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COD and AOX abatement in catalytic wet oxidation of halogenated liquid wastes using CeO_2-based catalysts

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Abstract

The treatment of halogenated containing compounds is one of the more promising applications of catalytic wet oxidation (CWO) reaction. The aim of this work is to compare the abatement of chemical oxygen demand (COD) and adsorbable organic halogen (AOX) parameters in three halogenated liquid wastes: a landfill leachate, a pulp and paper bleaching liquor and a heavily organic halogen polluted industrial wastewater, treated at 430–500 K in a batch bench-top pressure vessel. Two catalysts based on ceria were used: a pure CeO_2 and a SiO_2-doped ceria characterized by different surface area and oxygen storage capacity. The efficiency of the catalytic process was examined controlling COD and AOX parameters; the catalysts deactivation was observed by the measurement of the surface area and the increase of the carbon content of the catalysts after the reactions.

Keywords: Catalytic wet oxidation; Wastewaters; Adsorbable organic halogens; COD; AOX; CeO_2-SiO_2; Ceria; Oxygen-storage

1. Introduction

In the last years, intensive research effort aimed at the development of new technologies to remove organic pollution in wastewater, and particularly pollution related to the presence of organic halogens. The organic halogen content of a wastewater is characteristically related to refractivity, scarce biodegradation, bioaccumulation and health damages in the environment [1]. It is well known that a lot of wastewater containing high concentration of organic halogens compounds or other organic chemicals from industrial synthesis are scarcely treatable by traditional biological technologies and need to be pre-treated by severe actions to abate biological refractory and inhibitory effects.

Wet oxidation (WO) is a useful treatment method for reduction of aqueous pollution bound to heavily contaminated wastewater, in particular when it is necessary to treat low volumes. This process consists in the oxidation of dissolved or suspended aqueous solution of organic and inorganic substances by means of oxygen, at elevated temperature (450–590 K) and pressure (2–15 MPa), assuring wet conditions of reaction. Under these conditions organic waste streams too dilute to incinerate and too concentrated for biological treatment can be degraded to simpler, frequently more biodegradable, organic compounds or completely converted to CO_2 and H_2O [2]. This process is widely used in treatment of toxic or refractory substances [3] where biological treatments are not applicable, both in pure compound solution and in complex wastewaters [4]. Further, in WO process it is possible to recover energy operating with highly organic contaminated wastewater obtaining self-sustainability of the system [5]. In usual WO applications temperature and pressure range, respectively, from 400 to 590 K and 0.5 to 20 MPa, with most common applications and best efficiencies, in 500–560 K temperature and 3.5–12.8 MPa pressure ranges. In order to achieve less severe condition of temperature and pressure the WO process can be enhanced by the use of catalysts, carrying out catalytic wet oxidation (CWO), which has been presented as an optimal process in many aqueous wastes laboratory treatment studies and pilot experiences [6,7]. In spite of the operation costs (high temperature and pressure)

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the catalytic wet air oxidation appears as the most promising wastewater treatment in a wide range of environmental applications. Particular effort was given to studies involving CWO by cerium-based heterogeneous catalysts [8–11], because of their well known oxygen storage and exchanging capacities which were widely studied, exploited and developed especially in gas phase [12,13]. The majority of the past investigations were carried out with simulated wastewaters with single organic compounds, and very little attention has been paid to real high-strength halogenated industrial wastewaters. At present time, there is no investigation reported on the efficiency of ceria-based catalysts on the abatement of AOX parameter in industrial wastewaters; the present study was carried out to investigate for the first time the behavior of these oxides on the abatement of organic pollutants (measured as chemical oxygen demand (COD) and adsorbable organic halogen (AOX)) in three different heavily polluted wastewaters.

2. Experimental

Cerium oxide (CeO_2) catalyst (cat-A) was prepared by precipitation with ammonia from a solution of $Ce(NO_3)_3 \cdot 6H_2O$. The resulting precipitate was washed several times with water and with acetone/toluene/acetone mixture and then dried at 373 K for 15 h followed by calcination under air flow at 723 K temperature for 2 h. The resulting powder had a surface area of 77 m^2/g as measured by the B.E.T. method using N_2 adsorption at 77 K with a Sorptomatic 1990 apparatus (Carlo Erba).

The CeO_2-SiO_2 (Si 6 wt.%) catalyst (cat-B) was obtained mixing an aqueous solution of $Ce(NO_3)_3 \cdot 7H_2O$ with an aqueous solution of sodium silicate (containing a SiO_2 amount of 63 wt.%). After this, an ammonia concentrated solution was slowly added to reach a pH of 11.5. Then, this solution is stirred at 363 K for 24 h in a Nalgene autoclave. The yellow precipitate is filtered, washed with water, acetone and water, dried for 24 h at 333 K and calcined in a tubular furnace at 723 K for 2 h [14]. The resulting powder had a surface B.E.T. area of 166 m^2/g.

