Stability of carbon-supported iron catalysts for catalytic wet peroxide oxidation of ionic liquids

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ABSTRACT

The stability of two carbon-supported Fe catalysts in the catalytic wet peroxide oxidation (CWPO) of 1-Butyl-3-methylimidazolium acetate (BmimAc) was examined. One catalyst (Fe/AS) was obtained by chemical activation of dried sewage sludge with iron chloride at a $FeCl_3$:sewage sludge mass ratio of 3 and the other (Fe/HTCS) by hydrothermal carbonization of the sludge in the presence of $FeCl_3$ at a mass ratio of also 3. Fe/AS catalyst exhibited a well-developed porosity, whereas Fe/HTCS one did not show porosity. The carbon content was high in both catalysts, with a total Fe content of 5.2 and 6.6% (w/w) for Fe/AS and Fe/HTCS catalysts, respectively. An additional Fe catalyst prepared by incipient wetness impregnation on a commercial active carbon support (Fe/AC) was used for comparison with the previous two. All catalysts were active in experiments of H_2O_2 decomposition and long-term CWPO runs (0.133 kg_{Fe} h mol_{BmimAc}^{-1} at 80 °C). Whereas Fe/AC catalyst lost activity largely due to Fe leaching (90% of Fe_{Bulk}), Fe/AS and Fe/HTCS catalysts exhibited virtually no Fe leaching and hence fairly good stability. Fe/AS catalyst, which afforded complete removal of $Bmim^+$ and TOC conversion values around 30%, proved the most efficient catalyst.

1. Introduction

Ionic liquids (ILs) are salts formed by an organic cation and an organic or inorganic anion that possess a low vapor pressure and a melting point below 100 °C [1,2]. Because of their relative high solubility in water, ILs can be released to an aqueous medium during synthetic processes or used as solvents in many catalytic, biocatalytic, chemical and electrochemical processes [3,4]. The consideration of ILs as "green solvents" remains a subject of debate. Thus, ionic liquids exhibit a wide range of environmental toxicity depending mainly on their structural features and on the particular target biological system [5]. The imidazolium family of compounds is the most widely studied among ILs, which is unsurprising if one considers their excellent properties as solvents for a number of chemical processes [6]. Imidazolium-based ILs have a low ecotoxicity [7,8] which, however, increases with increasing length of the alkyl chain; also, they possess a low biodegradability [9–11] that can be improved by lengthening the alkyl chain to more than 6 C atoms [9,12]. Advanced oxidation processes (AOPs) have emerged as the best choice for removing poorly biodegradable compounds from wastewater under mild operating conditions [13]. For example, imidazolium-based ILs can be efficiently removed by electrochemical oxidation [14–16], ultraviolet photolysis

[17,18] and Fenton oxidation [19–21]. Catalytic wet peroxide oxidation (CWPO), which involves decomposing H_2O_2 into HO· radical in the presence of a suported Fe catalyst at an acid pH, has been sucessfully used for IL degradation [22]. The main advantage of this process is that Fe is immobilized and retained on a support, which dispenses with the need to remove the metal from wastewater [23]. Although CWPO reactions are usually conducted under mild conditions, some authors have found that raising the temperature improves mineralization [24–26]. However, conventional catalysts lose activity during the reaction, largely through Fe leaching [23,25–27]. The need thus remains to obtain active and stable catalysts for CWPO under operating conditions.

Carbon-based materials have been used as sorbents in wastewater treatments [28–30] and also as catalyst supports [31,32]. The best choices for this purpose have a high carbon content in addition to well-developed porosity, which leads to a high surface area and facilitates metal adsorption and dispersion as a result [33,34]. However, carbon-supported Fe catalysts for CWPO are prone to Fe leaching through poor fixation of the metal onto the carbon surface [23,32]. Also, some carbon materials impair H_2O_2 decomposition into hydroxyl radicals [35]. A varyety of carbonaceous residues such as agricultural waste including olive and grape bagasse [36], pomegranate seeds [37] or grape seeds

