis diffuse reflectance (UV–vis–DR) spectra were recorded in air on powdered samples using a Jasco V-570 spectrometer equipped with an integrating sphere for solid samples. The reference was BaSO₄.

Transmission electron microscopy (TEM) observations were carried out on a JEOL 2010 microscope (200 kV, resolution 0.19 nm). Samples for direct examination were prepared by suspending the powder in EtOH, and a drop of the suspension was allowed to dry on a copper grid. When the contrast was low, extractive replica were used. A drop of the suspension was deposited on freshly cleaved mica. After drying, the dispersed powder was covered by a carbon film. The mica was plunged into a solution containing a mixture of water, acetone and hydrofluoric acid to dissolve the support without dissolving the metal particles. These remained stuck to the carbon film, which was collected on a copper grid.

2.4. Oxidation of tyrosol

The catalytic oxidation of tyrosol was carried out in a stirred (stirring rates of between 500 and 1200 rpm) and thermostated Pyrex well-mixed slurry batch reactor of 250 mL. The reaction was performed in the 25–80 °C temperature range and at a pH of 5.6 (the natural pH of the solution) using a 500 ppm tyrosol (3.6 mmol L⁻¹) aqueous solution in contact with different catalysts loading under continuous stirring. After 5 min of stirring, a hydrogen peroxide solution was added (time zero of the reaction) in one time. The H₂O₂/tyrosol molar ratio was 19/1, which is the stoichiometric quantity needed to totally transform the tyrosol into CO₂ according to the reaction:



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