



Catalytic hydrogenation of Cl-oxyanion pollutants in water

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ABSTRACT

Pt and Pd catalysts supported on alumina have been tested and characterised for the catalytic hydrogenation of chlorates at room temperature and atmospheric pressure. Metallic nanoparticles are the catalytic active species, obtaining better results with the Pt than with the Pd catalysts. It is observed that the activity of the Pt catalysts depends on the metal precursor used for their preparation and the calcination temperature as these factors lead to different platinum dispersion on the alumina surface. The best results were obtained with the catalysts prepared from metal precursors containing Cl atoms and calcined at lower temperatures, as smaller metallic crystallites are formed. The chlorate reduction profiles displayed a pseudo-first order kinetic towards chlorate. The optimised catalyst was tested for the reduction of the different Cl-oxyanions, proving that the reaction rate depends on the chlorine valence of the ion following this order: $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^-$. This is due to the different molecular geometry of the anions that results in different stability of the ClO_x^- . The optimised catalyst was fully stable in successive uses, being active for the simultaneous reduction of chlorate, chlorite and bromate in water.

1. Introduction

Water is an essential resource for society being necessary to guarantee the supply of quality water. This is not simple as only 0.6–0.9% of the water on the planet is easily accessible as ground and/or surface water [1,2]. Nevertheless, the problem is not only the water availability but their pollution, affecting human health and aqueous ecosystems [3]. Some of the pollutants that may worsen water quality are Cl-oxyanions (ClO_4^- , ClO_3^- , ClO_2^-) [4]. Perchlorate ions interfere with the iodine uptake of the thyroid gland and thereby cause a decrease in the production of the thyroid hormone. In 2016 the World Health Organization (WHO) established a provisional maximum tolerable daily intake value of 0.01 mg perchlorate per kg body weight and based on this, a guideline perchlorate concentration of 0.7 mg L^{-1} in drinking water was calculated [5]. The main sources of this pollutant are the fabrication of ammonium perchlorate as well as the firework and rocket industry [6–8]. Chlorate and chlorite are usually found after water disinfection treatments based on chlorine dioxide or other chlorine compounds. These compounds present negative effects on health such as oxidative stress or haemoglobin size change and WHO set a provisional limit of 0.7 mg L^{-1} for both pollutants in drinking water [9,10].

Consequently, appropriate treatments must be developed and various approaches have been already investigated such as adsorption,

separation by membranes, biological treatments, ion exchange and chemical [11] or electrochemical reduction methods [12]. The use of ferrous ion, as a chemical reductor agent has been proposed as a method for the removal of chlorite [13]. However, to achieve high reaction rates, low pH values are required (<5) with an adverse impact on both economic and environmental aspects [13]. The removal of chlorate and perchlorate is more challenging as both compounds are quite stable due to the electron delocalisation. Then catalysis may be an alternative as it has been successfully used for the treatment of other pollutants [14–17].

The catalytic hydrogenation of chlorine and halogen-oxygen compounds has been previously proposed in some patents [18,19] and the same process has been used for removing different water pollutants such as NO_3^- , NO_2^- , and BrO_3^- [20–26]. This technique would have advantages not only in terms of costs and easy operation, but also regarding public acceptance as ClO_x^- pollutants will be reduced to innocuous Cl^- without the use of toxic chemicals. In general, noble metal-based catalysts have been used for the catalytic reduction of different oxyanions in water [27]. The key principle is the interaction between the noble metal and H_2 as the metallic active species dissociatively adsorb the H_2 , activating the hydrogen that will reduce the coadsorbed ions. Possible catalytic systems include metallic Pd, Pt, Ru, Ir and Rh [28] on different supports as alumina, silica, zeolites, activated carbon or nanosized supports [29–34]. Furthermore, supported bimetallic catalysts containing Pd, Pt

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and/or Rh with an additional promoter such as Cu, Sn, In or Re are employed [1,33]. In contrast to noble metals, the promoter usually do not dissociate H₂, instead, they facilitate the ion reduction by spillover of the adsorbed hydrogen [27,35]. The selection of an adequate support is also important in order to enhance the metal dispersion and to facilitate handling and phase separation after the treatment. Moreover, the choice of the support may have a significant influence on the reaction rate, as it can directly participate in the catalysis or may have an indirect effect through modification of the electronic properties of the metallic particles. The support can also influence on the density, size and morphology of the metallic particles which determine the distribution of the catalytic active sites. Additionally, mass transfer effects in supports with high specific surface area or microporosity can modify the activity and selectivity of the catalyst [27,36]. In this way, some authors pointed out that proper supports for this reaction may have a certain effective electronegativity and must be readily wettable [19]. Other authors [37] have shown that the presence of some inert metal hydroxides in the media accelerates the catalytic reduction rate as they enhance the mass transfer and minimise the metal dissolution from the support.

