Enhanced Electroreductive Removal of Bromate by a Supported Pd–In Bimetallic Catalyst: Kinetics and Mechanism Investigation

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Supporting Information

ABSTRACT: In this work, the electroreductive removal of bromate by a $\text{Pd}_1\text{-In}_4/\text{Al}_2\text{O}_3$ catalyst in a three-dimensional electrochemical reactor was investigated. A total of 96.4% of bromate could be efficiently reduced and completely converted into bromide within 30 min under optimized conditions. On the basis of the characterization results and kinetics analysis, a synergistic effect of Pd and In was observed, and $\text{Pd}_1\text{-In}_4/\text{Al}_2\text{O}_3$ had the highest reaction rate constant of 0.1275 min^{-1} (vs 0.0413, 0.0328, and 0.0253 min^{-1} for $\text{In}/\text{Al}_2\text{O}_3$, $\text{Pd}/\text{Al}_2\text{O}_3$, and Al_2O_3). The results of electron spin resonance and scavenger experiments confirmed that both direct electron transfer and indirect reduction by atomic H^* were involved in the bromate removal process, while the direct reduction played a more important role. Moreover, the introduction of In could increase the zeta potential of $\text{Pd}_1\text{-In}_4/\text{Al}_2\text{O}_3$, facilitating bromate adsorption and its subsequent reduction on the catalyst. Finally, a reaction mechanism for bromate reduction by $\text{Pd}_1\text{-In}_4/\text{Al}_2\text{O}_3$ was proposed based on all the experimental results.

INTRODUCTION

Bromate is an oxyhalide disinfection byproduct frequently detected in drinking water from ozonation of bromide-containing source waters.¹ Because of its carcinogenic and genotoxic properties, the World Health Organization (WHO) has promulgated a $10 \text{ }\mu\text{g/L}$ standard for bromate in drinking water.² To meet this strict limitation, numerous treatment methods have been explored, including filtration, chemical reduction, biodegradation, activated carbon techniques, and photocatalysis.^{3–8} Among these technologies, liquid phase catalytic hydrogenation has proven to be an efficient and clean method to eliminate bromate.^{9,10} Wang et al. reported the hydrogenation reduction of bromate using a core–shell-structured catalyst with encapsulated Pd nanoparticles.¹¹ However, the catalytic hydrogenation needs an external supply of H_2 , while the storage and transportation of H_2 may be a hidden danger. Alternatively, the electrochemical reduction of bromate is found to be a promising approach due to its low maintenance requirements and efficient minimization of toxic chemicals and secondary pollution.^{12–14} Kishimoto and Matsuda reported an efficient electrochemical method to reduce bromate to bromide using a two-compartment electrolytic flow cell with activated carbon felt as electrodes.¹⁵ The results showed that bromate contamination can be removed within a few minutes, but this process required acidic conditions. Zhao et al. studied the effectiveness of a boron-doped diamond electrode in bromate removal by electrochemical reduction, and nearly 90% of bromate could be removed with the bias potential of -1.0 V within 2 h.¹⁴ However, the application of these cathodes for water treatment would be limited due to the low A/V ratio (ratio of the electrode area and solution volume). Hence, it is necessary to design a new electrochemical reactor and electrode with high

efficiency. Recently, a three-dimensional electrochemical reactor using granular activated carbon (GAC) or modified GAC as particle electrodes exhibited higher efficiency in treatment of heavy oil refinery wastewater compared with a two-dimensional electrode reactor (without particles).¹⁶ Moreover, the removal rate of the target pollutants could also be increased by using three-dimensional electrodes with more available reactive sites and electrons compared to the conventional two-dimensional electrodes.^{17,18}

It is widely reported that Pd has the unique property of activating H_2 to produce continuously adsorbed atomic H^* and trapping electrons, which could serve as a strong reducing agent in catalytic reductive reactions.¹⁹ Moreover, Pd-based bimetallic catalysts were found to exhibit better activity and selectivity in many important chemical reactions compared with monometallic Pd catalysts.^{20–22} It has been reported that the enhanced catalytic activity could be attributed to the promotion effect of the second metal element such as Cu, Au, Bi, Sn, Fe, etc.^{23–27} For instance, the catalytic hydrogenation efficiency of Pd/SnO_2 and $\text{Pd}/\text{Al}_2\text{O}_3$ toward N-nitrosodimethylamine and nitrate reduction was greatly enhanced by the addition of Sn and In.^{28,29} The efficiency of Cu- and Sn-doped carbon nanofiber/sintered metal fiber filters was also evaluated by bromate and nitrate reduction in continuously operated reactors.³⁰ However, studies on the electroreduction of bromate in a three-dimensional electrochemical reactor by Pd-based three-dimensional suspended electrodes are still limited. In addition, the effect of the dosage of

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other transition-metal (Cu, Sn, Bi, and In) dopants on the catalytic activity of Pd also needs to be investigated.

