DEHALOGENATION OF CHLOROBROMOPHENOL BY OZONATION USING HETEROGENEOUS CATALYST

NDABANKULU V.O.
MADDILA S.
JONNALAGADDA S.B.*

School of Chemistry, University of KwaZulu-Natal
Westville campus, Chiltern Hills, Durban-4000, South Africa

ABSTRACT

Ozone initiated oxidation of 2-chloro,4-bromophenol, (CBP) in aqueous system catalyzed by 1, 2.5 and 5% loadings of 1:1 molar ratio of Ce-Zr oxide on TiO_2 were studied. The synthesized catalysts were characterized via BET, ICP, PXRD, TPD, TEM, SEM, and FT-IR analysis. The powder XRD data revealed that Ce-Zr exists in three different phases on titania. SEM and SEM-EDX confirmed well dispersed metal oxides on titania surface. ^{1}H NMR, IR and GC-MS positively confirm hydroxyfumaric acid (HFA) and oxalic acid (OA) as reaction products. 5% Ce-Zr/TiO_2 showed best performance with 100 % conversion in 4 h.

Key words: Chlorobromophenol; Ozonation; Ceria/Zirconia, TiO_2; Hydroxyfumaric acid; Oxalic acid.

1. Introduction

Halogenated organics are broadly used in various sectors of industry and in agriculture. Halophenols (chloro, bromo) are widely used as wood preservatives and they are also used in the synthesis of chemicals as industrial intermediates, insecticides, lubricants and dyes (Zhanga *et al*., 2009; Slack *et al*., 2005; Richardson and Ternes, 2014). They are considered risky pollutants as they are non-biodegradable, bioaccumulates, toxic, mutagenic and carcinogenic (Verschueren, 1983; Tamer *et al*., 2006; Maddila *et al*., 2014). Additionally, the halophenols are non-biodegradable in nature, after being released into environments they endure for long periods and then prone to accumulate in organic tissues [Maddila *et al*., 2013a, 2013b]. There appears the demand for efficient methods for removal of chloro, bromo functional groups in the organics from the industrial discharges which contaminate the ground water (Maddila *et al*., 2013; 2016a; 2016b). This has aroused interest in the dehalogenation of halophenols present in industrial effluents.

Ozonation is excellent method in treating wastewaters encompassed organics and is extensively used globally in the water treatment including for the effective microbial disinfection (Tamer *et al*., 2006; Jonnalagadda *et al.,* 2012). Nowadays, ozone consumption has expressively increased in treatment of water comprising various organic or inorganic compounds (Maddila *et al*., 2013a; 2016a; 2016b). The oxidation potential of ozone is higher than the chlorine compounds. Oxidation potential is the strength its reactions with refractory pollutants. Molecular ozone is not only a powerful oxidant but also selective in reactions with specific nucleophilic molecules, but its reaction with some organic compounds occurs in a slow manner. Ozone is unstable in aqueous medium and under basic pH conditions decomposes to hydroxyl radicals ($^{.}OH$) (Maddila *et al*., 2015a; 2015b). Compared to molecular ozone, $^{.}OH$ is much reactive and can attack variety of organic molecules, but with less selectivity (Kasprzyk-Hordern *et al*., 2003), which formed from ozone decomposition and reacts non-specifically with most of the substances (Chetty *et al*.,

2012). O_3 forms $^{\cdot}OH$ via decomposition reactions of $-OH$ ions and/or dissociated hydrogen peroxide (H_2O_2). The H_2O_2 formation in the process of ozonation of different organic compounds was detected (Maddila et al., 2013a; 2013b). The 'radical chain reactions' leading to $^{\cdot}OH$ generation are established with the involvement of various intermediate radical species (Kasprzyk-Hordern et al., 2003; Jonnalagadda et al., 2012). In the process of ozonation of the industrial wastewater [Maddila et al., 2016a, 2016b], the establishment of radical chain with $-OH$ ions and its expansion with H+ and change in reaction pH is not enough to increase the $^{\cdot}OH$ concentrations. In the advanced oxidation processes (AOPs) for treatment of industrial wastewaters, the use of ozone and heterogeneous catalysts has considerably increased (Jonnalagadda et al., 2012). The heterogeneous catalysts are widely used as they show good stability, negligible losses and improve the efficacy of ozone decomposition (Maddila et al., 2013a). These catalyst materials can also be easily recovered and reused. The efficacy of the catalytic ozonation process depends mainly on the surface properties of the catalyst and the pH of the solution (Kasprzyk-Hordern et al., 2003). The metals, metal oxides and metal oxides with or without support are the heterogonous catalysts used predominantly. The use of Ce based catalyst is has shown to improve the formation of hydroxyl radicals which play a key role in the mineralization of CBP and other organic pollutants (Maddila et al., 2013a; 2014). The catalysts with more than one metal generally exhibit synergistic behavior, which makes these catalysts more efficient.

