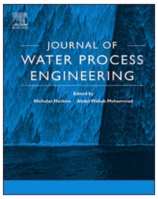
Journal of Water Process Engineering 19 (2017) 42–50

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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



Effect of vanadium on the catalytic activity of ceria towards wet peroxide oxidation of persistent and biorecalcitrant chlorinated organics

Christy Kunjachan, Asha Sreevalsan, Manju Kurian*

Department of Chemistry, Mar Athanasius College, Kothamangalam 686666, India

ARTICLE INFO

Keywords:
$Ce_xV_{1-x}O_2$
Wet peroxide oxidation
4-CP
2,4-D

ABSTRACT

Chlorinated aromatic compounds are recalcitrant to biodegradation and conventional treatment methods Herein, we investigate the efficiency of catalysts in the oxidation of 4-chlorophenol (4-CP) and 2,4-dichlorophenoxyacetic acid over $Ce_xV_{1-x}O_2$ (x: 0, 0.25, 0.5, 0.75, 1) nano oxides with hydrogen peroxide in water. The catalysts were characterised by temperature programmed reduction (H_2-TPR) and desorption (NH_3-TPD and CO_2-TPD) techniques. Effect of reaction variables like catalyst dosage, H_2O_2 and reactant concentrations and temperature, were investigated. The results show that 500 mg/L 4-CP is completely removed with 0.13 mol/L of H_2O_2 over 500 mg/L $Ce_{0.75}V_{0.25}O_2$, within 135 min with the total organic carbon (TOC) removal of 21.56%. Within 75 min, 250 mg/L 2,4-D is completely degraded by 0.08 mol/L H_2O_2 over 500 mg/L $Ce_{0.5}V_{0.5}O_2$ with 30.15% TOC removal. The major degradation intermediates are phenol, benzoquinone and 2,5-hexane dione as identified by gas chromatography mass spectrometry (GC–MS). Based on these, a possible reaction mechanism is proposed. The stability and reusability of the mixed oxides during five consecutive cycles was experimented by X-ray diffraction (XRD) and surface area measurements. The catalytic efficiency is retained after five successive runs and the catalysts are texturally stable Scavenging experiments revealed the activation of reaction through the formation of hydroxyl radicals.

1. Introduction

Chlorophenols considered as priority pollutant by the US Environmental Protection Agency (EPA) and European regulatory authorities [1–3] have been detected in waste sites, waste water, drinking water and also in soils as a result of partial degradation of herbicides. 2,4-dichlorophenoxyacetic acid (2,4-D) is a generally used pesticide found in surface and ground waters. Considering its toxicological effects, World Health Organization recommended a maximum contaminant level of 70 $\mu g\,L^{-1}$ for 2,4-D in drinking water [4]. The main sources of such pollutants are pharmaceutical drugs, disinfection byproducts, metabolites, transformation products, pesticides, surfactants and biocides [5–8]. Development of efficient techniques for degrading toxic, persistent and bio-recalcitrant organic pollutants which affect waste water treatment processes has got a great attention in the present science community. Waste water treatment and the use of treated waste water as an alternative water source, is presently of high priority in the policy agendas of many countries. Advanced oxidation processes (AOPs) for the treatment of waste waters containing organic compounds are much attractive in the environmental point of view. AOPs include many techniques, such as ultrasound/H_2O_2, ozone(UV/H_2O_2), Ozone/H_2O_2, sonophotochemical oxidation, photo–Fenton processes, catalytic advanced oxidation processes, use of advanced oxidation processes combine with biological oxidation, sonication followed by wet air oxidation (SNIWO), cavitation oxidation process (CAV– OX) etc [9–13]. Among these catalytic wet peroxide oxidation (CWPO) is one of the most important advanced oxidation processes.

CWPO is a low cost technology since it operates with simple equipment under mild conditions with hydrogen peroxide as oxidant and a suitable catalyst. H_2O_2 is green solvent, since its total decomposition products are oxygen and water and it acts as a free-radical initiator, providing OH· radicals that promote the degradation of organics. To enhance the decomposition of hydrogen peroxide to hydroxyl radicals the use of a catalytic system with a metal/metal oxide having two possible oxidation states M^{n+} and $M^{(n+1)+}$ where M represents the metal symbol is highly desirable. For CWPO generalized mechanism involve the following steps (i) $H_2O_2 + M^{n+} \rightarrow OH^- + HO\cdot + M^{(n+1)+}$ (ii) $H_2O_2 + HO\cdot \rightarrow HOO\cdot + H_2O$ (iii) $M^{(n+1)+} + HOO\cdot \rightarrow O_2 + H^+ + M^{n+}$, (HO· HOO· and OH^- represents hydroxyl radicals, hydroperoxyl radicals and hydroxide ion respectively) [14]. The photocatalytic degradation using selected metal oxides like TiO_2, ZnO, WO_3 etc have also been reported in literature for the degradation of