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[25,38]; tire waste [39,40]; polyethylene [41] and medical waste [42] have been the targets of increasing efforts at their valorization over the last decade. For example, sewage sludge is produced in very large amounts in wastewater treatment plants —as large as 85 g dry solids per population per day according to the International Water Assotiation (IWA). Spain produces an estimated 1.2 millions tonnes each year (Government of Spain, 2017). At present, sewage sludge is managed by composting, landfilling or incineration [43,44], which poses so serious a problem that efficiently handling of this waste has become a priority action in various strategic plans focusing on recycling (e.g., Council Directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment) or its banning from agriculture (e.g., Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture). There remains, however, the need to find sustainable ways of valorizing sewage sludge, which can be converted into effective catalytic supports by pyrolysis, activation or hydrothermal carbonization (HTC). In a previous work, carbon-supported Fe catalysts were obtained through pyrolysis of sewage sludge with $FeCl_3 \cdot 6H_2O$ as precursor of the active phase, showing good results in CWPO of phenol, bromophenol and dimethoate in terms of mineralization rates and Fe leaching (< 1%) [45]. Moreover, a new method for preparing supported Fe catalysts based on chemical activation of dried sludge with $FeCl_3$ at 750 °C in an N_2 atmosphere was developed, exhibing the catalyst a high mineralization rate (ca. 80%) and low Fe leaching (2.5%) in antipirine CWPO [46]. Unlike pyrolysis, HTC efficiently converts wet sewage sludge into a carbonaceous material by using less energy and minimizing CO_2 emissions [47]. The exothermic reactions involved take place in an aqueous environment at a moderate temperature (180–350 °C) at autogenous pressure (2–10 MPa) [48,49]. On the other hand, the carbonaceous materials obtained by HTC are characterized by a poor porosity development against that the obtained by pyrolysis or chemical activation processes [50,51]. HTC allows sewage sludge to be converted into char for use as an energy source (solid fuel) and/or an activated carbon precursor potentially useful as a sorbent [52,53] or catalytic support, for example.

The main aim of this work is to examine the stability of two different Fe carbon catalysts prepared by activation with $FeCl_3$ and HTC in the presence of $FeCl_3$ from sewage sludge in the CWPO of the ionic liquid 1-Butyl-3-methylimidazolium acetate (BmimAc). Stability was assessed mainly in terms of Fe fixation in the carbonaceous support.

2. Material and methods

2.1. Catalyst preparation and characterization

Aerobic granular sludge was obtained from a membrane bioreactor (MBR) of industrial cosmetic water located at Madrid (Spain). Before using, the sludge was washed with distilled water, dried at 105 °C for 24 h, ground and sieved to a particle size of 0.10-0.25 mm [45,46]. Fe/AS catalyst was prepared from mixing $FeCl_3 \cdot 6H_2O$ with dried biosolid in a mass ratio of 3 (mg $FeCl_3$/mg biosolid) and dried in an oven at 60 °C for 20 h. Following, the activation process consisted of a heating at 750 °C for 2 h, under an N_2 atmosphere (30 mL N min^{-1}), in a Nabertherm Series R tubular furnace (ramping up 10 °C min^{-1}). Finally, the catalyst was washed with 3 M HCl at 80 °C for 1 h and then to neutral pH with distilled water in order to remove excess activating reagent and dried at 60 °C.

The second catalyst (Fe/HTCS) was obtained by HTC of a mixture of $FeCl_3 \cdot 6H_2O$ salt and wet granular sludge in a mass ratio of 3 (mg $FeCl_3$/mg dried sludge; sludge moisture content, 85%) in a 250 mL stainless steel batch reactor with an inner Teflon lining. The HTC process was performed at 208 °C for 1 h, with heating at 10 °C min^{-1}. Then, the material was washed with a 3 M HCl solution at 80 °C to remove excess Fe.

A Fe/AC catalyst was prepared by incipient wetness impregnation

from a $FeCl_3 \cdot 6H_2O$ solution followed by drying at room temperature for 2 h and standing at 60 °C overnight before calcining at 200 °C for 3 h by heating at 10 °C min^{-1}. The activated carbon was supplied by Merck (BET surface area ≈ 950 m^2 g^{-1}, bulk density ≈ 0.5 g cm^{-3}).