Catalysts based on Re-Pd supported on carbon have been described as active materials for the reduction of perchlorate [7,38,39]. The dispersed Pd particles over the carbon surface bind with the adsorbed H₂. This is followed by a reaction between Re(VII) and the adsorbed hydrogen with a reduction of Re(VII) to Re(I) forming H₂O. In this way, an open site is available for ClO₄⁻. The cycle is completed by the oxidation of Re(I) to Re(IV) with the abstraction of an oxygen atom from ClO_x (x = 1, 2, 3, 4), thereby Cl⁻ is formed at the end [38,39]. These catalysts can be used for the reduction of chlorate, being this reaction 10 times faster than perchlorate reduction [40]. However, the formation of the promoting Re species in the bimetallic catalyst requires a relatively complex process due to the use of different organic ligands in the precursor material. Carbon-supported iridium catalysts have been also applied for catalytic hydrogenation of chlorate in concentrated sodium chloride solutions, showing that the reduction rate was dependent on pH, iridium content and metal dispersion [41]. Pd catalysts supported on different N-doped carbon nanotubes have been described as active catalysts for chlorate hydrogenation, obtaining a 90% of conversion at 50°C [32,33]. The same authors have discussed about the influence of the support in the catalytic activity [30]. Carbon was also proposed as a suitable support for Pd catalysts with MoO_x immobilised on the surface. This catalyst showed an improved activity and stability compared with the catalyst without Mo [29]. Recently the use of nickel and magnetite promoted carbonised cellulose bead-supported bimetallic Pd-Pt catalyst has been described for the hydrogenation of chlorate in water obtaining a 99% conversion after 45 min at 80 °C [31].

Hereby, we study the performance of different Pd and Pt catalysts supported on alumina for the hydrogenation of chlorate at room temperature and atmospheric pressure and evaluate the influence of diverse catalyst synthesis parameters on the final activity. The optimized catalyst has been tested for the reduction of different Cl-oxyanions and for the simultaneous removal of chlorate, chlorite and bromate ions in water phase.

2. Experimental

2.1. Catalyst preparation

Pd catalysts were prepared using commercial γ -alumina supplied by abcr GmbH as support. The alumina was first dried at 100 °C and an aqueous solution of PdCl₂ was added by wet impregnation to obtain 5% (w/w) of palladium in the final catalyst. After impregnation, the catalyst was heated with air at 1.25 °C·min⁻¹ till 550 °C and it was calcined at this temperature for 3 h. Before each reaction, the catalyst was activated with hydrogen at 200 °C for 4 h.

Pt-catalysts were prepared using commercial γ -alumina supplied by abcr GmbH. The alumina was previously dried at 100 °C and different

aqueous solutions of platinum precursors (PtCl₄, H₂PtCl₆·xH₂O, Pt(NH₃)₄(NO₃)₂, Pt(NH₃)₄Cl₂·xH₂O) were added by wet impregnation to obtain the desired platinum content in the final catalyst. After impregnation, catalysts were heated with air at 1.25 °C·min⁻¹ till the desired temperature (350°C, 450°C and 550°C) and calcined at this temperature for 3 h. Before each reaction, the catalysts were activated with hydrogen at 200 °C for 4 h or at 400 °C for 1 h.

2.2. Catalytic tests

The activated catalysts were tested in a batch reactor. The polluted water was prepared by dissolving NaClO₃ in Milli-Q water. The reaction was carried out at room temperature and atmospheric pressure in a batch reactor containing 0.6 L of water with 50 ppm of chlorate and stirred at 900 rpm with a mechanical Teflon stirrer. In certain experiments, the chlorate concentration was modified (25, 50, 100 and 125 ppm) and in others, 50 ppm of chlorite or bromate were added. The experiments were usually made using 1 g of catalyst, as powder. Before each test, the polluted water was hydrogenated for 2 h with a gas flow of 200 mL·min⁻¹. The same hydrogen flow was maintained throughout the reaction. Reactants and products were determined by an ionic chromatograph 883 Basic IC Plus (Metrohm®) equipped with a conductivity detector and a chemical suppressor. The anions were separated in a Metrosep A Supp 5–150/4.0 column. The reproducibility of the catalytic tests was verified, repeating at least 3 times, the most significant reactions.