Reaction tests were carried out in a 400 ml stainless steel pressure vessel (Parr Instruments, Model 4562) with internal parts covered by Teflon liners. The autoclave was adapted for batch working with inlet–outlet valves, mixer, cooling device and automatic control of temperature and pressure. A schematic illustration of the CWO apparatus is shown in Fig. 1. During the batch tests the pressure vessel was charged with the waste solution and the catalyst, then the oxygen was introduced at the required pressure. Finally the temperature was raised and the reaction was started while stirring all the mixture. The reaction time was 1 h for the general tests, while a range of reaction times was employed for kinetic study. After reaction, the mixing was stopped and the mixture was cooled to room temperature. At this point the liquid sample was drawn by the V3 valve (Fig. 1), decanted and analyzed.

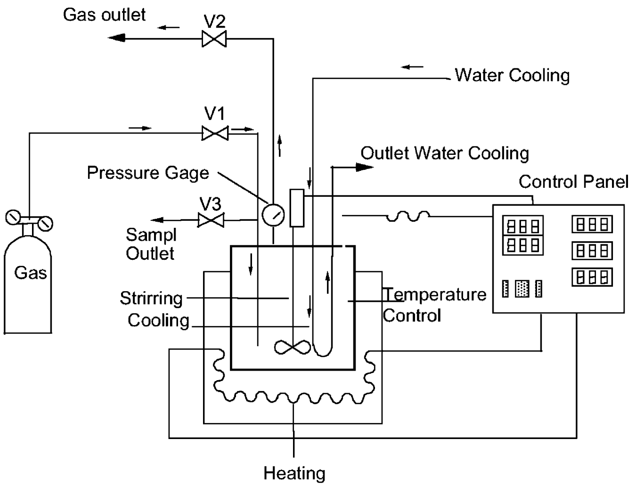

Fig. 1. Scheme of the CWO apparatus.

One hundred and fifty milliliters of the composite wastewater and 0.5 g (10 mM as CeO_2) of the catalyst was used for the experimental procedure while pressure (ranging between 2 and 3.5 MPa) was adapted to diverse temperatures to maintain wet condition by oxygen pressure addition. The absence of diffusional effects were checked by running tests at different stirring rates.

COD was determined respecting colorimetric procedure of Standard Methods for the Examination of Water and Wastewater [15] and AOX parameter was evaluated following ISO 9562 standard by an ECS1000 Euroglas AOX analyzer. Respirometric oxygen uptake rate (OUR) measures were conducted utilizing a WTW 320 oxymeter on 1 l open respirometer. The inoculated biomass was taken from an activated sludge reactor of a municipal wastewater treatment plant. The elemental analysis of C, H, N, S and O on the used catalysts was performed with a Carlo Erba Automatic Elemental Analyzer Model 1106. The study was carried out using three halogenated liquid wastes: a landfill leachate (LL), a pulp and paper bleaching liquor (BL) and a heavily organic halogen polluted industrial wastewater (IW). Table 1 shows the main characteristics of the different wastewaters used.

Table 1
Characterization parameters of landfill leachate (LL), pulp and paper bleaching liquor (BL) and a heavily organic halogenated industrial wastewater (IW)

Parameter	LL	BL	IW
pH	8	6	6.5
Conductivity[a]	4500	800	350
COD[b]	6750	1300	3250
AOX[b]	5.0	2.7	12
Suspended solids (SS)[b]	9000	110	50
Total nitrogen (TN)[b]	1100	1.7	1
Total phosphorous (TP)[b]	35	0.2	0.1
SO_4^{2-}[b]	700	400	<5
Ca^{2+}[b]	2000	200	80
Cl^-[b]	2500	90	<5

[a] μS/cm.
[b] mg/l.

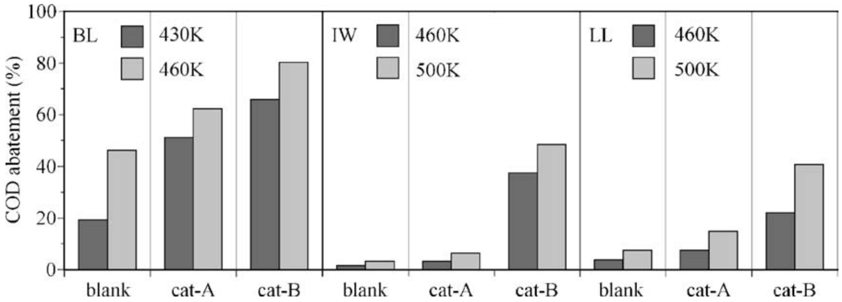

Fig. 2. COD removal (%) in BL, IW and LL sample.