Hence, in this study, different Pd-based supported catalysts (Pd-M/Al₂O₃, M = Cu, Sn, Bi and In) were synthesized for the first time and evaluated based on their bromate reduction efficiency. Pd₁-In₄/Al₂O₃ was proven to have the highest efficiency as particle electrodes in the electrochemical reductive removal of bromate in a three-dimensional electrochemical reactor. Moreover, the bromate reduction followed pseudo-first-order kinetics. The catalyst was further characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), and zeta potential analysis to study the synergistic effect of Pd and In within the catalyst. The effect of catalyst dosage, solution pH, and applied current on the bromate reduction over Pd₁-In₄/Al₂O₃ was also studied in detail. On the basis of electron spin resonance (ESR) scavenger experiments, both direct electron transfer and indirect reduction by atomic H^{*} were confirmed to be involved in the bromate removal process. Finally, an electrochemical reduction mechanism of bromate over Pd₁-In₄/Al₂O₃ was proposed according to all the experimental results. The findings in this study demonstrate the potential of the three-dimensional electrochemical reactor as an effective system for eliminating bromate contamination in water.

MATERIALS AND METHODS

The catalysts were prepared by a conventional impregnation method. Briefly, γ -Al₂O₃ was immersed in PdCl₂ solution containing 0.1 M hydrochloric acid, followed by ultrasonic treatment for 360 min. After standing for 24 h, the obtained samples were dried at 120 °C, calcined at 300 °C for 120 min, and finally

reduced at 200 °C in a H₂ atmosphere for 300 min (flow rate: 100 mL/min). The resulting supported Pd catalysts were denoted as $x\%$ Pd/Al₂O₃, where x is the Pd loading amount (wt %). Bimetallic Pd-M/Al₂O₃ catalysts (M = In, Cu, Sn, Bi) were obtained by the same impregnation method with the theoretical Pd/M ratio of 1:4. Pd-In/Al₂O₃ with different Pd/In ratios was denoted as Pd_{*x*}-In_{*y*}/Al₂O₃, where x/y is the theoretical Pd/In ratio.

A three-dimensional electrochemical reactor was used for the electrochemical experiments, which was separated into a cathode cell and anode cell by a proton-exchange membrane (Nafion117, Dupont). For each batch experiment, the cathode cell was filled with 50 mL of aqueous solution of bromate using Na₂SO₄ as the supporting electrolyte. RuO₂/Ti was used as the cathode and anode with an effective geometric surface area of 100 cm², and the distance between cathode and anode was 4 cm. The reactor was controlled by a DC power supply source AMERLLPS302A (Dahua instrument corporation of Beijing). The initial concentration of bromate was 100 μ g/L unless otherwise specified, and the experiments were performed at room temperature. The system was magnetically stirred at a rate of 800 rpm.

The concentrations of bromate and bromide were measured using a Dionex 2000 ion chromatograph (IC), equipped with an IonPac AS-19 anion-exchange analytical column, an IonPac AG19 guard column, and KOH solution as mobile phase eluent. Atomic H^{*} signals were measured on a Bruker model ESR 300E spectrometer, with a Quanta-Ray Nd:YAG laser system as the irradiation source and 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trap reagent. XRD patterns of the catalysts were recorded with an X'Pert PRO powder diffractometer (PANalytical Co.). TEM images and energy dispersive spectrometer (EDS)

Figure 1. (A) Effect of Pd loading, (B) cometals, and (C) Pd/In ratio on the electrochemical reduction of bromate. (D) Initial activity of the catalyst under varying conditions (catalyst dosage = 1.0 g/L, Pd content of the catalysts in B and C was 3.0%, initial bromate concentration = 100 μ g/L, 2 mM Na₂SO₄, pH = 7.0, current density = 0.9 mA/cm²).

images of the samples were obtained on a transmission electron microscope, JEM-2100F Field Emission Electron Microscope (JEOL Ltd.). XPS analysis was carried out with a Kratos AXIS Ultra X-ray photoelectron spectrometer. The specific surface area measurement was performed using the BET method using a surface area analyzer, ASAP 2020 HD88 (Micromeritics Co.). The surface potential of the samples was characterized by a Nano Particle Sizing and Zeta Potential Analyzer (DelsaNano C, Beckman Coulter Ltd.).