The main aim of the research was to explore the effect of Ce-Zr loaded on titania as heterogeneous catalysts for degradation of chlorobromophenol with ozone as an oxidant in aqueous solutions. In addition to comparing the activity of the loading of the catalyst on titania, a detailed analysis of the product profile and % conversion of the substrate was also carried out under varied conditions.

2. Materials and methods

2.1. Catalyst preparation

The synthesis of the metal oxide supported catalysts was done by wet impregnation method. Briefly, desired amount of cerium nitrate, zirconium nitrate were dissolved in double distilled water (20 ml). Into the 20 mL solution was added Titania (5.0 g) and stirred initially for 3 h at room temperature and thereafter for overnight. The as-prepared catalysts were dried at in an oven for 12 h at 110–130 °C and then calcined in air at 450 °C for 3 h the 1.0%, 2.5%, and 5.0% w/w of Ce-Zr/TiO_2 catalysts (Kasprzyk-Hordern et al., 2003; Maddila et al., 2014; Chetty et al., 2012).

2.2 Ozonalysis experiment

For ozone generation, a Fischer Ozone 500 generator was used. Ozone enriched oxygen stream was passed through a sintered glass (porosity 2) into the 50 cm^3 reactor at a flow rate of 10 ml per min. The reactor temperature was maintained at 19 ± 1 °C by circulating water through double walled jacket. For each run 20 ml 10 % w/v of 2-chloro,4-bromophenol (CBP) and fixed ozone concentration (0.05 M) and flow rate of 10 ml min^{-1}. The concentration of the pollutant used was a bit more than that is found in the wastewater systems. This was due to the fact that the instrument sensitivity and limit of detection had to be considered. I.e. for this work a double beam Shimadzu spectrometer was used to monitor the disappearance of CBP.

A magnetic stirrer was used to ensure continuous mixing. Ozone concentration in oxygen stream was determined using KI method (Kasprzyk-Hordern et al., 2003; Maddila et al., 2014). Before and after each of the experiment the flow rate and ozone content were monitored in duplicate runs. Experiments were done were done with 1, 2.5 and 5 wt % of Ce-Zr/TiO_2. The 5 wt% showed better efficiency in degradation of CBP and as a results it was used in all different conditions that were tested. In each experiment 100, 150, 200, and 250 mg l^{-1} catalyst was used. The results shown in the paper are for the optimum conditions which were 5 wt % Ce-Zr/TiO_2 (The deviation within the replicates was ±0.0005).replicates.

2.3. Instrumentation

All the catalyst characterization and product identification was achieved adopting the following techniques: PXRD, SEM-EDX, TEM, N_2 sorption, ICP, FTIR, ^{1}H NMR spectral analysis (Maddila *et al.*, 2013; 2014; Oseghe *et al.*, 2015) Products were analyzed using Perkin Elmer Clarus 400 Gas Chromatograph equipped with an EI mode Mass spectra photometer, the GC-MS analysis was executed in EI mode with 35-500 amu intervals. Furthermore, J & W DB5MS column of specifications, length (30 m), diameter (250 μm) and film thickness (0.25 μm) was used. Helium was used as a carrier gas, and the temperature ramp program used during the GC-MS analysis is as follows: 50 °C (2 min), 20 °C min-1 until 300 °C (10 min).

3.   Results and discussion

3.1 X-Ray diffraction

X-ray diffractograms of bimetallic catalyst are presented in Figure 1. XRD diffractograms showed the presence of cerium oxide and zirconium oxide on the TiO_2 support. The maximum intense and sharp peak at $2\theta \approx 25°$ corresponds to (101) plane of TiO_2 (PDF-ICDD 21-1272). The peaks obtained at approximately 48°, 55° and 69° corresponds to (220), (311) and (400) planes respectively and confirms the presence of pure CeO_2 (PDF-ICDD 34-0394) phase. XRD patterns showed the presence of ZrO_2 phase in the catalyst. Slight shift in peaks was observed due to variation in metal loadings on TiO_2 support.
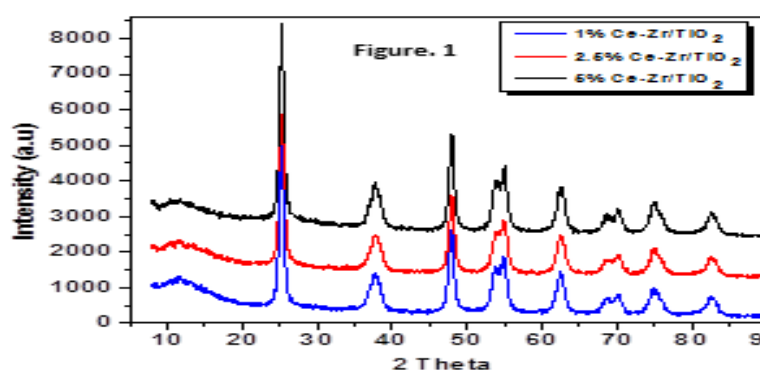

