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Anne Heponiemi

CATALYTIC WET AIR OXIDATION OF INDUSTRIAL WASTEWATERS

OXIDATION OF BISPHENOL A OVER CERIUM SUPPORTED METAL CATALYSTS

*UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU
FACULTY OF SCIENCE*

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CATALYTIC WET AIR OXIDATION OF INDUSTRIAL WASTEWATERS

Oxidation of bisphenol A over cerium supported metal catalysts

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Abstract

The large amounts of industrial wastewaters, contaminated by hazardous and toxic compounds together with ever tightening legislation, have challenged traditional wastewater treatment methods. Therefore, the development of discharge limits under, cost-effective and ecological wastewater treatment has become an essential concern. Catalytic water phase technologies are interesting alternatives for traditional wastewater treatment. Among them catalytic wet air oxidation (CWAO) has been used successfully in the management of various industrial effluents. However, the development of an active and stable catalyst for the severe reaction conditions of CWAO has proved truly challenging.

The aim of this thesis was to study the activity and stability of laboratory prepared cerium supported metal catalysts in the catalytic wet air and wet peroxide oxidation of aqueous organic pollutants. Ru supported on Ce-Zr mixed oxides and commercial activated carbon as reference were used in CWAO and catalytic wet peroxide oxidation (CWPO) of surface plating industry wastewater. Ag/Ce-Zr and Pt/Ce-Ti catalysts were catalyzed CWAO of aqueous solution of bisphenol A (BPA).

Both CWAO and CWPO improved the abatement of organic compounds from surface plating industry wastewater when comparing the non-catalytic experiments. Moreover, catalytic oxidation enhanced the biodegradability of organic matter in the wastewaters.

According to the results, Pt/Ce-Ti catalysts performed with higher activity in CWAO of BPA than Ag/Ce-Zr catalysts and almost 100% removal of BPA was achieved. The leaching of active metal during oxidation experiments affected the activity of Ag/Ce-Zr catalysts. Moreover, CWAO of BPA was not a surface area specific reaction but the activity of catalysts was related to the chemisorbed oxygen content on the catalysts' surface.

The results of this thesis showed that cerium supported metal catalysts are active and stable catalysts in CWAO of BPA and also in the treatment of industrial wastewater. Therefore, these catalysts could be applied next to pilot scale applications.

Keywords: bisphenol A, catalytic wet air oxidation, catalytic wet peroxide oxidation, cerium, platinum, ruthenium, silver, wastewater treatment, zirconium

Heponiemi, Anne, Teollisuuden jätevesien orgaanisten yhdisteiden katalyyttinen märkähapetus. Ceriumkatalyytit bisfenoli A:n hapetuksessa
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Tiivistelmä

Teollisuuden jätevedet sisältävät usein haitallisia ja myrkyllisiä yhdisteitä, joiden käsittely perinteisillä jäteveden käsittelymenetelmillä on hyvin haastavaa. Lisäksi alati kiristyvä ympäristölainsäädäntö asettaa omat vaatimuksensa jäteveden käsittelylle. Katalyyttiset vedenkäsittelymenetelmät ovat viime vuosina herättäneet paljon kiinnostusta. Yksi lupaavimmista tekniikoista on katalyyttinen märkähapetus, jota on käytetty sekä lukuisten malliaineiden että teollisten jätevesien käsittelyssä. Märkähapetuksen vaativissa reaktio-olosuhteissa aktiivisena säilyvän katalyyttimateriaalin kehittäminen on kuitenkin osoittautunut varsin haasteelliseksi.

Väitöskirjatutkimuksen tavoitteena oli kehittää aktiivisia ja kestäviä ceriumpohjaisia katalyyttimateriaaleja märkähapetusreaktioon. Tutkimuksessa valmistettiin Ru-, Pt- ja Ag-katalyyttejä, jotka impregnoitiin Ce-Zr- ja Ce-Ti-sekaoksideille. Ru/Ce-Zr-katalyyttejä sekä kaupallista aktiivihiiltä vertailumateriaalina käytettiin pintakäsittelyteollisuuden jäteveden märkähapetuksessa ja märkäperoksidihapetuksessa. Bisfenoli A:n (BPA) vesiliuoksen märkähapetusta katalysoitiin sekä Ag/Ce-Zr- että Pt/Ce-Ti-katalyyteillä.

Katalyyttisellä märkähapetuksella ja märkäperoksidihapetuksella pintakäsittelyteollisuuden jäteveden orgaanisten yhdisteiden konsentraatio väheni enemmän verrattuna ilman katalyyttiä suoritettuihin hapetuksiin. Lisäksi käsitellyn vesinäytteen biohajoavuusaste nousi eli jäteveden sisältämät orgaaniset yhdisteet olivat hapettuneet helpommin biohajoavaan muotoon.

Pt/Ce-Ti-katalyytit olivat Ag/Ce-Zr-katalyyttejä aktiivisempia BPA:n märkähapetusreaktiossa. Pt-katalyyttisessä reaktiossa saavutettiin lähes 100 % reduktio BPA:n pitoisuudessa. Ag-katalyyttien aktiivisuuteen vaikutti hopean osittainen liukeneminen hapetettavaan liuokseen märkähapetusreaktion aikana. Lisäksi havaittiin, että BPA:n märkähapetusreaktiossa katalyytin aktiivisuus oli riippuvainen katalyyttipintaan kemiallisesti sitoutuneen hapen määrästä eikä niinkään katalyytin pinta-alasta.

Väitöskirjatutkimuksessa saatujen tulosten perusteella valmistetut ceriumpohjaiset metallikatalyytit olivat aktiivisia ja kestäviä. Katalysoiduissa hapetusreaktiossa sekä BPA:n että pintakäsittelyteollisuuden jäteveden orgaaninen kuormitus pieneni. Siksi valmistettuja katalyyttimateriaaleja voitaisiin tutkia seuraavaksi pilotti-mittakaavan sovellutuksissa.

Asiasanat: bisfenoli A, ceriumoksidi, hopea, jäteveden käsittely, katalyyttinen märkähapetus, katalyyttinen märkäperoksidihapetus, platina, rutenium, zirkonium

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Oulu, August 2015 Anne Heponiemi

Abbreviations

AC	Activated carbon
ACF	Activated carbon fiber
AOP	Advanced oxidation process
BE	Binding energy
BET	Brunauer-Emmett-Teller Method
BPA	Bisphenol A
BOD	Biochemical oxygen demand [mg O_2 L^{-1}]
CNT	Carbon nanotubes
CNW	Carbon nanowires
COD	Chemical oxygen demand [mg O_2 L^{-1}]
CWAO	Catalytic wet air oxidation
CWPO	Catalytic wet peroxide oxidation
CX	Carbon xerogel
EDC	Endocrine disrupting chemical
EDS	Energy-dispersive X-ray spectroscopy
EPA	United States Environmental Agency
ER	Eley-Rideal adsorption model
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
ICDD	International Centre for Diffraction Data
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LHHW	Langmuir-Hinshelwood-Hougen-Watson adsorption model
MWCNT	Multi-walled carbon nanotube
PDF	Powder Diffraction File
SCWO	Supercritical wet oxidation
ThOD	Theoretical oxygen demand [mg O_2 L^{-1}]
TOC	Total organic carbon [mg C L^{-1}]
TPD	Temperature programmed desorption
UV-Vis	Ultraviolet-visible
WAO	Wet air oxidation
WPO	Wet peroxide oxidation
WW	Wastewater
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

List of original publications

This thesis is based on the following publications, which are referred throughout the text by their Roman numerals:

I Heponiemi A & Lassi U (2012) Advanced oxidation processes in food industry wastewater treatment – a review. In: Valdez B (ed) Food industrial processes – Methods and equipment, Chapter 17. InTech publishing: 313–338.

II Heponiemi A, Rahikka L, Lassi U & Kuokkanen T (2011) Catalytic oxidation of industrial wastewater under mild conditions. Topics in Catalysis 54: 1034–1041.

III Heponiemi A, Azalim S, Hu T & Lassi U (2015) Cerium oxide based catalysts for wet air oxidation of bisphenol A. Topics in Catalysis DOI 10.1007/s11244-015-0457-y.

IV Heponiemi A, Azalim S, Hu T & Lassi U (2015) Catalytic wet air oxidation of bisphenol A with platinum catalysts supported on cerium and cerium-titanium oxides, manuscript.

The author of this thesis was the primary author of Papers I–IV who was responsible for the planning, experimental and reporting of the results in all publications. The co-authors participated in the experimental design and analysis of the publications.

Table of contents

1 Introduction

1.1 Background

Large amounts of wastewaters are produced worldwide in several industrial sectors such as pharmaceutical, chemical, petrochemical, in addition to the pulp and paper industry as well as in households. Typically, domestic wastewaters are treated in municipal wastewater treatment plants while industrial effluents often acquire special technologies due to the highly toxic and refractory compounds of wastewaters. Traditional wastewater treatment techniques include physico-chemical, thermal and biological treatment methods which are widely applied for the removal of pollutants. However, conventional activated sludge methods require quite long residence times, large-scale treatment plants and are usually unsuitable for toxic compounds. Incineration is appropriate for effluents with chemical oxygen demand (COD) over 150 mg L^{-1} but it is extremely energy consuming and generates further problems due to the hazardous emissions of dioxin and furan. (Debellefontaine *et al.* 1996). Techniques such as flocculation, precipitation, adsorption, reverse osmosis and air stripping require post-treatment before discharging the effluent to the environment (Danis *et al.* 1998). Moreover, new regulations for the disposal and treatment of toxic and hazardous effluents will further strict the discharge limits of aqueous waste. These limitations have forced researchers to develop more ecological and efficient technologies for wastewater treatment.

Advanced oxidation processes (AOPs) are alternatives for traditional wastewater treatment techniques. These techniques involve the generation of a free hydroxyl radical ($HO^\bullet$) which is one of the most powerful oxidation agents known. AOPs can be split into “cold” and “hot” oxidation techniques according to their working temperature. Techniques operating near ambient temperatures such as ozonation, photolysis, photocatalysis, Fenton processes and combinations of these processes are suitable for effluents containing COD $\leq$ 5.0 g L^{-1}. For wastewaters with higher amounts of COD (5–150 g L^{-1}) hot oxidation techniques i.e. wet air oxidation, wet peroxide oxidation and supercritical wet air oxidation are more convenient. (Paper I). However, the energy requirements of “hot” AOPs have limited the use of these techniques but with and appropriate choice of catalysts these can be lowered. In recent years, catalytic wet air oxidation (CWAO) and catalytic wet peroxide oxidation (CWPO) have received a lot of attention in the research field of wastewater treatment (Perathoner & Centi 2005, Kim & Ihm 2011). Both homogeneous and heterogeneous catalysts have been studied in CWPO and particularly in CWAO. The need for an extra separation step of a homogeneous catalyst has been the driving force for the development of active and stable heterogeneous catalysts for water phase applications. Therefore, various materials such as metal oxides, carbon materials and noble metals have been widely studied in the abatement of organic pollutants from wastewater streams (Bhargava *et al.* 2006, Cybulski 2007). However, in spite of the vigorous research in the field of CWAO and CWPO there is still a need for an active, stable and cost-effective catalyst for industrial wastewater treatment.

1.2 Scope and objectives

The aim of this work was to study catalytic wet air oxidation as an alternative treatment method for aqueous pollutants in which great importance was placed upon the preparation and characterization of cerium based catalytic materials used in the catalytic experiments. Several characterization techniques such as X-ray diffraction and specific surface area measurement were utilized in order to understand the catalysts' activity, selectivity and stability. The applicability of multiple methods will provide a larger view of the catalysts' activity and stability.

In the first part of this thesis, surface plating industry wastewater was oxidized by CWAO and CWPO. Oxidation reactions were catalyzed by commercial activated carbon (AC) and laboratory prepared Ru catalysts supported on Ce-Zr mixed oxides. Therefore, the first research questions were: Whether CWAO or CWPO are suitable treatment methods for industrial effluent? Whether commercial AC work better in the oxidation experiments than laboratory prepared Ru catalysts? These research questions were discussed in Paper II.

Cerium based catalysts performed good catalytic activity in the CWAO of surface plating industry wastewater. However, Ru as an active metal is a rather expensive material and due to this fact silver was chosen as a cheaper alternative. Therefore, in Paper III Ag supported on Ce-Zr mixed oxides were used in CWAO of aqueous solution of bisphenol A (BPA). BPA is classified as an endocrine disrupting chemical (EDC) and it has been reported to affect sexual development (Meeker *et al.* 2010, Zeinab *et al.* 2012, Helmestam *et al.* 2014). Moreover, the removal of BPA from wastewaters by traditional biological treatment may cause further problems due to the accumulation of BPA into the activated sludge (Marttinen *et al.* 2003, Clara *et al.* 2004). Therefore, the second set of research questions were: Is CWAO an appropriate treatment method for the removal of BPA from aqueous streams? Does Ag affect the catalytic activity of Ce-Zr mixed oxides?