RESULTS AND DISCUSSION

Efficient Electroreduction of Bromate by Pd₁-In₄/Al₂O₃ Catalyst. The effect of Pd loading on Al₂O₃ on the bromate reduction was optimized first. As shown in Figure 1A, the removal efficiency of bromate increased to a maximum value, and then decreased with increasing Pd content (the initial activity of Pd/Al₂O₃ was 27.74, 39.48, 48.36, and 29.4 $\mu\text{g}\cdot\text{gCat}^{-1}\cdot\text{h}^{-1}$ when Pd content was 1.5%, 2.0%, 3.0%, and 4.0%, Figure 1D). Higher amounts of Pd will aggregate on the surface of Al₂O₃, which may result in locally excessive H₂ evolution³¹ and then inhibit the H₂ efficiency by restricting the access of bromate to the interior H₂ generation sites. Cu, Sn, Bi, and In as the promoting metals for Pd-M/Al₂O₃ were chosen, and their efficiency was also evaluated based on bromate reduction (Figure 1B). Compared with Pd/Al₂O₃, all the bimetal catalysts exhibited an improved electroreduction activity with the order of Pd-Cu/Al₂O₃ < Pd-Sn/Al₂O₃ < Pd-Bi/Al₂O₃ < Pd-In/Al₂O₃ (the initial activity was 49.12, 68.86, 80.24, and 145.58 $\mu\text{g}\cdot\text{gCat}^{-1}\cdot\text{h}^{-1}$, respectively, Figure 1D). Pd-In/Al₂O₃ had the highest activity toward bromate reduction, and the optimal atomic ratio of Pd to In was further evaluated. As depicted in Figure 1C, the electroreduction rate of bromate increased dramatically with In content, and the initial activity of Pd-In/Al₂O₃ was 34.26, 44.9, 55.24, 100.42, and 145.58 $\mu\text{g}\cdot\text{gCat}^{-1}\cdot\text{h}^{-1}$ with a Pd/In ratio of

4:1, 2:1, 1:1, 1:2 and 1:4 (Figure 1D). Hence, Pd₁-In₄/Al₂O₃ with a Pd loading amount of 3.0% was chosen in the subsequent experiments.

In addition, the bromate electroreduction and the generation of bromide were further investigated for different particle electrode materials, and the obtained results were found to follow pseudo-first-order kinetics. As shown in Figure 2, the bromate concentration decreased by 54.0%, 64.2%, and 71.4% in the presence of Al₂O₃, In/Al₂O₃, and Pd/Al₂O₃, while about 96.4% of bromate was reduced at 30 min with Pd₁-In₄/Al₂O₃. That is to say, when the initial concentration of bromate was 100 $\mu\text{g}/\text{L}$, the remaining bromate in solution was only 3.6 $\mu\text{g}/\text{L}$, which was much lower than the standard of 10 $\mu\text{g}/\text{L}$. Moreover, the reaction rate constant of Pd₁-In₄/Al₂O₃ was 0.1275 min^{-1} , which was also much higher than that of other catalysts (0.0413, 0.0328, and 0.0253 min^{-1} for Pd/Al₂O₃, In/Al₂O₃, and Al₂O₃). It was worthy to note that the reaction constants for bromide formation were a little lower than that for bromate reduction (0.099, 0.0371, 0.0278, and 0.0215 min^{-1}). The bromine balance will be analyzed subsequently. The above results indicated that a synergistic effect of Pd and In existed within the catalyst and that it could enhance the current efficiency (as shown in Figure S1, the electric energy consumption to remove 1 mg bromate was 0.0065, 0.0105, 0.0127, and 0.0166 KWh for Pd₁-In₄/Al₂O₃, Pd/Al₂O₃, In/Al₂O₃, and Al₂O₃, respectively). Hence, Pd₁-In₄/Al₂O₃ was proven to be an ideal particle electrode material for the removal of bromate in water by electroreduction.

