



Catalytic reduction of bromate over monometallic catalysts on different powder and structured supports



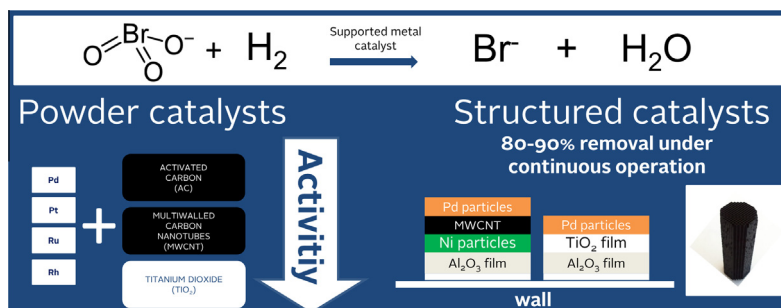
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HIGHLIGHTS

- Metal catalysts for the reduction of bromate under hydrogen in water were prepared.
- Different supports for the metal phase were evaluated to improve catalytic activity.
- The use of TiO₂ and MWCNT as supports improved the activity when compared with AC.
- Structured monolithic catalysts were prepared using TiO₂ and MWCNT supported Pd.
- Stable continuous removal of bromate was achieved between 80% and 90%.

GRAPHICAL ABSTRACT



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ABSTRACT

Bromate in water has been associated with cancer risks for lifetime exposures, and present technologies for its removal have important drawbacks that create a need for the development of new and more efficient alternatives. Heterogeneous catalysis has been explored for the removal of inorganic pollutants from water with promising results. In this work we aim to improve the efficiency of the catalytic reduction of bromate to bromide by exploring different supports (activated carbon, titanium dioxide and multi-walled carbon nanotubes) for the catalytic metallic phase (Pd, Pt, Rh and Ru). Improvements of the turn-over frequency in the order of 1000 from previously reported activated carbon supported catalysts were obtained with titanium dioxide and multi-walled carbon nanotubes for experiments using 10 mg L⁻¹ initial concentration of bromate; leading to complete conversion into bromide in under 5 min for TiO₂ and 30 min for MWCNT.

On the other hand, the use of structured catalysts for advanced water treatment processes has been recently shown as a promising alternative for conventional catalysts. We demonstrate the application of highly active metal-support pairings on a structured catalyst towards bromate removal during continuous operation, achieving up to 87% bromate conversion at steady-state.

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1. Introduction

Bromate is consistently found in water treatment plants at concentrations that represent a significant cancer risk for lifetime exposures. The main origin of bromate is the ozonation of bromide

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during the water treatment process [1]. Methods available for the removal of bromate from water, including adsorption, biological or electrochemical approaches, generally give origin to unwanted sludges and concentrated secondary streams, or present low efficiencies [2,3]. The lack of an efficient technology to control bromate concentrations in water has created a need for the development of new alternatives for its removal. Bromate reduction has been approached using different alternatives such as photoelectrocatalytic reduction using Ti/TiO₂ photocathode [4], heterogeneous redox catalysis [5] and heterogeneous catalysis under hydrogen [6].

The development of heterogeneous catalysts for reduction of bromate under hydrogen into bromide, a less harmful species, has been shown to be a potentially attractive method with interesting efficiencies, as in the case of bromate reduction by granular activated carbon [2], alumina supported metallic catalysts [6], carbon nanofibers supported metallic catalysts [3,7–9], zeolite supported metallic catalysts [10] and activated carbon supported metallic catalysts [1,11]. The use of different supports for active metallic phases to explore metal-support interactions, better metallic configurations or different reaction mechanisms have already been shown to be effective in similar catalytic reaction for reduction of inorganic pollutants in water under hydrogen [12–15]. In the case of bromate reduction into bromide, it has been demonstrated that the reaction can occur by different pathways. Bromate can be reduced by direct reaction with hydrogen in solution and also by adsorption and reduction by hydrogen on the surface of the metallic particles. In the last case, bromide is released in the solution and the metal becomes oxidized. To complete the cycle, hydrogen also reduces the metal phases, which are available again to further interaction with bromate and hydrogen [1]. Bromate can also be removed by adsorption, particularly when activated carbon is used as catalyst support [1], but also by reduction under hydrogen on the surface of the activated carbon and zeolite supports [1,10]. Supported noble metal catalysts like Pd, Pt, Ru and Rh efficiently promote the reduction of bromate into bromide ion under hydrogen at room temperature and pressure, the Pd catalyst being the most promising among them, independently of the support used [1,6,10]. Similarly to what is observed in the nitrate reduction [16], the Pd-Cu bimetallic catalysts is the most promising pair, presenting remarkable activity on the reduction of bromate into bromide under hydrogen [1,10].

