Journal of Molecular Liquids 177 (2013) 402–408

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

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

Preparation, characterizations and its application of heterogeneous Fenton catalyst for the treatment of synthetic phenol solution

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ARTICLE INFO

Article history:
Received 30 July 2012
Received in revised form 5 October 2012
Accepted 8 October 2012
Available online 23 October 2012

Keywords:
Phenol
CWPO
Heterogeneous Fenton-type catalyst
Sol–gel method
Hydrogen peroxide

ABSTRACT

Fe–Co–Al trimetal oxide (TMO) was prepared by the sol–gel route for the oxidation of phenol solution by catalytic wet peroxide oxidation (CWPO) method. The characteristic of Fe–Co–Al was carried out. The size of the catalyst was found to be between 1 and 5 μm with good porosity which was confirmed using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N_2 adsorption–desorption isotherms. The catalytic activity results showed almost complete oxidation of phenol up to 1000 mg/L. The oxidation process and the products formed were confirmed using various instrumental analyses. The TMO catalyst could be reused even after three cycles very effectively.

1. Introduction

Phenol and phenolic derivatives are identified as harmful aromatic compounds in industrial waste waters and have been considered on the EPA's priority pollutant list since 1976 [1]. These organic compounds are of serious environmental concern in several chemical industries, petroleum refineries, cooling plants etc., because of their widespread use and toxicity. Phenol is also considered as an intermediate product in the oxidation pathway of high molecular weight aromatic hydrocarbon and it is usually considered as a model compound for advanced waste water treatments [2].

Though there are many conventional biological processes which represent an environmentally friendly way of treatment with reasonable costs, they are not adequate to treat non-biodegradable wastewaters. In such cases, many alternative technologies are available such as adsorption, advanced oxidation processes (AOP), wet air oxidation (WAO), incineration etc. and other treatment methods such as sonochemical degradation [3,4], photochemical degradation [5–7], AOP with UV/H_2O_2 [8], catalytic oxidation [9] and the microwave-enhanced advanced oxidation processes [10–12] have also been used for the removal of phenol and phenolic derivatives in the wastewaters.

On the other hand, there are many non-catalytic treatment methods which need severe operating conditions such as high pressure and temperature, which makes the treatment process expensive. There has been increase in research on heterogeneous catalytic oxidation, thus significantly reduced the process high temperature and pressure and also increasing the oxidation rate of refractory organics [13,14].

Among metal oxides, iron oxides have been widely used because of their availability, non-toxic nature and catalytic generation of hydroxyl radicals, which is well known [15]. Development of supported iron catalysts is also gaining importance in AOP [16]. However, the environment of iron species in the iron-containing catalysts are also closely related to the method of synthesis, and the counter ions used during synthesis. One of the different possible routes for the production of $OH^{\bullet}$ radicals is the Fenton type reaction [17,18] comprising hydrogen peroxide and ferrous iron, which are capable of oxidizing different organic compounds completely [19]. In this type of system, pH control is necessary to avoid precipitation of iron to ferric hydroxide sludge, which requires being disposed. This process is known as CWPO process which is a very effective technology for the treatment of hazardous, toxic and highly concentrated organic compounds. Thus it is a very challenging task for the preparation of Fenton like heterogeneous catalysts for environmental chemists. The incorporation of catalyst in the CWPO could effectively decrease the limitations on operating conditions, shorten reaction time and increase the oxidation efficiency of organic compounds [20]. In the last few decades, various catalysts have been prepared and homogeneous catalysts were proved to have good catalytic activity, though it was also necessary to remove and regenerate metal ions in the effluents. To overcome this drawback, heterogeneous catalysts were prepared that seemed

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http://dx.doi.org/10.1016/j.molliq.2012.10.011

to be more effective and promising for the treatment of waste water [21–23]. In this category, transition metal oxide showed a good catalytic activity for the treatment of wastewater without leaching of metal ions [24,25].

Sol–gel considered a low temperature synthesis method that gives pure, homogeneous nano particles with good size distribution. In this paper, the Fenton type heterogeneous catalyst has been prepared containing the transition metals of aluminum, cobalt and iron. It has been reported that cobalt (II) compounds were very effective in the production of OH radicals [26] and oxidation of refractory organics such as aldehydes and phenol [27] while alumina widely used as a catalysis for a variety of reactions and also serves as a catalytic support. Since aluminum and cobalt play a major role in the Fenton type reaction for the oxidation process apart from iron, the combination of Fe, Co and Al was chosen for the preparation of an effective heterogeneous catalyst. Thus various stoichiometric combinations of the metal ions were prepared and the ratio with good catalytic activity for phenol oxidation by CWPO process was chosen and characterized using SEM, TEM, EDAX, DRS and N_2 adsorption–desorption isotherm. The activity of the metal oxide was checked in terms of phenol concentration and the oxidized products of phenol were analyzed using various instrumentation techniques. The stability of the catalyst was analyzed by recycling the catalyst three times.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by sol–gel method by dissolving of Fe $(NO_3)_3 \cdot 9H_2O$, Co $(NO_3)_2 \cdot 6H_2O$ and Al $(NO_3)_3 \cdot 9H_2O$ in the stoichiometric ratio of 1:1:6 in 100 mL distilled water and 20 g of citric acid were added to it. The solution was mixed for 4 h, using a magnetic stirrer at 500 rpm until a clear solution was obtained by heating at 70 °C. The resulting residue was dried in hot air oven at 110 °C for 12 h. Then the residue was calcined at 500 °C for 5 h using muffle furnace. The resultant product was brownish black in color, thus milled by a planetary ball mill (Ball ratio 1:10) (Fritsch Pulverisette) for 4 h to get a very fine powder. The nitrates of iron, cobalt and aluminum Citric acid were procured from Merck India Ltd.

