



Catalytic wet peroxide oxidation of phenol over iron or copper oxide-supported allophane clay materials: Influence of catalyst SiO₂/Al₂O₃ ratio

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ABSTRACT

Allophane clay materials with SiO₂/Al₂O₃ ratios of 1.0 (AlSi1) and 2.2 (AlSi2) were synthesized by a co-precipitation route and further impregnated with iron or copper species. The structure of the parent AlSi1 sample is similar to that of a typical Al-rich soil allophane, while the parent AlSi2 material resembles the structure of a hydrous feldspathoid with a large interspherule surface, thereby exhibiting a high surface area. The ability of the various iron or copper-based allophane samples to behave as efficient and stable catalysts in phenol oxidation using H₂O₂ was investigated in ambient conditions for the first time. Their structural and textural properties were determined by X-ray diffractometry, N₂ adsorption–desorption at 77 K, electrophoretic mobility measurements, infrared spectroscopy, transmission and scanning electron microscopy, as well as by thermo-gravimetric analysis. The catalytic activity of the iron or copper oxide-supported allophanes was markedly influenced by their SiO₂/Al₂O₃ ratio and by their respective structure. The iron-based AlSi2 catalysts with tail-like structure and high surface area proved to be far more active than their corresponding AlSi1 counterparts. The highest catalytic efficiency in terms of total organic carbon abatement was obtained at 40 °C for the calcined iron oxide-supported AlSi2 allophane sample, for which very low leaching level of iron species was noticed (0.37 mg L⁻¹). By contrast, large differences in terms of catalytic efficiency (conversion rates) and stability were observed for the copper-based counterparts, thereby indicating that the iron oxide-supported allophanes with a hydrous feldspathoid structure are highly active and stable in the catalytic wet peroxide oxidation of phenol.

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1. Introduction

In being able to generate strongly oxidizing hydroxyl radical species, advanced oxidation processes (AOP) are effective in decomposing a wide range of organic pollutants [1–3]. Typical AOP include ozonation, wet air oxidation, wet peroxide oxidation, Fenton-type reactions as well as photocatalytic processes. Depending on the type of oxidant (ozone, oxygen, hydrogen peroxide) and on several possible combinations, such as the use of both H₂O₂ and O₂ or O₃, H₂O₂/UV, H₂O₂/ultrasonic irradiation, the number of AOP processes may be higher. Catalytic wet peroxide oxidation (CWPO) based on the Fenton-type process involves reacting Fe²⁺ species with H₂O₂ under acidic conditions (pH ~ 3.0) to produce reactive hydroxyl radicals in mild reaction conditions, thereby limiting

investment costs. The redox properties of other transition metal ions, such as copper, cerium and manganese can similarly be used to generate hydroxyl radicals from hydrogen peroxide under atmospheric pressure and temperature closed to the ambient [4–6]. However, in this homogeneous Fenton process, many problems typical of homogeneous catalysis are encountered, such as catalyst separation and regeneration, as well as the application of a strict control of pH to prevent precipitation of iron hydroxide. These drawbacks may be overcome by using Fenton-like heterogeneous catalysts (i.e., solids containing transition metal cations, mostly iron or copper ions) that can operate over a wide range of pH, are easily recovered after use and remain active during successive cycles of reaction [7].

A variety of solid catalysts have been prepared and described on the basis of their activity and stability in the catalytic wet peroxide oxidation of various organic pollutants [2]. Such Fenton-type heterogeneous catalysts include transition metal-exchanged zeolites [7,8], pillared interlayered clays containing iron or copper species [4,9,10,11–13], activated carbon impregnated with iron or copper

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oxide [14,15], iron-supported mesostructured silica supports [16,17], iron-based perovskite or spinel oxides [18,19], and iron-oxide minerals [20]. The efficiency and stability of solid catalysts are strongly related to the nature and dispersion of the active phase and the interaction between the active centers and the support. In this respect, catalytic supports exhibiting high surface area, as well as large and uniform pores are preferred because they can facilitate the dispersion of active sites and enhance diffusion of reactants/products in liquid phase reactions [21].

Allophane is a clay-size mineral of widespread occurrence in volcanic ash soils. The unit particle of allophane is a hollow spherule with an external diameter between 3.5 and 5.5 nm and a wall thickness of 0.7–1.0 nm. Defects in the wall structure give rise to openings of about 0.3 nm in diameter [22–25]. Three types of naturally occurring allophane minerals are known to exist: (1) Al-rich soil allophane with an imogolite-like structure and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ~ 1.0 ; (2) Si-rich soil allophane with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ~ 2.0 ; and (3), stream-deposit allophane with a hydrous feldspathoid-like structure exhibiting a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.1–2.2 [26,27]. Some synthetic aluminosilicates with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio > 2.2 have also been included in the stream-deposit allophane category [28].