Moreover, the use of monolithic catalysts structured at the nano- and micro-scale in water treatment has already been demonstrated to present advantages when compared with other methods for continuous operations [17]. Their use can enhance conversion, selectivity and catalyst life due to the high contact efficiencies between the support and flow streams [18]; besides, it eliminates the need for filtration of catalyst particles, especially important in liquid phase systems. Palomares et al. [8] reported the catalytic reduction of bromate over Pd catalysts supported on carbon-based structured materials. On the other hand, Thakur et al. [3] observed that Ru catalysts supported on carbon nanofibers gradually deactivate when tested in bromate reduction using ethanol as a reducing agent in silicon micro-reactors, despite good initial activity.

In this work we aim to further improve the catalytic reduction of bromate by exploring the use of different supports for the catalytic metallic phase. The most promising catalytic systems will then be applied in the continuous reduction of bromate using a structured catalyst.

Three different supports for the metal catalysts were selected: activated carbon (AC), multiwalled carbon nanotubes (MWCNT) and titanium dioxide (TiO₂). They have shown promising results as catalyst supports in the reduction of nitrate in water under hydrogen [15], as well as other hydrogenation reactions. Bromate removal using AC has been discussed in a previous work [1], while

several works on the use of TiO₂ [12,14,19–24] and MWCNT [3,7,8,15,25–28] for similar reactions may be found in the literature.

Series of AC, MWCNT and TiO₂ supported monometallic catalysts were prepared and their performance in the hydrogen reduction of bromate in water was evaluated. Selected catalysts were then prepared under structured form, supported on a honeycomb monolith, and were applied in the catalytic reduction of bromate in water under continuous operation.

2. Experimental

2.1. Catalysts preparation

2.1.1. Powder catalyst

Powder catalysts of Pd, Pt, Rh and Ru supported on each of AC, MWCNT and TiO₂ were prepared and used in the semi-batch reduction of bromate under hydrogen. The detailed preparation methods of the powder catalysts, by incipient impregnation, are described elsewhere [15,16,25,26,29]. Briefly, aqueous solution of the precursor salts were prepared at the adequate concentrations to achieve the desired metallic loading. Prior to impregnation, the supports were degassed by ultrasonication in a low pressure system. The impregnated catalysts were dried at 110 °C for 24 h, heat treated under nitrogen flow during 1 h and reduced under hydrogen flow for 3 h at a previously optimised temperature for each metal/support pairing [14,15,25,29].

2.1.2. Structured catalyst

Structured catalysts of Pd supported on MWCNT and TiO₂ on a structured support were prepared and used in the continuous reduction of bromate under hydrogen. The catalysts were prepared in separated steps for the support layer and the deposition of the metallic phase. Structured cordierite honeycomb monoliths (22 mm × 60 mm, 400 channels per square inch) were used as support for the catalytic phases, which in turn were both supported on TiO₂ and MWCNT.

The honeycomb cordierite monoliths were initially heat treated at 900 °C under air (50 cm³ min⁻¹; 1 h, 10 °C min⁻¹) to remove impurities. Afterwards, the monoliths were dipped into a nyacol alumina suspension (25% nyacol in water; 30 mm min⁻¹ dip rate, 1 min dipped in suspension). The alumina washcoated monoliths were then rinsed with distilled water and dried overnight at room temperature; followed by a final drying stage at 110 °C in air for 1 h. The dried alumina washcoated monoliths were then heat treated under air flow at 450 °C (50 cm³ min⁻¹; 1 °C min⁻¹), in order to achieve a γ -alumina coating [30,31], using a low heating rate to avoid cracking of the alumina layer [32].

The monoliths coated with carbon nanotubes (MWCNT monoliths) were prepared following a procedure adapted from the literature [31–35]. The CNT growth catalyst (nickel) was then impregnated on the surface of the monoliths, by adsorption from a pH neutral nickel solution. The nickel solution was prepared using 29 g Ni(NO₃)₂·6H₂O as precursor on a 1 L solution, together with 80 g NH₄NO₃ and 4 mL ammonia solution (25%). The monoliths were kept overnight in this solution (12 h) and the liquid was continuously flowed through the channels, which was achieved by keeping the solution stirred while the monolith was fixed on a horizontal position, oriented in the direction of the flow. The monoliths were then rinsed with distilled water and dried overnight at room temperature, followed by drying at 110 °C in air for 1 h. Afterwards, the monoliths were heat treated under nitrogen flow at 450 °C for 2 h (50 cm³ min⁻¹; 1 °C min⁻¹). Finally, the growth of the carbon nanotubes was carried out under a C₂H₆: H₂ mixture (0.6:0.4) at 600 °C for 210 min. The temperature and

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