2.3. Characterization studies

X-ray diffraction (XRD) patterns were recorded in a PANalytical CUBIX diffractometer equipped with a PANalytical X'Celerator detector. X-ray radiation of Cu K α ($\lambda_1 = 1.5406 \text{ \AA}$, $\lambda_2 = 1.5444 \text{ \AA}$, I₂/I₁ = 0.5) was used with a tube voltage of 45 kV and with an intensity of 40 mA. The measurements were made with a length of the goniometer arm of 200 mm and a slit of variable divergence with an irradiated sample area of 3 mm. The measurement range was from 2.0 to 90.0 with a step of 0.02° and a measurement time of 17 s per step.

Textural properties of the catalysts were determined by N₂ adsorption with Micromeritics ASAP 2040. A temperature of – 196 °C was set and 0.2 g of the sample with a particle size between 0.4 and 0.6 mm was used to analyse each catalyst. The samples were outgassed at 400 °C and 10–5 mbar for 12 h prior to the N₂ adsorption measurements. To determine the specific surface area, the BET isotherm model was applied to obtain the value of the monolayer. Besides, the determination of the specific surface area was accomplished through analysis of the pressure and volume data of the adsorbed gas.

The chemical composition was measured by inductively coupled plasma (ICP-OES) in a Thermo Scientific™ iCAP PRO ICP-Optical Emission Spectrometer. Prior to analysis, 40 mg of each solid sample was digested with concentrated hydrofluoric and nitric acid for 24 h. Subsequently, the solutions were analysed by ICP-OES.

TPR profiles were obtained using a Micromeritics Autochem 2910 automated chemisorption analysis instrument. After placing the sample in the holder, a mixture of 10% H₂ in Ar flowed at a rate of 50 mL·min⁻¹ and the temperature was gradually increased from 40 to 500 °C at a rate of 10 °C per minute.

The High-Angle Annular Dark-Field Imaging (HAADF) measurements were conducted on a Cs-Probe Corrected Titan microscope (Thermo-Fischer Scientific) outfitted with a GIF Quantum (Gatan Inc.) and Super-X EDXS detectors (Thermo-Fischer Scientific). Images were acquired at the same acceleration voltage (300 kV) at varying magnifications.

3. Results

3.1. Catalyst characterisation

Alumina based catalysts with 5 wt% of platinum were prepared from diverse Pt precursors *i.e.*, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$, $\text{H}_2\text{Pt}_4\text{Cl}_6 \cdot x\text{H}_2\text{O}$, PtCl_4 and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ using the wet impregnation method and the samples were calcined at different temperatures and reduced with hydrogen. All the catalysts had a Pt content close to the target value (5 wt%) and a surface area of about 190–220 m^2/g . The surface areas of the Pt catalysts were quite similar to the support. The materials presented type II isotherms typical of mesoporous materials.

XRD patterns of the Pt-catalysts showed the characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ at $2\theta = 37.6, 39.5, 45.8, 60.9, 66.8$ and 85.0° that are practically coincident with the main patterns of Pt^0 . Nevertheless, some differences are observed, for the different catalysts patterns, in the intensity and definition of the diffraction peaks that appear at $2\theta = 39.3^\circ$ and 81.3° assigned to the 111 and 311 peaks of Pt^0 . These differences are related to the use of different Pt precursors and calcination temperatures. As seen in Fig. 1, those peaks are smaller and less defined in the patterns of the catalyst prepared with a Cl-containing precursor and calcined at lower temperature. On the contrary, the catalyst prepared with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ and calcined at 550°C shows high, narrow and well-defined peaks of Pt indicating the formation of larger crystallites.

The reduced samples were characterised by electron microscopy in order to determine the catalyst morphology and analyse the distribution of Pt crystallites on the support. The results showed that the materials had a low crystallinity with a homogeneous dispersion of the platinum atoms over the support, forming Pt nanoparticles of different size depending on the precursor and on the calcination temperature. Fig. 2 shows the micrographs obtained with the catalysts prepared with PtCl_4 and calcined at 350 or 550°C . As observed calcination at lower temperature results in a more homogeneous distribution of the Pt crystallites centered around 1–2 nm, while the calcination at higher temperature gives a heterogeneous distribution around 15–25 nm.

Catalyst prepared with Pd displays similar features to those described with platinum, as it was described in a previous work [23]. The dark field scanning-transmission electron microscopy of this catalyst shows that nanoparticles of palladium are formed on the alumina surface without large aggregates and with an average crystal size close to 5–6 nm [23].

