



Metal assessment for the catalytic reduction of bromate in water under hydrogen

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HIGHLIGHTS

- Noble metals supported on activated carbon promote the reduction of bromate under H₂.
- Palladium, platinum, ruthenium and rhodium are the most efficient catalysts.
- Bromate removal corresponds to complete conversion into bromide.
- Activity is related to the dissociative adsorption energy of hydrogen.
- The role of H₂ is clarified and the catalytic mechanism is discussed.

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ABSTRACT

The presence of bromate ion in water and wastewater is a known problem due to its carcinogenic potential, and other toxic effects on human health. The catalytic reduction under hydrogen is an attractive process for its removal by conversion into bromide ion.

Different metals (Pd, Pt, Ir, Rh, Ru, Fe, Sn, Cu, Zn and Ni) supported on activated carbon were assessed for the catalytic reduction of bromate under hydrogen at room temperature and pressure. All these catalysts are active in the conversion of bromate into bromide. Ruthenium, palladium, platinum and rhodium were shown to be the most efficient metals. When the available metal surface for reaction was considered, platinum showed the best activity. The trend of activities was associated to (and discussed on the basis of) the dissociative chemisorption energy of hydrogen over the metals.

A mechanism for the reduction of bromate was proposed, involving reactions in the liquid phase, on the surface of the activated carbon support, and on the surface of the supported metal particles. It is proposed that the reaction mechanism on the surface of the metal catalysts comprises the decomposition of hydrogen and subsequent reaction with bromate. This reaction leads to the release of bromide ion and water. The oxidized metal is then reduced by hydrogen, thus closing the catalytic cycle.

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1. Introduction

Bromates removal from drinking water has been subject to recent attention, since they were classified by the International Agency for Research on Cancer in Group 2B (possibly carcinogenic for humans) [1]. In fact, it is estimated that 3.9 µg/L correspond to a cancer risk of 10⁻⁵ for life-time exposures [2]. Additionally, other source of information indicates that life-time exposures to 5, 0.5 and 0.05 µg/L lead to cancer risks of 10⁻⁴, 10⁻⁵, and 10⁻⁶, respectively [3]. The main risks are associated with the kidneys, both as targets for cancer and for toxic action of bromate. The peritoneum

and the thyroid are also considered as cancer targets, and there is also the possibility that exposure to bromate may result in low sperm counts [4].

As a consequence of this classification, the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) have established a provisional guideline for bromates in drinking water of 0.01 mg/L [2,3]. Bromate ions are very stable in water, and their presence is mainly due to the ozonation of bromide containing water during the respective treatment for human consumption. Bromide has various natural and anthropogenic sources, such as seawater intrusion, pesticide run-off, industrial wastes and impurities from road de-icing salts [5].

The alternatives for bromate removal from drinking water are biological treatment, photocatalysis, electrochemical reduction and catalytic reduction [6]. The catalytic route presents advantages

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in terms of efficiency and rate of removal, without producing secondary waste streams with the accumulated remnants [6].

The heterogeneous catalytic reduction of water pollutants (e.g. nitrates) using metallic catalysts has already been demonstrated to be an efficient process, using different supports for the metal phase, such as: activated carbon cloths [7], activated carbon [8–12], multi-walled carbon nanotubes [13,14], titanium oxide [15–17], cerium oxide [18–20] and carbon-coated monolithic supports [21–23].

Nevertheless, few systems have been tested in the reduction of bromate ion. The reduction of bromate to hypobromide and subsequently to bromide in the presence of activated carbon, through the formation of surface oxides, has been reported [4,5,24,25]. The adsorption and reduction of bromate is proposed to be influenced by the particle size, the pore volume and the presence of surface oxygenated groups, particularly carboxylic groups. The influence of the surface oxygen content on the activated carbon capacity for bromate reduction has also been reported, as well as the influence of pH and of some organic and inorganic species usually present in water [5]. However, the reaction rates for these systems are not satisfactory, and it is not always clear whether actual conversion of bromate or just adsorption is taking place.

A silicon-based structured microreactor was recently used to test the catalytic activity of Ru supported on carbon nanofibers for the reduction of bromate [6]. Although redox reactions involving oxidation of water are possible, they are too slow and bromate is too stable in water. Thus, methanol was used as a proton donor. Turn-over frequencies of 0.032 s^{-1} were achieved for this system, but deactivation was observed. It was proposed that RuO_2 is responsible for the reduction of bromate, being oxidized to RuO_3 . The latter is then reduced to the former species by the alcohol present in solution. However, hydroxylation occurs simultaneously, which leads to deactivation of the catalyst.

