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A Research on Some Mechanism of Catalytic Wet Oxidation for Wastewater

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Abstract – Wastewater from manufacturing or chemical industries constitutes a very important source of water pollution. Industrial wastewater usually contains specific and readily identifiable chemical compounds. These include a variety of organic compounds. Many of these compounds, particularly the aromatic organic compounds are either carcinogenic or mutagenic in nature, which resist biological oxidation processes normally used by the industries for treating wastewater. These compounds are stable and persistent in nature with long-lasting adverse effects and they get dispersed over large areas before undergoing transformation into some other compounds. Many of these organic compounds are synthesized in the laboratory and even in very low concentration, they present a long term hazard as they are likely to accumulate either in food chain or in water sediment. Wet air oxidation (WAO) is the process of oxidizing organic matter in the presence of liquid water. Oxidation reactions take place in the aqueous environment where the water is an integral part of the reaction. Water provides a medium for the dissolved oxygen to react with the organics and can also react in part with the organics. The chemistry of wet oxidation involves free radical formation with oxygen derived radicals attacking the organic compounds and resulting in the formation of organic radicals. The efficiency of aqueous phase oxidation can be largely improved by the use of catalysts, either in the form of solids or as homogeneous catalysts. Catalysts, such as Cu2+ and Fe3+ in homogeneous system, their heterogeneous counterparts, or precious metal catalysts are used to enhance the effectiveness of the WAO process. In contrast to thermal oxidation, WAO does not produce any noxious gases like NOx, SO2, HC1, dioxins, furans, etc. Achieving complete mineralization of the organics through WAO process may not be always possible, since some low molecular weight oxygenated compounds (especially acetic and propionic acids as well as methanol, ethanol, and acetaldehyde), originally present in the wastewater or accumulated in the liquid-phase during the oxidation process, are resistant to further transformation to carbon dioxide.

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INTRODUCTION

Wastewater produced in many industrial processes contains organic compounds such as phenol and its derivatives, which cannot be treated by conventional biological oxidation. Other processes such as chemical oxidation, electrochemical treatment, photo-catalytic oxidation, photo-electrochemical oxidation, and wet oxidation processes under sub- and supercritical conditions and incineration have been tested in some countries (Mishra 1995). The application of a particular method depends on the nature of the pollutant, the concentration of the pollutant, the desired removal efficiency, effectiveness, ability to form secondary toxic product and cost The incorporation of a catalyst has also been considered in combination with all types of oxidants aiming to reduce the operating temperature and pressure, and/or to treat pollutants that cannot be destroyed during non-catalytie liquid phase oxidation processes. The classical Fenton’s reaction, which combines iron salts with hydrogen peroxide has also given good results for various organic pollutants (Bigda 1995).

Nonetheless, the addition of a homogeneous catalyst has the inherent disadvantage of the posterior catalyst removal from the treated effluent, because the metal ions are pollutants themselves in the range of concentrations used. Heterogeneous catalysts, on the other hand, do not need any extra separation step and are thus more attractive. A first attempt by (Lticking 1998, Andreozzi et al. 1999), led to the technology map in which WAO appears to be the most suitable technology for wastewater containing between 20 and 200 g/L of COD (Chemical Oxygen Demand). The suitability of WAO would be further reinforced if a heterogeneous catalyst is successfully incorporated in the process. Thus, particular emphasis has to be dedicated to the study of the Catalytic Wet Air Oxidation (CWAO) process.

Current literature shows that among the wastewater treatment techniques, catalytic wet oxidation (CWO) of organic wastes in water seems to be effective and promising (Mishra 1995, Luck 1999, Matatov-Meytal 1998).

Catalytic wet oxidation is a process involving an organic compound in water and oxygen over a catalyst. Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst. Heterogeneous systems have the advantages over homogenous systems because the catalysts can be separated much more easily after the process.

Although homogeneous catalytic systems using transition metal catalysts (especially salts of Cu, Fe, Mn) are generally more effective than solid catalysts, the dissolved catalysts however, are in many cases toxic and their use requires a separation step such as precipitation to remove or recover the catalyst ions from the treated effluent Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst. Due to this, heterogeneous catalyzed wet oxidation seems to be more promising since only one down-stream separation step, filtration, is required to remove the catalyst from the liquid phase Catalytic wet oxidation (CWO) of organic compounds and organic-containing wastewaters over homogeneous or heterogeneous catalysts can be carried out under much milder conditions than non-catalyzed processes. Catalytic wet oxidation (CWO) using solid catalysts, involves the following steps: diffusion of the reactants to the catalytic or support surface, adsorption of the reactants onto the surface, reaction on the surface, desorption of products off the surface, and diffusion of products from the surface. Because of these steps, heterogeneous processes are usually more complicated to control. Since the catalyst surface plays an important role in adsorption and desorption, appropriate selection of both the active part and the support of the catalyst therefore can have a remarkable effect on the reaction rate.