The pore structure of the catalysts was established from N_2 adsorption–desorption isotherms at −196 °C obtained with a MicromeriticsTristar 3020 automated volumetric gas adsorption instrument. Prior to the adsorption measurements, a sample of 0.15 g of each catalyst was degassed to vacuum in a glass container at 150 °C for 7 h by using a Micromeritics VacPrep 061 degassing apparatus. The iron content of the catalysts was determined by total reflection X-ray fluorescence (TXRF) spectroscopy on an Extra-II Rich & Seifert spectrometer equipped with a Si–Li detector. The C, H, N and S contents of the catalysts were determined with a LECO CHNS-932 analyzer. Ash was quantified according to ASTM D1506-99 and the oxygen content calculated by difference from 100%. Available Fe in the outer catalyst surface was determined by X-ray photoelectron spectroscopy (XPS) on a Physical Electronics 5700C Multitechnique instrument using MgKa radiation (1253.6 eV) and energy dispersive X-ray spectroscopy (EDAX).

2.2. CWPO tests

The activity of the three catalysts in H_2O_2 decomposition was assessed in a stirred batch reactor (400 mL) equipped with a magnetic stirrer (500 rpm) and temperature control. Tests were conducted at pH 3 at 80 °C, using a catalyst mass equivalent to a concentration of 40 mg$_{Fe}$ L^{-1} based on the Fe$_{Bulk}$ content of each catalyst. CWPO long-term experiments (80 h on stream) were performed in a continuous stirred tank reactor (CSTR, 400 mL) fitted with an autosampler (Gilson FC 203B) to collect aliquots of reaction medium. All CWPO runs were conducted at atmospheric pressure in duplicate. IL and H_2O_2 solutions were pumped to the reactor at a 1 mL min^{-1} flow rate in order to feed an IL concentration of 1 mM and the stoichiometric H_2O_2 dose, the resulting space–time being 0.133 kg$_{Fe}$ h mol$_{BmimAc}$$^{-1}$. The imidazolium concentration was determined with Varian Prostar 325 high performance liquid chromatography (HPLC) using UV–Vis detection at 218 nm, a Phenomenex Synergy 4 mm Polar-RP 80 A column (15 cm long, 4.6 mm i.d.) as stationary phase and a mixture of phosphate buffer and acetonitrile (95:5% v/v) at a flow rate of 0.75 mL min^{-1} as mobile phase. Acetate anion (Ac), short chain organic acids (formic, malonic and oxalic) and anionic species (nitrite and nitrate) were quantified on a Dionex ICS-900 ion chromatograph with chemical suppression and furnished with a Dionex IonPac AS22 4 × 250 mm column, using a stream of 1.4 mM NaHCO$_3$/4.5 mM Na$_2$CO$_3$ at 1 mL min^{-1} as mobile phase. Total organic carbon (TOC) and total nitrogen (TN) were determined with a Shimadzu TOC-VCSH analyzer. Finally, H_2O_2 was determined with a Cary 60 UV/Vis spectrophotometer from Agilent Technologies that was operated at 410 nm [54] to monitor the colorimetric titration leading to the formation of Ti(IV)–H_2O_2 complex. Iron leached from the catalyst to the liquid phase being measured by the same apparatus at 510 nm with the o-phenanthroline method [55].

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the main characteristics of the sewage sludge and the catalysts. As can be seen, Fe/AC catalyst exhibited a well-developed micropore structure with a fair contribution of mesopores. Fe/AS catalyst was essentially microporous and had a BET area similar to that of the catalyst prepared from commercial activated carbon as a result of $FeCl_3$ being used as activating agent [46,56]. Finally, the catalyst obtained by HTC and activation with $FeCl_3$ barely developed BET area. The N_2 adsorption-desorption isotherms plots are presented in the supplementary material (Fig. 1S). The Fe/HTCS isotherm corresponds to a non-porous material, whereas Fe/AC and Fe/AS isotherms are