Catalysis Today 151 (2010) 143–147

Contents lists available at ScienceDirect

Catalysis Today

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

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

S. Keav *, A. Martin, J. Barbier Jr., D. Duprez

Université de Poitiers, LACCO UMR 6503, 40 Avenue du Recteur Pineau, F-86022 Poitiers Cedex, France

ARTICLE INFO

Article history:
Available online 11 February 2010

Keywords:
Catalytic Wet Air Oxidation
Phenol
Noble metal
Doped-ceria
Deactivation

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.

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,

* Corresponding author. Tel.: +33 549453523; fax: +33 549453741.
E-mail address: sylvain.keav@univ-poitiers.fr (S. Keav).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.01.025

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 (λ = 270 nm) and an Aminex HPX87H Biorad column (Ø = 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 (m^2 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

ratio $C\%_t$ was calculated from Eq. (2) in which $[PhOH]_0$ and $[PhOH]_t$ are respectively the initial and instantaneous phenol concentration values. Total Organic Carbon removal ratio $\Delta(TOC)\%_t$ is expressed in Eq. (3) where TOC_t is the instantaneous TOC value.

$$M\% = \frac{[CO_2]_{tot(t)}}{TOC_0} \times 100 \quad (1)$$

$$C\%_t = \frac{[PhOH]_0 - [PhOH]_t}{[PhOH]_0} \times 100 \quad (2)$$

$$\Delta(TOC)\%_t = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \quad (3)$$

3. Results and discussion

3.1. Single run experiments

Each support and catalyst presented in Table 1 was first tested during a classic single run experiment. A blank run was also performed in the absence of catalyst, in order to gauge the conversion of phenol achievable by the non-catalytic thermal oxidation reaction. Fig. 1 plots phenol conversion, TOC abatement and mineralization against time for each of these experiments. TPO and elemental analysis results for carbon contents in used catalysts are also presented in Table 2. Both techniques give similar results.

In comparison with the uncatalyzed reaction, cerium-based oxides improve the overall efficiency of the process (except for ZrCePr catalyst mineralization curve which is below that of blank experiment). Even though tested bare supports were calcined at a lower temperature (650 °C) than metallic catalysts (800 °C), so that they have higher specific surface areas, they are considerably less active than the latter ones. Platinum always appears to be more active than ruthenium. It is tempting to connect this observation with the fact that platinum is also better dispersed. However, while the dispersion of RuCe catalyst is smaller than that of RuZrCePr, its activity is more important. Metal dispersion, although probably playing a role in activity, may not be the only factor to take into account and since only four metallic catalysts were tested in the present study, no conclusion should be drawn without additional information.

When no metal is deposited, both Ce and ZrCePr conversion curves are similar and the same observation can be made concerning ΔTOC curves. This is also true if comparing PtCe with PtZrCePr and RuCe with RuZrCePr during the first 10 min of reaction. After this period, an increasing gap between the curves corresponding to Ce and ZrCePr supported catalysts – the first ones being more active than the latter ones – can be observed. This difference in supports behaviour can be related to mineralization rates which are smaller for ZrCePr based catalysts, thus suggesting that these catalysts cannot easily degrade the adsorbed phase. Therefore ZrCePr support is initially as active as ceria but is more disposed to fouling.

Table 2
Carbon contents in used catalysts obtained from TPO and elemental analysis.

Catalyst	$n(C)$ (mmol g^{-1})	
	TPO	Elemental analysis
Ce	3.5	3.2
ZrCePr	7.2	7.8
PtCe	6.0	4.6
PtZrCePr	11.3	10.8
RuCe	7.2	8.3
RuZrCePr	10.9	8.8