Allophane nanoparticles in Chilean Andisols are commonly associated with iron oxide of short range order, among them ferrihydrite, which is a hydrated ferric iron oxide compound [29,30]. However, owing to numerous surface reactive hydroxyl groups, natural allophanic nanoclays are shown to strongly retain a substantial fraction of organic matter from the Andisols. This organic matter is found to be intimately associated with the allophane particle surface. Calaby-Floody et al. [25] highlighted the difficulty to isolate allophane nanoparticles from the soil with high purification degree even after repeated treatments with hydrogen peroxide. Such drawback has stimulated research on the synthesis of allophane clay materials with defined properties and their interaction with iron oxide [30–35]. This strategy constitutes an attractive alternative to natural contaminated allophanic nanoclays for practical applications. In this way, synthetic allophane nanoparticles have been already used as good adsorbents of organic pollutants [36,37], iron oxide-supported synthetic allophane can also act as support for enzyme immobilization [38]. In addition, when deposited on a glassy carbon electrode, the iron-based material is able to electro-oxidize phenol [39]. The use of iron oxide-supported allophane clays materials as catalysts in the degradation of organic pollutants by a Fenton-like reaction has been recently reviewed by Garrido-Ramírez et al. [40].

The main objective of the present study is to elaborate environmentally friendly catalysts based on allophane-type structure, fulfilling important requirements in the Fenton-like reaction, such as activity in ambient conditions (atmospheric pressure and temperature close to the ambient), stability and low cost. For that purpose, two allophane clay materials with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are synthesized by a co-precipitation route and further act as support for iron or copper oxide. Various characterization techniques, such as X-ray diffraction, nitrogen sorption isotherms, thermal analysis, infrared spectroscopy, electron microscopy coupled to EDX analyses, as well as electrophoretic mobility measurements are used to evaluate the final structural and textural properties of the parent allophane materials and their corresponding iron or copper oxide-supported counterparts. Their catalytic performances are determined for the first time in total phenol oxidation using hydrogen peroxide as oxidant, with the aim of investigating the influence of the allophane $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the phenol elimination activity and total organic carbon (TOC) decay. The stability of both iron and copper active species during the catalytic reaction is also evaluated. Phenol is used as a model molecule, because of the high toxicity exhibited by phenolic wastes, which are one of the most

prevalent forms of pollutants in waste water stemming from industry.

2. Experimental

2.1. Allophane supports preparation

Allophane clay materials were synthesized by co-precipitation of potassium silicate and aluminum chloride following the procedures described by Mora et al. [30] and Diaz et al. [31]. Briefly, 0.47 L of potassium silicate solution (2 mol L^{-1}) was prepared by dissolving 50 g of silica in concentrated KOH (5.3 mol L^{-1}) solution. In parallel, an aluminum chloride solution (2 mol L^{-1}) was prepared by dissolving 14 g of aluminum in 500 mL of HCl (1:1). A given amount of aluminum chloride acting as Al_2O_3 source (45 mmol) was placed in a Teflon beaker to which 330 mL of deionised water was added. A quantity of potassium silicate as silica source (135 mmol) was then added dropwise under continuous stirring. The pH of the suspension was adjusted to pH 5.0 (by addition of HCl or KOH solutions) at a constant temperature (25°C). After stirring for 45 additional minutes, the suspension was centrifuged and repeatedly washed (by centrifugation) until the supernatant solution was free of chloride. The resulting as-synthesized allophane sample has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.2 (determined by energy dispersive X-ray spectroscopy) and was labelled as AlSi2. Allophane with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ~ 1.0 , designated as AlSi1, was obtained by mixing an aqueous solution of aluminum chloride (2.15 mol L^{-1}) with a solution of potassium silicate (1 mol L^{-1}) as described above.

2.2. Iron or copper oxide-supported allophanes

AlSi2 sample was impregnated with iron or copper oxide by a wet impregnation method [30], using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as iron and copper source, respectively. The pH of iron nitrate and copper nitrate stock solutions was fixed to 3.0 and 5.0, respectively. Briefly, appropriate amounts of iron (corresponding to 2 or 6 wt.% Fe) or copper nitrate solutions (corresponding to 6 wt.% Cu) were added to 2 g of AlSi2 allophane suspension and made up to 60 mL with deionised water. Each solution was then concentrated in a rotary evaporator at 25°C . The resulting product was separated by centrifugation, homogenized by washing three times with 1 mol L^{-1} KCl solution, before being repeatedly washed with deionised water until no chloride ion was detected in the supernatant solution. The samples, labelled as AlSi2Fe2 (2 wt.% of iron), AlSi2Fe6 (6 wt.% of iron) and AlSi2Cu6 (6 wt.% of copper) were air-dried, ground and oven-dried at 105°C for 24 h. Portions of the AlSi2Fe6 and AlSi2Cu6 samples were calcined in air at 300°C for 1 h. The corresponding thermally treated samples were referred to as AlSi2Fe6(T300) and AlSi2Cu6(T300), respectively. The same methodology was used to impregnate the AlSi1 sample with 6 wt.% of iron (AlSi1Fe6).

2.3. Characterization of the catalysts

The textural properties of the parent allophane materials and of their corresponding synthesized and calcined iron or copper oxide-supported counterparts were evaluated by N_2 adsorption-desorption at 77 K on a Micromeritics ASAP 2010 instrument. Prior to N_2 adsorption, the samples were degassed under vacuum at 250°C for at least 6 h. The specific surface area was determined from the linear part of the BET plot. The isoelectric point (IEP) values were obtained with a Malvern Zetasizer 2000 instrument, by determining zeta potentials over the pH range 3–10, derived from electrophoretic mobility measurements using 0.5 mg samples in

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