3. Results and discussion

A series of preliminary tests were performed to assure that in the absence of oxygen the organic compounds are not adsorbed on the high-surface area catalyst during experimental runs. The results, not shown here, confirm that no adsorption occurs on the catalyst surface at the reaction temperature investigated. Figs. 2–3 show the results of the catalytic reactions carried out on the wastewater samples; these are characterized by a different degree of refractivity and therefore COD and AOX abatement strongly differ in the three cases. Pulp and paper bleaching liquor is the sample less refractory to oxidative treatment; the results of a 1 h test performed on this sample at 430 and 460 K are reported. The abatement of COD and AOX after oxidation is particularly evident with the utilization of the catalyst. The performance of the doped CeO_2-SiO_2 is better than that of pure ceria and the removal of ca. 80% of COD and 90% of AOX are reached at 460 in 1 h reaction. COD abatement is in agreement with previous results on similar effluents [2]. A surface area drop caused by deposition of organics is observed in both catalysts (see Table 2).

The results obtained on halogenated industrial wastewater and on landfill leachate indicate the higher refractoriness of these wastewaters. Tests were performed at 460 and 500 K; in both cases the abatement of COD parameter is evident after 1 h treatment and reaches a maximum of ca. 50 and 40%, respectively, with CeO_2-SiO_2 catalyst. AOX abatement is limited to 50% in IW whereas with LL there is a slight increase of AOX during reaction. A mechanism of reaction of organic pollutants with the chloride to form organic halogen compounds could be proposed in this case because of the very high concentration of chlorides in LL wastewater (see Table 1) [16]. Table 2 shows carbon content and surface area of the catalysts after reactions. It is evident that there is a loss of surface area with a corresponding increase of carbon content more relevant at lower temperature. Overall surface area drop and carbon deposition are lower than those observed after treatment of BL, which is connected to the lower reactivity under these conditions. The adsorption of reagents and/or intermediate products may in fact result in the formation of heavy by-products, which form a carbonaceous deposit hampering the accessibility of the reactants to the catalyst surface. This aspect has a key role on catalyst practical importance since in a long-term operation it would cause a loss of catalytic activity.

Table 2
Carbon content and surface area in landfill leachate (LL), pulp and paper bleaching liquor (BL) and halogenated industrial wastewater (IW) catalytic wet oxidation tests with cerium oxide (cat-A) and CeO_2-SiO_2 (cat-B) catalysts

Wastewater	Reaction temperature (K)	Cat-A		Cat-B	
		SA (m^2/g)	% C	SA (m^2/g)	% C
–	298	77	0	160	0
BL	430	12	15	30	10
	460	17	25	32	30
LL	460	20	6	46	10
	500	32	4	70	5
IW	460	20	4	107	13
	500	32	2	114	7

CWO reaction time: 1 h.

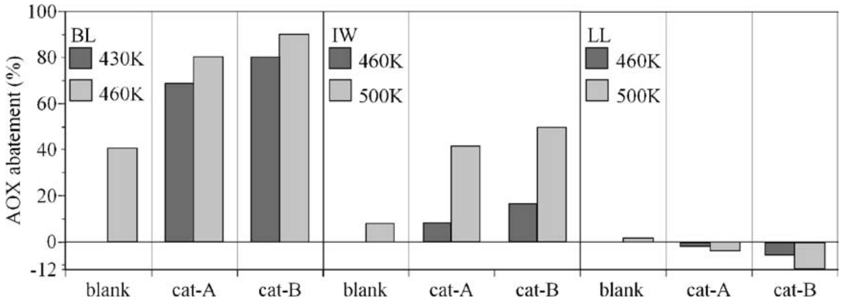

Fig. 3. AOX removal (%) in BL, IW and LL sample.

Table 3
OUR measures (mg/l min) after 1 h reaction at 500 K (460 K)[a]

Sample	No reaction	Cat-A	Cat-B
IW	0.07	0.17 (0.09)	0.27 (0.17)
LL	0.28	0.42 (0.36)	0.64 (0.50)
BL	0.37	0.70 (0.51)	0.75 (0.57)

[a] For BL temperatures of 460 K (430 K) were used.

Table 4
Activation energies for removal of COD and AOX in IW sample

	ΔE (KJ mol^{-1})	
	1st step	2nd step
COD	24.9	34.5
AOX	12.9	10.4

Table 3 shows for each wastewater the OUR before and after the catalytic tests. The OUR measure gives an indication of the biodegradability of a wastewater. It can be seen that in all samples oxygen uptake is increased after CWO, with higher values obtained by using CeO_2-SiO_2 catalysts. In particular with BL and LL wastewaters for treatment of 1 h, respectively, at 460 K and 500 K with doped ceria catalysts, OUR values larger than 0.6 mg/l min are obtained indicating a good biodegradability. IW wastewaters are the most refractory to biological treatment due most likely to the presence of a higher AOX concentration. Also in this case however, biodegradability is increased by CWO.