TPR of the Pt catalysts calcined at different temperatures and prepared with PtCl_4 are shown in Fig. 3. As it can be seen, in both cases two

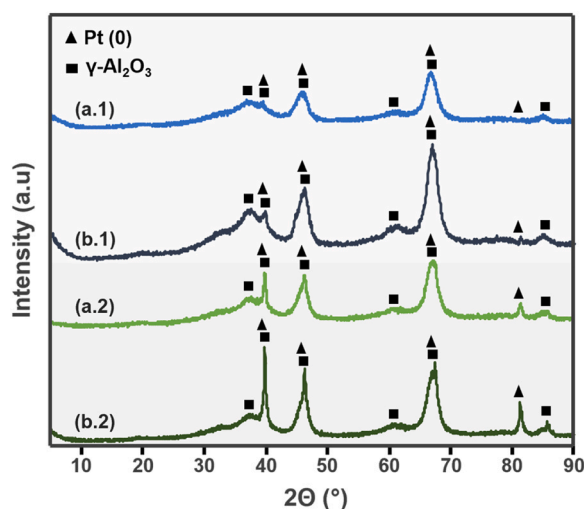


Fig. 1. XRD patterns of the activated 5%Pt- Al_2O_3 catalysts prepared using: (1) PtCl_4 precursor or (2) $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ precursor; calcined at (a) 350°C or (b) 550°C .

broad peaks are observed, one at low temperatures ($140\text{--}160^\circ\text{C}$) and another at higher temperatures ($260\text{--}400^\circ\text{C}$) They are ascribed to the different platinum species that are weakly and strongly interacting with the alumina. Most authors [42–45] assumed that the first peak could be attributed to the reduction of oxy- or hydroxychloride platinum species, while the high temperature peak can be attributed to the two-dimensional dispersive oxychlorinated platinum species, which strongly interact with the support. The position of these peaks is shifted to lower temperatures in the catalyst calcined at 350°C , indicating that the metallic active sites formed on the catalyst calcined at lower temperature interact more easily with the hydrogen molecules.

3.2. Catalytic results

The catalysts were tested for the catalytic reduction of chlorate in water. A blank reaction was previously carried out without any catalyst and the results (not shown) demonstrate that the reduction of chlorate by hydrogen does not occur at room temperature and atmospheric pressure in the absence of catalyst. After the addition of the catalyst, chlorate is successfully reduced to chloride. In all the reactions studied, chlorite or hypochlorite were not detected in the reaction media, confirming the absence of stable intermediates or by-products with a complete selectivity to the desired product, *i.e.* chloride.

The activity of the Pt and Pd catalysts for the chlorate reduction was compared and the results are shown in Fig. 4. It has been described that palladium catalyst has an improved activity for the reduction of bromates [23,24] and when combined with a non-noble metal (Cu or Sn) it is also active for the reduction of nitrates [20–22]. Nevertheless, for the reduction of chlorate, the activity of the catalyst containing Pd is lower than the activity of the Pt catalysts, probably due to the preferential adsorption of Cl^- on Pd active sites or/and to a better dispersion of the Pt active sites.

The activities of different Pt catalysts prepared with different metal precursors and calcined at different temperatures are shown in Figs. 5 and 6. It is observed that different reaction rates are obtained depending on the Pt precursor and the calcination temperature. The best results are achieved using the catalysts prepared with precursors containing Cl atoms and calcined at the lowest temperature. This is related to the formation of metal nanoparticles with different crystallite size leading to catalysts with different metal dispersion. This can be inferred from the XRD patterns of the catalysts. As can be seen in Fig. 1 the catalyst prepared with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ has larger and better defined peaks at $2\theta = 39.3^\circ$ and 81.3° that are assigned to the 111 and 311 peaks of metallic Pt, indicating the formation of larger metal crystallites in this catalyst. The same feature is observed with the catalyst calcined at 550°C when compared with the XRD pattern of the catalyst calcined at 350°C . This was also confirmed by electronic microscopy as it can be observed in Fig. 2 where are shown some microographies of the catalysts calcined at different temperatures and the particle distribution. Pt crystallites of 10–20 nm were formed in the catalyst calcined at 550°C , whilst the size of the nanoparticles is one order magnitude smaller when calcined at 350°C .

