



Bimetallic activated carbon supported catalysts for the hydrogen reduction of bromate in water



J. Restivo, O.S.G.P. Soares, J.J.M. Órfão, M.F.R. Pereira*

Laboratory of Catalysis and Materials – Associate Laboratory LSRE/LCM, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

The association of bromate in drinking water with several public health risks, namely related to its carcinogenic potential and its toxic nature, has led to an interest in the development of sustainable alternatives for its removal from water. The hydrogen reduction of bromate over supported heterogeneous metallic catalysts has already been shown to be an interesting alternative for the reduction of bromate into less hazardous species, without formation of additional sludges.

In this work, the coupling of a noble metal with a second metal supported on activated carbon has been studied for this reaction. Several metals were used for this goal, resulting in a wide array of combinations of noble and promoter metals. All the combinations showed remarkable activity for the complete conversion of bromate into bromide, without accumulation of by-products.

The role played by the second metal was extensively studied, for which experiments were conducted using physical mixtures of the corresponding monometallic catalysts and also different metal amounts on the supported bimetallic catalysts. In most cases, the presence of a second metal hindered the activity of the noble metal, when compared with the respective monometallic catalyst. In the case of the Pd–Cu bimetallic catalyst, it is possible to improve the activity obtained with the Pd catalyst. The activity of the bimetallic catalyst was shown to be dependent on the composition.

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1. Introduction

Concentrations of bromate in the range 1–50 $\mu\text{g/L}$ have been detected in water at full scale water treatment plants [1]. Average concentrations in the United States have been reported to be as high as 100 $\mu\text{g/L}$ [2]. Bromate is mainly derived from the ozonation of bromide containing waters, which reacts with molecular ozone, as well as with the OH^\bullet radicals formed during the process [1–3]. Bromate ion in water may also originate from other sources, such as seawater intrusion, pesticide run-off, industrial wastes and impurities in road de-icing salt [2].

Regarding the dangers associated with the presence of bromate in water, it has been estimated that a concentration of 3.9 $\mu\text{g/L}$ corresponds to a cancer risk of 10^{-5} for life-time exposures [4]. On the other hand, the United States Environmental Protection Agency (USEPA) reports that life-time exposures to 5, 0.5 and 0.05 $\mu\text{g/L}$ lead to cancer risks of 10^{-4} , 10^{-5} , and 10^{-6} , respectively [5]. 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 [1]. Both the World Health Organization (WHO) and USEPA's provisional guidelines limit the concentration of bromate in source water to 0.01 mg/L [4,5].

The consequent classification of bromate by the International Agency for Research on Cancer in Group 2B (possibly carcinogenic for humans) [6] has led to an interest from the scientific community in the development of technologies for their efficient removal from water.

There are several methods available to remove bromate ion from water, namely adsorption, biological or electrochemical technologies. Nevertheless, the formation of unwanted sludge, and the low efficiency or accumulation in secondary streams leaves space for the development of new technologies [2,3].

Heterogeneous catalysis has already been demonstrated to be an efficient method for the removal of bromate from water by hydrogen reduction to more desirable species, such as bromide [2,3,7–12]. Nevertheless, to the best of our knowledge, the potential application of bimetallic catalysts has yet to be tested in this process. Such systems have demonstrated potential to enhance the

* Corresponding author. Tel.: +351 22 508 1468.
E-mail address: fpereira@fe.up.pt (M.F.R. Pereira).

Table 1
Bimetallic catalysts supported on AC.

1% Noble metal–1% second metal	
Pd	Cu; Fe; Sn; Zn
Pt	Cu; Sn
Ru	Cu; Ni
Rh	Sn
Ir	Cu
x% Pd	x% Cu
1	0.1; 0.3; 0.6; 1; 2; 5
2	1

hydrogen reduction of nitrites in water [13–16], which have been reported to have a mechanism similar to that of bromate [7].

The aim of the present work is to determine whether the coupling of a promoter metal and a noble metal supported on activated carbon is advantageous in the catalytic hydrogen reduction of bromate in water, at room temperature and pressure. For that effect, several bimetallic pairs were tested, and some of them were selected to be used in experiments using physical mixtures, which were done to provide information regarding the role of the promoter metal in the reaction. Furthermore, different weight loading ratios were also tried out for a selected bimetallic supported catalyst.