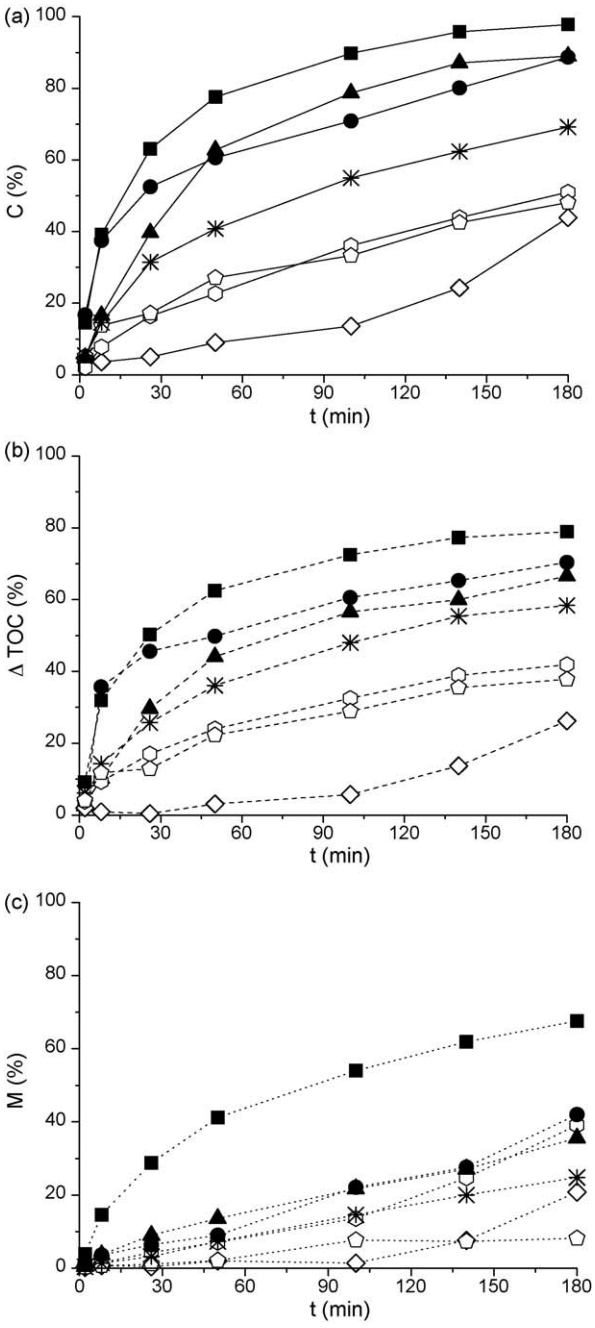

Fig. 1. Evolution of phenol conversion (a), TOC abatement (b) and phenol mineralization (c) during single run catalytic tests for blank run (◇); Ce (⬡) and ZrCePr (⬠) supports; and PtCe (■), PtZrCePr (●), RuCe (▲) and RuZrCePr (*) catalysts.

3.2. Deactivation phenomenon and reactivation protocol

In order to better understand the deactivation phenomenon, cyclic experiments were performed to compare the activities of fresh, used and reactivated catalysts. PtCe, PtZrCePr and RuCe catalysts were chosen for this study. RuZrCePr catalyst was considered unnecessary to be studied in this part since the comparisons of PtCe with RuCe, on one hand, and of PtCe with PtZrCePr, on the other hand, would give information about the respective influences of metal and support phases toward regeneration.

A typical catalytic test with fresh catalyst (Cycle I) was first performed as a reference experiment. Pre-fouled catalyst (recovered

from a previous run, rinsed and dried) was also tested (Cycle II) under the same experimental conditions. For all results to be comparable, every test was carried out using a same mass of "fresh" catalyst. Since the sample used in Cycle II was "pre-coked", the mass of catalyst to be loaded in the reactor was corrected to take into account the presence of adsorbed molecules. Cycle III consisted in testing a fouled catalyst after the ex situ degradation of its carbonaceous overlayer in a tubular reactor with a 5% O_2/N_2 mixture (30 mL min^{-1}, 350 °C). The sample was reduced for 60 min under H_2 (30 mL min^{-1}, 350 °C) before reuse. Regeneration step was carried out in diluted rather than in pure oxygen to (i) avoid uncontrolled overheating due to the exothermicity of the combustion reaction and (ii) prevent metal losses resulting from the formation of volatile RuO_4 oxide when ruthenium was the active phase. Phenol conversion, TOC abatement and mineralization curves are given in Fig. 2 for each experiment.

Whatever the catalyst may be, fouling led to activity decline while ex situ regeneration contributed to a complete recovery of activity. Hamoudi and Larachi also observed the important loss of activity of a 1 wt.% Pt–MnO_2/CeO_2 catalyst tested in two consecutive CWAO runs without regeneration [9].

