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

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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.

Keywords: bromate, hydrogen reduction, bimetallic catalysts, activated carbon

28 1 INTRODUCTION

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

36 Regarding the dangers associated with the presence of bromate in water, it has been
37 estimated that a concentration of 3.9 $\mu\text{g/L}$ corresponds to a cancer risk of 10^{-5} for life-
38 time exposures [4]. On the other hand, the United States Environmental Protection
39 Agency (USEPA) reports that life-time exposures to 5, 0.5 and 0.05 $\mu\text{g/L}$ lead to cancer
40 risks of 10^{-4} , 10^{-5} , and 10^{-6} , respectively [5]. The main risks are associated with the
41 kidneys, both as targets for cancer and for toxic action of bromate. The peritoneum
42 and the thyroid are also considered as cancer targets, and there is also the possibility
43 that exposure to bromate may result in low sperm counts [1]. Both the World Health
44 Organization (WHO) and USEPA's provisional guidelines limit the concentration of
45 bromate in source water to 0.01 mg/L [4, 5].

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

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

54 Heterogeneous catalysis has already been demonstrated to be an efficient method for
55 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 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 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 , $\text{Ni}(\text{NO}_3)_2$, $(\text{NH}_4)_3\text{IrCl}_6$, $\text{Fe}(\text{NO}_3)_3$, 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 H₂ 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 cm³/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 N₂ adsorption isotherms, 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 cm³/min during 15 min to remove oxygen. After that period, 20 mL of a bromate solution, prepared from NaBrO₃, were added to the reactor, in order to obtain an initial BrO₃⁻ concentration equal to 100 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 x 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl:CH₃OH (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 Na₂CO₃ stationary phase.

3 RESULTS AND DISCUSSION

3.1 CHARACTERIZATION

From H₂ chemisorption experiments it was possible to obtain the metal dispersion of the monometallic catalyst [17], but for the bimetallic catalysts no H₂ 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 H₂ chemisorption.

Table 2 shows that the BET surface area of the support is 869 m²/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. Figure 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.

3.2 CATALYTIC EXPERIMENTS

3.2.1 BIMETALLIC CATALYSTS

The bromate reduction in the presence of hydrogen was evaluated using several different bimetallic catalysts. To assess this effect, the same activated carbon support

was used for all the metal pairs. The bromine mass balance throughout the experiments presented here showed that the BrO_3^- was removed from water due to conversion into Br^- , with no contribution from adsorption or formation of secondary products.

On a first approach, palladium was coupled with different metals. The corresponding bromate removals are shown in Figure 2.

The coupling of Pd with Cu was shown to be the most efficient combination among those tested, even surpassing the performance of the Pd monometallic catalyst. All the other combinations present similar or lower performances than the Pd monometallic catalyst. A similar trend was observed for the second metal alone, as presented elsewhere: $\text{Cu} > \text{Sn} > \text{Fe} > \text{Zn}$ [17]. Comparison of the performances of the second metals tested alone showed them to be less active than the bimetallic catalysts prepared with Pd.

Among the metals tested, the Cu monometallic catalyst shows the best activity both alone [17] and also paired with Pd. Therefore, bimetallic catalysts containing Cu and different noble metals (Pd, Ir, Pt, Ru) supported on activated carbon were tested in the bromate reduction in the presence of hydrogen, as seen in Figure 3.

Once again, the Pd-Cu catalyst showed the best performance of those tested, closely followed by the Pt-Cu catalyst. Ir-Cu and Ru-Cu catalysts are outperformed by the Cu monometallic catalyst in the first 10 and 15 min, respectively, but eventually overpass it, promoting 100% bromate conversion after 25 and 30 minutes respectively; with the Cu monometallic catalyst total bromate reduction was only achieved after 60 min of reaction. Overall, the performance of every Cu-containing bimetallic catalyst tested here is between that of the Pd-Cu and the Cu monometallic catalyst.

To assess the performance of different noble metals in the reduction of bromate using bimetallic catalysts, some noble metals (Pd, Pt, Ru or Rh) were paired with other metals (Sn or Ni) and evaluated in the reaction (Figure 4).