Silver did not improve the catalytic activity of Ce-Zr mixed oxides in CWAO of BPA. Consequently, in the last part of this thesis Pt was chosen as an active metal while Ce-Ti mixed oxides were used as supports in CWAO of BPA. The purpose of this research was to determine if Pt supported on Ce-Ti mixed oxides perform higher catalytic activity in the abatement of BPA by CWAO than Ag/Ce-Zr catalysts. This research question has been discussed in Paper IV.

2 Wet air oxidation

The basic idea of the wet air oxidation (WAO) process is to use air or molecular oxygen to oxidize organic matter at elevated temperatures (200–325 °C) and pressures (5–15 MPa). In these severe reaction conditions organic waste is decomposed via free radical mechanisms to intermediates (e.g. carboxylic acids and other low molecular weight organic compounds) and to end products, CO_2 and water (Mishra *et al.* 1995). At about 250 °C almost all organic compounds can be eliminated except acetic and propionic acids (Debellefontaine & Foussard 2000). Acetic acid is the most refractory compound and it requires a reaction temperature of around 320 °C for decomposition (Debellefontaine *et al.* 1996). The success of the oxidation reaction depends strongly on the operating pressure and temperature as well as the reaction time and treated effluent. WAO is a suitable method for wastewaters which are both too diluted to incinerate and too concentrated or toxic for biological treatment and so the COD of the treated effluent is typically between 20–150 g L^{-1} (Kolaczkowski *et al.* 1999).

2.1 Process description

Fig. 1 shows a typical flow diagram for a WAO system with a bubble column reactor where the oxidizable wastewater is brought to the system using a high-pressure pump. At the same time compressed air is preheated in the heat exchanger and further mixed with treated effluent. This mixture of gas and liquid is pumped to the bubble column reactor in which it is oxidized by air or oxygen for a sufficient period of time in order to achieve the desired oxidation level (typically 15–120 min). After oxidation the effluent is cooled down in the heat exchanger and depending on the oxidation level it is then discharged to the watercourse or treated further biologically. The formed gases are then treated via adsorption, scrubbing or incineration techniques. The reactor is typically adiabatic and the temperature of the reaction is controlled by adjusting the total pressure. Furthermore, when water vaporizes in the gas phase the heat is absorbed and it is released after the oxidation of organic compounds in the liquid phase. The energy of the outlet streams (gas, liquid) is usually enough for preheating of the coming effluent. Typically, no additional energy is required for a WAO system if the COD of the coming effluent exceeds 15 g L^{-1}. (Debellefontaine & Foussard 2000).

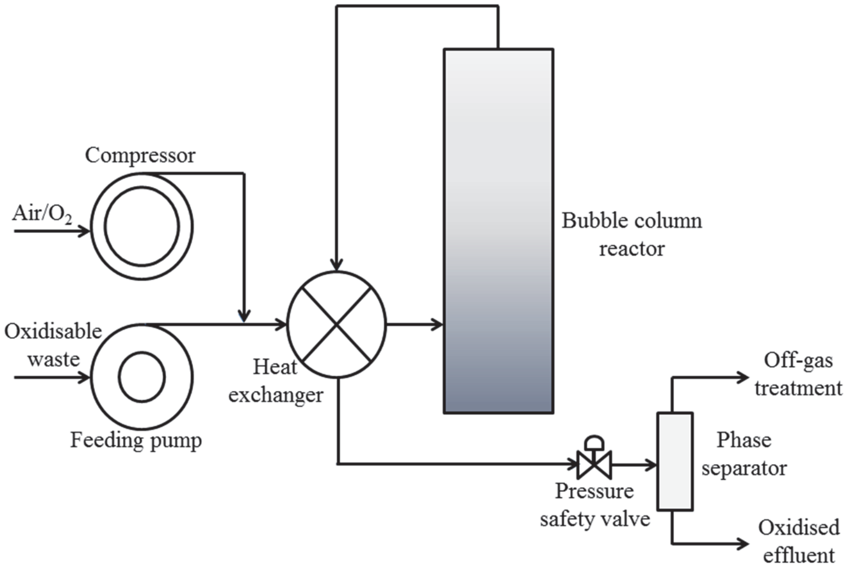

Fig. 1. Simplified flow diagram of the wet air oxidation process (Debellefontaine & Foussard 2000).

Typically, around 90% COD removal can be achieved in industrial scale wet air oxidation systems so the treated effluent cannot be discharged directly into the environment. However, the oxidized effluent is more biodegradable and it can be treated biologically before final release. (Debellefontaine & Foussard 2000).

Nowadays, over 400 commercial WAO units are operating all over the world treating wastewaters from pharmaceutical, chemical and petrochemical industries as well as urban sludge from biological treatment plants. Most of the commercial WAO units are non-catalytic such as Zimpro® (US Filter), Wetox® and Kenox® or homogeneously-catalyzed systems: Simo (Ciba Geigy), Loprox® (Bayer and Bertrams) and Athos® (Veolia Environment). Heterogeneously catalyzed wet oxidation facilities are working only in Japan by Nippon Shokubai® and Osaka gas®. (Larachi 2005).

2.2 Reaction mechanisms of WAO

The reaction mechanisms of WAO are rather complex and not well understood. However, several researchers have concluded that WAO involves chain reactions in which oxygen and hydroxyl, hydroperoxyl and organic hydroperoxy free radicals participate (Debellefontaine *et al.* 1996).

Wet air oxidation reaction mechanism can be divided into four steps (Emanuel *et al.* 1967). The oxidation reaction starts with the formation of free radicals. In this first step oxygen reacts with the weakest C-H bonds of the oxidized organic compound forming hydroxyl radical ($HO_2^{\bullet}$), organic radical ($R^{\bullet}$) and further hydrogen peroxide (H_2O_2):

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot} \tag{1}$$
$$RH + HO_2^{\cdot} \rightarrow R^{\cdot} + H_2O_2 \tag{2}$$

Typically, these initial reactions are the limiting ones for most of the organic molecules and depend strongly on temperature. The activation energy of the initial reaction can exceed 150 kJ mol^{-1} which explains why air oxidation is rather fast at temperatures over 250 °C. However, the following propagation reactions are typically rapid and have high rate constants. (10^7–10^9 L mol^{-1} s^{-1}) (Debellefontaine *et al.* 1996). In the propagation step, the radical $R^{\bullet}$ reacts further with oxygen forming peroxy radical ($RO_2^{\bullet}$) (Equation (3)) which abstracts a hydrogen atom from the organic molecule, producing organic hydroperoxide (ROOH) and more organic radicals (Equation (4)).

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \tag{3}$$
$$RO_2^{\cdot} + RH \rightarrow R^{\cdot} + ROOH \tag{4}$$

The organic hydroperoxide is a relatively unstable compound which decomposes via degenerate branching:

$$ROOH \rightarrow RO^{\cdot} + OH^{\cdot} \tag{5}$$

The chain reaction will end when free radicals $R^{\bullet}$ and $RO_2^{\bullet}$ form stable compounds:

$$R^{\cdot} + R^{\cdot} \rightarrow R - R \tag{6}$$
$$R^{\cdot} + RO_2^{\cdot} \rightarrow ROOR \tag{7}$$
$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow ROH + R_1COR_2 + O_2 \tag{8}$$

The formed organic molecules are typically low molecular weight organic compounds such as alcohols and ketones which will further decompose to acetic or formic acids. This decomposition is usually the rate determining step in the oxidation reaction. Eventually, organic acids convert into final products, CO_2 and water. (Li *et al.* 1991). The schematic representation of the wet air oxidation reaction mechanism is described in Fig. 2 (Debellefontaine *et al.* 1996).

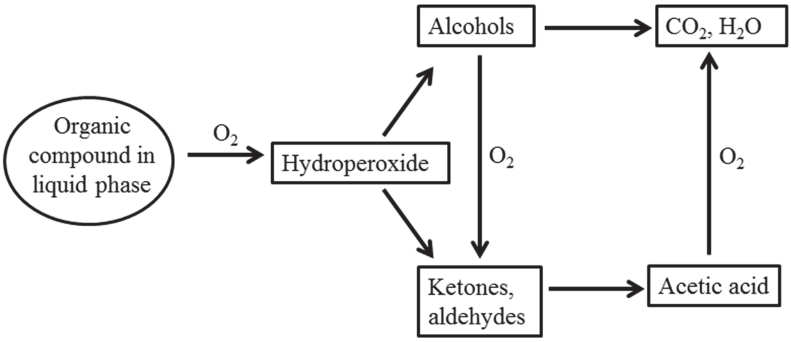

Fig. 2. Simplified diagram for wet air oxidation reactions (Debellefontaine *et al.* 1996).

2.3 Oxygen transfer and solubility during WAO

The wet air oxidation reaction mechanism involves two steps. One is the chemical reaction between organic matter and dissolved oxygen forming carbon dioxide. The physical step is the diffusion of oxygen from the gaseous to the liquid phase and the transfer of produced CO_2 from liquid to the gaseous phase. (Debellefontaine *et al.* 1996). Typically, the transport of slightly soluble gases such as oxygen is more rapid in the gas than in the liquid phase. Therefore, the reaction rate controlling step is the oxygen transfer between the gas-liquid interfaces. This gas transfer process can be described according to Equation (9),

$$r_m = k_L a\left(C_{O_2}^* - C_{L,O_2}\right) \tag{9}$$

in which r_m is the oxygen mass transfer rate, k_L is the liquid side mass transfer coefficient, a is the gas-liquid interfacial area, C^*_{O2} is the saturated oxygen concentration and $C_{L,O2}$ is the oxygen concentration in the bulk liquid. (Kolaczkowski *et al.* 1999). When temperature and pressure of the reaction increase, the saturated oxygen concentration rises significantly. The concentration of the saturated oxygen, C^*_{O2}, can be determined from Henry's law,

$$k_H = \frac{p_{O_2}}{C_{O_2}^*} \tag{10}$$

in which k_H is the Henry's constant and p_{O2} the partial pressure of dissolved oxygen. The dependency of Henry's constant from temperature is described in Fig. 3 (Cramer 1980). Usually it is assumed that the solubility of oxygen decreases when the temperature increases but as it can be observed from Fig. 3, the solubility of oxygen is greater at above 250 °C than at room temperature. The efficiency of the WAO process is based particularly on this high solubility of oxygen at increased temperatures and pressures. In WAO units, dissolved oxygen concentration as high as 3000 mg L^{-1} can be easily achieved. (Debellefontaine *et al.* 1996).

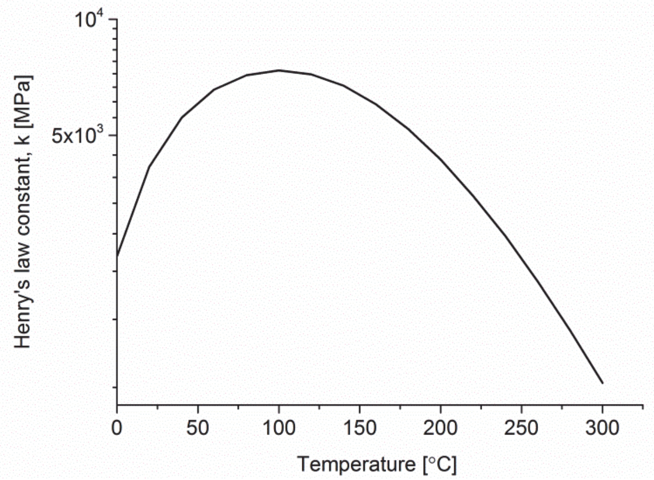

Fig. 3. The dependency of the Henry's law constant, k_H, for O_2 solubility on the temperature (Cramer 1980).

3 Catalytic wet air oxidation

The severe reaction conditions (high pressure and temperature) of WAO require special equipment resulting in the need for high investments and large operational costs. To reduce these costs and increase the reaction rate of oxidation reaction considerable amount of both homogeneous and heterogeneous catalysts have been tested in the catalytic wet air oxidation (CWAO) of model compounds and industrial effluents. Moreover, the use of catalysts in WAO enables the oxidation of refractory compounds such as acetic acid and ammonia in much lower temperatures than in the absence of catalysts. (Luck 1999).

The catalyst of WAO should have special properties due to the reaction conditions of oxidation reaction (temperature 125–200 °C, maximum pressure 5 MPa). Those are: i) physically and chemically stable compound in hot acidic medium, ii) mechanically strong, iii) exhibit high oxidation rate in diffusion limited reaction, iv) maintain active for several runs and be non-sensitive to poisons in the treated effluents and v) display nonselective, complete oxidation. (Matatov-Meytal & Sheintuch 1998).

