



On the effect of Ce incorporation on pillared clay-supported Pt and Ir catalysts for aqueous-phase hydrodechlorination



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ABSTRACT

Hydrodechlorination (HDC) of chlorinated pollutants in water such as 4-chlorophenol (4-CP) and 4-chloroaniline (4-CA) was carried out with catalysts based on Pt and Ir supported pillared clays. Almost complete dechlorination was achieved at short reaction time under mild operation conditions with the Pt catalyst. The incorporation of cerium oxide to the Pt and Ir catalysts (PtCe and IrCe catalysts, respectively) led to a higher dispersion than that of the monometallic ones. The catalyst loaded with Pt showed low reaction rates and conversion while the one modified with increasing amounts of cerium oxide was highly active for conversion of the chlorinated pollutants. On the contrary, the IrCe catalysts were found poorly active due to partial coverage of Ir crystallites by cerium oxide.

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1. Introduction

The removal of chlorinated organic compounds represents one of the priorities in water treatment due to their harmful effects and the new and more restrictive environmental legislation. Chlorinated and chloronitrogenated aromatic compounds such as chlorophenols and chloroanilines are usually classified as harmful or toxic agents [1] that can cause cancer [2] and other harmful effects. Nevertheless, these molecules are widely used in the production of pesticides, antioxidants, dyes or other chemicals. Chlorophenols have been regarded as useful industrial products with a broad range of applications, being used as versatile anti-microbial and disinfecting agents, fungicides, insecticides, algicides, herbicides and as synthetic precursors for a variety of pharmaceuticals, glues, paints, dyestuffs and inks. Chlorinated anilines are harmful pollutants, forbidden in some countries for their carcinogenic effects and their high toxicity [3]. The European Union (EU) restricted some azo-dyes in textile industry due to possible formation of this kind of compounds (EU 2002/61/CE and Regulation 1907/2006, REACH directive). The 4-chloroaniline (4-CA) is

used in the production of pesticides, approved by the EU for use such as pyraclostrobin and diflubenzuron, different drugs, dyes and biocides widely used in healthcare products like chlorhexidine or triclocarban.

Catalytic HDC has been investigated during the last decades being very effective in the elimination of chlorinated pollutants in aqueous phase such as chlorophenols with H₂ [4–7] or formic acid [8,9] as reducing agents, pesticides [10–14] or chloronitrogenated pollutants [15], diminishing the toxicity of the effluents containing these compounds.

Cerium oxide catalysts are commonly used in fuel cells, solar cells and three-way catalysts [16,17]. Nanostructured CeO₂ materials generally improve the properties compared to microsized or bulk materials [18]. The ability to store oxygen under oxidizing conditions and release it under reducing conditions makes these materials ideal for several environmental applications. Cerium oxide has been also used in the synthesis of precious metal catalysts to prevent the sinterization of metallic nanoparticles, increasing the catalyst dispersion [19], as it has been demonstrated when incorporating cerium oxide to Pt/Al₂O₃ [20], Rh-Mo/ZrO₂ [21] and Al-PILC catalysts supporting Pd [22,23], Pt [24] or transition metals such as Mn [25]. On the other hand, CeO₂ can be used to increase the stability of some catalysts [25]. It has been also used in the synthesis of pillared clays with Fe for phenol oxidation in aqueous phase, improving its catalytic activity [26,27].