Metal contents and dispersion values of regenerated catalysts were measured. Except for PtZrCePr for which metal loading and dispersion dropped from 2.5 wt.% to 1.9 wt.% and from 21% to 12%, respectively, no significant change was observed in comparison with fresh catalysts. Unexpectedly, the alterations of PtZrCePr did not affect its activity since the regenerated catalyst had the same activity as the fresh one. However, since these alterations were not observed in the case of ceria supported catalysts and that a diminution of Pt content is not likely to occur during the ex situ regeneration treatment, the instability of PtZrCePr results from an instability of ZrCePr ternary oxide which is therefore not an adequate choice as a support phase for CWAO. For unfouled catalysts (i.e. Cycles I and III), quasi-superimposition of C and ΔTOC curves during the first 10 min of reaction indicates that phenol is converted but neither into aqueous intermediates nor into carbon dioxide, an important amount of phenol adsorbs over the catalytic surface and is rapidly changed into a polymeric phase. For all catalysts, $C - \Delta$TOC difference is almost constant after 50 min of reaction, which demonstrates the accumulation of refractory intermediates such as acetic acid. This accumulation phenomenon is well known to occur in CWAO of organic compounds [25] and was confirmed by HPLC analyses.

For PtZrCePr catalyst, carbon content was identical after each run (%C = 13%) and all mineralization curves were linear and superimposed. A little %C increase (from 10% to 10.5%) was observed between Cycles I and II for RuCe catalyst while mineralization curve changed from non-linear to linear shape. Finally, PtCe catalyst carbon content doubled from 6% to 11%, as a consequence of the second run, and Cycle II non-linear mineralization curve was much below those of Cycles I and III. From those observations, mineralization activity is in direct connection with the amount of adsorbed carbon. During CWAO of phenol, carbon is deposited over the catalytic surface but this deposition is limited to a certain amount of adsorbed species. This phenomenon was also observed by Hamoudi et al. [26] and Delgado et al. [27] in the case of cerium–manganese composite oxides. Before surface saturation state is attained, both aqueous intermediates and carbonaceous overlayer oxidation reactions occur simultaneously. Apparent mineralization rate is then the sum of the mineralization rates corresponding to each of these reactions. Once surface is saturated with adsorbed compounds, all active sites are occupied and unable to catalyze the oxidation of aqueous intermediates. In those conditions, the carbonaceous deposit becomes the only organic compound to be mineralized and reaction proceeds through its degradation – which frees active sites – immediately followed by the formation of new adsorbed compounds. It is also to be noticed that when a catalyst has its surface saturated, as it is always the case for PtZrCePr catalyst, all its mineralization curves are straight lines of same slope. Total oxidation of adsorbed molecules into CO_2 occurs at a steady rate. Since C and ΔTOC curves also become linear, phenol conversion is limited by mineralization rate. The period necessary to reach surface saturation state varies in accordance with catalysts composition. It lasts only a few minutes for PtZrCePr catalyst while saturation only occurs after hours for RuCe and PtCe. As explained in Section 3.1, ZrCePr oxide is less active than Ce support to mineralize adsorbed compounds, which explains why it is saturated and deactivated faster.