3.1 Homogeneous catalysts

The advantage of homogeneous catalyst is its operation in the same liquid phase with the treated effluent. Therefore, the interaction of mass transfer and reaction kinetics are similar with non-catalytic WAO. The main disadvantage of homogeneous catalyst is the need for an extra separation step in the process which also increases capital cost. (Kolaczkowski *et al.* 1999). However, homogeneous catalysts have been proven to be effective in WAO of several model compounds and industrial effluents (Kolaczkowski *et al.* 1999, Bhargava *et al.* 2006) while copper salts have performed with the highest activity in the oxidation reaction (Shende & Mahajani 1994, Chen *et al.* 1999, Kayan *et al.* 2004). Table 1 describes examples from homogenous catalysts in WAO of various organic compounds and industrial effluents.

Table 1. Homogeneously catalyzed WAO of organic compounds and industrial effluents.

Catalyst	Treated effluent	Reaction conditions	Removal efficiency	Reference
$Cu(NO_3)_2$	acetic acid	247 °C, $p(O_2)$ 1.0 MPa	TOC, 87%	Imamura *et al.*1986
$CuSO_4$	phenol	175 °C, $p(O_2)$ 0.69 MPa	COD, 95%	Vaidya & Mahajani 2002
$CuSO_4$ + $FeSO_4$	sewage sludge	210 °C, p(air) 5.6 MPa	TOC, 71%	Bernardi *et al.* 2010
$Zn(NO_3)_2$	p-coumaric acid	130 °C, $p(O_2)$ 2.8 MPa	TOC, 40%	Mantzavinos *et al.* 1996

The effectiveness of homogenous WAO can be improved by adding radical promoters or co-oxidants to the process. In the study of Vaidya and Mahajani (2002) cupric sulphate catalyzed phenol oxidation was enhanced with the addition of hydroquinone to the reaction mixture. This model compound was used as a free radical generator which accelerated the degradation of phenol but increased the formation of acetic acid. Positive synergistic effects have also been observed while two or more transition metal salts have been used in combination. The performance of homogeneous $CuSO_4$ and $FeSO_4$ salts were compared in the CWAO of sewage sludge (Table 1). The mixing of these salts improved the abatement of TOC and also the highest amount of carboxylic acids was observed while copper and iron salts were used in combination. (Bernardi *et al.* 2010).

3.1.1 Reaction mechanisms of homogeneous CWAO

The homogeneously catalyzed WAO reaction undergoes a free radical mechanism which consists of initiation, propagation and terminations steps as described in WAO, Chapter 2.2. However, the free radicals of the catalytic process are assumed to be quite different in comparison to non-catalytic WAO due to the milder reaction conditions of CWAO. Wu *et al.* (2003) have proposed the pathway for the phenol (denoted as ROH in Equation (11)) oxidation in the homogeneously catalyzed WAO. The reaction starts at the initiation step in which homogeneous catalyst (denoted by M in Equation (11)) such as Cu^{2+}, Fe^{3+}, Co^{3+} accelerates the oxidation of phenol by transferring electron to it to initiate the free radicals:

$$ROH + M^{n+} \rightarrow RO^{\cdot} + M^{(n-1)} + H^{+} \qquad (11)$$

Propagation and termination steps follow initiation and reactions proceed as described in Equations (3) and (4) in Chapter 2.2. The free-radical reaction continues while the catalytic metal donates or accepts electron for the hydroperoxide (ROOH) formed in the termination step and free radicals further compose (Equations (12) and (13)). (Mikulová 2007).

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + OH^{-} + M^{(n+1)+} \tag{12}$$

$$ROOH + M^{(n+1)+} \rightarrow RO_2^{\cdot} + H^{+} + M^{n+} \tag{13}$$

This reaction mechanism is called homolytic due to the forming of free-radicals via a homogeneous mechanism. The free-radicals forms in a catalytic cycle through the reduction-oxidation homolytic reactions of hydroperoxides as described in Equations (12) and (13). (Bhargava *et al.* 2006).

3.2 Heterogeneous catalysts

In the 21th century research in the field of catalytic wet air oxidation has concentrated mainly in heterogeneous systems. The main advantage of heterogeneous catalysts over homogeneous ones is the removal of an extra separation step after catalytic oxidation. Metals and those mixed oxides as well as carbon materials have been widely studied in CWAO of organic effluents. Typically, supported noble metals have been observed to be more efficient catalysts than transition metals. (Bhargava *et al.* 2006, Levec & Pintar 2007).

However, to identify an active and stable catalyst in water phase oxidation has turned out to be rather challenging due to the hot acidic environment of CWAO. The main deactivating factors of heterogeneous catalysts are leaching of the active phase and loss of surface area due to the sintering of support. (Luck 1999). The leaching of catalytic material can be actually convert the reaction to homogeneous when it is supposed to be heterogeneous (Sheldon *et al.* 1998). Furthermore, sintering can be controlled by using metal oxides such as Al, Hf, Zr and Ti which has been observed to be stable even in supercritical wet oxidation (SCWO) conditions (Ding *et al.* 1996) or by mixing a more thermally stable oxide to an unstable one e.g. Zr with Ce (Mikulová *et al.* 2007a). The leaching of an active metal can be prevented by similar manners as sintering and also by pH control during the oxidation experiment. Moreover, the life-time of the heterogeneous catalyst can also be reduced due to the poisoning of the active sites. The deposition of organic or inorganic compounds on the surface of the metal oxide can be one of the deactivating factors of a catalytic material. (Luck 1999).

3.2.1 Metal and metal oxide catalysts

Metals and metal oxides have been widely studied in CWAO although noble metals have shown higher activity in the treatment of organic effluents. However, precious metals are rather expensive materials and cheaper alternatives have been explored. Several transition metal oxides such as Cu, Fe, Mn, Co and Ni have been tested for example in CWAO of phenol, ammonia, and industrial wastewaters (Table 2). (Kim & Ihm 2011).

Table 2. Heterogeneous metal catalysts used in CWAO of organic compounds and industrial wastewaters.

Catalyst	Treated effluent	Reaction conditions	Removal efficiency	Reference
CeO_2-TiO_2	phenol	140 °C, p(air) 3.5 MPa	TOC, 77%	Yang *et al.* 2008a
CuO	epoxy acrylate containing wastewater	250 °C, p(O_2) 3.5 MPa	COD, 77%	Yang *et al.* 2010
Cu-Al-O	ammonia	230 °C, p(air) 2.0 MPa	ammonia, 50%	Kaewpuang-Ngam *et al.* 2002
Cu/Al_2O_3	phenol	150 °C, p(air) 2.0 MPa	phenol, 100%	Kim & Ihm 2005
Mn/Ce	high-strength alcohol-distillery liquors	240 °C, p(O_2) 1.5 MPa	TOC, 75%	Belkacemi *et al.* 2000
Mn/Ce	formaldehyde containing wastewater	200 °C, p(O_2) 1.5 MPa	TOC, 92%	Silva *et al.* 2003
Ag/Al_2O_3-ZrO_2	p-cresol	160 °C, p(O_2) 1.5 MPa	p-cresol, 96%	Núñez *et al.* 2011
Pt/CeO_2	acetic acid	200 °C, p(O_2) 2.0 MPa	mineralization, 90%	Mikulová *et al.* 2007c
Pt/$Ce_{0.9}Zr_{0.1}O_2$	succinic acid	190 °C, p(air) 5.0 MPa	succinic acid, 100%	Yang *et al.* 2015
Ru/CeO_2	aniline	200 °C, p(O_2) 2.0 MPa	aniline, 100%	Barbier *et al.* 2005
Ru/Ce-Ti	p-hydroxybenzoic acid	140 °C, p(air) 5.0 MPa	p-hydrobenzoic acid, 99%	Triki *et al.* 2009
Ru/TiO_2	formic acid	110 °C, p(O_2) 1.0 Mpa	TOC, 100%	Pintar *et al.* 2008
Ru/ZrO_2	olive oil mill wastewater	190 °C, p(air) 7.0 MPa	TOC, 31%	Minh *et al.* 2008
RuPd/CeO_2	ammonia	200 °C, p(O_2) 2.0 MPa	N_2 yield, 70%	Barbier *et al.* 2002

Generally, copper catalysts have performed with high activity in heterogeneous CWAO but according to several studies leaching of Cu during oxidation experiments was partly responsible for the catalyst's efficiency (Posada *et al.* 2006, Hung 2009, Kim *et al.* 2009). Several attempts have been investigated to avoid the leaching of copper during CWAO. For example, Arena *et al* (2003) prepared a $CuCeO_x$ catalyst by the co-precipitation method. The leaching of Cu during CWAO was lower than with commercial $CuZnAlO_x$ but the prepared catalyst showed poor activity. Instead the sol-gel method prepared with a $Ce_{1-x}Cu_xO_{2-\delta}$ catalyst performed with higher activity and selectivity in CWAO of phenol. The dispersion of the copper oxide phase to the ceria oxide prevented the leaching of Cu effectively. (Hocevar *et al.* 2000).

Ceria-based materials have been widely studied in CWAO due to their oxygen storage and mobility properties. These special characteristics of ceria enable the formation of oxygen defect sites in the ceria lattice which promotes the production of active radicals i.e. enhance the oxidation reaction (Trovatelli 1996). Pure CeO_2 has shown good performance for example in CWAO of phenol (Lina *et al.* 2002) and wastewaters from the pulp and paper industry and landfill leachates (Goi *et al.* 2006). The introduction of transition metals into the lattice of ceria was observed to improve oxygen storage, release and mobility and also the redox properties, surface area and thermal stability of the material (Larachi *et al.* 2002). Different amounts of Mn, Cu, Ti and Zr incorporated into CeO_2 has resulted in higher abatement of phenol (Hocevar *et al.* 2000, Chen *et al.* 2001, Yang *et al.* 2008a), 2-chlorophenol (Li *et al.* 2007), acetic acid (Yang *et al.* 2006) and organic concentration from coking wastewater (Han *et al.* 2009) compared with pure cerium oxide. Moreover, when ceria is used as a support observations have shown it to affect the dispersion of the active metal whilst improving the reduction and oxidation of the supported metal (Trovatelli 1996).

However, most metal and mixed metal oxides are used as catalysts' supports in noble metal catalysts. The main purpose of the support is to enable the thorough dispersion of an active metal onto the large surface area possessing carrier. Supports can also prevent the sintering of an active metal and improve the catalysts' hydrolytic, thermal and chemical stability or other desired properties. (Matatov-Meytal & Sheintuch 1998).

3.2.2 Noble metal catalysts

Noble metals such as Pt, Ru, Pd, Ir and Ag have been shown to possess the highest activity in CWAO and no leaching of the active metal has been observed (Cybulski 2007). However, the deactivating of precious metal catalysts has occurred due to coking and also poisoning by sulphur, halogen and phosphorus containing compounds (Matatov-Meytal & Sheintuch 1998). The durability of a noble metal catalyst can be improved by the appropriate choice of support.

Typically, alkaline- and alkaline-earth metals are known to be suitable for this purpose. (Cybulski 2007).

The metal content in precious metal catalysts is typically 0.1–5% while CeO_2, ZrO_2, TiO_2, Al_2O_3 or related mixed oxides and carbon materials are used as supports in catalysts (Cybulski 2007). Supported noble metal catalysts have been studied in the oxidation of several model compounds such as phenol and other aromatic compounds, carboxylic acids, aliphatic compounds and wastewaters (Table 2). Typically, precious metal catalysts are more effective than pure metal or metal oxides due to their ability to oxidize refractory compounds such as acetic acid (Levec & Pintar 2007). Especially Ru and Pt supported on CeO_2 and Ce-Zr mixed oxides have been observed to be very active in CWAO of acetic acid (Mikulová *et al.* 2007b, Mikulová *et al.* 2007c, Wang *et al.* 2008).

3.2.3 Carbon materials

Carbon materials such as activated carbon (AC), graphite, carbon nanotubes (CNT) and carbon nanowires (CNW) are widely used as supports in wet air oxidation catalysts (Kim & Ihm 2011). They can be also used as pure catalysts in liquid phase oxidation due to their electronic properties which range from a semiconductor to an insulator. The most studied carbon material, AC, is a relatively cheap material compared to metal oxides or noble metal catalysts and it does not have the leaching problem. Moreover, AC can be used over a wide pH range due to its stability in various reaction conditions and its large surface area enables the high adsorption of organic molecules. (Stüber *et al.* 2005). Studies on the CWAO of model compounds and industrial wastewaters over carbon materials are described in Table 3.

Table 3. Carbon materials as catalysts and their supports in CWAO.

