# Catalytic wet air oxidation of phenol over metal catalyst (Ru,Pt) supported on TiO$_2$–CeO$_2$ oxides

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## ABSTRACT

The catalytic performances of Ru and Pt supported on TiO$_2$–$x$ wt% CeO$_2$ were studied in catalytic wet air oxidation (CWAO) of phenol at 160 °C and 20 bar of pure oxygen pressure. Contrary to expectations, improved oxygen storage capacities of the materials prove to be detrimental to catalytic performances since they favor the formation of polymers in solution and the accumulation of adsorbed species. On the opposite, the presence of Lewis acid sites promotes the phenol total oxidation. They would favor the activation of the hydroxyl function, thus promoting the ortho-oxidation of phenol and finally the formation of CO$_2$. On the other hand, platinum appears to be more efficient than ruthenium for CWAO of phenol.

## 1. Introduction

High concentration, toxicity and low biodegradability of waste waters are still the major difficulty of environmental pollution. Consequently, the United Nations General Assembly declared 2013 as the United Nations International Year of Water Cooperation. In Europe, new environmental regulations are expected with tighter restrictions, and therefore it is obvious that advanced technologies for (waste)water treatment should be available for efficient elimination of emerging pollutants in order to face the incoming challenges.

Catalytic Wet Air Oxidation (CWAO) is an efficient and promising oxidative pollution removal process that has made many achievements in the research of wastewater treatment [1]. It consists in oxidizing an aqueous organic pollutant at mild temperature and under oxygen or air pressure. Different heterogeneous catalysts have been tested, offering the advantage of being easily recoverable and reusable [2–4]. Transition metal oxides (Cu, Fe, Co, Mn, Ni, Sn, and many other oxides in various combinations) and supported noble metals (Pt, Pd, Ru, and Rh) have been proposed for the CWAO. For heterogeneous transition metal oxides, partial leaching of metal ions has been observed during the reaction, and a recovery step is necessary. Noble metal catalysts have proved their effectiveness for the CWAO of a wide range of pollutants, including carboxylic acids [5,6], phenol [7–10], and nitrogen compounds [11–13]. Thus, noble metals are still being used, despite their high price, because they show higher catalytic activity and high resistance to metal leaching. They are usually supported on oxides or carbon materials [4].

The major drawback of CWAO is the low solubility of oxygen in the reaction media. The key factor is to improve the efficiency of this process using catalysts with high Oxygen Storage Capacities (OSC). OSC is indeed favorable to promote the catalyst activity by increasing oxygen mobility. Thereby, cerium-based heterogeneous catalysts have been widely studied, used, and developed due to

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the well-known oxygen storage capacity (OSC) and high oxygen mobility of ceria [14–18]. In CWAO technique, when no noble metal is present, $CeO_2$–$TiO_2$ mixed oxides show higher activity for acetic acid and phenol oxidation in a packed-bed reactor than that of pure ceria and titania [19,20]. The optimal atomic ratio Ce/Ti was found to be equal to 1. When a noble metal is present, such as Ru for the CWAO of *p*-hydroxybenzoic acid, the decrease in the molar ratio of Ce/Ti from 3 to 1/3 improves the activity of the catalysts [21]. More recently, $Rh/TiO_2$–$CeO_2$ were successfully tested for the CWAO of methyl tert-butyl ether (MTBE) in a batch reactor [22]. The best results were obtained for Rh supported on $TiO_2$ doped with 5 wt% $CeO_2$. A correlation was found between the catalytic performance and the number of Lewis acid sites on the surface of the materials. Thus, it was assumed that the Lewis acid sites are acting as a trap for the MTBE molecule increasing the conversion on the Rh particles joined to an additional supply of oxygen provided by the cerium oxide redox process.

This paper deals with CWAO of phenol in the presence of Pt and Ru catalysts supported on $TiO_2$–$CeO_2$ mixed oxides. In order to examine the influence of ceria loading on the catalytic properties, $TiO_2$–$CeO_2$ supports with different loadings of ceria were investigated.

## 2. Experimental

### 2.1. Catalyst preparation

$TiO_2$, $CeO_2$, and $TiO_2$–*x* wt% $CeO_2$ were used as supports in this study. They were synthesized by sol–gel method as follows: an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ and/or $Ti(C_4H_9)_4$ in 1-butanol was progressively added, at 70 °C, under vigorous stirring, to a mixture of water and 1-butanol. The pH was adjusted to 3 by use of ammonia. After 24 h reflux at 70 °C, the resulting pseudo-gel was dried in a rotating evaporator at 100 °C for 12 h. To avoid the influence of surface area on the CWAO reaction, the supports were then calcined at different temperatures, for 12 h with a heating ramp of 2 °C/min, so that the surface is similar for all materials.