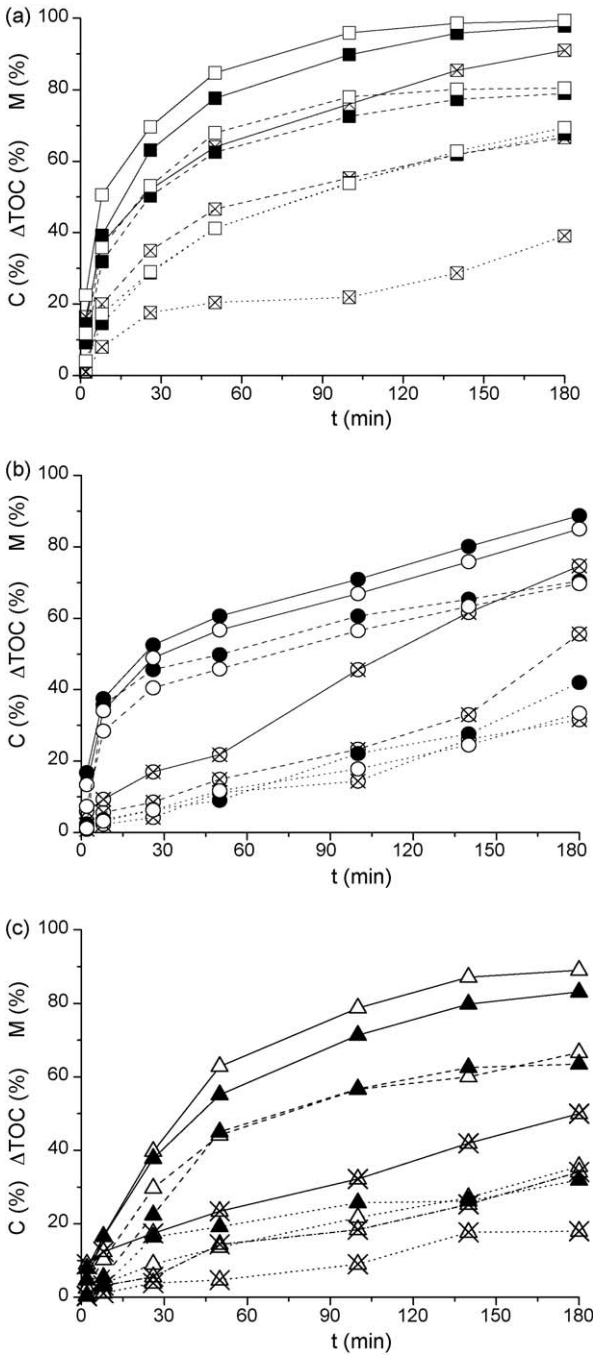

Fig. 2. Evolution of phenol conversion (– – –), TOC removal (– – –) and phenol mineralization (. . . . . .) during Cycle I (■, ● and ▲), Cycle II (☒, ⊠ and ⊗) and Cycle III (□, ○ and △) for PtCe (a), PtZrCePr (b) and RuCe (c) catalysts.

Table 3
Phenol conversion, TOC removal, and phenol mineralization obtained after 180 min with a fresh PtCe catalyst and after one, two or three deactivation–reactivation cycles.

	Fresh catalyst	After 1st regeneration	After 2nd regeneration	After 3rd regeneration
C (%)	97.8	99.4	98.3	98.2
Δ(TOC) (%)	78.9	80.4	79.3	79.6
M (%)	67.7	69.4	68.5	68.9

3.3. Successive CWAO-regeneration experiments

Amongst the catalysts tested in the previous parts, PtCe was found to be the most active in the CWAO of phenol and it could be ex situ regenerated without any alteration. Its stability toward successive deactivation–regeneration cycles was tested. Experimental conditions for CWAO runs and for regeneration treatments were exactly the same as those described above.

Results, given in Table 3, show that both activity and selectivity were recovered after each regeneration run, confirming that PtCe, considering its activity, stability and its behaviour toward regeneration, is a good candidate for CWAO.

4. Conclusion

CWAO catalysts can suffer multiple causes of deactivation. The lixiviation of active components is undoubtedly responsible for a definitive loss of activity. On the contrary, the deposition of carbonaceous materials on the catalyst is reversible. However, only few studies were dedicated to the removal of this adsorbed phase despite its practical interest.

A decrease in activity was confirmed to occur during the CWAO of phenol over platinum and ruthenium catalysts supported on cerium-based oxides and was attributed to the fouling of the catalytic surface by a layer of adsorbed intermediates. Mineralization activity declined because occupied active sites became unable to directly oxidize aqueous intermediates. The nature of the support phase plays an important role in the degradation of adsorbed compounds.

An easy-to-perform ex situ solvent-free reactivation procedure was proposed, consisting in the total degradation of the carbonaceous deposit by combustion with diluted oxygen at moderate temperature. Effective successive regeneration runs were shown to be feasible without damaging the catalyst structure. The use of air as a regenerating agent instead of a 5% O_2/N_2 mixture would make the procedure cheaper and thus even more attractive.