Catalyst	Treated effluent	Reaction conditions	Removal efficiency	Reference
AC[a]	phenol	160 °C, $p(O_2)$ 1.6 MPa	phenol, 70%	Cordero *et al.* 2008
CX[b]	aniline	200 °C, $p(O_2)$ 0.69 MPa	aniline, 100%	Gomes *et al.* 2008
MWCNT[c]	phenol	160 °C, $p(O_2)$ 2.0 MPa	phenol, 100%	Yang *et al.* 2008b
Cu/ACF[d]	ammonia	190 °C, $p(O_2)$ 3.0 MPa	ammonia, 95%	Hung 2009
Pt/AC	phenol	200 °C, $p(O_2)$ 0.42 MPa	phenol, 100%	Cao *et al.* 2003
Ru/AC	resin effluent	200 °C, $p(O_2)$ 1.5 MPa	COD, 92%	Liu *et al.* 2010
Ru/MWCNT	aniline	200 °C, p(air) 5.0 MPa	aniline, 100%	Garcia *et al.* 2006

[a]AC: activated carbon, [b]CX: carbon xerogel, [c]MWCNT multi-walled carbon nanotube, [d]ACF: activated carbon fiber

However, exposing AC to oxygen can cause a loss in material due to the combustion of carbon even at reaction conditions of CWAO (Fortuny *et al.* 1998). Furthermore, a decrease in the surface area of micropores and deposits of carbonaceous species on the surface of activated carbons have been reported to affect the deactivation of catalysts (Cordero *et al.* 2008).

Chemical or physical activation of carbon materials has been observed to improve the catalytic activity of these materials. In the study of Yang *et al.* (2008b) multi-walled carbon nanotubes were chemically modified by acidic treatment. The chemical modification of MWCNT was assumed to lead to a higher concentration of functional groups in the catalyst whilst the treated MWCNT performed high activity and stability after several runs. Carbon xerogel (CX) was activated physically by gas phase treatment to increase the amount of oxygen functional groups (Gomes *et al.* 2008). It was observed that physically treated CX has a higher mesoporous surface area than with commercial AC which was assumed to affect the catalytic activity of the sample.

3.2.4 Reaction mechanisms of heterogeneous CWAO

The reaction mechanism of heterogeneous CWAO differs from those proposed to non-catalytic and homogenous WAO due to the oxidation reaction occurring on the surface of the catalyst. The most used surface catalysis models in CWAO are the Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) adsorption models in which one reactant (ER) or all reactants (LHHW) adsorb on the surface and react. (Bhargava *et al.* 2006). The schematic description of heterogeneous CWAO based on the LHHW model is presented in Fig. 4.

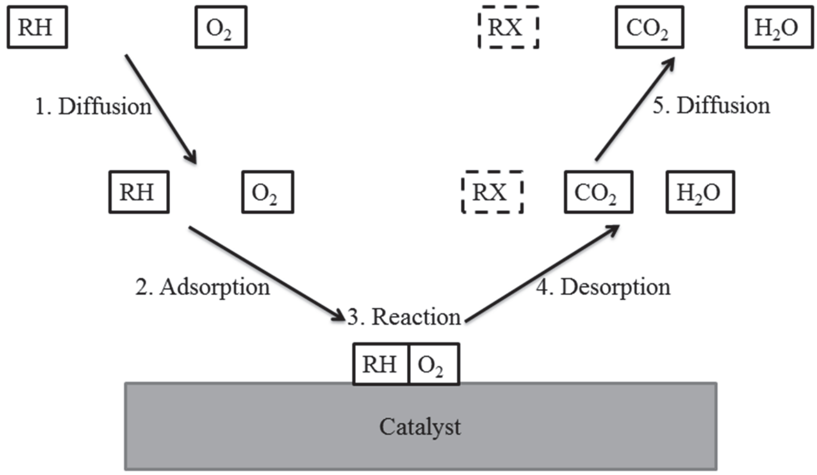

Fig. 4. Reaction pathway of heterogeneous CWAO (Mikulová 2007, Arena *et al.* 2010).

In the first step oxygen diffuses from a gaseous to a liquid phase while the solid organic material transfers to the liquid phase. Next the reactants absorb on to the surface of the catalyst where the oxidation reaction happens. In the fourth step the formed products i.e. intermediates, CO_2 and H_2O desorb by reoxidizing the catalyst's surface. Finally, CO_2 diffuses to the gaseous phase (Mikulová 2007, Arena *et al.* 2010).

Heterogeneous catalysts can initiate free radicals in the same way as was previously described in Chapter 3.1.1 in homogeneous catalysis (Equations (11)–(13)). The redox potential of the catalyst metal is an important factor affecting the oxidation efficiency (Kim & Ihm 2011). Typically, a low redox potential enhances the radical-chain initiation and propagation (Arena *et al.* 2010). Moreover, the catalyst is also able to transfer an oxygen atom to aqueous reactant molecules through complexation and activation (Cavani & Trifiro 1997). The CWAO of organic compounds may begin either by the activation of oxygen or reactant molecules while either lattice or chemisorbed oxygen may participate in the oxidation reaction. Therefore, the solid catalyst improves the oxidation reaction due to the formation of the ionic environment. (Kim & Ihm 2011). For CWAO of organic compounds both homolytic (free radical) (Sadana & Katzer 1974, Sadana 1979) and heterolytic (ionic) (Arena *et al.* 2007) reaction mechanisms have been observed.

The reaction conditions and treated effluent affect the reaction mechanism of CWAO. Typically, several reaction pathways may occur and one can dominate the oxidation reaction. If the catalyst has high activity, a heterolytic reaction mechanism will predominate in the oxidation reaction. On the contrary, for the catalyst with low activity the CWAO undergoes through a free radical mechanism while a higher concentration of catalyst may cause a longer induction time. Moreover, the interaction between catalyst and free radicals may lead to a lower oxidation rate due to the chain termination. This phenomenon could explain the lower removal of treated effluent over some catalysts compared to a non-catalytic reaction. (Kim & Ihm 2011).

4 Wet peroxide oxidation

In wet peroxide oxidation (WPO) liquid hydrogen peroxide is used to decompose organic compounds from wastewaters in the form of a two-step process (compared to a three phase WAO. The homogeneous catalytic WPO is adopted from the classical Fenton's reaction but it operates at a temperature range of 20–140 °C i.e. a higher oxidation efficiency can be achieved (Debellefontaine *et al.* 1996). In the catalyzed WPO reaction metallic ion, typically Fe^{2+} or Cu^{+} is decomposed by H_2O_2 generating hydroxyl radicals (Perathoner & Centi 2005):

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + HO^{-} + HO^{\cdot} \qquad (14)$$

The formed hydroxyl radical can further oxidize organic compounds as was depicted in WAO (Equation (2)). However, homogeneous WPO has its disadvantages such as limitations in the operation pH and difficulty in recycling the catalyst. Therefore, WPO research has nowadays focused more on the heterogeneous catalysis and especially on the supported transition metals which can operate in a wide pH range (Melero *et al.* 2009). Nevertheless, as observed from Equation (14), the transition metal (Fe or Cu) has to be in the reduced form for the decomposition of hydrogen peroxide to hydroxyl radical. The stabilization of iron or copper ions has been performed by dispersion of metals on a suitable support (Tu *et al.* 2012, Messele *et al.* 2014) or by attaching them to microporous materials such as zeolites (Fajerwerg & Debellefontaine 1996, Centi *et al.* 2000). Moreover, different iron materials such as Al-Fe pillared clays (Barrault *et al.* 2000), Fe-exchanged pillared beidellite (Catrinescu *et al.* 2003) and Fe-exchanged Y zeolite (Neamţu *et al.* 2004) have been used in WPO systems.

The decomposition of hydrogen peroxide can occur also on the surface of carbon materials through an electron transfer similar to the Fenton mechanisms (Gomes *et al.* 2010), hence activated carbon (Dehkordi & Ebrahimi 2009, Domínguez *et al.* 2013), graphite, carbon black (Domínguez *et al.* 2014) and other carbon based materials (Tu *et al.* 2012) have been widely studied in WPO. Moreover, the surface properties of carbon materials can be easily modified by proper chemical and physical treatments which make them very suitable catalytic materials for a wide range of reaction conditions (Gomes *et al.* 2011, Messele *et al.* 2014).

5 Materials and methods

5.1 Water samples

Water samples studied in this research were wastewater originating from the Finnish surface plating industry (Paper II) and an aqueous solution of bisphenol A (Papers III and IV).

5.1.1 Surface plating industry wastewater

The slightly basic (pH ~ 9), light blue surface plating industry wastewater sample contained large amount of organic compounds (Fig. 5). Through water sample analysis, these were mainly short chain alcohols but also small amounts of toxic solvents such as dichloromethane, trichloroethane and xylenes were detected. Due to the high organic concentration (COD ~ 5000 mg L^{-1}) and toxic compounds the wastewater sample was treated as a hazardous waste. Thus, CWAO was studied as an alternative treatment method for the sample (Paper II).

Fig. 5. Surface plating industry wastewater sample before treatment.

5.1.2 Aqueous solution of bisphenol A

Bisphenol A (BPA; 4,4'-(propane-2,2-diyl)diphenol) (Fig. 6) is used in the production of epoxy resins and plastic materials. Unfortunately, BPA can be discharge to the environment via manufacturing, use and from landfills, and so the exposure to the chemical is rather widely recognized. (Rubin 2011).

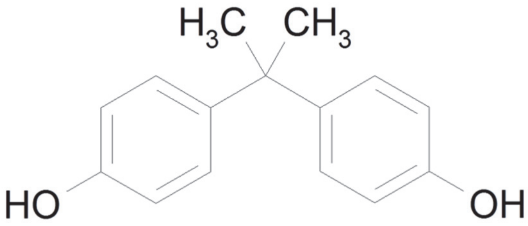

Fig. 6. Bisphenol A, 4,4’-(propane-2,2-diyl)diphenol.

The US Environmental Agency (EPA) has regarded BPA as an endocrine disrupting chemical which has caused negative health effects to animals and possibly to humans (Keri *et al.* 2007). BPA has been reported to imitate the structure and function of the estradiol hormone by binding and activating the same estrogen receptor as the natural hormone (Okada *et al.* 2008). Due to the harmful health effects of BPA an efficient treatment method for the removal of it is essential before discharging to the environment. Conventional biological treatment has been reported to decrease the BPA concentration in wastewater (Jiang *et al.* 2005, Qiang *et al.* 2013), however, the adsorption of BPA into the activated sludge may cause further problems in the sludge treatment (Clara *et al.* 2004). Therefore, other wastewater treatment techniques are needed for the removal of BPA. In this research, CWAO is studied as a one alternative for the treatment of BPA in water (Papers III and IV).

5.2 Analysis of water samples

The organic concentration of surface plating industry wastewater (Paper II) was analysed by TOC (total organic carbon), COD (chemical oxygen demand) and BOD (biological oxygen demand). The BPA content was determined by measuring the absorbance of samples by using UV-Vis spectrophotometer (Papers III and IV). The dissolved oxygen concentration and pH were determined by a Hach Lange HQ40D portable meter by using LDO and pH probes. Furthermore, possible leaching of the catalyst’s metals of both water samples were also determined. Detailed descriptions of analysing methods are shown in the next Chapters.

5.2.1 Chemical oxygen demand (COD)

Chemical oxygen demand (COD) defines the amount of an oxidant which reacts with oxidable compounds of a water sample under controlled conditions (APHA 2012). For surface plating industry wastewater samples (Paper II), COD was determined according to Standard Method 5220D: Closed Reflux, Colorimetric Method using Hach Lange cuvette tests (APHA 2012). In method 5220D, the dichromate ion ($Cr_2O_7^{2-}$) oxidized at acidic conditions both in inorganic and organic matter of the water sample while at the same time chromium is reduced from Cr^{6+} to Cr^{3+} state. The green coloration of the Cr^{3+} was measured by a Hach Lange DR 2800 spectrometer at a wavelength of 605 nm. (APHA 2012).

5.2.2 Biochemical oxygen demand (BOD)

Biochemical oxygen demand (BOD) describes the amount of molecular oxygen consumed during a specified time period for the biodegradation of organic matter (APHA 2012). For surface plating industry wastewater (Paper II) BOD was determined according to OECD guideline 301 F: Manometric respirometry test, using a WTW Manometric BOD OxiTop® instrument (OECD 1992). In the 301 F test the consumption of oxygen by micro-organisms of the sample is determined by measuring the pressure change in the closed bottle. BOD OxiTop® instrument calculates the BOD value in [mg L^{-1}] using the modified ideal gas law for closed bottle conditions. For surface plating industry wastewater BOD_7 and BOD_{28} were measured.