As can be seen in Figure 4, the Pd-Sn catalyst shows the best catalytic activity. Nevertheless, the performance of this catalyst is inferior to that observed with the pair Pd-Cu (Figure 3) and also with the Pd monometallic catalyst. In fact, of all the metals that were coupled with the noble metals, copper was the only one that was observed to act as a promoter, while the remaining metals (Fe, Sn, Zn, Ni) used as secondary metals in the bimetallic catalysts were observed to result in worse performances than the corresponding monometallic catalysts. It has been reported that the coupling of Ru and Ni reduces the total adsorption capacity for CO in microcalorimetry experiments, approaching that of Ni alone, probably due to alloy formation [18]. So, the decrease in the bromate reduction performance from the Ru monometallic catalyst to the Ru-Ni bimetallic catalyst must be related to the interaction of the two metals on the surface of the support. In addition, it is known that H₂ chemisorption on Ni is strong [19]. Thus, Ni might be competing with Ru for H₂ chemisorption. For nitrite reduction, it has been shown that strong absorption of H₂ results in lower catalytic activity, with Ni catalysts supported on activated carbon showing no activity [15]. The Pd, Pt and Rh monometallic catalysts in Figure 4 show better performance than the bimetallic catalysts containing Sn. The coupling of Pt with Sn in a bimetallic catalyst supported on alumina and prepared at low reduction temperatures has been observed to result in a loss of activity in the hydrogenation of crotonaldehyde, mostly due to the partial blocking of Pt active sites by Sn [20]. The same effect was observed for the conversion of isobutene when the Sn content was higher than 0.5% [21]. A similar reason can explain why the addition of Sn reduces the activity of Pd, Pt and Rh in our case.

3.2.2 PHYSICAL MIXTURES

Since the monometallic catalysts supported on activated carbon have shown good activities in the hydrogen reduction of bromate in water [17], it is necessary to compare the performance of the monometallic and bimetallic catalysts to understand if there is a synergic effect in the coupling of two different metals, or if the increase in the performance, when observed, is merely due to the higher metal loading available. Therefore, experiments were made using physical mixtures of monometallic catalysts supported on activated carbon. As already mentioned (Figures 2 to 4), the bimetallic catalyst does not always perform better than the monometallic catalyst. When other

metals were coupled with Pd, only Cu managed to improve the removal of bromate from water. Thus, the effect of Cu as a promoter metal was studied when coupled with Pd.

The SEM-EDS spectra obtained for the post-reaction recovered catalysts are presented in Figure 5. This analysis was made for recovered catalysts from the experiments using bimetallic catalysts and physical mixtures of monometallic catalysts. The observations shown here were compared with the SEM-EDS spectra obtained with fresh catalysts, as well as those for the corresponding monometallic catalysts [22].

It is observable from the EDS data that, for the bimetallic catalyst, both metals were identified in close contact (Figure 5-a). Similar spectra were obtained for the fresh bimetallic catalysts, as reported elsewhere [22], This suggests that no changes, such as metal leaching or migration, occur during the bromate reduction reactions in the conditions used in the present work, with this catalyst.

For the physical mixture of 1%Pd/AC and 1%Cu/AC, both metals were identified in the metal particles where Pd was observed on the surface of the support (Figure 5-d). Only individual Cu particles were observed (Figure 5-e). This is due to the leaching of Cu, which has also been witnessed when similar experiments were carried out for the hydrogen reduction of nitrates in water [22]. In fact, the leaching of copper in similar supports has been observed by several authors, which leads to the conclusion that in the case of the Pd/Cu physical mixture, a bimetallic catalyst, with the metals in close contact, is formed in-situ under the reaction conditions used [22, 23].

In Figure 6 the bromate conversions obtained using the Pd and Cu system as monometallic catalysts, as a bimetallic catalyst and as a physical mixture of the two monometallic catalysts are compared.

From Figure 6 it is possible to see that the bimetallic catalyst shows better performance than the corresponding monometallic catalysts, as was already stated. Most importantly, the physical mixture of Pd and Cu monometallic catalysts presents even higher performance in the bromate reduction than the bimetallic catalyst. This must be related with the disposition of the metals on the support. When a mixture of