The use of ceria-based catalysts in environmental applications is well known and is connected with both the redox and morphological properties of these materials [12]. As a matter of fact, doping of ceria with a transition metal induces an enhancement of the redox properties mainly driven by structural modifications in the lattice that induce an increase of the diffusion rate of oxygen; at the same time doping increases the surface area and the thermal stability under reaction conditions. Recently, gas-phase deep oxidation of chlorinated hydrocarbons has been reported over ceria-zirconia-based catalysts [17] and similar catalyst compositions were previously shown to be active for oxidation of hydrocarbons [18,19]. The mechanism of action has been ascribed to a combination of surface acidity and availability of lattice oxygen. Although the action of the catalyst in wet oxidation has not been totally clarified, the principal role of ceria is likely to act as a good medium for oxygen activation and transport. This characteristic is connected with the formation of oxygen defect sites, and should contribute to oxygen activation by promoting a mechanism for production of active radicals or by promoting direct redox reaction [20]. In our preliminary experiments, the higher oxygen storage of silica-modified ceria due to the presence of defective sites [14] coupled with the high surface area of the catalyst may contribute to the increased reactivity.

A more detailed kinetic investigation has been carried out for the IW sample in order to compare the mechanism of removal of COD and AOX. It is known that the removal of organics in wastewaters occurs with a first order two-stage mechanism [2]. According to previous reports on simulated compositions, the reasons of this behavior is that the primary pollutants are decomposed in the first stage into less oxidable organic molecules that are further converted into CO_2 and H_2O. Since in the present investigation the oxidation content in the liquid phase was maintained at an excess level for the complete oxidation of all organic compounds, the oxidation kinetic of the WAO process can be represented by:

$$\frac{dC}{dt} = -kC^n \tag{1}$$

where C is either COD or AOX concentration, k the reaction rate coefficient, t the time and n is the reaction order. A first order kinetic model was used to represent the experimental data. Fig. 4 displays the plot of $\ln(C/C_0)$ versus t for either COD and AOX parameter. In both cases a two-stage first order reaction kinetics has been used to describe the catalytic behavior although it is evident that the slowdown of activity is clearly observed in the removal of COD and not in AOX. Activation energies for COD removal (Table 4)are consistent with the elimination in the second step of the more refractory pollutants derived from the primary pollutants. For the AOX curve, the two steps are barely visible and in agreement with this the activation energies are comparable and lower than those observed for COD removal. The lower activation energy is more likely related to the mechanism of removal of chlorine from the organo halogenated molecules according to a mechanism were R–Cl is first transformed to RH and

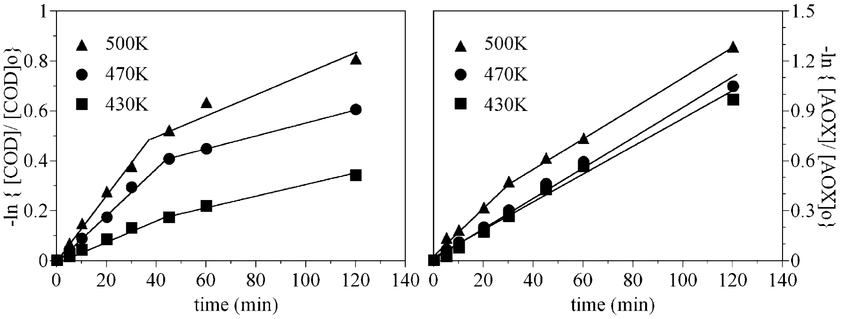

Fig. 4. Effect of temperature on first order kinetic plots of COD and AOX removal.

Cl^- and then RH (now contributing to overall COD) is oxidized to CO_2 and H_2O.

4. Conclusions

Catalytic wet air oxidation of three high strength composite halogenated liquid wastes using CeO_2-based catalyst was investigated and in comparison with WO, the CWO provides a higher efficiency in abatement of COD and AOX (with up to 90% AOX and 80% COD abatement). In addition it enhances the biodegradability of heavily polluted wastewaters to a degree that allows wastewaters to be then treated in a biological reactor. The comparison between pure and silica doped ceria catalysts evidences the importance of enhanced oxygen storage capacity and increased surface area. Preliminary kinetic studies reveal that the oxidation can be well represented by a first-order kinetics for both COD and AOX removal. In the former, in agreement with previous reports, a two-stage kinetics is observed, with the second stage reaction being much slower than the first.

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