2.2. Analytical method

The surface morphology of the Fe–Co–Al catalyst was captured, using Scanning electron Microscopy (SEM, FEI Quanta 200) and Transmission electron microscopy (TEM model — Philips CM 12) with EDS detector for microanalysis with an accelerating voltage of 80 kv. The diffuse reflectance UV–visible spectra of Fe–Co–Al catalyst was recorded, using Cary100 UV–visible spectrophotometer to estimate their energy band gap. The surface area, pore diameter and pore volume were determined by Micromeritics ASAP 2020 porosimeter. The thermal stability of the catalyst was determined, using TGA/DSC (Netzsch STA 409, Germany).

2.3. Catalyst activity

The catalytic activity of Fe–Co–Al was estimated by oxidation of synthetic phenol solution through CWPO process in a stoppered glass conical flask under 100 rpm stirring speed at 30 °C. 200 mL of synthetic phenol solution pH was adjusted to 3.5, and then the 0.5 g of Fe–Co–Al catalyst was added with H_2O_2 at a concentration of 9.96 mmol/L. The experiments were also conducted by varying the initial concentration of phenol (250, 1000 and 2000 mgL^{-1}) and by varying the amount of the catalyst loading (0.25 to 2 g). At subsequent time interval during the reaction time aliquant samples was withdrawn and filtered before being analyzed. The concentration of phenol was estimated by adopting the methodology described in APHA [28]. Simultaneously, the pH changes were monitored, using a pH meter (Systronics 362). Consequently, the UV-visible spectrum of the initial and the oxidized aqueous solutions were recorded in the wavelength region of 200–800 nm. FTIR spectroscopy (Thermo Nicolet 6700) by direct method was also recorded in the region 400–4000 cm^{-1} for the initial (phenol + H_2O_2 at pH 3.5) and after oxidation of phenol solution. The oxidized solution (after 1 h) was lyophilized and this product was dried over $CaCl_2$ and analyzed using ^1H NMR spectroscopy (JEOL).

Further, the catalyst reusability was checked by washing the catalyst with distilled water and dried at 120 °C and then reused for next batch experiment.

3. Results and discussion

3.1. Physical surface characterization of Catalyst

The electronic microscopic images of the Fe–Co–Al catalyst were captured as shown in Fig. 1. Fig. 1a and b, show images with an average particle size of 1–5 μm at a magnification of 300x and 2000x respectively. Similarly Fig. 1c (5000×) and d (10,000×) illustrate the surface with pores in structure on the catalyst surface.

The TEM image of the Fe–Co–Al catalyst sample is shown in Fig. 2a. The average size of the particle was found to be 5 μm. The EDAX analysis of the particular particle (Fig 2a) is depicted in Fig. 2b, and the corresponding atomic and weight percentage of the composite is shown in Fig. 2c. The results confirmed the formation of the homogeneity of the trimetal oxide with the exact composition as synthesized. The N_2 adsorption–desorption of calcined TMO is depicted in Fig. 3, which represents the reversible type IV as defined by IUPAC for mesoporous materials. A hysteresis loop in the adsorption and desorption cycle upon pore condensation was obtained, which can be attributed to the different sizes and the pore distribution of the particles. The energy band gap of Fe–Co–Al catalyst was obtained from the optical diffuse reflectance spectra (DRS) recorded at room temperature and is shown in Fig. 4. It displays an absorption inflection point at around 636 nm, which should be assigned to the oxidation feature of TMO. The maximum reflectance at a wavelength corresponding to 800 nm shows a Energy gap (Eg) value was 1.95 eV which falls in the extrinsic semiconductor range. The surface area, average pore radius and pore volume deduced from the sorption isotherm were found to be 43.4 m^2/g, 19.4 Å and 0.11 cm^3/g respectively. Fig. 5 portrays the thermo gravimetric analysis (TGA) and differential thermal analysis (DSC) of the Fe–Co–Al catalyst after calcination. Generally, thermal degradation of the dried nitrate–citrate consists of three steps namely dehydration, decomposition of citrate to carbonate and formation of ferrite [29]. The observed weight loss at 150 °C is attributed to the loss of physical or chemical desorption of water, while the loss above 250 °C is due to the decomposition of capped organic molecules as reported by Ponpandian et al. [30]. An endothermic peak at 700 °C (Fig. 4) is due to the thermally induced anionic oxidation–reduction reaction of the gel. Here, citrate ion acts as a reductant and nitrate ions act as an oxidant [31].

3.2. Catalytic oxidation of phenol Instrumental analysis

The results of the catalytic tests performed for phenol oxidation with H_2O_2 and the TMO catalyst at 30 °C at varying intervals of time as shown in Fig. 6. With an initial concentration of phenol, 100 + 10 mg/L; H_2O_2, 0.2 mL/L of and mass of catalyst, 0.5 g/L. Fig. 6 reveals that the complete oxidation of phenol could be achieved by 1 h of interaction time. The pH of the reaction mixture increased from ≈3.4 to 5.3 in 1 h. It was also observed that there was a drop in pH presumably due to the addition of H_2O_2 and may also be attributed to the formation of acid intermediates. In the sequel, the pH value increased slowly from 30 min to 1 h, most likely, due to the