monometallic catalysts is used, all the metal active sites are accessible on the catalyst surface for the bromate reduction, whereas the same may not occur when bimetallic catalysts are used [22], since the most active metal could be covered by the other metal. In fact, during the hydrogen chemisorption analyses no H₂ chemisorption was observed on the Cu and Pd-Cu catalysts, as was expected since Cu does not chemisorb H₂ [24]. This may indicate that some interaction between the noble metal and Cu occurs, forming an alloy, and/or that Cu is covering most of the noble metal, which may result in a strong limitation in the amount of H₂ chemisorbed in the bimetallic catalyst. In addition, it has been reported [25] that the heat of adsorption during CO adsorption microcalorimetry experiments using a 1%Pd-0.3%Cu catalyst supported on an activated carbon (similar to that used in this work) decreases when compared to the Pd monometallic catalyst. This behavior was observed for catalysts heat treated at or above 200 °C, which was explained by the formation of alloys. Such observations have also been confirmed by XRD [26]. Thus, since the catalysts used in this study were heat treated at 200 °C, the different activities obtained in the experiments with the physical mixtures and bimetallic catalysts could be related with some alloy formation in the bimetallic catalyst leading to a decrease in the bromate reduction, which is known to involve the dissociation of hydrogen on the surface of the noble metal [7, 17]. SEM/EDS data show that the particles on the surface of the activated carbon contain both metals. This was observed for the bimetallic catalysts and for the physical mixtures of monometallic catalysts after reaction. Similar results were reported for the same type of catalysts when physical mixtures were used in the nitrate reduction [22], where the physical mixture of Pd and Cu catalysts performs equal or even better than the corresponding bimetallic catalyst. Thus, it is possible to conclude that for the Pd-Cu pair, while there is an improvement in the bromate reduction when compared with the Pd monometallic catalyst, the activity of the bimetallic catalyst could be partially hindered by the interaction between the Cu and Pd on the surface of the activated carbon support. An additional experiment was made using homogeneous Cu²⁺ as catalyst, where an amount equal to that present on the corresponding activated carbon supported catalysts was used. Only a residual improvement of the performance was achieved when compared with the experiment only with H₂. Thus,

the leaching of Cu into solution should not contribute significantly to the reduction of bromate in the case of the physical mixtures of monometallic Pd and Cu catalysts.

Different proportions of the pair Pd-Cu as a bimetallic catalyst were tested in the catalytic reduction of bromate, and the removals obtained after 10 minutes of reaction are depicted in Figure 7 as a function of the atomic percentage of copper. Since the removal of bromate was complete after 30 minutes of reaction for all the proportions, an intermediate stage of reaction was selected to allow the comparison between the catalysts.

The performance of the bimetallic Pd-Cu catalysts with different loadings of both metals can be arranged in the following order: 1% Pd-2% Cu > 1% Pd-1%Cu $\approx$ 1% Pd-0.6% Cu > 1%Pd $\approx$ 2% Pd-1%Cu > 1% Pd-0.3% Cu > 1% Pd-5% Cu $\approx$ 1% Pd-0.1% Cu. When considering the atomic compositions presented, it is clear that a fraction of Cu at least equal to 0.5 is needed to improve the performance of the bimetallic catalyst relatively to the monometallic palladium catalyst. However, a large atomic fraction was shown to actually hinder the reduction rate of bromate (see 1% Pd-5% Cu/AC). It has been suggested for the Pd-Cu bimetallic catalysts supported on activated carbon that the increase in the relative amount of the promoter metal decreases the availability of isolated noble metal particles [26]. Additionally, it has been observed than on a Pd-Cu catalyst, applied to the catalytic hydrogenation of nitrite, the Pd promotes the dissociation of H₂ to react with nitrite ions, while also reducing oxidized Cu, which is then able to participate in the reaction, thus increasing the reaction rate by providing two active centers for reaction [13]. In regard of the textural characterization of the catalysts, particularly the information relative to metal particle size, significant changes have not been detected [26, 27]. Therefore, the presence of the promoter metal increases the reactivity of the system on a certain range of atomic ratios; outside this interval the available noble metal surface necessary to interact with hydrogen and bromate ion decreases [25, 26]. It has been observed that the addition of Cu to supported Pd catalysts reduces the availability of high coordination sites for reaction [28]. The low coordination sites, which become more predominant on the Pd surface with the addition of Cu, are known to have higher activity in hydrogenation reactions [29, 30]. This behavior has been observed in the reduction of nitrates over Pd-Cu

bimetallic catalysts, where the selectivity to the desired product (nitrogen) is hurt due to over hydrogenation [31]. In the case of bromate reduction, the conversion into bromide is always complete; so there is an improvement on the reaction rate when Cu is coupled with Pd. However, when the ratio of Cu to Pd is too high, the performance of the catalyst decreases, probably because the low coordination sites on the Pd surface become blocked by the added Cu.