MECHANISM OF CATALYTIC WET OXIDATION – SOME METHODS

Various attempts have been made to study reaction mechanisms for pure organic compounds during liquid phase oxidation. For engineering purposes, it is important to quantify the reaction rate by identifying the major oxidation pathways as well as understanding the reaction controlling steps, catalytic oxidations of organic molecules can proceed via different mechanisms, namely: [1] enzymatic oxidation; [2] free radical auto-oxidations initiated by transition metal cations; [3] metal ion oxidation of coordinated substrates; [4] oxygen transfer to the substrate mediated by metaioxo or peroxo complexes and [5] oxidative dehydrogenation on metal surfaces (Gallezot 1997).

In alcohol oxidations, oxidative dehydrogenation on metal surfaces is commonly reported (Gallezot 1997, Mallat 1994). The mechanism of alcohol oxidation on a noble metal catalyst involves the dehydrogenation of the organic substrate on the metal surface, while oxygen is needed to scavenge the adsorbed hydrogen from the surface.

Phenol and its derivatives has been the subject of many studies in CWO as a model reaction. Studies on the mechanisms for oxidation of phenol require some knowledge of the short-lived intermediates as well as the final reaction products. For transition metal oxide catalysts, the reaction is believed to occur by free-radical initiation on the catalyst surface, homogeneous propagation, and either a homogeneous or a heterogeneous termination process. Radical initiation could occur by dissociative adsorption of phenol or hydroperoxide decomposition on the catalyst.

Generally, the reaction intermediates reported on phenol oxidation catalyzed by supported metal oxides, like copper, zinc, manganese and other metal catalysts, are similar to those of non-catalysed phenol oxidation. The reaction products that have been reported from the oxidation of phenol by oxygen and ozone can be attributed to three classes: primary intermediates (hydroquinone, catechol, p-benzoquinone, o-benzoquinone), secondary intermediates (maleic acid, formic acid, pyruvic acid, oxalic acid, oligomers of primary intermediates), and end products (formic acid, acetic acid, carbon dioxide and water). Phenol supercritical water oxidation (SCWO) have been recently reviewed (Savage, 1999), in which the formation of dimers and other intermediates like single-ring compounds (e.g. hydroquinone), ring-opening products (e.g. maleic acid, glyoxylic acid, acetic acid and other organic acids) and gases (e.g. CO, C02) are reported. Some of these partial oxidation products and intermediates, especially the dimers, are relatively more toxic than phenol. The oxidation of phenol has in most cases involved oxidation, decarboxylation, dehydration and rearrangement of the molecules or some combination of these steps (Matatov-Meytal 1998, Pintar 1995).

MATERIALS

Catalysts used in the present work-

In the present investigation, seven different catalysts have been selected for evaluating their suitability for oxidative degradation of phenol, 4-chlorophenol and 2,4-dichlorophenol in presence and in absence of hydrogen peroxide as the oxidizing agent.

The catalysts are

A. Hematite (Fe203)

B. Goethite (FeOOH)

C. Mn02

D. TiCh

E. Fe2C>3+Mn02(l:l mixture)

F. Fe203 + Ti02 (1:1 mixture)

G. Mn02+ Ti02 (1:1 mixture)

A brief description of the catalysts along with their important physical characteristics is given below.

A. Hematite

Hematite, with its high iron content is a very useful mineral. Its chemical composition contains a high percentage of Iron (70%) and it is the primary ore used to create Iron. The ore sometimes contains a small amount of titanium. It is soluble in concentrated hydrochloric acid. Hematite is harder than pure iron, but much more brittle. The red powdered hematite is used as a pigment and as rouge in polishing. When shaped into ornaments, it is often called black diamond. Hematite is an antiferromagnetic material below 260 K, and is weakly ferromagnetic above this temperature.

Hematite in this work is obtained from Howards of Ilford Limited, England and it has the following characteristics Color = reddish brown.

Systematic name = Hematite

Chemical Formula = Fe**2**C**>3**

Molar mass = 159.69 g

Density and phase = 5.26 g/cm3, solid

Crystal System: Trigonal-Hexagonal Scalenohedral

Cell Parameters: a = 5.0317, c = 13.737, a : c = 1:2.73009

B. Goethite

The catalyst goethite was prepared in the laboratory by ageing ferric hydroxide precipitates produced from ferric nitrate solution at pH 13 and 343 K for 60 h. The final synthesized goethite was separated from suspension by centrifugation; washed with deionized water till the pH value of supernatant was reduced below pH 7 and then dried at 313 K for 48h. Goethite has the following physical characteristics:

Color: Yellowish brown

Chemical Formula = Fe3+0(0H)

Molar mass = 88.85 g

Density and phase = 4.27 g/cm3, solid

Crystal System: Orthorhombic

Cell Parameters: a = 4.6, b = 9,95, c = 3.02; a:b:c = 0.462 :1 : 0.304

C. Manganese (TV) oxide (MnC^)

MnOa was used for production of chlorine in the eighteenth century, before being displaced by eletrolytic methods. This blackish solid occurs naturally as the mineral pyrolusite, which is the main ore of manganese. It is also present in manganese nodules.

The principal use for Mn02 is for making dry-cell batteries such as the alkaline batteries and it is also used for production of permanganates. Manganese dioxide is used extensively as an oxidant in organic synthesis. MnC**>2** catalyses the decomposition of hydrogen peroxide to oxygen and water.