Figure 1. XRD spectra 1%, 2.5% & 5% Ce-Zr loaded on TiO_2 catalyst

3.2. BET Surface and elemental analysis

Surface area and pore volume of the prepared bimetallic catalysts are presented in Table 1. All three bimetallic catalysts show minor difference in both pore volume and surface area. It is clear from the table that, addition and dispersion of Ce and Zr in TiO_2 support enhances the surface area of all catalyst. Mixture of ceria, zirconia and TiO_2 enhances the surface area of TiO_2 have been reported in the literature (Reddy *et al.*, 2003). The study indicates that bimetallic catalysts show high surface area and low pore volume than TiO_2 support without metal addition. Figure 2 shows the N_2 sorption isotherm of the catalyst typical for type IV isotherms which therefore implies mesoporous materials. Table 1 also indicates the actual metal loadings of catalyst determined by ICP.

Table 1. BET surface area, elemental analysis and TPD data of Ce-Zr loaded supports

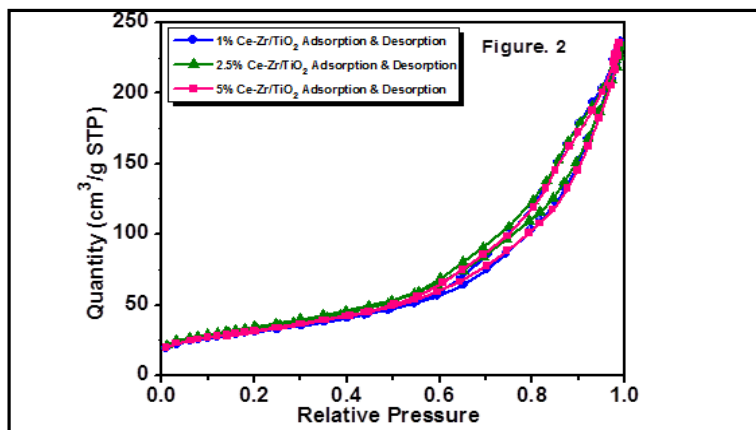| Catalyst	ICP (mol%)		Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore diameter (Å)	EDX		Acidity (mmol $NH_3 g^{-1}$)	Specific acidity (mmol $NH_3 g^{-1}$)
	Ce	Zr				Ce	Zr		
TiO₂	-	-	88	0.42	115	-	-	620	7.04
1% Ce-Zr/TiO₂	0.44	0.48	124	0.33	108	0.37	0.41	541	4.39
2.5% Ce-Zr/TiO₂	1.22	1.24	111	0.33	97	1.11	1.12	422	3.81
5% Ce-Zr/TiO₂	2.47	2.45	114	0.32	94	2.46	2.44	363	3.11

Figure 2. N_2 Adsorption-Desorption Isotherms of catalysts

3.3 SEM and TEM

Figure 3(a,b,c) show SEM micrographs of bimetallic catalysts prepared with 1, 2.5 and 5 wt% Ce-Zr on TiO_2 support. Figure 3(d,e,f) reveal that all catalysts having similar morphology and clusters of metal particles are present on the support surface. Cerium and zirconium metal particles were evenly dispersed on the surface of TiO_2 support. It has been also observed that with the increase in metal loadings, the agglomeration of particles increases. Surface of the TiO_2 support seems more covered with metals in the case of 5% Ce-Zr/TiO_2. Figure 3 (d,e,f) display the TEM images of CeZr/TiO_2 catalysts. An examination of the TEM images indicates that agglomeration of the catalyst. The TEM micrograph shows that particles are of less than 10 nm in size and randomly oriented with round, oval and elongated shaped metal oxide particles.
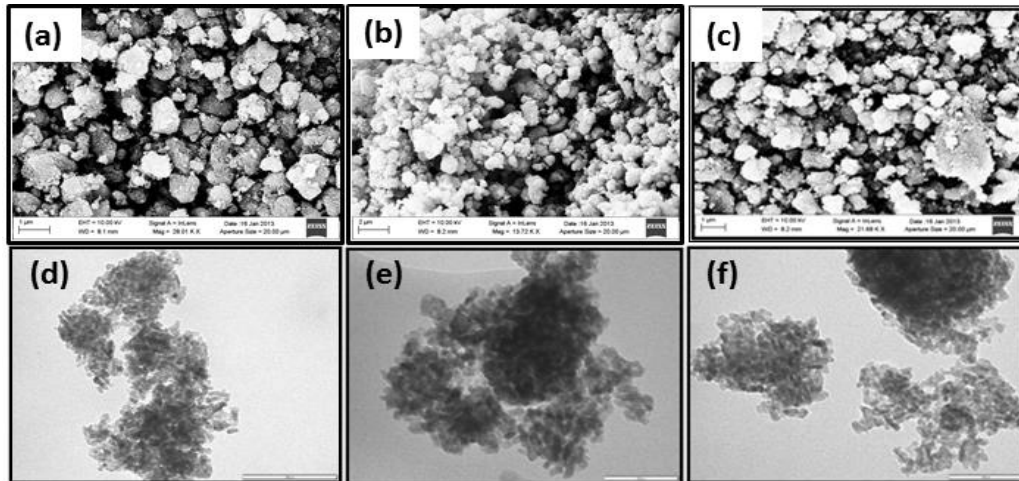