Monometallic catalysts were obtained by ion exchange method to favor the dispersion of metal species, using $RuCl_6^{3-}$ in acidic medium and $Pt(NH_3)_4^{2+}$ in alkaline medium. Metal contents were set at 1.25 wt% for Ru and 2.50 wt% for Pt. These values correspond to similar molar amounts of metal species. The mixture of precursor solution and support was stirred for 3 h and evaporated under vacuum at 40 °C. Final catalysts were obtained after overnight drying at 100 °C followed by reduction in $H_2$ (60 mL min$^{-1}$) for 4 h at 400 °C.

Catalysts with different ceria loading were synthesized in order to evaluate the influence of support and metal phase on activity and selectivity to $CO_2$. The following notation system was used to name the catalysts: MTiCeX where M is the deposited metal (Ru or Pt), Ti is titania ($TiO_2$), Ce is ceria ($CeO_2$), and X is the cerium oxide weight percent.

### 2.2. Catalyst characterization

The Ru, Pt, and Ce contents of the different catalysts were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES; model optima 2000 DV) after digestion in an acid solution.

The BET specific surface areas were measured by nitrogen adsorption–desorption at −196 °C using a Micromeritics Tristar apparatus. The BJH method was used to determine the mean pore size. Prior to these physisorption measurements, the samples were degassed at 250 °C for 5 h.

Metal particle size was determined by high-resolution transmission electron microscopy (HRTEM) and deduced from the metal dispersion obtained by hydrogen chemisorption. HRTEM measurements were carried out on a Jeol JEM 2100 UHR equipped with a $LaB_6$ filament. The apparatus has a linear resolution of 0.14 nm and is equipped with a Gatan Ultrascan CCD camera with a resolution of 2k × 2k. Hydrogen chemisorption was performed in a chromatographic microreactor at −85 °C to avoid the participation of cerium-based supports in $H_2$ consumption. This temperature was obtained by mixing acetone with liquid nitrogen. Hydrogen pulses were injected in regular intervals after reduction under $H_2$ (400 °C, 1 h) and degassing under argon (400 °C, 120 min).

Oxygen Storage Capacity (OSC) values were measured at atmospheric pressure and 400 °C in a U-shaped reactor continuously purged with He. The sample was first saturated with oxygen and then purged for 10 min. OSC values were determined from the amount of $CO_2$ formed consecutively to CO injections under $CO/O_2$ alternate pulse conditions, as described elsewhere [23,24].

The surface acidity of the solids was investigated through Fourier transform infrared (FTIR) spectroscopy of pyridine adsorption. Pyridine FTIR spectra were recorded on a Thermo Nicolet Nexus FTIR spectrometer. Samples were compacted into thin pellets and activated at 450 °C under a secondary vacuum ($10^{-6}$ mbar) overnight. After cooling until room temperature, pyridine adsorption was performed for 5 min after pressure stabilization. The cell was then kept under a secondary vacuum for 1 h. The thermodesorption of pyridine was carried out at 150 °C for 30 min. The IR spectra were recorded at room temperature in a spectrometer equipped with a DTGS detector (Deuterium TriGlyceride Sulfur) and KBr beam splitter, with a resolution of 2 cm$^{-1}$ and 64 scans.

### 2.3. Catalytic test

Catalytic wet air oxidation reactions were carried out in a 0.44 L Hastelloy C22 autoclave equipped with a magnetically driven stirrer, as described elsewhere [25]. In a typical experiment, 160 mL of an aqueous solution containing phenol (2.098 g L$^{-1}$) and the catalyst (4 g L$^{-1}$) were poured into the autoclave that was flushed with helium. The reactor was heated up to 160 °C and the stirring speed was set at 1000 rpm. At the initial time of the reaction, 20 bar of pure $O_2$ was introduced into the reactor. The pressure was maintained constant throughout the experiment by regularly refilling with $O_2$. Gas-phase and liquid-phase samples were simultaneously and periodically collected for analysis.

Carbon dioxide present in the gas phase was determined by a gas chromatograph equipped with a catharometer and a Porapak Q packed column. Liquid phase was previously filtered by the use of a Durapore membrane (0.2 μm; Ø = 4.7 cm) to eliminate all catalyst residues and then analyzed by HPLC using a 250 × 4.6 mm C18 reversed-phase column (Microsorb-MV 100-5, Varian). The mobile phase was a mixture of 45 vol.% methanol and 55 vol.% water (flow rate: 1 mL min$^{-1}$). The HPLC system is equipped with a UV-visible detector set at 270 nm. The HPLC is calibrated with standard solutions of phenol in water. The Total Organic Carbon (TOC) values were measured using a total organic analyzer (Shimadzu LCPH/CPN).

After 180 min of reaction, the reactor was cooled down to room temperature. ICP analysis of the remaining solutions were performed to ensure that noble metals did not leached from the materials. The catalysts were recovered, washed with ultra-pure water, and dried overnight at 120 °C. Carbon contents in used catalysts were quantified by elementary analysis. It is worth noted that the reproducibility of the experimental protocol was verified for several reference catalysts and the experimental error was found to be lower than 5%.