These results indicate that the highest activity of the catalyst prepared from a chlorine salt and calcined at a lower temperature can be related to a more homogeneous distribution of metal nanoparticles and to the absence of Pt aggregates. Similar results were obtained with Pd catalyst in a similar reaction, *i.e.* bromate reduction [46] and were related to the formation of $\text{Pd}_x\text{O}_y\text{Cl}_z$ species during the calcination of the catalyst prepared with a Pd precursor containing Cl atoms. These species prevent palladium agglomeration during catalyst activation with hydrogen. Then, similar results are expected with the catalysts prepared with Pt salts containing Cl. On the other hand, the effect of the temperature on the metallic dispersion has been also discussed in previous papers [47] concluding that during heat treatment above 500°C of Pt-alumina catalysts, in an oxidative atmosphere, agglomeration of platinum takes place and large particles are formed. In agreement, the

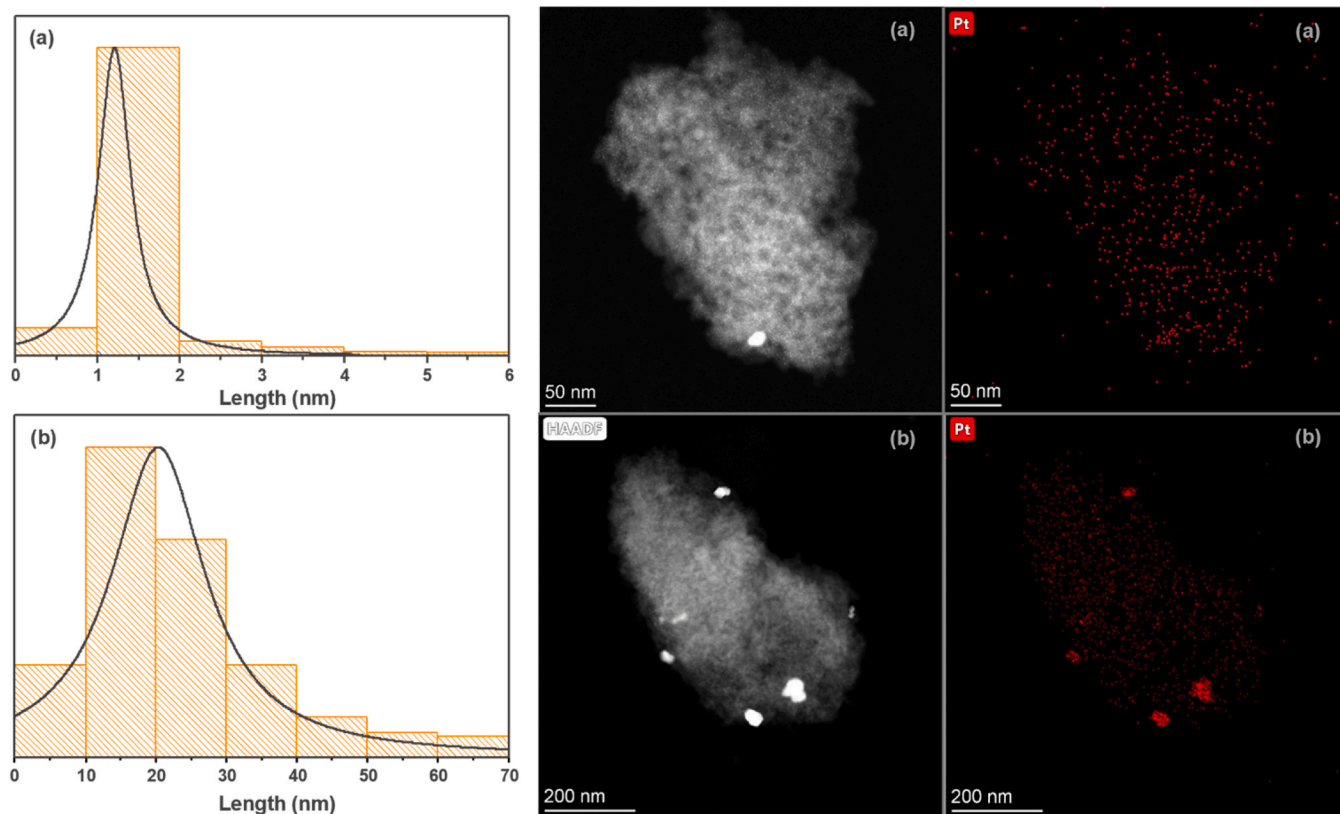


Fig. 2. HAADF-STEM images, Pt-EDX mapping and particle size distribution plot of the Pt-catalysts prepared with PtCl_4 and calcined at (a) 350°C or (b) 550°C .