Characterization of Pd₁-In₄/Al₂O₃. The changes of physicochemical properties responsible for the higher efficiency of Pd₁-In₄/Al₂O₃ were characterized by TEM, XRD, BET, and XPS analysis. As depicted in Figure 3A and B, the lattice spacing of 0.228 nm belonged to the Pd(111)-In(111) bimetal. The average metal particle size was found to be ca. 7.7 nm. The measured ratio of Pd/In at different sites of the composite was

Figure 2. Electrochemical reduction of bromate and the generation of bromide with different catalysts (catalyst dosage = 1.0 g/L, initial bromate concentration = 100 $\mu\text{g}/\text{L}$, 2 mM Na₂SO₄, pH = 7.0, current density = 0.9 mA/cm²).

Figure 3. (A) TEM image of Pd₁–In₄/Al₂O₃. (B) EDX images for Pd₁–In₄/Al₂O₃ element mapping, and (C) XRD patterns of (a) Al₂O₃, (b) Pd/Al₂O₃, and (c) Pd₁–In₄/Al₂O₃.

determined to be from 1:2.78 to 1:4.96. Additionally, Pd particles aggregated to some extent, while In was highly dispersed on the surface of Al₂O₃. The diffraction peaks assigned to the (111), (200), and (220) reflections of metallic Pd were observed for the Pd/Al₂O₃ catalyst (Figure 3C), reflecting the typical face centered cubic crystallographic structure,¹⁰ while the new peak at 39.6° can be attributed to the Pd–In alloy.³² Table 1 shows the

Table 1. BET Results for Different Catalysts

	BET area (m ² /g)	pore volume (cm ³ /g)	pore size (nm)
Al ₂ O ₃	67.97	0.27	15.65
Pd/Al ₂ O ₃	63.70	0.34	21.27
Pd–In/Al ₂ O ₃ (4:1)	74.62	0.35	19.13
Pd–In/Al ₂ O ₃ (1:4)	41.90	0.22	21.31

BET results for different catalysts. The average pore size of the mesoporous Al₂O₃ was 15.65 nm, which was larger than the size of the metal nanoparticles (7.7 nm). The BET area and pore volume were similar for Al₂O₃, Pd/Al₂O₃, and Pd₄–In₁/Al₂O₃. However, a significant decrease of BET area and pore volume was observed for Pd₁–In₄/Al₂O₃ (42 m²/g and 0.22 cm³/g vs 64–74 m²/g and 0.34–0.35 cm³/g), which meant that some of the loaded metals might have occupied the volume in the mesopores. This result indicates that the specific surface area was not a critical factor for the high activity of Pd₁–In₄/Al₂O₃. In addition, the impact of In introduction on the valence state of Pd was studied by XPS (Figure 4). With the increase of In loading (Pd, Pd₄–In₁, and Pd₁–In₄), the binding energy of Pd_{3d} shifted toward a higher value from 334.4 eV (3d_{5/2}) and 339.7 eV (3d_{3/2}) to 334.8 and 340.0 eV and 335.8 and 341.1 eV. Meanwhile, the position of the peak assigned to In (0), with a binding energy of 444.79 eV (3d_{5/2}) and 452.39 eV (3d_{3/2}), did not change with In

Figure 4. XPS spectra of Pd in Pd/Al₂O₃, Pd₄–In₁/Al₂O₃, and Pd₁–In₄/Al₂O₃ catalysts and XPS spectra of In for Pd₄–In₁/Al₂O₃ and Pd₁–In₄/Al₂O₃ catalysts.

content. This proved that a Pd–In alloy was formed and that In could change the chemical environment of Pd.³³

Effect of Different Parameters on Pd₁–In₄/Al₂O₃ Efficiency. Figure S2 explores the influence of different parameters such as catalyst dosage, solution pH, and current density on the electroreduction performance of Pd₁–In₄/Al₂O₃. The bromate removal rate increased with the dosage of Pd₁–In₄/Al₂O₃ (0.2–1.0 g/L) and then maintained a steady level when the catalyst concentration was further increased to 1.5 g/L, while the effect of initial solution pH was not significant and almost 100% of the bromate was degraded after reaction for 25 min. The weak pH effect reflects that the electrocatalytic reduction of bromate with the Pd₁–In₄/Al₂O₃ can be performed under a wide pH range. Since the generation of atomic H* through the Volmer reaction is favored in acid solutions,³⁴ the high efficiency of