Figure 3. SEM images (a, b, c) and TEM images (d, e, ef) of 1%, 2.5% and 5% Ce-Zr on TiO_2

3.4 IR spectra

The absorption bands observed at 788, 796 and 790 cm^{-1} endorse the existence of Ce-Zr on TiO_2 (Figure 4). While 1% Ce-Zr on titania showed IR bands at 518 cm^{-1} and 1124 cm^{-1}; 2.5% Ce-Zr displayed 542 cm^{-1} and 1057 cm^{-1} bands; plus the 5% Ce-Zr on titania exhibited bands at 548 cm^{-1} and 1053 cm^{-1}. The peaks corresponding to Ce-Zr-O can be witnessed in all three samples as absorption bands at 1636 cm^{-1} and 1635 cm^{-1}. The Ce-O vibrational stretching peaks for the three catalysts respectively can be observed at 425 cm^{-1}, 427 cm^{-1} and 434 cm^{-1}. The absorption bands observed at 3213 cm^{-1}, 3258 cm^{-1} and 3255 cm^{-1} for 1%, 2.5% and 5% Ce-Zr/TiO_2 respectively confirm the manifestation of hydroxyl groups on their surfaces.
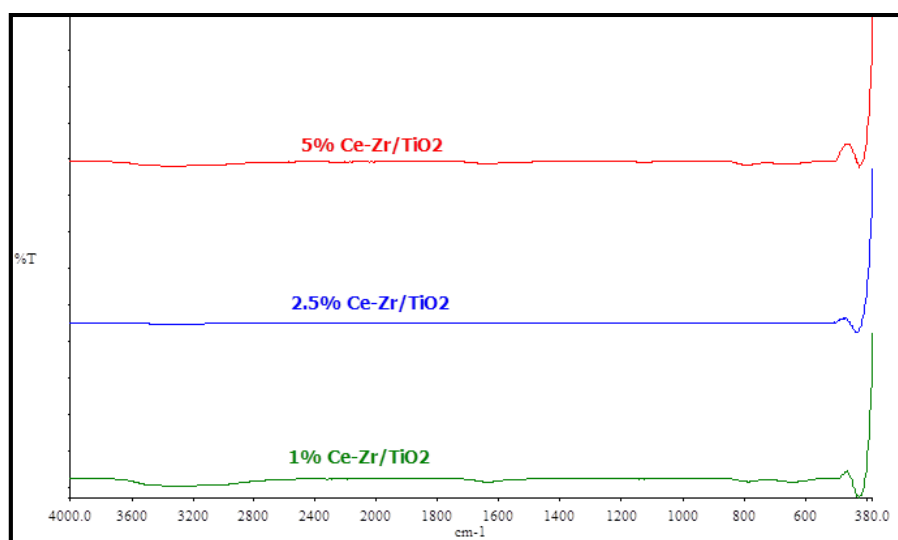
Figure 4. IR spectra of 1%, 2.5% and 5% Ce-Zr loaded on TiO_2 supports