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* Corresponding author.
E-mail address: mk@macollege.in (M. Kurian).

http://dx.doi.org/10.1016/j.jwpe.2017.07.007
Received 21 January 2017; Received in revised form 10 July 2017; Accepted 12 July 2017

pollutants. The addition of radical precursors enhances the photocatalytic oxidation for degradation of organic contaminants in water. Both CWPO and photocatalytic oxidation, involve electron transfer, reductive conversion of hydrogen peroxide to hydroxyl radical and reduction of $M^{(n+1)+}$ to M^{n+} [15]. Gannoun et al. studied the chlorobenzene oxidation using Ce doped V_2O_5 based catalyst and obtained 100% conversion at 400 °C [16]. Xu et al. experimented the degradation of chlorophenols using Fe^0/CeO_2 composites and concluded the extent of removal as the following order PCP > 2,4-DCP > 2,4,6-T-CP > 4-CP [17]. Li et al. and Yang et al. reported catalytic wet air oxidation of cholophenols using $Ru/Ce_xZr_{1-x}O_2$, $Ru/Ce_xZr_{1-x}O_2$ and Ru-Pt loaded $Ce_xZr_{1-x}O_2$ under mild conditions [18–20]. Our previous studies showed that $Ce_xFe_{1-x}O_2$ are effective catalysts for wet peroxide oxidation of 4-CP, 2,4-DCP and 2,4-D with 100% conversion at mild conditions and $Ce_xV_{1-x}O_2$ are efficient catalysts for the removal of 2,4-DCP [21,22]. Aim of the present work is to clarify the conversion of 2,4-D and 4-CP over $Ce_xV_{1-x}O_2$ (x – 0, 0.25, 0.5, 0.75, 1) nanocatalysts by Wet Peroxide Oxidation and effect of different reaction variables on reaction rate. A suitable kinetic model and reaction mechanism has been proposed. The reusability of the catalysts was examined and the reused catalysts' structural examination by XRD and surface area measurements has been conducted.

2. Experimental

2.1. Chemicals

Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) by Aldrich Chemical Co. Inc. (St. Louis, MO, USA), vanadium(IV) oxide sulphate pentahydrate by Loba Chemie and ammonia (Merck Chemicals, Mumbai, India) were used for preparation of oxide catalysts [22]. For catalytic activity studies 4-chlorophenol (Loba Chemie), 2,4-dichlorophenoxy acetic acid (Himedia Laboratories), hydrogen peroxide, *n*-butanol, silver sulphate, mercury sulphate, sulphuric acid, ferrous ammonium sulfate and potassium dichromate (Merck Chemicals, India) were used as obtained.

2.2. Characterisation of prepared catalysts

$Ce_xV_{1-x}O_2$ (x: 0, 0.25–1) oxides were prepared by coprecipitation method. The pre-cursors used were cerium(III) nitrate hexahydrate and vanadium(IV) oxide sulphate pentahydrate. Requisite quantities of Ce and V pre-cursors were dissolved separately in deionized water and mixed together. Dilute aqueous solution of ammonia was added drop wise to this solution with magnetic stirring at ambient temperature until the precipitation was complete (pH ~ 10). The resulting slurry was stirred for further 2 h, filtered off and washed several times with distilled water until free from anionic impurities. The obtained precipitate was oven dried at 110 °C and calcined at 700 °C for 5 h to obtain highly crystalline and phase pure oxides.

Temperature Programmed Reduction experiments were performed in a Micromeritics TPx system using 10% H_2 in He flowing at 5 mL/min. Experiments were carried out in the range of 30–850 °C at heating rate of 5 °C/min. Total acid-base property was evaluated by temperature-programmed desorption of ammonia/carbon dioxide in Micromeritics TPx system. Before NH_3/CO_2 desorption, the sample was pre-treated under He flow of 10 mL/min at 200 °C. NH_3/CO_2 adsorption was performed under ambient conditions by flowing 10% NH_3 in He/10% CO_2 in He over the oxide until saturation and then desorption of NH_3/CO_2 by temperature-programmed treatment under He from 30 to 850 °C at a heating rate of 10 °C/min. X-ray diffractograms of the reused catalysts were obtained using a Rigaku MiniFlex 600 X-ray diffractometer using CuKα radiation. Phase identification was carried out by comparison with JCPDS database cards. The average crystallite size was determined by Scherrer equation: $D = K\lambda/(\beta\cos\theta)$ where D is the average crystallite size, K the shape factor (0.89), λ the wavelength of the incident X-rays (1.5418 Å), θ the diffraction angle, and $\beta_{h,k,l}$ the full width at half maximum in radian of the Bragg peak corrected using the corresponding peak in micron-sized powder. Specific surface area measurements were done by nitrogen physisorption at 77 K using a Micromeritics Gemini VII instrument. The specific areas of the samples were determined according to the standard Brunauer-Emmett-Teller (BET) procedure using nitrogen adsorption taken in the relative equilibrium pressure interval.