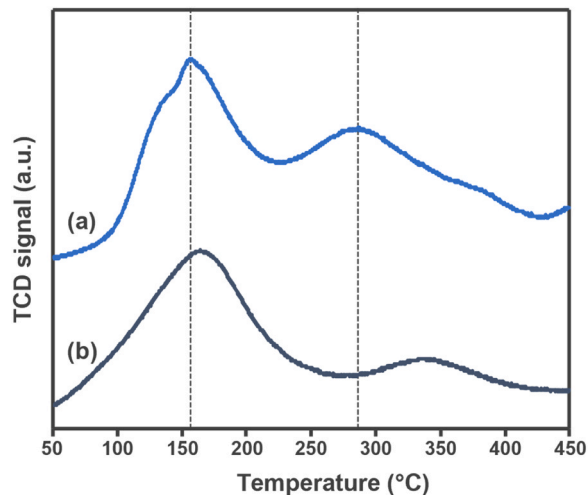


Fig. 3. TPR profiles of the pre-oxidized Pt-catalysts prepared with PtCl_4 and calcined at (a) 350°C or (b) 550°C .

TPR results have also shown that the platinum species formed in the catalyst calcined at lower temperatures interact more easily with hydrogen improving the activity of this catalyst for chlorate hydrogenation.

The evolution on time of the reaction when using different chlorate concentrations (25, 50, 100, $125\text{ mg}\cdot\text{L}^{-1}$), while keeping the partial pressure of H_2 constant, is shown in Fig. 7. The initial reaction rates increases linearly with the bromate initial concentration. A linear correlation is obtained in both cases with R^2 coefficients close to one and with the line passing through the origin. These results indicate a pseudo-first order reaction with respect to chlorate, similar to the results

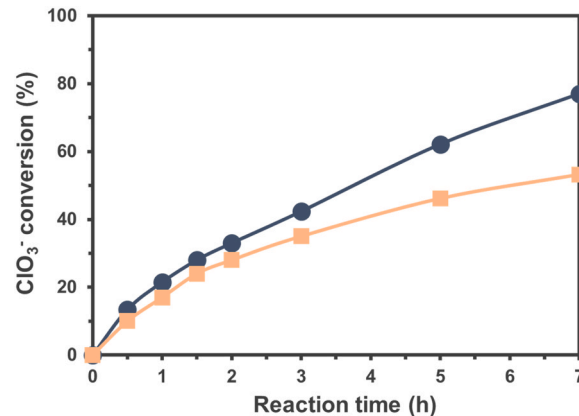


Fig. 4. Activity of the (●) Pt and (■) Pd catalysts for the hydrogenation of chlorate (1 g. of catalyst, 50 ppm of ClO_3^- , room temperature and atmospheric pressure).

obtained in the bromate hydrogenation reaction [24] and for the perchlorate reduction [40].

The optimised Pt catalyst was also tested in the reduction of other Cl-oxyanions. According to thermodynamics and the reduction potential, the most favourable reaction must be the reduction of perchlorate to chloride [1] as the ΔG of the perchlorate reduction is more negative (-2585 kJ/mol) than the ΔG of the chlorate reduction (-1244 kJ/mol) and the ΔG of the chlorite reduction (-1221 kJ/mol). Nevertheless, the catalytic results (Fig. 8) show the opposite trend, observing that the reaction rate for the hydrogenation of the ions was $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^-$. These results must be related to the different geometry of the anions that will result in different stability of the species to be reduced. Chlorite has a bent shaped geometry, whilst chlorate has a trigonal pyramidal

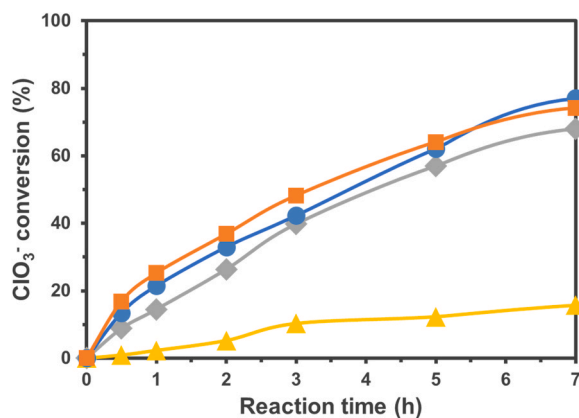


Fig. 5. Activity of the Pt-catalysts calcined at 550°C and prepared with different metal precursors (●) PtCl₄, (■) H₂PtCl₆ · 6 H₂O, (◆) Pt(NH₃)₄Cl₂ · x H₂O and (▲) Pt(NH₃)₄(NO₃)₂ for the hydrogenation of chlorate (1 g. of catalyst, 50 ppm of ClO₃⁻, room temperature and atmospheric pressure).

