Deactivation and reactivation of noble metal catalysts tested in the Catalytic Wet Air Oxidation of phenol

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ABSTRACT

Ceria and doped-ceria supported platinum and ruthenium catalysts were tested at 160 °C for the Catalytic Wet Air Oxidation of phenol. This work focused on the catalyst deactivation phenomenon caused by the formation of a carbonaceous layer during the oxidation reaction. Its degradation is favoured when cerium simple oxide is used as the support phase. Ex situ oxidative treatment, with diluted oxygen, revealed to degrade efficiently adsorbed compounds, thus leading to a total recovery of activity.

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1. Introduction

Wet Air Oxidation (WAO) is an efficient and promising oxidative pollution removal process which consists in totally oxidizing aqueous organic pollutants at high temperature (125–320 °C) and under oxygen or air pressure (5–200 bar) [1]. Those severe conditions of reaction can be lowered by the use of adequate catalysts, those latter being divided into three main categories:

- homogeneous catalysts, such as copper and iron salts, are very effective but their use implies an additional precipitation treatment aiming at recovering the catalyst from the treated effluent [1,2],
- oxides of transition metals, and particularly copper oxide CuO, are quite active but suffer fast deactivation due to the leaching of active species into the reaction medium [3–5],
- supported noble metals, although more expensive than metal oxides, offer the advantages of higher activity and resistance to leaching [6].

Cerium-based oxides appear to be interesting supporting materials for Catalytic Wet Air Oxidation (CWAO) catalysts both in terms of stability and activity. On the basis of Pourbaix diagrams, Béziat et al. concluded that CeO_2, as well as TiO_2 and ZrO_2 oxides, was stable enough to be used in the hot, acidic and oxidative CWAO medium [7]. This was experimentally confirmed by the very low levels of cerium leaching reported in the literature for ceria [8] and

cerium-based materials [9]. Moreover, ceria is well-known for its redox properties, resulting from its ability to store and release oxygen. These redox properties, known as Oxygen Storage Capacity (OSC), are an important factor controlling activity in CWAO [3,8] and can be further improved by doping with trivalent (La^{3+}, Pr^{3+}) or tetravalent (Zr^{4+}) cations [10,11].

Phenol uncatalyzed oxidation mechanism was studied in detail by Devlin and Harris who suggested an aqueous phase mechanism scheme [12]. Phenol heterogeneously catalyzed WAO was the subject of many studies. Both oxide of transition metals [13] and noble metals [14] based catalysts were reported to be prone to deactivation as a result of partial coverage of the catalytic surface by carbonaceous species. It is noteworthy to mention that fouling was not necessarily responsible for activity losses, as observed by Quintanilla et al. in their work concerning the CWAO of phenol on a 2.5 wt.% Fe/activated carbon catalyst [15].

The stability and the formation pathway of this carbonaceous deposit are of great interest. Authors generally agree that it is constituted by a strongly adsorbed polymer but only a quick review was done concerning regeneration possibilities.

From an industrial point of view, regeneration is generally preferred to be performed ex situ rather than in situ for several reasons including safety, time considerations and better activity recovery [16]. Strategies for the ex situ removal of fouling species include oxidation by an oxidizing agent (oxygen [17], ozone [18] or nitrous oxide [19]), hydrocracking at elevated temperature under high hydrogen pressure [20] and extraction by liquid solvents [18] or by supercritical fluids [21]. Considering that CWAO is a pollution abatement process, regeneration by potentially non-environmental-friendly organic solvent washing, although probably effective, may not be the best option. Reactivation by oxidation with oxygen,

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which is known to easily and rapidly remove all surface deposits [17,19], was selected for this study. Because of the exothermic nature of the combustion reaction, particular attention must be given to regeneration conditions: oxygen should be diluted with an inert gas while temperature should be carefully controlled to prevent overheating and subsequent thermal degradation of the catalyst [17].

Concerning the reactivation of CWAO catalysts, Chen et al. experimented regeneration of a spent copper promoted CeO_2/γ-Al_2O_3 catalyst via acetone, HCl and HNO_3 solution rinsing [22]. Acetone rinsing revealed to be efficient but two consecutive CWAO-regeneration cycles led to a much smaller activity. Authors attributed this phenomenon to residual carbon deposits and to the extended lixiviation of the metal species in the second run. Hamoudi and Larachi observed that the deposit could be completely removed below 300 °C [9], which was confirmed by Wang et al. [23]. Pintar and Levec verified that the catalyst could be regenerated by burning out the polymeric product but the study of CWAO catalysts reactivation was not the primary objective of their work and no further details were given [13].

The present work deals with the CWAO of phenol in presence of platinum and ruthenium catalysts supported on CeO_2 and $Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$ oxides. It aimed at improving knowledge about the effects of the carbonaceous deposit formed during this reaction and at developing a regeneration treatment for fouled catalysts. Experimental conditions favouring the formation of adsorbed species were thus selected for this study.

2. Experimental

2.1. Catalysts preparation

The various catalysts tested in the present study, along with their abbreviations and some of their physico-chemical properties, are presented in Table 1.