A different reaction mechanism is proposed in two other studies. Mills and Meadows [26] applied a ruthenium oxide heterogeneous catalyst to the reduction of bromate in water, with and without the addition of an organic alcohol to the solution. The influence of the initial bromate concentration, loading of the catalyst and the presence of other anions in solution were evaluated. It was also observed that the presence of an alcohol in the solution led to faster reduction of bromate into bromide ion. It was suggested that the Ru heterogeneous catalyst used is capable of promoting the hydrolysis of water, thus leaving available hydrogen for reaction with bromate ions on the surface of the catalyst, which ultimately lead to the reduction of bromate into bromide coupled with the release of oxygen. Nevertheless, they observed that the addition of an alcohol increased the reaction rate due to its faster oxidation relatively to water. Chen et al. [27] used palladium supported on alumina as heterogeneous catalyst for bromate reduction in the presence of hydrogen. Other supports were also tested, including silica and activated carbon. Adsorption of bromate is stated as essential for initiation of the reaction, acting as the controlling step. The influence of pH was also tested, since negatively charged surfaces may cause repelling of bromate anions and consequent decrease of the bromate reduction rate. Metallic palladium supported on alumina showed the best activity, which correlates with the hydrogen adsorption capacity of the metal. A similar mechanism to the one proposed by Mills and Meadows [26] was considered, in which the slow oxidation of water over the catalyst was overcome by the introduction of oxygen into the reaction system. Thus, they propose that hydrogen is adsorbed and dissociated on the surface of palladium, and then reacts with adsorbed bromate.

Finally, the reduction of bromate has also been tested using Pd supported on macro structures, such as honeycomb monoliths, sintered metal filters or carbon felts, which were previously covered

with carbon nanofibers [28], where the influence of the type of macro structure used as support for the carbon nanofibers was assessed. A life cycle assessment of the application of these type of catalysts to the reduction of bromate in water was also performed [29]. Similarly, other mono and bimetallic catalysts were also tested, using the same types of structured carbon nanofibers supports [30]. Furthermore, the N-doping of the carbon nanofibers on a structured support did not influence the activity of supported Pd or Ru catalysts [31].

In this work, the assessment of several monometallic catalysts supported on activated carbon for the catalytic reduction of bromate under hydrogen was carried out. To the best of our knowledge, this is the first systematic study for this reaction. The reaction mechanism was also clarified.

2. Materials and methods

2.1. Preparation of catalysts

A commercial activated carbon (NORIT GAC 1240 PLUS, 0.5% max acid soluble ash, 0.01% max acid soluble iron) was used as support for the metal phases. Before impregnation, the activated carbon was ground to a controlled particle diameter between 0.1 and 0.3 mm. 1 %wt monometallic catalysts were prepared by incipient wetness impregnation from aqueous solutions of the corresponding metal salts (H_2PtCl_6 , PdCl_2 , $\text{Cu}(\text{NO}_3)_2$, SnCl_2 , RhCl_3 , RuCl_3 , $\text{Ni}(\text{NO}_3)_2$, $(\text{NH}_4)_3\text{IrCl}_6$, $\text{Fe}(\text{NO}_3)_3$ and ZnCl_2). After impregnation, the samples were dried at $100\text{ }^\circ\text{C}$ for 24 h, heat treated under nitrogen flow at $200\text{ }^\circ\text{C}$ for 1 h, and finally reduced at $200\text{ }^\circ\text{C}$ in hydrogen flow for 3 h. The selected temperatures have been shown to be adequate for the preparation of these catalysts, avoiding sintering or alloy formation [11,32].

2.2. Characterization of catalysts

Selected catalysts were characterized using different techniques: N_2 adsorption at $-196\text{ }^\circ\text{C}$, H_2 chemisorption and transmission electron microscopy (TEM).

The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at $-196\text{ }^\circ\text{C}$ with a Nova 4200e (Quantachrome Instruments) equipment. BET surface areas (S_{BET}) were calculated.

Metal dispersions were determined by chemisorption of H_2 at $35\text{ }^\circ\text{C}$ and atmospheric pressure in an Altamira Instruments AMI-200 apparatus, using the pulse method, and assuming a stoichiometric ratio $\text{H}_2/\text{metal} = 1/2$. Pulses of $58\text{ }\mu\text{L}$ (from a calibrated loop) were successively injected in the carrier gas ($25\text{ cm}^3(\text{STP})/\text{min}$ of Ar), which passes through the catalyst bed (150 mg), until saturation of the catalyst surface. The non-adsorbed hydrogen is measured with an online thermal conductivity detector. The amount of H_2 corresponding to saturation was calculated by summing the differences between the amounts injected and detected at outlet.

TEM analyses were obtained using a LEO 906E microscope operating at a 120 kV accelerating voltage.

2.3. Evaluation of catalysts

Bromate reduction was carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 180 mL of deionised water and 400 mg of catalyst were introduced into the reactor, the magnetic stirrer was adjusted to 700 rpm and hydrogen was fed to the reactor at $100\text{ cm}^3(\text{STP})/\text{min}$ during 15 min to remove oxygen. After that

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