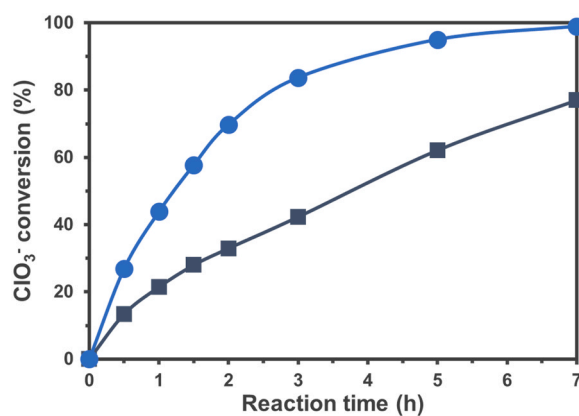


Fig. 6. Activity of the Pt-catalysts prepared with PtCl₄ and calcined at (●) 350°C or (■) 550°C for the hydrogenation of chlorate (1 g. of catalyst, 50 ppm of ClO₃⁻, room temperature and atmospheric pressure).

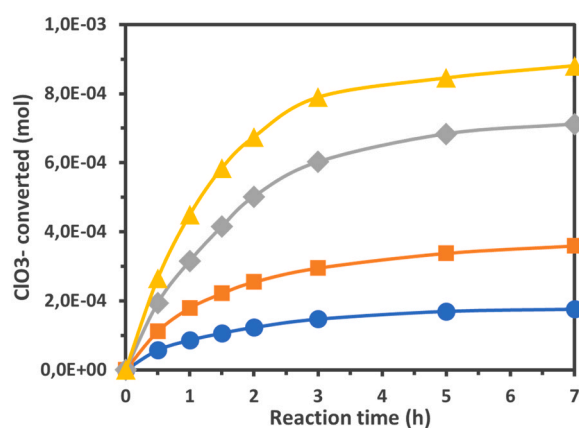


Fig. 7. Converted chlorates when using different chlorate initial concentrations: (●) 25 ppm, (■) 50 ppm, (◆) 100 ppm and (▲) 125 ppm (catalyst prepared with PtCl₄ and calcined at 350°C (1 g. of catalyst, 50 ppm of ClO₃⁻, room temperature and atmospheric pressure).

geometry and perchlorate has a tetrahedral geometry that stabilizes the Cl atoms and prevents its reduction [48]. Then reaction rate is controlled by the high activation energy resulting from the ion stability and the

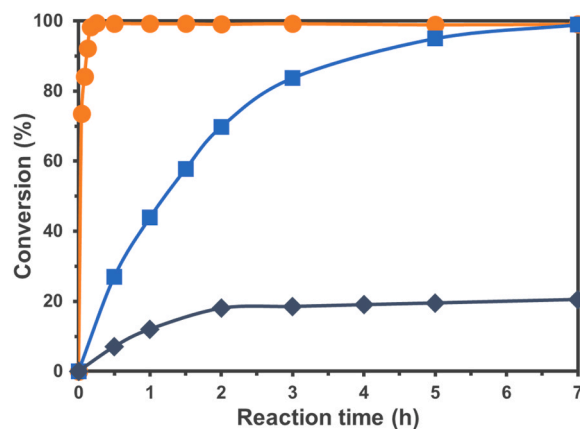


Fig. 8. Activity of the Pt-catalyst prepared with PtCl₄ and calcined at 350°C for the reduction of: (●) ClO₂; (■) ClO₃; (◆) ClO₄. (1 g. of catalyst, 50 ppm of ClO_x⁻, room temperature and atmospheric pressure).

kinetic of the reaction limits the reduction of the anions. Similar results have been described with other type of catalysts [40] used in perchlorate reduction studies.

The results obtained suggest that this catalyst will not be adequate for the reduction of perchlorate but will be active for the reduction of chlorate and chlorite. As these anions usually appear together after disinfection treatments, the activity of the catalyst for the simultaneous removal of both pollutants was evaluated. It is observed that the catalyst is active for the reduction of both anions when both species are simultaneously present in water. As can be seen in Fig. 9a, chlorite is first reduced and later the chlorate reduction starts. This is probably related to the easiest accessibility of the chlorine atom in the chlorite ion that favours the adsorption and reduction of the ClO₂ on the catalyst's active phase surface. Similar results are obtained when bromates and chlorates are simultaneously present in water (Fig. 9b), indicating that this is a multifunctional catalyst that can be used for the removal of different pollutants in the water phase.

The stability of the catalyst was studied in successive reaction cycles. Any deactivation was observed after 3 cycles of reaction demonstrating that the catalyst is not deactivated by the Cl⁻ ions formed during the reaction. The analysis of the water phase after these successive reactions did not show the presence of any trace of Pt which evidence the absence of metal leaching during reaction.