3.5 Product characterisation

During aeration of the samples with ozone enriched oxygen, the organic contents were extracted from the reaction mixture and analyzed at 60 min intervals in every reaction All samples were analyzed during the start of the reaction, i.e. t=0, but degradation of the pollutant was only observed after 60 min, therefore the results which are shown are only after degradation has started. Each run was carried out in triplicates and data obtained was with ± 2% error. Ozone concentration in oxygen stream was determined using KI method. After separation of the oxidation products from the parent compound (CBP) using column chromatography and the product mixture was characterised using GC-MS (Figure 5).
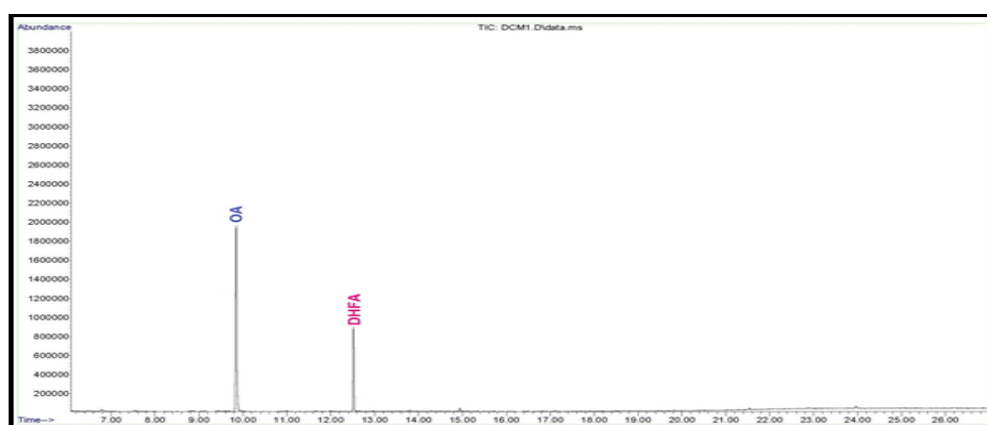

Figure 5. GC-MS chromatogram of product mixture

The mass spectra consequently confirmed the presence of two products namely hydroxyfumaric acid (HFA) and oxalic acid (OA). The proton NMR spectra of HFA displayed two singlets at δ 14.23 ppm and δ 10.29 ppm confirming the presence of COOH, CH groups respectively (Figure 6.a). Infrared spectra of HFA revealed the representative absorption bands at 1629, 3082, 3320 cm^{-1} for the C=C C−H and COOH stretching vibrations respectively (Figure 6.b). Further, the mass spectrum exhibited m/z peak at 149 (M+H) (Figure 6c). Likewise, the oxidant product OA showed a broad singlet for COOH protons at δ 13.10 ppm (Figure 7a). The absorption bands were obtained for the stretching frequencies of COOH, CH and C=O groups at 3444, 3069, and 1890 cm^{-1} respectively by the IR spectra of the OA product (Figure 7b). In addition, the mass spectrum indicated the m/z peak at 91 (M+H) (Figure 7c). The functional groups of oxidant products examined by IR and data of ^{1}H-NMR, mass spectra were consistent with one another.

The partial mineralization of products and formation of CO_2 during the ozonation process was positively verified by bubbling the gases through lime water, which turned milky. Ozone initiated oxidations are generally known to produce small chain biodegradable acids as the oxidation products Ozone was quantified using the KI method, where the Iodometric titration was done using sodium thiosulfate and potassium Iodate. This method was done so that the concentration of Ozone before and after the reaction.
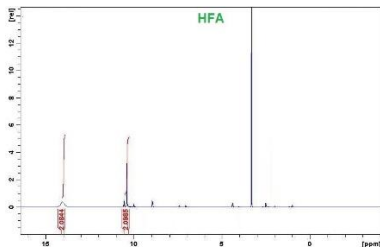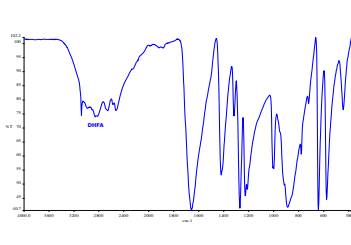