CeO_2 support was commercial Rare Earth Ceria HSA 5 provided by Rhodia while $Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$ mixed oxide was prepared through sol–gel method, according to the procedure previously described by Mikulová et al. [10]. Support phases were calcined for 300 min under air at 650 °C or 800 °C. These high temperature treatments were applied to increase the thermic stability of prepared catalysts. Since this work was devoted to the study of deactivation by fouling, all other potential causes of activity loss – in that case sintering of support particles – were tried to be avoided.

Noble metal was added by the impregnation method. In order to obtain comparable results, catalysts presenting identical molar amounts of metal were prepared. Metal contents were set at 1.25 wt.% for ruthenium and at 2.50 wt.% for platinum. Ruthenium and platinum-based catalysts were respectively synthesized from $RuCl_3 \cdot nH_2O$ and $Pt(NH_3)_4(OH)_2$ precursor salts. In each case, the mixture was stirred for 240 min before being evaporated in vacuum at 30 °C in a rotating evaporator. The catalysts were dried overnight at 120 °C and activated in a glass packed bed reactor under a flow rate of 30 mL min^{-1} of H_2 for 180 min at 350 °C.

2.2. Experimental set-up and procedure

Oxidation reactions were performed in a 0.44 L batch reactor made of Hastelloy C22 alloy and equipped with an electrically heated jacket and a turbine agitator. Model effluent was a 0.16 L aqueous solution containing phenol and catalyst at respective concentrations of $[PhOH]_0 = 2.098$ g L^{-1} and $C_{catalyst} = 4$ g L^{-1}. The typical operating conditions were 1000 rpm stirring speed, 20 bar oxygen partial pressure, 160 °C reaction temperature and 180 min reaction time. Gas phase samples as well as liquid phase samples were simultaneously and periodically collected and analyzed. Used catalysts were recovered by filtration, washed with ultra-pure water and dried overnight at 120 °C.

2.3. Analytical methods

Carbon dioxide present in the gas phase was determined by a gas chromatograph equipped with a catharometer and a Porapak Q packed column. Aqueous CO_2 was quantified from the amount of gaseous CO_2, on the basis of a specific study concerning carbon dioxide equilibrium between gaseous and liquid phases under 20 bar and at 160 °C [24].

Phenol concentration in liquid samples was determined by High Performance Liquid Chromatography (HPLC), using an UV6000LP diode array detector ($\lambda = 270$ nm) and an Aminex HPX87H Biorad column ($\emptyset = 7.8$ mm, $l = 300$ mm, mobile phase: 0.004 mol L^{-1} H_2SO_4 solution, 0.80 mL min^{-1}). Total Organic Carbon (TOC) values were measured in a 1020A TOC Analyzer (O.I. Analytical).

Specific surface areas were measured with a Micromeritics Tristar 3000 BET apparatus by nitrogen adsorption at -196 °C after degassing for 120 min under vacuum at 250 °C. The metal loadings of final catalysts were verified by inductively coupled plasma (ICP) analyses performed on an ICP/OES Perkin Elmer Optima 2000 DV apparatus. Metal dispersion values were determined by hydrogen chemisorption after a 60 min reduction under hydrogen (30 mL min^{-1}, 350 °C) and a 180 min degassing under argon (30 mL min^{-1}, 350 °C). Hydrogen pulses were afterwards injected at -95 °C (this temperature was attained by mixing acetone with liquid nitrogen) to measure metal accessibility.

Carbon contents in used catalysts were quantified by both (i) temperature programmed oxidation (TPO) using a 1% O_2/He mixture (12 mL min^{-1}) within the 30–700 °C temperature range (heating rate: 7 °C min^{-1}) and (ii) CHN elemental analysis using a NA 2100 PROTEIN machine from CE Instruments. The relative uncertainties associated with these carbon content values were 10% for TPO and 5% for elemental analysis.

2.4. Data analysis

Phenol mineralization molar ratio $M\%_t$ (Eq. (1)) corresponds to the ratio of the total amount of formed carbon dioxide ($[CO_2]_{tot(t)}$ expressed in grams of carbon per litre of solution) to the maximum amount of CO_2 being likely to form ($[CO_2]_{max}$ corresponding to the initial phenol solution TOC value, TOC_0 (g_C L^{-1})). Phenol conversion

Table 1
Abbreviations, compositions, calcination temperatures (T_{calc}), specific surface areas (S) and metal dispersion values (D) for tested supports and catalysts.

Catalyst abbreviation	Metal content (wt.%)	Supported metal	Support	T_{calc} (°C)	S (m² g^{-1})	D (%)
Ce	0	–	CeO_2	650	97	–
ZrCePr	0	–	$Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$	650	43	–
PtCe	2.4	Pt	CeO_2	800	45	44.0
PtZrCePr	2.5	Pt	$Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$	800	18	21.0
RuCe	1.1	Ru	CeO_2	800	44	3.0
RuZrCePr	1.2	Ru	$Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$	800	21	9.1