Degree of biodegradability

The degree of biodegradability for organic compounds in water sample can be calculated if the BOD and carbon content of the sample are known. The inorganic carbon content of the surface plating industry wastewater was negligible thus carbon concentration was assumed to be the same as TOC of the sample (Paper II). The theoretical oxygen demand (ThOD) for the surface plating industry wastewater was calculated by using Equation (15) in which c(C) is the TOC of the wastewater sample and $M(O_2)$ and M(C) are the molecular weights of oxygen and carbon respectively.

$$ThOD = c(C)\frac{M(O_2)}{M(C)} \tag{15}$$

The degree of biodegradability for organic compounds in surface plating industry wastewater was further determined according to Equation (16):

$$Degree\ of\ biodegradation\ [\%] = \frac{BOD}{ThOD} 100\% \tag{16}$$

5.2.3 Total organic carbon (TOC)

Total organic carbon (TOC) in water and wastewater is composed of a variety of organic compounds. Comparing to BOD and COD, TOC is a more convenient and direct expression of total organic content because the unit of the TOC value is [mg C L^{-1}] while measuring BOD and COD uses the unit of [mg O_2 L^{-1}]. TOC is independent on the oxidation states of the organic matter and so does not measure other organically bound elements, such as hydrogen and nitrogen, and other inorganics which can participate to the oxygen demand measurement by BOD and COD. (APHA 2012).

The TOC of wastewater (Paper II) and bisphenol A aqueous solution (Papers III and IV) was measured by a Sievers 900 Portable TOC analyser using the Standard Method 5310C, Persulfate-Ultraviolet Oxidation Method. In this method, the organic carbon is oxidized to CO_2 by persulfate in the presence of ultraviolet light (APHA 2012). In the Sievers 900 Portable instrument, formed CO_2 is determined by measuring the electrical conductivity while TOC of the sample is calculated automatically (GE Water & Process Technologies Analytical Instruments 2006).

5.2.4 Analysis of bisphenol A

Bisphenol A concentration (Papers III and IV) was determined by using an UV-Vis spectrophotometer (Shimadzu, model UV-1800) to measure the absorbance of water samples at a UV wavelength of 276 nm. The BPA concentration was calculated by applying the absorbance to the calibration curve within the 0–30 mg L^{-1} BPA range.

5.2.5 Metal content measurement

The possible leaching of catalysts' metals was determined from water samples after CWAO by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 5300 DV ICP-OES instrument.

5.3 Catalysts

In this study, 15 different laboratory prepared cerium based catalysts and two commercial ones, namely activated carbon and CeO_2 (supplied by Merck and Sigma Aldrich respectively), were used in the removal of organic compounds from surface plating industry wastewater and in the abatement of bisphenol A. Ag, Pt and Ru were used as active metals in the catalysts. Table 4 lists the studied supports and catalysts.

Table 4. Studied supports and catalysts.

Sample	Studied in
Activated carbon[a]	WW (Paper II)
CeO_2[a]	BPA (Paper III)
CeO_2	BPA (Paper IV)
$Ce_{0.8}Ti_{0.2}O_2$	BPA (Paper IV)
$Ce_{0.2}Ti_{0.8}O_2$	BPA (Paper IV)
$Ce_{0.85}Zr_{0.15}O_2$[b]	WW (Paper II)
$Ce_{0.2}Zr_{0.8}O_2$[b]	WW (Paper II)
$Ce_{0.85}Zr_{0.15}O_2$[c]	BPA (Paper III)
$Ce_{0.2}Zr_{0.8}O_2$[c]	BPA (Paper III)
Ag/CeO_2w[d]	BPA (Paper III)
$Ag/Ce_{0.85}Zr_{0.15}O_2w$[d]	BPA (Paper III)
$Ag/Ce_{0.2}Zr_{0.8}O_2w$[d]	BPA (Paper III)
$Ag/Ce_{0.85}Zr_{0.15}O_2c$[e]	BPA (Paper III)
$Ag/Ce_{0.2}Zr_{0.8}O_2c$[d]	BPA (Paper III)
Pt/CeO_2	BPA (Paper IV)
$Pt/Ce_{0.8}Ti_{0.2}O_2$	BPA (Paper IV)
$Pt/Ce_{0.2}Ti_{0.8}O_2$	BPA (Paper IV)
$Ru/Ce_{0.85}Zr_{0.15}O_2$	WW (Paper II)
$Ru/Ce_{0.2}Zr_{0.8}O_2$	WW (Paper II)

ww: wastewater, BPA: bisphenol A, [a]commercial catalyst, [b]support for Ru, [c]support for Ag, [d]prepared by wet impregnation, [e]prepared by complexation

5.3.1 *Preparation methods*

Cerium oxide (Paper IV), cerium zirconium (Papers II and III) and cerium titanium (Paper IV) mixed oxides were prepared by the sol-gel method. Detailed descriptions of supports preparation techniques are depicted in Papers III ($Ce_{0.85}Zr_{0.15}O_2$, $Ce_{0.2}Zr_{0.8}O_2$) and IV (CeO_2, $Ce_{0.8}Ti_{0.2}O_2$, $Ce_{0.2}Ti_{0.8}O_2$). Active metals were loaded to supports via wet impregnation and complexation (only Ag). The target metal contents were 1.25 wt% for Ru and 2.5 wt% for Ag and Pt. The impregnation methods of metals are descripted in Ref. (Heponiemi *et al.* 2009) for Ru and in Papers III and IV for Ag and Pt respectively.

5.4 Catalysts characterization techniques

In this study, several techniques were used for the characterization of catalysts. Metal content, specific surface area and X-ray diffraction were examined before and after CWAO for all catalysts. Moreover, field emission scanning electron microscopy were used for the characterization of fresh catalysts and used activated carbon while fresh Ag and Pt catalysts were studied also by X-ray photoelectron spectroscopy.

5.4.1 Inductively coupled plasma optical emission spectroscopy

The metal content of fresh and used catalysts was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 5300 DV ICP-OES instrument. The decomposition of Pt, Ru, Ce, Zr and Ti containing catalysts was performed via acidic digestion in a sand bath while Ag was determined after pre-treatment the catalysts with NH_4OH solution.

5.4.2 Physisorption

The specific surface areas and pore sizes of catalysts were determined from nitrogen adsorption-desorption at liquid nitrogen temperature (-196 °C) performed on a Micromeritics ASAP 2020 analyser. The surface areas were calculated by applying the Brunauer, Emmett and Teller (BET) theory to the data obtained from relative adsorbate pressures p/p_0. Pore sizes (Papers III and IV) were determined as a N_2 adsorption average pore width.

5.4.3 X-ray diffraction

The phase composition and average crystallite sizes of catalysts were determined from X-ray powder diffraction (XRD) analysis performed on a Siemens D5000 powder diffractometer (Paper II) and PANalytical X-Pert Pro X-ray diffraction equipment (Papers III and IV). CuKα1 radiation at a wavelength 0.15406 nm was used as an X-ray radiation source and diffractograms were collected at 2θ range 20–90°. Crystalline phases of catalysts were identified by comparison with a Powder Diffraction File (PDF) database supplied by International Centre for Diffraction Data (ICDD) (International Centre for Diffraction Data 2013). The average crystallite sizes (D) of catalysts were calculated from the Scherrer equation,

$$D = \frac{K\lambda_{K\alpha}}{\beta_c cos\theta} \tag{17}$$

in which K = 0.9, βc = full width high medium and θ = Bragg's angle for the considered peak.

5.4.4 Field emission scanning electron microscopy

Zeiss ULTRA plus field emission scanning emission microscope (FESEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) was used for the morphology analysis of catalysts. Before analysis catalysts were coaled in order to avoid the accumulation of charge.

5.4.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to study the chemical state of the catalyst's metals (Papers III and IV). Analysis were performed with an ESCALAB 250Xi (Thermo Fisher Scientific) spectrometer using monochromatic Al Kα radiation (1486.7 eV) operating at 20 mA and 15 kV. Charge compensation was used to acquire the desired spectra and binding energies (BE) were calibrated by applying the carbon 1s line at 284.6 eV as a reference (Paper III). For Pt catalysts (Paper IV) Ce 3d u´´´ peak at 916.7 eV was used for the charge compensation due to the charging of samples during XPS measurement. Furthermore, CasaXPS processing software was used for the spectral analysis.

5.5 Wet air oxidation studies

Two different reactor systems were used for wet air oxidation experiments (Fig. 7). For surface plating industry wastewater (Paper II) WAO studies were carried out in a 0.5 L stainless steel batch reactor (Fig. 7b) at temperatures of 130 °C and 150 °C for 2 h. In the beginning of the experiment, 0.28 L of treated effluent and 4 g L^{-1} of catalyst ($Ru/Ce_{0.85}Zr_{0.15}O_2$, $Ru/Ce_{0.2}Zr_{0.8}O_2$ or AC) were introduced to the reactor. While the desired reaction temperature was reached, the reaction was activated with the addition of air at a pressure of 0.6 MPa. At appropriate time intervals, water samples were taken from the reactor.

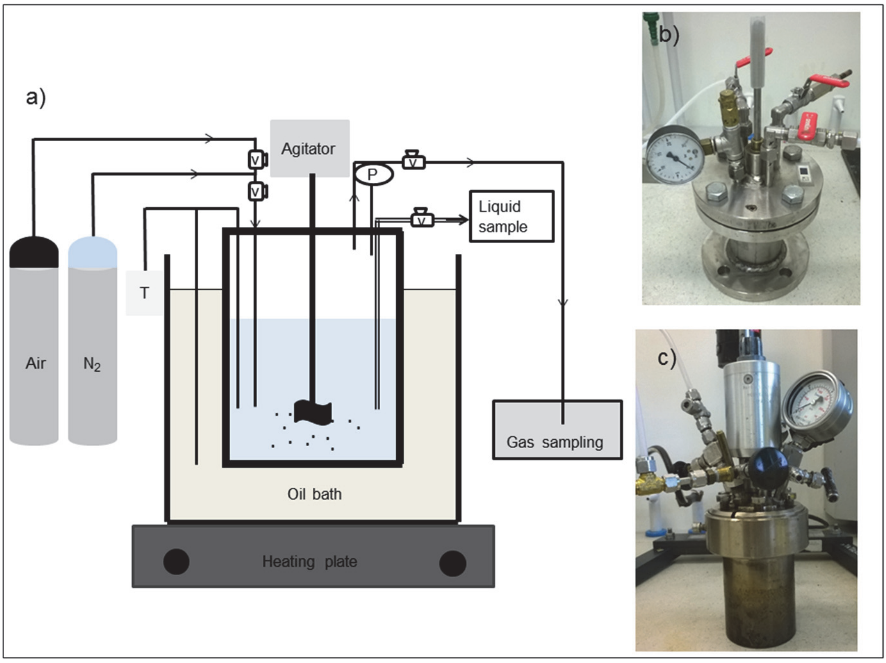

Fig. 7. A schematic description of the catalytic wet air oxidation reactor system (a), batch type reactor used in CWAO of surface plating industry wastewater, Paper II (b) and CWAO of BPA, Papers III and IV (c).

CWAO experiments with BPA (Papers III and IV) were performed in a 0.3 L stainless steel reactor (Fig. 7c). In this reactor system higher operating pressures than in a 0.5 L reactor can be achieved. BPA (60 mg L^{-1}) oxidations were conducted at a reaction temperature of 160 °C and at an air pressure of 2.0 MPa with 4 g L^{-1} concentration of Pt and Ag catalysts for 3 h. The oxidation efficiency was followed by taken water samples from the reactor at appropriate time intervals.

5.6 Wet peroxide oxidation studies

Wet peroxide oxidation experiments with surface plating industry wastewater (Paper II) were performed at atmospheric pressure in a 1.0 L three-necked flask connected to a reflux condenser (Fig. 8). At the reaction temperature of 100 °C, 0.28 L of wastewater was oxidized with 30 wt% H_2O_2 in the presence of Ru or AC catalyst (4 g L^{-1}) for 2–3 h. The stoichiometric amount of hydrogen peroxide for wastewater with unknown composition was evaluated according to the following reaction:

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \qquad (18)$$

Following the stoichiometry of the reaction, 5.6 mass ratio of H_2O_2 was needed for complete mineralization of the organic carbon. However, the wastewater sample typically contains also oxidable inorganic compounds and thus H_2O_2 was added in excess. In the experiments hydrogen peroxide was introduced to the reaction in batches in order to achieve a total concentration of 50 g L^{-1}. During experiments water samples were taken from the reactor.