The comparison of the performance of the bimetallic catalyst with different loadings (Figure 7) with the performance of the physical mixtures of the same pair (Figure 6) is useful to better understand the role of the bimetallic catalysts in the reduction of bromate in water using hydrogen. The performance of the physical mixture of the pair Pd-Cu is noticeably better than that of the corresponding bimetallic catalyst, regardless of the Pd/Cu ratio chosen (results not shown). It has been shown that for the remaining pairs tested, the addition of other metal did not improve the removal of bromate obtained with the noble metal monometallic catalyst. Thus, it seems that the utilization of a bimetallic catalyst is only beneficial for this reaction in specific cases. Accordingly, for the Pd-Cu pair, the addition of Cu as promoter metal to the Pd catalyst improves the reaction rate due to interaction between the metals, when they are found in a specific range of atomic ratios; this was not observed for the remaining metal pairs studied. The observed increase in performance of the physical mixture of Pd and Cu monometallic catalysts supported on AC when compared with the corresponding bimetallic catalyst might then also be attributed to the close interaction of Pd and Cu coming from solution (leached from the Cu monometallic catalyst) in an atomic ratio that is highly favorable for the studied reaction. On the other hand, in the mild experimental conditions used (room P and T), alloy formation on the surface of AC is not to be expected. It is possible that the higher performance of the physical mixture is related to the close interaction between Pd and Cu (leached from 1%Cu/AC) without the formation of alloys that might hinder the hydrogen chemisorption capability of Pd, as likely occurs when the bimetallic catalysts are heat treated and reduced at 200 °C.

4 CONCLUSIONS

Several bimetallic pairs supported on activated carbon were studied as catalysts for the hydrogen reduction of bromate in water. All the tested catalysts showed remarkable activity on the reduction of bromate under hydrogen. Furthermore, the conversion of bromate into bromide was observed to be complete for all the cases, without formation or accumulation of by-products in solution.

The Pd-Cu pair was shown to be the most promising catalyst, completely converting bromate in less than 10 minutes of reaction. Most of the other pairs resulted in reduced activity when compared to the corresponding monometallic noble metal catalysts.

Experiments using physical mixtures were carried out, and it was observed that the presence of a second metal, in most cases, can decrease the available surface of the noble metal for reaction, or can decrease the capacity of the most active metal to adsorb hydrogen. However, for the Pd-Cu pair, the experiment carried out using the corresponding physical mixture outperformed the bimetallic catalyst; nevertheless, during the physical mixtures experiments, in-situ formation of bimetallic catalyst was observed. This suggests that the interaction between the two metals improved the removal of bromate.

The influence of the composition in Pd-Cu catalysts was investigated, and it was shown that some improvement can be obtained regarding the reduction of bromate ion in water, when this pair was compared with the Pd monometallic catalyst. The improved performance of the Pd-Cu catalyst was observed to only occur in a specific range of atomic ratios.

Acknowledgments

Support for this work was provided by LSRE/LCM LA financing from Programa Operacional Factores de Competitividade (COMPETE), project FCOMP-01-0124-FEDER-022706 (Ref. FCT Pest-C/EQB/LA0020/2011), by Fundação para a Ciência e a Tecnologia (FCT) and Fundo Europeu de Desenvolvimento Regional (FEDER). J. Restivo and O.S.G.P. Soares thank FCT for their research grants (SFRH/BD/95751/2012 and SFRH/BPD/80435/2011, respectively).

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434

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436 **Table 1.** Bimetallic catalysts supported on AC.

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

439

440 **Table 1**

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

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445 **Table 2**

Sample	S_{BET}	$S_{\text{meso}}^{\text{a}}$	$V_{\text{micro}}^{\text{a}}$
	(m^2/g)	(m^2/g)	(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

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

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449 LIST OF FIGURES

450 **Figure 1.** TEM micrograph of 1%Pd-1%Cu/AC bimetallic catalyst.

451 **Figure 2** – Evolution of the dimensionless concentration of bromate for reduction
452 experiments using H₂ and bimetallic palladium catalysts supported on activated
453 carbon.

454 **Figure 3** - Evolution of the dimensionless concentration of bromate for reduction
455 experiments using H₂ and bimetallic catalysts containing Cu, supported on activated
456 carbon.

457 **Figure 4** - Evolution of the dimensionless concentration of bromate for reduction
458 experiments using H₂ over Pd and Pt (a), and Ru and Rh (b), bimetallic catalysts
459 containing Sn or Ni, supported on activated carbon.

460 **Figure 5** – EDS spectra of metallic particles found in the surface of the catalysts after
461 reaction: a) 1% Pd - 1% Cu/AC; b) 1%Pd/AC + 1%Cu/AC; c) 1%Pd/AC + 1%Cu/AC
462 (copper particle).

463 **Figure 6** - Evolution of the dimensionless concentration of bromate for reduction
464 experiments using H₂ over the bimetallic Pd-Cu catalyst and physical mixture of the
465 corresponding monometallic catalysts.

466 **Figure 7** - Removal of bromate after 10 min during reduction experiments using H₂
467 over different bimetallic Pd-Cu catalysts vs. atomic copper content.

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469 **Figure 1**

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472 **Figure 2**

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475 **Figure 3**

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481 Figure 5

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486 **Figure 6**

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