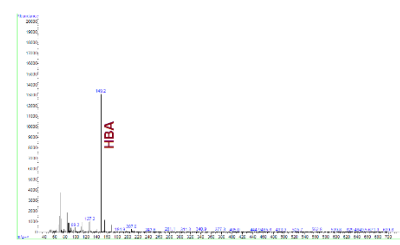**Figure 6a.** ^{1}H NMR Spectra of HFA

Figure 6b. Infrared Spectra of HFA

Figure 6c. Mass of HFA
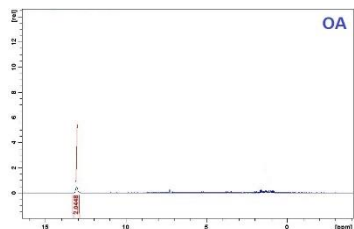

Figure 7a. ^{1}H NMR Spectra of OA

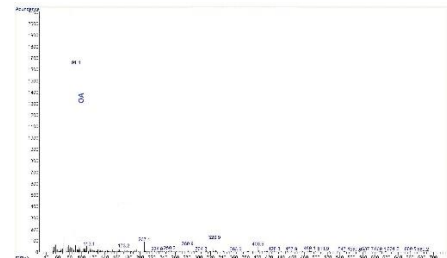**Figure 7b.** Infrared Spectra of OA

Figure 7c. Mass Spectra of OA

3.6 % Conversion and selectivity

Using 10% CBP (w/v), ozone aeration experiments were carried under uncatalysed and catalysed conditins (with three different loadings of catalysts) and under three pH conditions, 3, 7 and 11. Uncatalysed studies reveal that an increase in pH enhances the % conversion (Figure 8a), which proposes that $^•$OH is reactive species driving the oxidation of CBP. A perusal of % conversion data for catalyzed reactions (Figure 8b) indicates that while the catalyzed reactions are invariably faster, similar to the uncatalysed reaction the increase in pH enhanced the % conversions, suggesting alkaline pH 11 is optimum conditions for all the reactions. An examination of the % conversion profiles in Fig. 4b explicit that the composite material with 5% Ce-Zr/TiO_2 as catalyst gave 100% conversion in 4 h of ozonation, whereas the 1 and 2.5% Ce-Zr doped titania catalyst took 5h to achieve the 100% conversion. The Figure 9a-c also summarises the trends in % conversion of CBP with different wt% of Ce-Zr on titania at pH 11 together with the product selectivity. The current results suggest that mixed metal loaded on support catalysts yielded good catalytic activity facilitating the ozone decomposition and enhancing the substrate conversions.

3.7 Reaction mechanism

The process of heterogeneous catalysis is influenced by the catalyst surface properties, target contaminants and pH of the solution. As a result, the establishment of formation of reactive species becomes more difficult. In the catalysed reaction, the surface Lewis acid sites especially play a vital role (Maddila *et al.*, 2014). It is proposed that active sites on the surface of the catalyst enable the substrate binding, probably on the ceria site and the decomposed ozone attacks the organic molecule from its adjacent site. The active adsorptive sites, in addition to binding of organic molecules, also could facilitate

the formation of activated complexes with other reactive molecules/oxy radicals minimizing the activation energy for the reaction. Adsorption of the substrate on the catalyst surface may consequently generate a five or six-membered chelate ring appears to be anionic. Overall, this will improve the oxidative dehalogenation and degradation process of the organic molecules. The reaction intermediates on the catalyst surface or desorbed into solution can easily be attacked by O_3 or $^•OH$ like species, generating secondary and tertiary oxidation products (Jonnalagadda *et al.*, 2012; Maddila *et al.*, 2013). Finally, oxidation by-products are formed due to the oxidation of surface complex by O_3 or $^•OH$ on surface of the catalyst by either desorption or adsorption. Essentially in this mechanism, the acidic nature of the metal contained catalysts, together with organics forms the chelate which can be further oxidised by O_3 or $^•OH$. Thus, the proposed mechanism describes the good adsorptive properties and advantages of presence of ideal catalyst in an ozonation process.
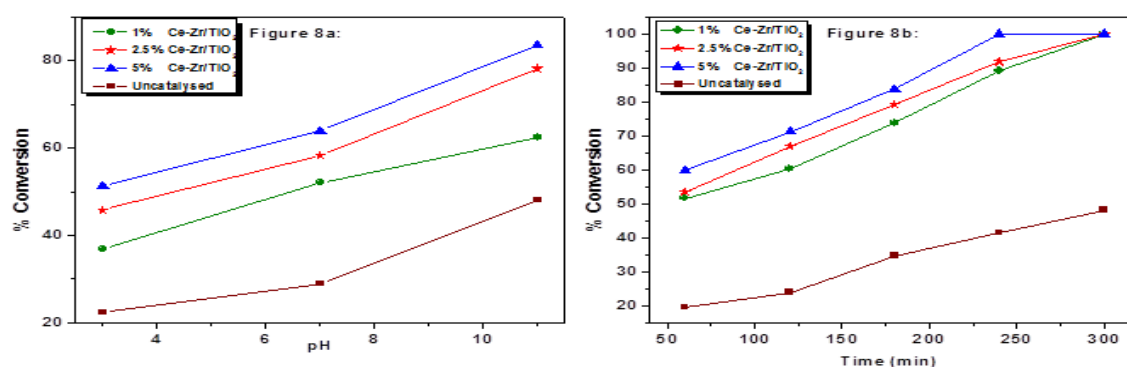

Figure 8. (a) %Conversion of CBP ozonation with different pH, (b) %Conversion of CBP with time (min)
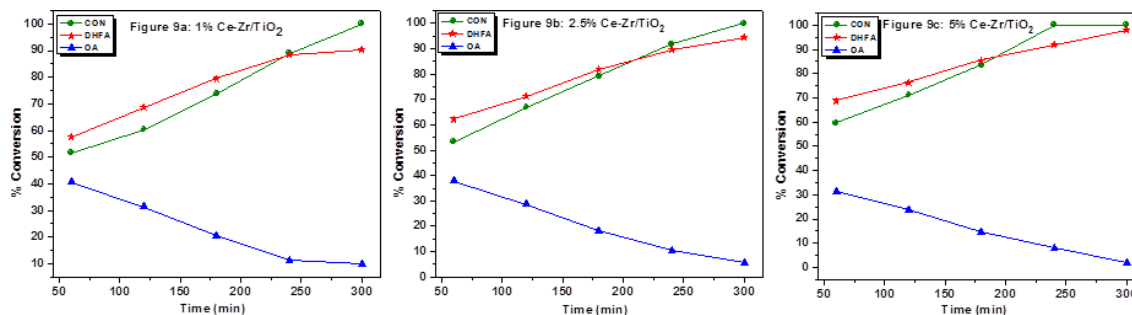