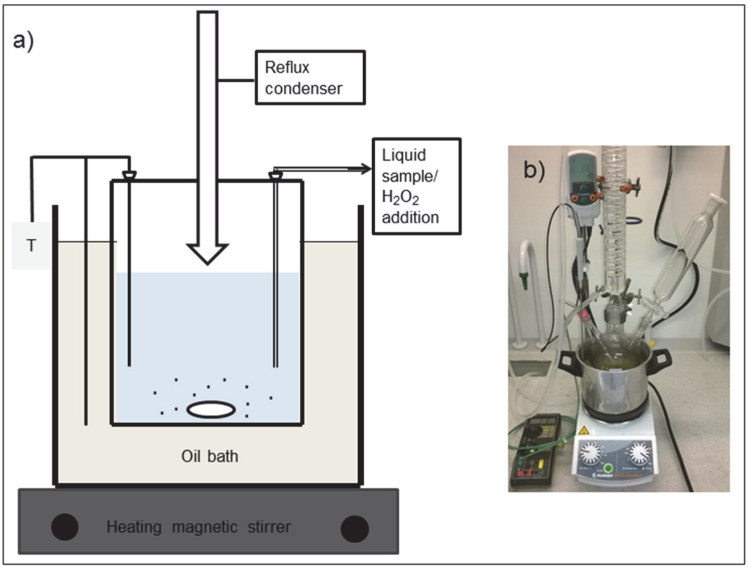

Fig. 8. A schematic description of the catalytic wet peroxide oxidation system (a) and the reactor set-up of CWPO for surface plating industry wastewater (b) (Paper II).

6 Results and discussion

6.1 Characterization of catalysts

6.1.1 Specific surface area and X-ray diffractogram

Specific surface areas, crystallite sizes and pore widths of studied catalysts are shown in Table 5 in which it can be seen that sol-gel prepared CeO_2 had advantages over Sigma Aldrich supplied cerium oxide.

Table 5. Specific surface area, average pore width and crystallite size of Ru, Pt and Ag catalysts.

Sample	Specific surface area [m^2 g^{-1}]	Pore width [nm]	Crystallite size [nm]
Activated carbon[a]	580	n.d.	-
CeO_2[a]	31	16	43
CeO_2	98	12	9.2
$Ce_{0.8}Ti_{0.2}O_2$	96	7.5	8.1
$Ce_{0.2}Ti_{0.8}O_2$	194	3.6	n.d.
$Ce_{0.85}Zr_{0.15}O_2$[b]	89	n.d.	7.1
$Ce_{0.2}Zr_{0.8}O_2$[b]	47	n.d.	14
$Ce_{0.85}Zr_{0.15}O_2$[c]	65	16	10
$Ce_{0.2}Zr_{0.8}O_2$[c]	34	12	7.6
Ag/CeO_2w[d]	12	35	58
Ag/$Ce_{0.85}Zr_{0.15}O_2$w[d]	45	21	14
Ag/$Ce_{0.85}Zr_{0.15}O_2$c[e]	29	32	16
Ag/$Ce_{0.2}Zr_{0.8}O_2$w[d]	18	18	8.2
Ag/$Ce_{0.2}Zr_{0.8}O_2$c[e]	18	17	8.3
Pt/CeO_2	91	13	9.1
Pt/$Ce_{0.8}Ti_{0.2}O_2$	83	7.8	8.2
Pt/$Ce_{0.2}Ti_{0.8}O_2$	137	4.4	n.d.
Ru/$Ce_{0.85}Zr_{0.15}O_2$	65/54[f]	n.d.	6.3
Ru/$Ce_{0.2}Zr_{0.8}O_2$	44	n.d.	15

n.d.: not determined, [a]commercial catalyst, [b]support for Ru, [c]support for Ag, [d]prepared by wet impregnation, [e]prepared by complexation, [f]different batches

The specific surface area of laboratory prepared CeO_2 was over three times higher than in commercial one due to the smaller crystallite size of sol-gel prepared oxide. However, according to X-ray diffractograms of cerium oxides (Fig. 1 in Paper III and Fig. 2 in Paper IV) both samples showed the typical face-centered cubic structure of CeO_2 (JCPDS: 01-081-0792) (International Centre for Diffraction Data 2013).

The Ce-Zr mixed oxides had been prepared in different batches which could explain the higher surface areas of carriers used in Paper II. Due to the overlapping of cubic CeO_2 and tetragonal $Ce_{0.16}Zr_{0.84}O_2$ (JCPDS 00-03801437) (International Centre for Diffraction Data 2013) phases with a smaller crystallite size in $Ce_{0.2}Zr_{0.8}O_2$ (Paper III) could be observed than in the corresponding one used for surface plating industry wastewater oxidation (Paper II). However, the use of Scherrer equation for the broadened peaks crystallite size determination underestimations in the calculations may occur (Hori *et al.* 1998). Moreover, the crystallite size and surface area of $Ce_{0.85}Zr_{0.15}O_2$ used for wastewater oxidation were in agreement with other studies (Mikulová *et al.* 2007b, Mikulová *et al.* 2007c).

In $Ce_{0.8}Ti_{0.2}O_2$ the face-centered cubic structure of CeO_2 was still present and no peaks of Ti could be observed in the X-ray diffractogram of the sample (Fig. 2 in Paper IV), suggesting the forming of homogeneous Ce-Ti-O solid solution during sol-gel preparation. Therefore, the preparation method performed with Ce-Ti oxides, in which aqueous solutions of precursors was mixed with ethanol, appeared to be more convenient than that one used with Ce-Zr in the preparation of mixed oxides. However, in the case of $Ce_{0.2}Ti_{0.8}O_2$ a weak peak at diffraction angle of 25.5° could be attributed to anatase titania (JCPDS: 01-089-4921) (International Centre for Diffraction Data 2013) and an amorphous structure of the sample was observed in X-ray diffractogram (Fig. 2 in Paper IV). Due to the insertion of titanium ions into the cerium oxide lattice and replacement of Ce ions, CeO_2 particles tended not integrate the crystalline phase (Yang *et al.* 2006, Yang *et al.* 2008a). Moreover, the amorphous structure i.e. the distortion in ceria lattice was responsible for the large surface area of $Ce_{0.2}Ti_{0.8}O_2$ (Table 5) (Zhao *et al.* 2011).

The adding of Pt and Ru to Ce-Ti and Ce-Zr oxides decreased the specific surface areas of supports slightly. However, on the loading of Ag to the commercial CeO_2 and Ce-Zr mixed oxides a remarkable loss of surface areas, especially in Ag/CeO_2 was observed (Table 5). One explanation to this phenomenon could be the high calcination temperature of supports (650 °C) which may lead to the sintering of CeO_2. The more thermally stable structure of Ce-Zr prevented the agglomeration of mixed oxides (Mikulová *et al.* 2007a) i.e. the decrease in the surface area was not so big. Moreover, the pore widths of Ag catalysts were also notably larger than in Pt catalysts (Table 5) which support the agglomeration theory. Furthermore, in X-ray diffractograms of Pt/$Ce_{0.8}Ti_{0.2}O_2$ and Ag/$Ce_{0.2}Zr_{0.8}O_2$ the main peaks of Pt and Ag were clearly seen at diffraction angles of 39.9° and 38.1° respectively, while no peaks of Ru could be observed in the X-ray diffractogram of Ru/$Ce_{0.85}Zr_{0.15}O_2$ (Fig. 9). This could be due to the low amount of Ru (1.25 wt%) in the catalyst. Other changes in X-ray diffractograms were not detected (Fig. 9) when comparing the pure oxides.

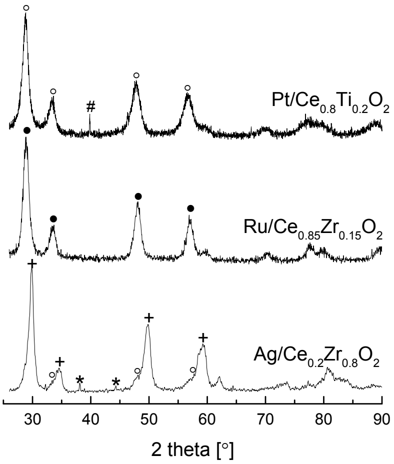

Fig. 9. X-ray diffractograms of Pt/$Ce_{0.8}Ti_{0.2}O_2$, Ru/$Ce_{0.85}Zr_{0.15}O_2$ and Ag/$Ce_{0.2}Zr_{0.8}O_2$. (°) PDF: 01-081-0792 (CeO_2); (#) PDF: 00-004-0802 (Pt); (•) PDF: 00-028-0271 ($Ce_{0.75}Zr_{0.15}O_2$); (+) PDF: 00-038-1437 ($Ce_{0.15}Zr_{0.84}O_2$); (*) PDF: 00-004-0783 (Ag).

6.1.2 FESEM and ICP-OES

The morphology and composition of catalysts' surface were investigated by FESEM-EDS. Examples of images can be seen in Fig. 10 a) and b). According to FESEM images of Ru/$Ce_{0.85}Zr_{0.15}O_2$ spherical shape particles with a diameter in the range of 10–20 μm were observed in samples (Fig. 10a). The amorphous structure detected in the X-ray diffractogram of Pt/$Ce_{0.2}Ti_{0.8}O_2$ (Fig. 2 in Paper IV) could also be seen in the FESEM image of sample (Fig 10b). The catalyst particles were characterized by an angular shape with a wide particle size distribution.

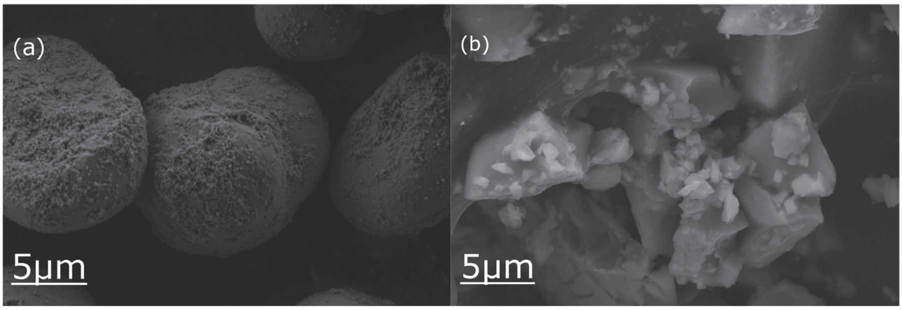

Fig. 10. FESEM images of Ru/$Ce_{0.85}Zr_{0.15}O_2$ (a) and Pt/$Ce_{0.2}Ti_{0.8}O_2$ (b).

Metal composition of catalysts was investigated both by FESEM-EDS (surface) and by ICP-OES (bulk). Examples of FESEM-EDS results are described in Table 6 and ICP-OES measurements in Table 7. In CeO_2 and Ce-Ti mixed oxides metal concentrations were in good agreement with the target values both on the surface and in the bulk of the supports, and no changes in the compositions after impregnation of active metal could be observed. However, EDS analysis of Ce-Zr mixed oxides revealed the same heterogeneity on the surface of Ce-Zr mixed oxides which was already detected in the XRD measurement (Paper III). More results from FESEM-EDS analysis are presented in Papers III and IV.

Table 6. Surface composition of Ru/$Ce_{0.85}Zr_{0.15}O_2$ and Pt/$Ce_{0.2}Ti_{0.8}O_2$ determined by FESEM-EDS.

Sample	Ce [wt%]		Zr [wt%]		Ti [wt%]		Ru [wt%]		Pt [wt%]	
	Target	EDS	Target	EDS	Target	EDS	Target	EDS	Target	EDS
Ru/$Ce_{0.85}Zr_{0.15}O_2$	72	70	8.3	10	-	-	1.25	0.5	-	-
Pt/$Ce_{0.2}Ti_{0.8}O_2$	29	28	-	-	39	37	-	-	2.5	2.2

According to ICP-OES analysis Pt content of catalysts was in good agreement with the target value, 2.5 wt%, of active metal (Table 7). However, the dispersion of Pt was not homogeneous (Table 6 in Paper IV) except in Pt/$Ce_{0.2}Ti_{0.8}O_2$, which is probably due to the larger particle size (Fig 10b) of this support. The active metal concentration in Ru catalysts was 0.6 wt% both in the bulk (Table 7) and on the surface of samples (Table 6) i.e. only half from the desired value 1.25 wt%. In the impregnation of Ru the pH of the solution was acidic. However, the precursor salt, $RuCl_3$, was Lewis acid. Thus, the exchange with Ce or Zr was impossible due to the CeO_2 and ZrO_2 isoelectric points which are near 6.7 (Terribile *et al.* 1998). Therefore, Ce and Zr were in the cationic form in the acidic solution as was Ru which could explain the low concentration of an active metal in Ru catalysts. Moreover, the rather low Ag content of silver catalysts could be explained also with the impossible exchange between support and active metal due to the acidic pH of the impregnation solution. Furthermore, the rather high calcination temperature (650 °C) of Ag catalysts and forming of volatile RuO_4 during ICP-OES analysis of Ru could also be partly responsible for the low active metal concentration in Ag and Ru catalysts.

Table 7. Concentration (wt%) of catalysts' active metals determined by ICP-OES.