Finally, in order to decrease the noble metal content, a catalyst with 1 wt% of platinum was prepared and its activity was compared with the 5 wt% Pt catalyst. The results are shown in Fig. 10, observing a small decrease of the reaction rate when decreasing the metal content. Nevertheless, considering the activity as the mols of chlorate converted per second and per mol of Pt, the activity of the catalyst containing 1 wt % of platinum is higher than the activity of the catalyst with larger amount of platinum, probably due to a better dispersion of the noble metal on the surface support [23].

4. Conclusions

Pt and Pd supported on alumina catalyze the reduction of chlorate in water with hydrogen to non-toxic chloride anions. Pt catalysts are more active than Pd catalysts for the specific reaction. Metal nanoparticles are the active sites, but their dispersion on the alumina support relies on the metal precursor used for the catalyst preparation and on the calcination temperature. The best results are achieved using the catalyst prepared with a Pt-precursor containing Cl atoms and calcined at 350 °C. A preliminary kinetic study of chlorate reduction with this catalyst suggests a pseudo-first order mechanism towards chlorate. It is observed that when the catalyst is used for the reduction of other Cl-oxyanions, the reaction

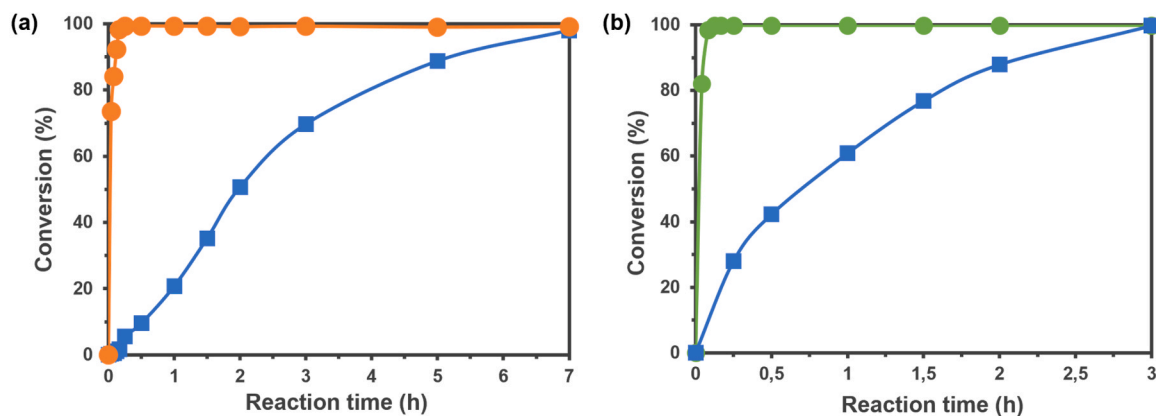


Fig. 9. Activity of the Pt-catalyst prepared with PtCl_4 and calcined at 350°C for the (a) simultaneous hydrogenation of (■) chlorate and (●) chlorite and for the (b) simultaneous removal of (■) chlorate and (●) bromate (1 g. of catalyst, 50 ppm of ClO_3^- and 50 ppm of ClO_2^- or 50 ppm of ClO_3^- and 50 ppm of BrO_3^- , room temperature and atmospheric pressure).

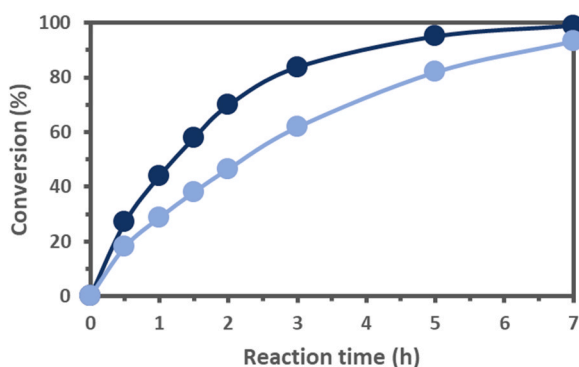


Fig. 10. Converted chlorates when using catalysts with different Pt content: (●) 1 wt% Pt, (●) 5 wt% Pt (1 g. of catalyst, 50 ppm of ClO_3^- , room temperature and atmospheric pressure).

rate depends on the geometry of the anion, following this trend $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^-$ indicating that this reaction is controlled by the accessibility and stability of the Cl atoms. The catalyst remains stable during successive chlorate reduction reaction cycles and no metal leaching is detected, evidencing the high stability of the Pt active species. The optimized catalyst is also active for the simultaneous reduction of chlorate and chlorite as well as for the simultaneous reduction of chlorate and bromate, indicating that it is a multifunctional catalyst that can be utilized for removing different pollutants in water.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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