References

[1] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Reviews: Wet Air Oxidation, Ind. Eng. Chem. Res. 34 (1995) 2–48.
[2] F. Luck, Wet Air Oxidation: past, present and future, Catal. Today 53 (1999) 81–91.
[3] S.-K. Kim, S.-K. Ihm, Nature of carbonaceous deposits on the alumina supported transition metal oxide catalysts in the Wet Air Oxidation of phenol, Top. Catal. 33 (2005) 171–179.
[4] A. Fortuny, C. Bengoa, J. Font, A. Fabregat, Bimetallic catalysts for continuous Catalytic Wet Air Oxidation of phenol, J. Hazard. Mater. B 64 (1999) 181–193.
[5] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. Garcia-Ochoa, Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: causes and effects, Appl. Catal. B: Environ. 61 (2005) 323–333.
[6] M. Besson, P. Gallezot, Deactivation of metal catalysts in liquid phase organic reactions, Catal. Today 81 (2003) 547–559.
[7] J.-C. Béziat, M. Besson, P. Gallezot, S. Durécu, Catalytic Wet Air Oxidation of carboxylic acids on TiO_2-supported ruthenium catalysts, J. Catal. 182 (1999) 129–135.
[8] A. Trovarelli, C. De Leitenburg, M. Boaro, G. Dolcetti, The utilization of ceria in industrial catalysis, Catal. Today 50 (1999) 353–367.
[9] S. Hamoudi, F. Larachi, Wet oxidation of phenol catalyzed by unpromoted and platinum-promoted manganese/cerium oxide, Ind. Eng. Chem. Res. 37 (1998) 3561–3566.
[10] J. Mikulová, S. Rossignol, J. Barbier Jr., D. Mesnard, C. Kappenstein, D. Duprez, Ruthenium and platinum catalysts supported on Ce, Zr, Pr–O mixed oxides prepared by soft chemistry for acetic acid Wet Air Oxidation, Appl. Catal. B: Environ. 72 (2006) 1–10.
[11] F. Deganello, A. Martorana, Phase analysis and oxygen storage capacity of ceria–lanthana-based TWC promoters prepared by sol–gel routes, J. Solid State Chem. 163 (2002) 527–533.
[12] H.R. Devlin, I.J. Harris, Mechanism of the oxidation of aqueous phenol with dissolved oxygen, Ind. Eng. Chem. Res. Fundam. 23 (1984) 387–397.
[13] A. Pintar, J. Levec, Catalytic oxidation of organics in aqueous solutions, J. Catal. 135 (1992) 345–357.
[14] S. Nousir, S. Keav, J. Barbier Jr., M. Bensitel, R. Brahmi, D. Duprez, Deactivation phenomena during Catalytic Wet Air Oxidation (CWAO) of phenol over platinum catalysts supported on ceria and ceria–zirconia mixed oxides, Appl. Catal. B: Environ. 84 (2008) 723–731.
[15] A. Quintanilla, N. Menéndez, J. Tornero, J.A. Casas, J.J. Rodríguez, Surface modification of carbon-supported iron catalyst during the Wet Air Oxidation of phenol: influence on activity, selectivity and stability, Appl. Catal. B: Environ. 81 (2008) 105–114.
[16] P. Dufresne, Hydroprocessing catalysts regeneration and recycling, Appl. Catal. A: Gen. 322 (2007) 67–75.
[17] P. Ammendola, R. Chirone, G. Ruoppolo, G. Russo, Regeneration of spent catalysts in oxy-combustion atmosphere, Exp. Therm. Fluid Sci., in press.
[18] I.V. Kozhevnikov, S. Holmes, M.R.H. Siddiqui, Coking and regeneration of $H_3PW_{12}O_{40}/SiO_2$ catalysts, Appl. Catal. A: Gen. 214 (2001) 47–58.
[19] G.J. Hutchings, R. Hunter, L.J. Van Rensburg, Methanol and dimethyl ether conversion to hydrocarbons using tungsten trioxide/alumina as catalyst – a study of catalyst reactivation, Appl. Catal. 41 (1988) 253–259.
[20] R. Klingmann, R. Josl, Y. Traa, R. Gläser, J. Weitkamp, Hydrogenative regeneration of a Pt/La-Y zeolite catalyst deactivated in the isobutane/n-butene alkylation, Appl. Catal. A: Gen. 281 (2005) 215–223.
[21] D.M. Ginosar, D.N. Thompson, K.C. Burch, Recovery of alkylation activity in deactivated USY catalyst using supercritical fluids: a comparison of light hydrocarbons, Appl. Catal. A: Gen. 262 (2004) 223–231.
[22] I.-P. Chen, S.-S. Lin, C.-H. Wang, S.-H. Chang, CWAO of phenol using CeO_2/γ-Al_2O_3 with promoter – effectiveness of promoter addition and catalyst regeneration, Chemosphere 66 (2007) 172–178.
[23] J. Wang, W. Zhu, S. Yang, W. Wang, Y. Zhou, Catalytic Wet Air Oxidation of phenol with pelletized ruthenium catalysts, Appl. Catal. B: Environ. 78 (2008) 30–37.
[24] L. Oliviero, Thesis of University of Poitiers, 2001.
[25] L. Li, P. Chen, E.F. Gloyna, Generalized kinetic model for wet oxidation of organic compounds, AIChE J. 37 (11) (1991) 1687–1697.
[26] S. Hamoudi, K. Belkacemi, F. Larachi, Catalytic oxidation of aqueous phenolic solutions catalyst deactivation and kinetics, Chem. Eng. Sci. 54 (1999) 3569–3576.
[27] J.J. Delgado, J.A. Pérez-Omil, J.M. Rodríguez-Izquierdo, M.A. Cauqui, The role of the carbonaceous deposits in the catalytic wet oxidation (CWO) of phenol, Catal. Commun. 7 (2006) 639–643.