2. Experimental

2.1. Preparation

A commercial activated carbon (NORIT GAC 1240 PLUS) was used as support. The activated carbon (AC) was ground to a controlled particle diameter between 0.1 mm and 0.3 mm. The monometallic catalysts were prepared by incipient wetness impregnation and the bimetallic catalysts by incipient wetness co-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). The contents of both noble and promoter metals were varied between 0.3 and 5 wt.%. After impregnation, the samples were dried at 100 °C for 24 h, calcined under a nitrogen flow at 200 °C for 1 h, and finally reduced at 200 °C in hydrogen flow for 3 h. The catalysts prepared are listed in Table 1.

2.2. Characterization

Selected catalysts were characterized using different techniques: H_2 chemisorption (all bimetallic pairs supported on AC), N_2 adsorption at -196 °C (AC, 2%Pd–1%Cu/AC, 1%Pt–1%Cu/AC, 1%Rh–1%Cu/AC), transmission electron microscopy (TEM; 1%Pd–1%Cu) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS; catalysts characterized after reaction: 1%Pd–1%Cu/AC; 1%Pd/AC + 1%Cu/AC).

The chemisorption of H_2 was carried out at 35 °C and atmospheric pressure in an Altamira Instruments AMI-200 apparatus, using the pulse method. The samples were previously calcined and reduced in situ, replicating the treatment conditions used in the preparation of the catalysts described in the previous section. Pulses of 58 μL (from a calibrated loop) were successively injected in the carrier gas (25 cm^3/min of Ar), which passes through a catalyst bed (150 mg), until saturation of the catalyst surface. The non-adsorbed hydrogen is measured with an online thermal conductivity detector.

Textural characterization of the support and of the supported catalysts was based on the analysis of N_2 adsorption isotherms,

Table 2
Textural characterization of the activated carbon (AC) and some of the catalysts.

Sample	S_{BET} (m^2/g)	S_{meso}^a (m^2/g)	V_{micro}^a (cm^3/g)
AC	869	97	0.318
2%Pd–1%Cu/AC	870	90	0.330
1%Pt–1%Cu/AC	876	168	0.275
1%Rh–1%Cu/AC	862	104	0.280

^a Micropore volume (V_{micro}) and mesopore surface area (S_{meso}) calculated by the t -method.

measured at -196 °C with a Nova 4200e (Quantachrome Instruments) equipment.

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

SEM-EDS analyses were performed using a FEI QUANTA 400 FEG ESEM/EDAX PEGASUS X4M apparatus.

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 fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and hydrogen was fed at 100 cm^3/min during 15 min to remove oxygen. After that period, 20 mL of a bromate solution, prepared from NaBrO_3 , were added to the reactor, in order to obtain an initial BrO_3^- concentration equal to 10 mg/L.

Small samples were taken from the reactor for determination of bromate and bromide concentrations after defined periods. Bromate ion concentrations were measured by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm \times 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M $\text{NaCl}:\text{CH}_3\text{OH}$ (45:55). Bromide ion concentrations were followed using a MetroHM 881 Compact Pro ion chromatography apparatus coupled with a 863 Compact Autosampler. An appropriate MetroHM chromatography column for anions was used with a 3.6 mM Na_2CO_3 stationary phase.

3. Results and discussion

3.1. Characterization

From H_2 chemisorption experiments it was possible to obtain the metal dispersion of the monometallic catalyst [17], but for the bimetallic catalysts no H_2 chemisorption was noticed. This may be an indication that some interaction exists between the noble metal (Pd, Pt, Ru, Rh or Ir) and the other metal (Cu, Sn, Ni, Zn or Fe), eventually forming an alloy, or the second metal is covering the noble metal, strongly limiting H_2 chemisorption.

Table 2 shows that the BET surface area of the support is 869 m^2/g . Moreover, it can be observed that the textural parameters of the supported metal catalysts remained practically unchanged compared to the unloaded carbon.

Selected catalysts were analyzed by TEM. In general, the metal is well dispersed on the support, most of the catalysts presenting metal particle diameters between 3 and 7 nm, but in some cases a few larger particles are also observed. Fig. 1 shows a representative TEM image of the 1%Pd–1%Cu/AC. It was also observed that there are no significant differences in the metal particle size when the amounts of Pd or Cu in the Pd–Cu bimetallic catalysts were modified.

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