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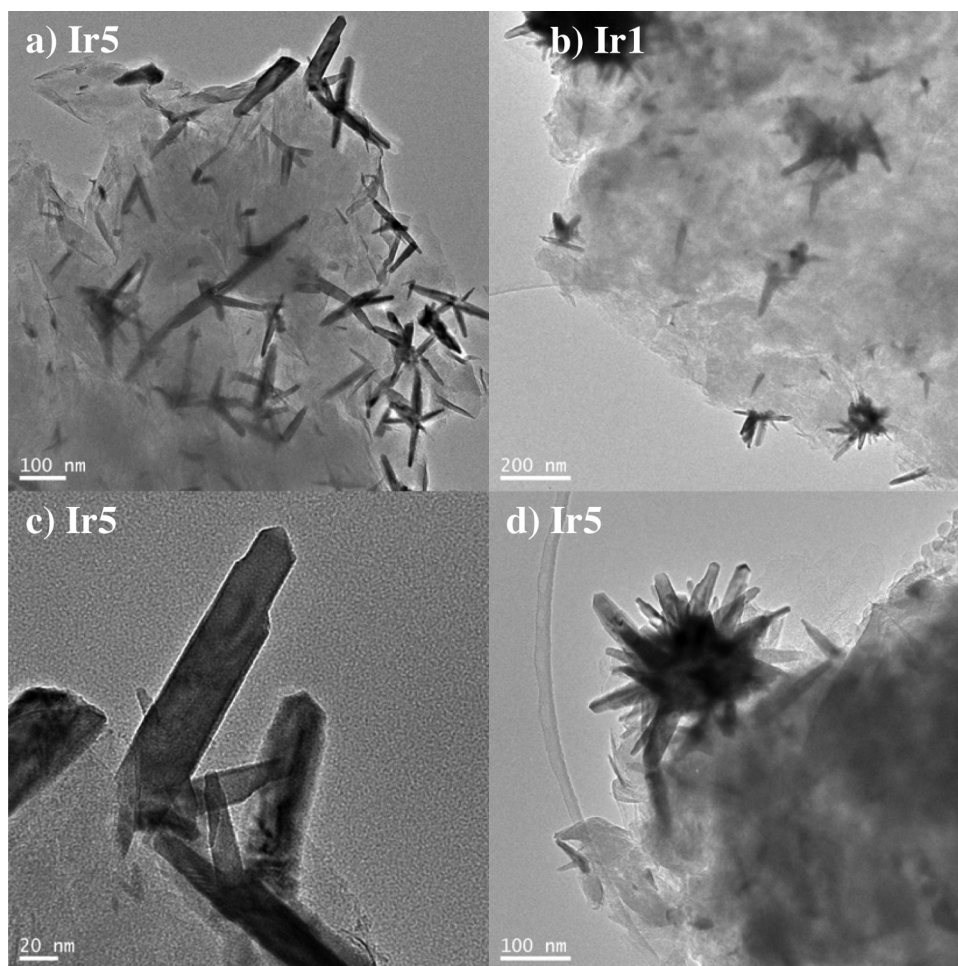


Fig. 1. TEM images of Ir1 (b) and Ir5 (a, c, d) at different scales.

The Pt and Ir catalysts have been less studied for HDC than those of Pd and Rh and they have shown less activity and a faster deactivation [7,28]. Nevertheless, the activity can be improved with the addition of promoters or other metals that allow a higher dispersion of the active phase avoiding the nucleation and growth of the nanoparticles over the support. The strong metal-CeO₂ interactions favour a higher metal dispersion compared to other supports [29–32]. In line with above, this work was undertaken with the aim to study the aqueous phase HDC of 4-CP on Pt and Ir catalysts and the HDC/HDN of 4-CA on PtCe catalyst focusing on the effect of Ce incorporation on their catalytic performance.

2. Materials and methods

2.1. Pillared clays preparation

The Pt catalyst was prepared using an Al-pillared clay (Al-PILC) as support. The starting material used in its preparation was a purified-grade bentonite supplied by Fisher Scientific Company (Loughborough, Oregon, USA). The chemical analysis (wt%) of this bentonite was: SiO₂, 52.22; Al₂O₃, 16.81; Fe₂O₃, 3.84; Na₂O, 1.26; MgO, 0.88; CaO, 0.74; K₂O, 0.80. Briefly, an aluminium pillaring solution was prepared (OH/Al = 2 molar ratio) and added to a bentonite suspension (1 wt%) providing 10 mmol of Al per gram of clay. The resulting material was washed by centrifugation with deionized water, dried overnight at 110 °C and calcined at 350 °C for 2 h. The cation-exchange capacity (CEC) was 97 meq per 100 g of clay.

Al-PILC was obtained following the method described elsewhere [9].

The monometallic Pt and Ir catalysts were prepared by wet impregnation of Al-PILC using a solution of H₂PtCl₆ (8%wt) or IrCl₃·H₂O. The bimetallic PtCe and IrCe catalysts were prepared by co-impregnation of H₂PtCl₆ or IrCl₂·H₂O and Ce(NO₃)₃·6H₂O, dissolved in an aqueous solution of HCl (1 M). These solutions were impregnated on 1 g of Al-PILC prior to calcination. The impregnated solid was dried at room temperature for 2 h, then at 110 °C for 14 h and, finally, calcined for 2 h at 500 °C. The resulting Pt, Ir, PtCe and IrCe catalysts, were loaded with 1 wt% in the case of Pt, 1 or 5 wt% of Ir and 3, 5 or 10 wt% of Ce(x) are referred to hereafter as Pt1, Ir1, Ir5 and Pt1Cex or Ir1Cex, respectively.

2.2. Catalyst characterization methods

A Micromeritics Tristar 3000 apparatus was used to obtain the N₂ adsorption-desorption isotherms at –196 °C. The samples were previously degassed at 160 °C and 5 × 10^{–3} Torr for 16 h. Specific areas were obtained according to Brunauer–Emmet–Teller (BET) method. The Pt, Ir and Ce loadings of the catalysts were determined by inductively coupled plasma mass spectroscopy (ICP-MS) by means of a Model Elan 6000 Sciex PerkinElmer apparatus. The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a JEOL 2100F microscope with a point resolution of 0.19 nm coupled with an energy-dispersive X-ray spectrometer (EDXS; INCA x-sight, Oxford

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