2 H**2**O**2** (aq) = **02**(g) + 2 H20 (1).

In pyrolusite (P-MnC^), single chains of edge-sharing Mn(fV)06 octahedra share comers with neighboring chains to form a framework structure containing tunnels with square cross sections that are one octahedron by one octahedron on a side.

Manganese dioxide used in the present work is obtained from BDH, England and has the following characteristics:

Color: Black

Systematic name = Manganese (TV) dioxide

Chemical Formula = Mn02

Other name = Pyrolusite

Molar mass = 86.94 g/mol

Density and phase = 5.026 g/cm3, solid

Solubility in water = insoluble

Melting point = 535 °C

D. Titanium (IV) dioxide (Ti02)

Titanium dioxide (also called titanium(IV) oxide, titanium white, or even titania) is cheap, nontoxic, readily available in bulk, and very widely used as a white pigment in paint, enamel, lacquer, plastic and construction cement. Ti02 powder is chemically inert, resists fading in sunlight, and is very opaque: this allows it to impart a pure and brilliant white colour to the brown or gray chemicals that form the majority of household plastics. Paint made with titanium dioxide does well in severe temperatures, is somewhat self-cleaning, and stands up to marine environments.

Pure titanium dioxide has a very high index of refraction and an optical dispersion higher than diamond. In nature, this compound is found in the minerals anatase, brookite, and rutile.

Titanium dioxide (Ti02) is a wide band gap semiconductor, crystallizing as rutile, anatase or brookite. Due to its physical properties (including high refractive index and dielectric constant) as well as its chemical behaviour in photosensitive reactions, Ti02 is a highly attractive material for a wide variety of industrial applications, such as photocatalysis, catalysis, charge separating devices, chemical sensors, solar cells, microelectronics and electrochemistry (Alexandrescu et al, 2004).It has the physical characteristics as given below:

Color: White

Systematic name = Titanium (IV) dioxide

Chemical Formula = Ti02

Molar mass = 79.87 g/mol

Density and phase = 4.23 g/cm3, solid

Solubility = insoluble

Melting point = 1850 °C

RESULTS

Catalytic wet oxidation of phenol - In the present investigation, wet oxidation of phenol over seven solid catalysts at room temperature and under near neutral conditions (pH~7), was studied in the presence and absence of H2O2 as an oxidizing agent. The other variables were the ratio of phenol and H2O2 in the reaction mixture, catalyst load, phenol concentration, etc,.

Catalytic wet oxidation of 4-chloro phenol - 4-chlorophenol (4-CP) is a toxic and persistent hazardous pollutant and it is very important to develop suitable techniques for the treatment of water contaminated with 4-CP. In this work, wet catalytic oxidation of 4-CP was investigated under different conditions.

Catalytic wet oxidation of 2,4-dichlorophenol - Wet oxidation of 2,4-dichlorophenol (2,4-DCP), another persistent phenol derivative, was also carried out following the same procedures with all the catalysts.

CONCLUSION

In the present investigation, seven different catalysts were investigated for evaluating their suitability for oxidative degradation of phenol, 4-ehlorophenol and 2,4-dichlorophenol in presence and in absence of hydrogen peroxide as the oxidizing agent. The catalysts used were (i) Hematite (Fe20 3), (ii) Goethite (FeOOH), (iii) Mn02, (iv) Ti02 (v) Fe20 3 + Mn02(l:l mixture), (vi) Fe20 3 + T i02 (1:1 mixture), and (vii) Mn02+ Ti02 (1:1 mixture). The reactions were carried out under variable conditions of (i) reaction time, (ii) catalyst load, and (iii) reactant concentration under two sets of situations, i.e. with the presence of I I20 2 as the externally added oxidant (in this case, reactant: H20 2 mole ratio was also varied) and in absence of H20 2 (wet air oxidation).

The catalysts used were commercial materials except goethite which was prepared in the laboratory. All the characteristics of the catalysts are well known and these are further confirmed by XRD, FTIR, SEM and CEC measurements. The catalysts exhibited various levels of activity towards oxidation of phenol and its two chloro-derivatives. This work showed that Mn02 catalyst could convert as much as 94.4 % phenol even at room temperature to harmless, non-toxic end products with phenol: H20 2 ratio of 1:10 and catalyst load of 10 g/L The conversion of phenol showed an increase as the reaction time was increased from 60 to 300 min in all the cases except with the catalyst Fe2C>3, when the reaction almost stopped at 60 min. When the relative amount of H20 2 in the reaction mixture was increased, more phenol is destroyed. The catalyst, Mn02, was more active in absence of H20 2 It was found that a catalyst loading of 10 g/L with respect to Mn02 could oxidize 77.3 % of phenol when phenol: H20 2mole ratio was 1:10. The same loading of Mn02 could destroy about 94.4 % phenol in absence of H20 2 through wet air oxidation. The 1:1 mixture of Mn02 + Ti02 was found to be the best giving 100 % conversion for a catalyst load of > 6 g/L in absence of H20 2.

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