Figure 9 (a-c). The conversion and selectivity with 1%, 2.5% and 5% loadings of Ce-Zr on TiO_2

Ernst *et al.*, have observed that, the organic molecule's adsorption on the surface of catalyst may not be essential to afford the catalytic effect. Besides, the adsorption would possibly hinder the activity caused by shrouding of the OH species (Jonnalagadda *et al.*, 2012). In ozonation process, the O_3 is initially adsorbed on the surface of the catalyst and subsequently decomposed rapidly due to the existence of OH species. Upon ozone decomposition, active oxygen is formed and it then reacts with support's hydroxyl surface groups to produce highly negative ions (OH^- or O_2H^-) which in turn react rapidly with another O_3 molecule to form radicals ($^•OH$ or $^•O_2H$). These formed radicals further react with a new ozone molecule to produce a $^•O_3^-$. This radical is decomposed into O_2, a free $^•OH$ which can play a part in organic compound's oxidization either in solution or on the surface of catalyst. In consequence, the characteristics of organic substrate play a crucial role in its oxidative degradation during the ozone facilitated oxidations in presence of catalyst. The pH of solution influences the binding and desorption of organic molecules on the catalyst surface. For the many interfacial reactions, adsorption is known to be the rate limiting step, which dictates the overall removal or degradation of the organics or pollutants. The catalyst activity for accelerated generation of $^•OH$ radicals, is linked with the metal oxide's surface properties. Different reaction intermediates and products could possibly form during ozonation of chlorophenols. During the

ozone initiated oxidation of chlorophenols, dechlorination and formation carboxylic acids and other hydroxylation products has been reported (Jonnalagadda *et al.*, 2012; Chetty *et al.*, 2012; Maddila *et al.*, 2013). From the current study, based on the reaction products, an electrophilic attack the aromatic ring by hydroxyl radical and other species is proposed. The carbon-carbon double bonds of the oxidation products formed as a result of breaking of the aromatic ring get further attacked by ozone and hydroxyl radicals (Proposed mechanism).
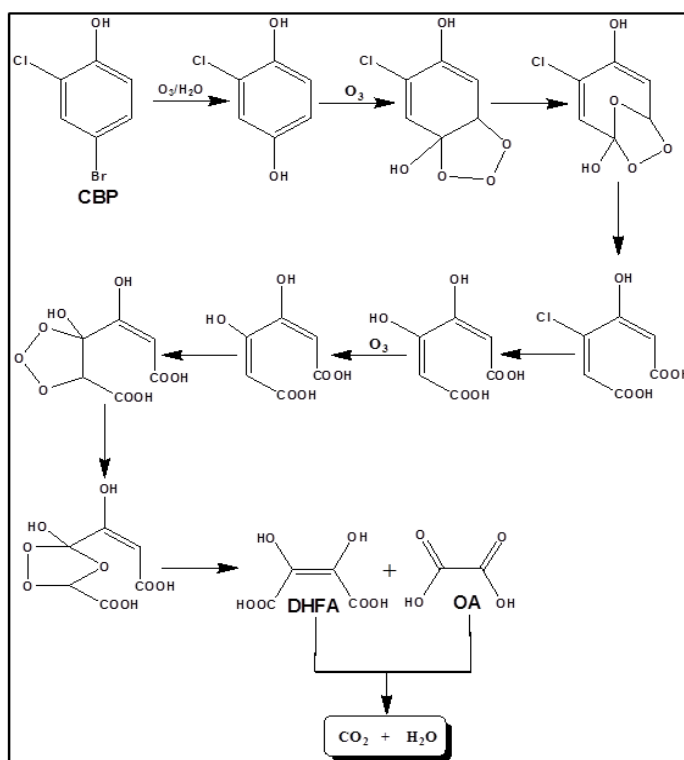
Proposed Mechanism: Mechanism of the Scheme

As reported in the literature aliphatic acids were anticipated and were found as reaction products. The prolonged reaction leads to mineralized products. Gratifyingly, the heterogeneous Ce-Zr/TiO$_2$ could be recovered effectively from the reaction mixture by simple filtration and by washing the catalyst twice with acetone and dried at 70-80 °C under reduced pressure for 2 h to make it ready for a later run. There is no loss of Ce-Zr loading on titania was observed which is confirmed by ICP-OES analysis. The catalyst was tested for next runs.