Sample	Ag [wt%]	Pt [wt%]	Ru [wt%]
Ag/CeO_2w	1.5	-	-
$Ag/Ce_{0.85}Zr_{0.15}O_2w$	1.6	-	-
$Ag/Ce_{0.85}Zr_{0.15}O_2c$	1.1	-	-
$Ag/Ce_{0.2}Zr_{0.8}O_2w$	1.0	-	-
$Ag/Ce_{0.2}Zr_{0.8}O_2c$	0.9	-	-
Pt/CeO_2	-	2.2	-
$Pt/Ce_{0.8}Ti_{0.2}O_2$	-	2.2	-
$Pt/Ce_{0.2}Ti_{0.8}O_2$	-	2.4	-
$Ru/Ce_{0.85}Zr_{0.15}O_2$	-	-	0.6
$Ru/Ce_{0.2}Zr_{0.8}O_2$	-	-	0.6

6.1.3 XPS

The chemical state of the catalysts' metals was investigated by X-ray photoelectron spectroscopy (Papers III and IV). Due to the coexistence of both Ce^{4+} and Ce^{3+} Ce 3d spectra of Ag and Pt catalysts were asymmetric (Fig. 11). The main peak of Ce at around 882 eV, attributed to CeO_2 (Dauscher *et al.* 1990, Galtayries *et al.* 1998), was obvious in all samples and the oxidation state of cerium on the surface of both Ag and Pt catalysts was mainly Ce^{4+}. The addition of higher amount of Zr or Ti to the Ce lattice increased slightly the Ce^{3+} content on more Zr or Ti containing catalysts which was in agreement with other studies (Galtayries *et al.* 1998, Yang *et al.* 2006).

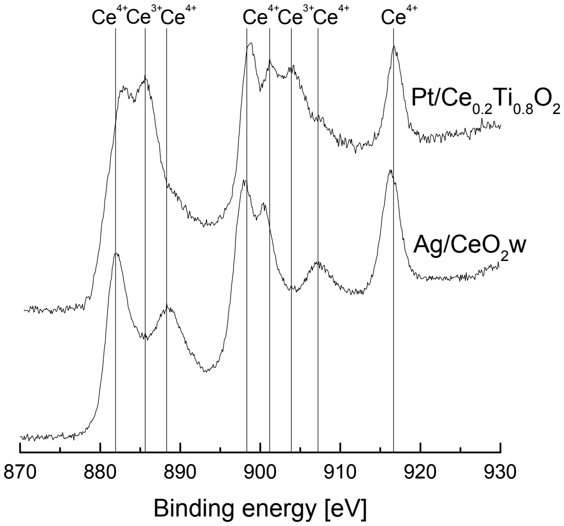

Fig. 11. XPS Ce 3d spectra of Ag/CeO_2 and $Pt/Ce_{0.2}Ti_{0.8}O_2$ catalysts.

An increase in Ce^{3+} concentration may change the chemical state of oxygen on the catalyst's surface. Therefore, the O 1s spectra of Ag and Pt catalysts were also measured. An example of O 1s spectra of Ag and Pt catalysts has been presented in Fig 12. The O 1s spectra consisted of three peaks which could be referred as the lattice oxygen (O I), chemisorbed oxygen (O II) which has been found to be the most reactive oxygen species on the catalyst's surface and oxygen of CO_3^{2-} groups (O III) (Larachi *et al.* 2002, Alifanti *et al.* 2003, Yang *et al.* 2006). The O I and O II species were present in all Ag and Pt catalysts while the oxygen specie related to carbonate groups occurred only in samples which had a strong C 1s peak i.e. CeO_2 (laboratory prepared), all Ag catalysts expect $Ag/Ce_{0.2}Zr_{0.8}O_2c$ and Pt catalysts supported on Ce-Ti mixed oxides. After fitting of O 1s spectra, slight changes in the amount of O II between different catalysts were observed but the content of lattice oxygen was higher than chemisorbed oxygen in all Ag and Pt catalysts (Table 4 in Papers III and IV). Typically, the existence of Ce^{3+} on the catalyst's surface could create vacancies and unsaturated chemical bonds which further enables the forming of chemisorbed oxygen (Yang *et al.* 2006). However, this was not in agreement with our results. One explanation could be that Ti^{4+} and Zr^{4+} with a smaller ionic radius than Ce^{4+} (0.68 Å, 0.84 Å and 0.97 Å respectively) could enter the CeO_2 lattice to substitute for Ce^{4+}. As a consequence the charge imbalance was weakened and the amount of chemisorbed oxygen decreased on the surface of Ti and Zr richer catalysts. (Lin & Yu 1998, Bozo *et al.* 2000).

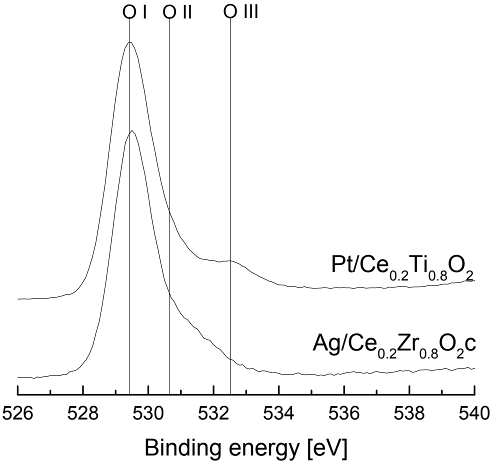

Fig. 12. XPS O 1s spectra of $Ag/Ce_{0.2}Zr_{0.8}O_2c$ and $Pt/Ce_{0.2}Ti_{0.8}O_2$.

The peaks de-convolution of XPS 3d spectra of Ag catalysts (Paper III) revealed the existence of Ag^+ at binding energies at around 368 eV and 373 eV (Gao *et al.* 2004) in all catalysts. Ag^{2+} was present at binding energies of 366 eV and 372 eV (Wang *et al.* 2012) in all Ag catalysts except $Ag/Ce_{0.2}Zr_{0.8}O_2$ prepared via complexation while Ag in its metallic form was not observed. Moreover, in the XPS analysis of Pt 4f spectra (Paper IV) Pt was mainly in the oxidized form (Pt^{2+}, Pt^{4+}) and only a small amount of Pt^0 was present on the catalysts' surfaces. Therefore, the reduction procedure performed with Ag and Pt catalysts was not effective probably due to the strong interaction between the support and active metal (Bera *et al.* 2003). Furthermore, binding energies of Zr and Ti XPS spectra were in agreement with existing literature (Galtayries *et al.* 1998, Francisco *et al.* 2001, Yang *et al.* 2006) (Papers III and IV).

6.2 Catalytic wet air and wet peroxide oxidation of wastewater

Surface plating industry wastewater was treated by CWPO and CWAO at reaction temperatures of 100 °C, 130 °C and 150 °C using 50 g L^{-1} H_2O_2 and 0.6 MPa of air as oxidizing agents (Paper II). Oxidation reactions were catalyzed by commercial AC and laboratory prepared Ru catalysts supported on Ce-Zr mixed oxides with concentration of 4 g L^{-1}. In Table 8 oxidation efficiencies has been described as a TOC removal occurred during a 2 h reaction.

Table 8. TOC removal [%] of surface plating industry wastewater after 2 h oxidation at different reaction temperatures.

Sample	100 °C [CWPO]	130 °C [CWAO]	150 °C [CWAO]
Non-catalytic	28	19	21
AC	32	42	53
$Ru/Ce_{0.85}Zr_{0.15}O_2$	33	28	39
$Ru/Ce_{0.2}Zr_{0.8}O_2$	28	22	43

In catalyzed WPO reactions only a slight improvement in the abatement of TOC after 2 h oxidation compared to non-catalytic experiment was observed (Table 8). Adsorption during the heating period was responsible for 5% (AC and $Ru/Ce_{0.2}Zr_{0.8}O_2$) and 18% ($Ru/Ce_{0.85}Zr_{0.15}O_2$) of TOC removal while no thermal decomposition of organic compounds was observed in the non-catalytic experiment. In all experiments, the H_2O_2 was added in batched in order to achieve the total concentration of 50 g L^{-1} after 90 minutes of oxidation. According to the dissolved oxygen measurements the concentration of O_2 in water samples after 2 h wet peroxide oxidation experiments were over 21 mg L^{-1} in non-catalytic and AC catalyzed reactions and between 5–8 mg L^{-1} in Ru catalyzed effluents. Therefore, the reactions continued until the basic level in the dissolved oxygen content i.e. around 8 mg L^{-1} (at 25 °C) (Karttunen 2003) was reached. These results have been presented in Paper II. However, too fast addition of H_2O_2 has been reported to affect negatively on the TOC removal in the CWPO of organic compounds (Melero *et al.* 2009) which could explain the rather low TOC abatement of catalyzed experiments. Moreover, the ICP-OES analysis of terminal water samples from Ru catalyzed WPO reactions revealed the leaching of cerium referring to the reaction of H_2O_2 and Ce. This could explain the lower dissolved oxygen content of Ce-Zr catalyzed reactions. Furthermore, the pH of terminal water samples was decreased to near five which refers to the forming of carboxylic acids during WPO reactions.

Comparing TOC removals of WPO at 100 °C and WAO at 130 °C (Table 8) higher reaction temperature only improved the TOC abatement in the AC catalyzed reaction which was probably due to excess oxygen available in WPO reactions. However, at 130 °C almost 30% of TOC removal had occurred during the heating period due to the absorption of organics on AC. Considering TOC removals of WAO after 2 h experiments increasing the reaction temperature from 130 °C to 150 °C higher abatement of organics was observed both in non-catalytic and catalytic runs. Nevertheless, at 150 °C adsorption was responsible for 41%, 86% and 87% of TOC abatement in Ru/$Ce_{0.85}Zr_{0.15}O_2$, Ru/$Ce_{0.2}Zr_{0.8}O_2$ and AC catalyzed reactions respectively. Table 9 describes the active surface areas of catalysts i.e. the part of the catalyst's surface in which the oxidation reaction takes place in each reaction temperatures.

Table 9. Active surface areas of Ru and activated carbon catalysts at different reaction temperatures.

Sample	Adsorption during heating [%]			Active surface area [m^2 g^{-1}]		
	100 °C	130 °C	150 °C	100 °C	130 °C	150 °C
AC	5.0	32	46	29	187	269
Ru/$Ce_{0.85}Zr_{0.15}O_2$	19	6.9	16	12	3.7	11
Ru/$Ce_{0.2}Zr_{0.8}O_2$	5.0	12	37	2.2	5.2	16

Considering the active surface areas of catalysts, Ru/$Ce_{0.2}Zr_{0.8}O_2$ was the most active catalyst at 100 °C and Ru/$Ce_{0.85}Zr_{0.15}O_2$ at both CWAO reactions (Table 9). AC with it high specific surface area (Table 5) performed rather poorly for its catalytic activity although the highest TOC removal, 53%, was achieved with this sample at 150 °C (Table 8). According to post characterization of samples, Ru/$Ce_{0.2}Zr_{0.8}O_2$ was the most stable catalyst in both CWPO and CWAO. The tetragonal structure of $(Zr_{0.88}Ce_{0.12})O_2$ (International Centre for Diffraction Data 2013) was still present in all used Ru/$Ce_{0.2}Zr_{0.8}O_2$ catalysts (Fig.9a in Paper II) and no changes in the diffractograms and surface areas were observed after the reaction. On the other hand, the surface area of Ru/$Ce_{0.85}Zr_{0.15}O_2$ decreased over 40% and around 60% during CWPO and CWAO respectively. Therefore, the addition of more Zr to the Ce lattice improved the durability of the Ru catalyst (Delgado *et al.* 2012). Furthermore, in ICP-OES analysis of terminal water samples of CWAO no leaching of catalysts' metals was detected.

The degree of biodegradation of organic compounds in terminal water samples from CWAO was determined by the BOD OxiTop® method. After a seven-day measuring period the degree of biodegradations for water samples catalyzed by Ru/$Ce_{0.85}Zr_{0.15}O_2$ and AC at 150 °C were 50% and 53% respectively (Fig. 7b in Paper II). Therefore, catalytic oxidation of surface plating industry wastewater improved the removal of TOC compared to the non-catalytic experiments and also enhanced the biodegradability of organics in the treated effluent.

6.3 Catalytic wet air oxidation of bisphenol A aqueous solution

Catalytic wet oxidation experiments of aqueous solution of bisphenol A (60 mg L^{-1}) were carried out at reaction temperature of 160 °C with air pressure of 2.0 MPa. Ag supported on commercial CeO_2 and laboratory prepared Ce-Zr mixed oxides (Paper III) and Pt supported on CeO_2 and Ce-Ti mixed oxides (Paper IV) with a concentration of 4 g L^{-1} were used as catalysts in these reactions.

Table 10. BPA and TOC removal after 3 h oxidation at 160 °C and air pressure of 2.0 MPa.