2.3. Catalytic activity studies

Catalytic activity experiments were performed by placing the reaction mixture containing 50 mL of 500 mg/L 4-CP or 250 mg/L 2,4-D solutions, 500 mg/L mixed oxide catalyst and requisite amounts of hydrogen peroxide in a 100 mL round bottom flask connected to a condenser and immersed into a thermo stated oil bath and agitating with a magnetic stirrer at 150 rpm. At specific intervals, aqueous sample of 0.3 mL was withdrawn and filtered immediately by Whattman grade1 filter paper to remove the catalyst particles before analysis. The samples were quantitatively analysed using Perkin Elmer Clarus 580 Gas Chromatograph equipped with an Elite-5 capillary column and expressed as percentage conversion of 4-CP and 2,4-D. The extent of oxidation and total organic carbon removal was measured using COD measurements with standard dichromate method and Shimadzu TOC-L analyzer respectively. Removal percentage of chemical oxygen demand (COD) was calculated as $\{([COD]_0 - [COD]t)/[COD]_0\}100$ where $[COD]_0$ and $[COD]_t$ are CODs at initial and at time t respectively. The residual amount of peroxide was back calculated by dichrometry. The error percentage between the results of analyses is less than 5%. The active species trapping experiments were carried out by adding 200 mM/L *n*-butanol (·OH scavenger) to the 4-CP/2,4-D degradation solution in the presence of catalyst to throw light on the mechanism of the reaction. The reaction intermediates of 4-CP and 2,4-D were identified by GC–MS analysis on a Varian 1200 L Single Quadruple spectrometer using Helium as the carrier gas. The pH was measured with a EUTECH digital pH meter. All experiments were repeated and averages are reported.

3. Results and discussions

3.1. Catalyst characterisation

Ceria shows a typical XRD pattern of cubic fluorite structure with characteristic peaks at 2θ values of 28.6°, 33.2°, 47.5°, 56.5°, 59.2°, 69.3°, 76.8°, 79.1° corresponding to (111), (200), (220), (311), (222), (400), (331) and (420) planes respectively, comparable with JCPDS card (34-0394). The X-ray diffractograms of Ce–V oxide powders with different Ce/V molar ratios revealed the coexistence of CeO_2 with a tetragonal $CeVO_4$ and orthorhombic V_2O_5 phase. Tetragonal $CeVO_4$ phase is seen with peaks located at $2\theta = 18.239°$, 24.150°, 32.522°, 34.328°, 39.161°, 43.645°, 46.352°, 47.998° and 49.298° which are due to (1 0 1), (2 0 0), (1 1 2), (2 2 0), (3 0 1), (1 0 3), (321), (312) and (400) planes. V_2O_5 shows orthorhombic phase with peaks at 2θ values of 20.1°, 21.6°, 26.0°, 30.8°, 41.1°, 47.6° due to the reflections of (010), (110), (101), (310), (020) and (320) planes [22]. The Brunauer-Emmet-Teller (BET) surface areas and pore volumes of synthesised composites were in the range of 26.21–1.26 m^2/g and 0.01–0.0007 cm^3/g respectively. FT-Infra Red and FT-Raman measurements confirmed the formation of different mixed oxides. Surface area of CeO_2 is found to be 26.21 m^2/g. With the addition of vanadium, the surface area and pore volume decrease to 1.26 m^2/g and 0.0005 cm^3/g respectively. TEM images of CeO_2 nanoparticles indicate crystals in the range of 13–15 nm. With increase in vanadium content, samples exhibit enhanced grain size and it is in the range of 50 nm–90 nm (Fig. 1). CeO_2 exhibits an intense Raman band at 464 cm^{-1}. The main bands of $CeVO_4$ are 228, 260, 378, 786, 798, and 861 cm^{-1}. Crystalline V_2O_5 has