4.   Conclusions

Our study showed that the wet impregnation method permits the synthesis of bi-metallic catalysts with good metal dispersion. The size of catalyst particles, and reaction parameters play a significant role in ozonolysis, so catalytic properties are strongly affected by the preparation method of the catalyst. Titania is a suitable support for loading the bimetallic Ce-Zr oxide catalysts. The CBP oxidation was quantitative with 100% dechlorination. HFA and OA were main products of which OA was the secondary product, with partial mineralization. Catalysed ozonation is proved to be an effective method to remove chloro, bromo and hydroxy groups from substituted organic molecules.

References

Chetty E.C., Maddila S., Dasireddy V.D.B.C. and Jonnalagadda S.B. (2012), Efficient conversion of 1, 2-dichlorobenzene to mucochloric acid with ozonation catalyzed by V_2O_5 loaded metal oxides, *Appl. Catal. B: Environ.*, **117–118**, 18–28.

Jonnalagadda S.B., Pullabhotla V.S.S.R., Maddila S. and Chetty E.C. (2012), Ozone for drinking and wastewater treatment and for value added products, *Int. J. Chem.* **1**(1), 119-129.

Kasprzyk-Hordern B., Ziolek M. and Nawrocki J. (2003), Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, *Appl. Catal B: Environ.*, **46**, 639-669.

Maddila S., Dasireddy V.D.B.C. and Jonnalagadda S.B. (2013a), Ozone initiated dechlorination and degradation of trichlorophenolusing Ce–Zr loaded metal oxides as catalysts, *Appl. Catal. B: Environ.*, **138-139**, 149-160.

Maddila S., Dasireddy V.D.B.C. and Jonnalagadda S.B. (2013b). Dechlorination of tetrachloro-o-benzoquinone by ozonation catalysed by cesium loaded metal oxides, *Appl. Catal. B: Environ.*, **138-139,** 149-160.

Maddila S., Dasireddy V.D.B.C. and Jonnalagadda S.B. (2014). Ce-V loaded metal oxides as catalysts for dechlorination of chloronitrophenol by ozone, *Appl. Catal. B: Environ.*, **150-151**, 305-314.

Maddila S., Oseghe E.O. and Jonnalagadda S.B. (2016a), Photocatalyzed ozonation by Ce doped TiO_2 catalyst degradation of pesticide Dicamba in water, *J. Chem. Tech. & Biotech.*, **91**, 385-393.

Maddila S., Palakondu L. and Jonnalagadda S.B. (2015b), Degradation, mineralization of bromoxynil pesticide by heterogeneous photocatalytic ozonation, *J. Indu. & Eng. Chem.* **24**, 334-341.

Maddila S., Rana S., Maddila S.N., Chandrasekhar V. and Jonnalagadda S.B. (2015a), Ozone driven photocatalyzed degradation and mineralization of pesticide, Triclopyr by Au/TiO_2, *J. Environ. Sci. & Heal. Part B*, **50**, 1-13.

Oseghe E.O., Ndungu P.G. and Jonnalagadda S.B. (2015), Synthesis of mesoporous Mn/TiO_2 nanocomposites and investigating the photocatalytic properties in aqueous systems, *Environ Sci Pollut Res Int.*, **22**(1), 211-222.

Reddy B.M., Khan A., Yamada Y., Kobayashi Y., Loridant S., and Volta J.C. (2003), Raman and X-ray photoelectron spectroscopy study of CeO_2-ZrO_2 and V_2O_5/CeO_2-ZrO_2 catalysts, *Langmuir,* **19**, 3025-3031.

Richardson S.D. and Ternes T.A. (2014), Water analysis: emerging contaminants and current issues, *Analytical Chemistry*, **86**, 2813–2848.

Slack R.J., Gronow J.R. and Voulvoulis N. (2005), Household hazardous waste in municipal landfills: contaminants in leachate, *Science of the Total Environment*, **337**, 119–137.

Tamer E., Hamid Z., Aly A.M., Ossama El.T., Bo M. and Benoit G. (2006), Sequential UV-biological degradation of chlorophenols, *Chemosphere.* **63,** 277–284.

Valand J., Maddila S., Friedrich H.B. and Jonnalagadda S.B. (2016b), Heterogeneous catalysed ozonation using Cu-Ni-Co oxides for degradation of dichlorophenol, *Ozone: Sci. & Eng.,* **38**(1), 14-24.

Verschueren K. (1983). Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold, New York.

Zhanga Z., Cissokoa N., Woa J. and Xua X. (2009), Factors influencing the dechlorination of 2,4-dichlorophenol by Ni–Fe nanoparticles in the presence of humic acid, *J Hazd Mat.,* **165**, 78–86.