Sample	BPA removal [%]	TOC removal [%]
CeO_2[a]	76	75
CeO_2	77	83
$Ce_{0.8}Ti_{0.2}O_2$	73	77
$Ce_{0.2}Ti_{0.8}O_2$	76	82
$Ce_{0.85}Zr_{0.15}O_2$	76	76
$Ce_{0.2}Zr_{0.8}O_2$	70	72
Ag/CeO_2w[a]	52	40
$Ag/Ce_{0.85}Zr_{0.15}O_2w$	76	73
$Ag/Ce_{0.85}Zr_{0.15}O_2c$	76	74
$Ag/Ce_{0.2}Zr_{0.8}O_2w$	70	64
$Ag/Ce_{0.2}Zr_{0.8}O_2c$	69	63
Pt/CeO_2	97	83
$Pt/Ce_{0.8}Ti_{0.2}O_2$	96	83
$Pt/Ce_{0.2}Ti_{0.8}O_2$	89	81

[a]commercial support

Before each catalytic runs WAO of BPA was carried out at the used reaction conditions at pH 5 (Paper III) and pH 9 (Paper IV). No removals of BPA and TOC occurred after 3 h of oxidation. Considering the catalytic oxidations, over 70% BPA and TOC removals was achieved with pure supports (Table 10). The oxidation reaction was very fast and after 90 minutes the maximum removals were almost achieved (Fig. 13).

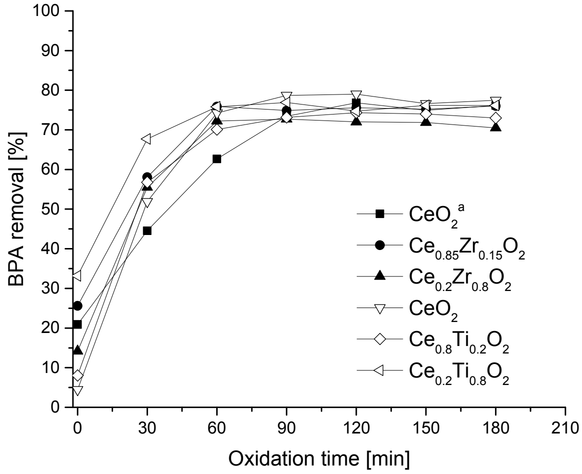

Fig. 13. Bisphenol A removal as a function of oxidation time for CeO_2, Ce-Zr and Ce-Ti mixed oxides. Temperature 160 °C, air pressure 2.0 MPa, concentration of the catalyst 4 g L^{-1}, ^{a} commercial support.

Only slight differences between carriers were observed while sol-gel prepared CeO_2 performed with the highest activity with 77% BPA abatement. The activity of CeO_2 was related to the high chemisorbed oxygen content of support (Paper IV) and rather low adsorption of BPA during the heating period. Furthermore, adsorption was responsible for a 21%, 26% and 14% decrease in BPA content in water samples with commercial CeO_2, sol-gel prepared $Ce_{0.85}Zr_{0.15}O_2$ and $Ce_{0.2}Zr_{0.8}O_2$ respectively (Fig. 13). Therefore, Zr richer support was actually the most active catalyst of that series although it expressed the lowest removal of BPA (Table 10). Moreover, $Ce_{0.2}Ti_{0.8}O_2$with its rather high surface area (194 m^2 g^{-1}) compared to other supports (Table 5) did not show any special activity in BPA abatement i.e. CWAO of BPA was not a surface area specific reaction. This same phenomenon was observed in the study of Erjavec *et al* (2013) in which CWAO of BPA was carried out with titanate nanotube-based catalysts. Furthermore, in post characterization of supports no changes in X-ray diffractograms or specific surface areas of both CeO_2, Ce-Zr mixed oxides and $Ce_{0.8}Ti_{0.2}O_2$ were detected (Papers III and IV). However, in $Ce_{0.2}Ti_{0.8}O_2$ 55% loss of specific surface area and a change in the phase structure was observed. In X-ray diffractogram of used $Ce_{0.2}Ti_{0.8}O_2$ diffraction peaks at 2θ value 25.5°, 38.1°, 48.0° and 54.4° could be attributed to anatase titania (JCPDS: 01-089-4921) (International Centre for

Diffraction Data 2013) while only weak peak at diffraction angle around 25° was observed in the fresh support (Fig. 14).

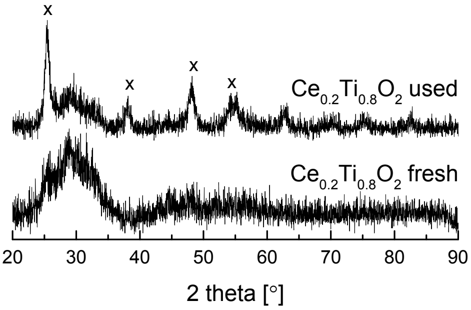

Fig. 14. X-ray diffractograms of fresh and used $Ce_{0.2}Ti_{0.8}O_2$. (x) PDF: 01-078-2486 (TiO_2).

Even with the addition of silver to Ce-Zr mixed oxides no increase in the BPA and TOC removal occurred (Table 10). The activity of Ag/CeO_2 was actually worse than with a pure support. Similar observations were made in the study of Silva *et al.* (2003) in which CWAO of formaldehyde industry was catalyzed by Ag/CeO_2. The addition of Ag to CeO_2 had a negative effect on the catalytic activity. In this study, the rather low surface area and thus large crystallite size of support (Table 5) were probably responsible for the decrease in the BPA abatement of Ag/CeO_2 compared to CeO_2. In the post characterization of Ag/Ce-Zr catalysts no changes in the specific surface areas and neither in X-ray diffractograms of used catalysts were observed. Moreover, the addition of Ag to supports decreased the adsorption of BPA during the heating period especially with Ag catalysts prepared via complexation (Fig. 15).

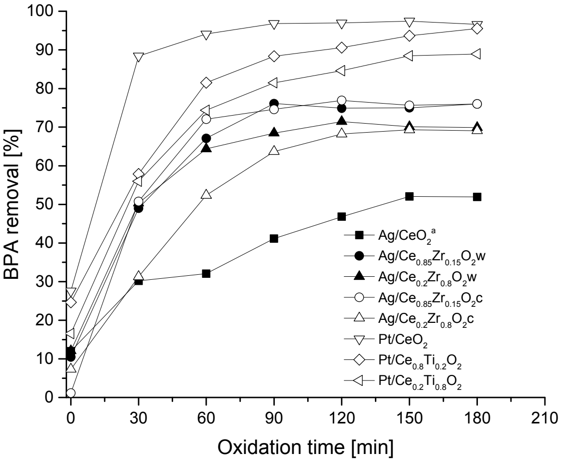

Fig. 15. Bisphenol A removal as a function of oxidation time for Ag and Pt catalysts. Temperature 160 °C, air pressure 2.0 MPa, concentration of the catalyst 4 g L^{-1}, ^{a} commercial support.

However, due to the rather low metal content (Table 7) and the leaching of silver during oxidation reactions no improvement in the abatement of BPA with Ag/Ce-Zr catalysts compared to pure supports was observed. Furthermore, according to XPS analysis of Ag 3d spectra silver was present in the oxidation state and no metallic Ag was detected which also explains the poor activity of Ag catalysts in the removal of BPA.

The addition of Pt to supports enhanced the abatement of BPA to 89% with Pt/Ce$_{0.2}$Ti$_{0.8}$O$_2$ and almost 100% with Pt/CeO$_2$ and Pt/Ce$_{0.8}$Ti$_{0.2}$O$_2$ (Table 10). However, adsorption of BPA during the heating period was responsible for quite significant amounts of removal (17–28%) with impregnated catalysts i.e. pure CeO$_2$ were catalytically slightly better than with the active metal (73% vs. 69%) (Fig. 15). Considering XPS O 1s results, the concentrations of O II species were higher in Pt catalysts than in pure supports (Paper IV). Therefore, the impregnation of Pt to CeO$_2$ and Ce-Ti mixed oxides was beneficial for the chemisorbed oxygen content. However, the higher amount of non-lattice oxygen could affect the forming of carbonaceous species during CWAO which would explain the lower removal of TOC than BPA with Pt catalysts (Table 10). It has been reported in a few studies that the high oxygen storage capacity (OSC) of a catalyst could promote the accumulation of deposits on catalysts surface in the CWAO of phenol (Keav *et al.* 2014) and acetic acid (Mikulová *et al.* 2007c).

Although it was not possible to draw direct conclusions between OSC and chemisorbed oxygen content, lower removal of TOC than BPA referred the deactivation of Pt catalysts due to the carbonaceous deposits. Moreover, the dissolving of catalysts' metals could also cause a reduction in catalyst activity but according to ICP-OES analysis of terminal water samples no leaching of Pt, Ti or Ce occurred. Furthermore, according to post characterization of Pt catalysts Pt/$Ce_{0.8}Ti_{0.2}O_2$ was the most stable catalyst in CWAO of BPA while no changes in the phase structure, specific surface area and metal content was observed.

7 Conclusions

In this thesis cerium based catalysts were studied for the removal of aqueous pollutants by CWAO and CWPO. Therefore, the first research question was related to the treatment of surface plating industry wastewater using both techniques. According to the results presented in Paper II both CWAO and CWPO were effective in the removal of organic compounds from wastewater. The highest TOC removal (53%) was achieved in AC catalyzed CWAO at 150 °C with air pressure of 0.6 MPa. However, adsorption during the heating period was responsible for quite a significant amount of TOC removal with AC. Therefore, laboratory prepared Ru catalysts performed higher catalytic activity in the treatment of surface plating industry wastewater while Ru/$Ce_{0.2}Zr_{0.8}O_2$ was the most stable catalyst in CWAO and CWPO. According to post characterization of catalysts no changes in the phase structure, specific surface area and metal content of Ru/$Ce_{0.2}Zr_{0.8}O_2$ was observed.

Due to the good performance of cerium based catalysts in CWAO of surface plating industry wastewater the second research question was: Could CWAO be an appropriate technique for the abatement of BPA from aqueous solutions? This research question was discussed in Paper III. However, due to the high-price of Ru cheaper alternative, Ag, was impregnated as an active metal to the Ce-Zr supports. The results presented in Paper III showed that in the Ce-Zr catalyzed CWAO of BPA over 70% removal of BPA was attained during 3 h of oxidation. With the addition of Ag to the Ce-Zr supports no improvement in the abatement of BPA by CWAO was detected. According to the ICP-OES results the amount of silver was low in fresh catalysts due to the too high calcination temperature (650 °C). Moreover, during the oxidation experiments leaching of Ag was detected which further decreased the concentration of the active metal and thus the activity of Ag catalysts.

The addition of silver to Ce-Zr supports did not affect the activity of catalysts in CWAO of BPA. Therefore in Paper IV the activity of Pt/Ce-Ti catalysts in CWAO of BPA was studied which then led to third research question: Could Pt/Ce-Ti catalysts perform higher activity in the removal of BPA by CWAO than Ag catalysts? The results presented in Paper IV showed that in Pt/CeO_2 and Pt/$Ce_{0.8}Ti_{0.2}O_2$ catalyzed CWAO almost 100% removal of BPA was achieved. However, as in Paper II with Ru catalysts, adsorption of BPA during the heating period was responsible for a significant part of the abatement. Therefore, a pure

CeO_2 support, prepared by the sol-gel method, performed with higher catalytic activity (73% vs. 69%) in the CWAO of BPA than with an active metal.

As a summary, cerium based catalysts performed with high activity and stability in the CWAO of industrial wastewater and especially in the catalytic oxidation of aqueous solution of BPA. The catalytic oxidation of wastewater improved the biodegradability of organic compounds in the effluent. Thus, CWAO could be one alternative as a pretreatment process before traditional biological management to achieve the required level of purification of surface plating industry wastewater. Moreover, the activity of Ag/Ce-Zr and Pt/Ce-Ti catalysts in CWAO of BPA was not related to the specific surface area of these samples but the chemisorbed oxygen content on the catalysts' surface.

7.1 Future work

In this thesis promising results from the activity and stability of cerium based catalysts have been attained. However, all the oxidation experiments in this study have been performed in a batch reactor while a more convenient way to evaluate the real performance of these catalysts would be the use of a continuous wet air oxidation reactor system under steady state reaction conditions. Moreover, to get more information about the oxidation reaction and the activity of catalysts' determination of the amount of produced CO_2 by gas phase chromatography and analysis of absorbed carbon-based compounds by elemental analysis would be needed. These techniques are already under study in our research group. Additionally, valuable information on the structure-activity relationship of catalysts could be achieved by studying the acidity of catalysts by Fourier transform infrared spectroscopy (FTIR) or temperature programmed desorption (TPD). These characterization methods will be used in our future catalytic research.

However, noble metals are rather expensive materials and thus cheaper alternatives should be look for as catalysts. One option could be the utilization of modified industrial by-products such as fly ashes, carbon residues and silicate minerals etc. as catalysts in the water phase applications. Those by-products would provide more economical and cost-effective catalysts in the catalytic wet air oxidation process in the near future.

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