Figure 5. (A) The adsorption of bromate using different catalysts without applying any electrochemical potential (catalyst dosage = 1.0 g/L, initial bromate concentration = 100 $\mu\text{g/L}$, 2 mM Na_2SO_4 , pH = 7.0). Inset shows the surface zeta potentials of different catalysts at pH 7.0. (B) Bromine mass balance during the electrochemical reduction process (catalyst dosage = 1.0 g/L, initial bromate concentration = 10 mg/L, 2 mM Na_2SO_4 , pH = 7.0, current density = 2 mA/cm²). Inset shows the bromine balance with different catalysts under the same other conditions.

bromate removal at neutral pH indicated that the contribution of atomic H^{*} to bromate reduction is likely to be insignificant. In addition, the influence of current density on the Pd₁-In₄/Al₂O₃ efficiency was also examined at 0.3 to 1.2 mA/cm². The reduction rate markedly increased with current density (0.3 to 0.9 mA/cm²) and then remained constant at a higher current of 1.2 mA/cm². Higher current density will produce more available electrons,³⁵ leading to higher efficiency in bromate reduction. The similar efficiency of Pd₁-In₄/Al₂O₃ at 1.2 and 0.9 mA/cm²

should be attributed to the limitation of active sites in the catalyst, interfering with the electron transfer to bromate.

Proposed Mechanism of Bromate Reduction on Pd₁-In₄/Al₂O₃. Figure 5A depicts bromate removal by adsorption over different materials without the addition of applied current. Compared with Al₂O₃ without bromate adsorption, only 7% and 11% of bromate was adsorbed on Pd/Al₂O₃ and In/Al₂O₃. Pd₁-In₄/Al₂O₃ exhibited the highest adsorption capacity, and 48.6% of bromate could be removed under the same conditions. However, there were no bromide species detected during the adsorption process. This was because of the much higher zeta potential of Pd₁-In₄/Al₂O₃ than the other three catalysts at neutral pH (inset of Figure 5A). Hence, the more positive surface charge facilitated the adsorption of the negatively charged bromate on Pd₁-In₄/Al₂O₃. After the addition of applied current, the removed bromate was almost completely reduced to bromide for all the tested catalysts (inset of Figure 5B). For example, the sum of bromate and bromide at 30 min accounted for 99.1% of the total bromine added into the reactor for Pd₁-In₄/Al₂O₃, which indicated that the decreased bromate was completely converted into bromide. Regarding the slight decrease in the sum of bromate and bromide during the reaction process (5–20 min), this was due to the formation of other bromine species such as BrO₂⁻, HBrO₂, and HOBr/OBr⁻.³⁶ However, they were finally converted into bromide, since the mass balance of total bromine was recovered at 30 min.

The electroreduction mechanism of bromate by Pd₁-In₄/Al₂O₃ was further investigated because direct electron transfer and atomic H^{*} may be both involved in the reaction process.^{37,38} As shown in Figure 6A, nine characteristic peaks of DMPO-H^{*} with strong intensity were detected by ESR in the presence of catalyst compared with the control experiment (no catalyst). This confirmed that atomic H^{*} was indeed produced and involved in the bromate reduction process. However, the peak intensity of DMPO-H was similar for Pd/Al₂O₃, In/Al₂O₃, and Pd₁-In₄/Al₂O₃, which indicated that the introduction of In had no positive effect on the atomic H^{*} generation for Pd₁-In₄/Al₂O₃. *tert*-BuOH is a quenching reagent toward atomic H^{*}; therefore its influence on bromate electroreduction was also studied. As shown in Figure 6B and C, a significant inhibition of bromate removal in the presence of *tert*-BuOH (10 mM) was

Figure 6. (A) The DMPO spin-trapping ESR spectra with different catalysts at a current density of 0.9 mA/cm². (B) Electrochemical reduction of bromate in different systems with various C₄H₁₀O concentrations (catalyst dosage = 1.0 g/L, initial bromate concentration = 100 $\mu\text{g/L}$, 2 mM Na_2SO_4 , pH = 7.0, current density = 0.9 mA/cm²). (C) Bromate removal with and without C₄H₁₀O under different conditions at a reaction time of 20 min.

observed for Pd/Al₂O₃ and Pd₁-In₄/Al₂O₃ catalysts with efficiency decreases of 27.5% and 19.2%, while the negative effect of *tert*-BuOH was not significant for the control experiment, with only 5% inhibition. It can be speculated that the 37% bromate removal in the control should come from direct electron transfer, and both direct electron transfer and indirect atomic H^{*} reduction contributed to the bromate removal in the presence of catalysts. The higher contribution of direct electron reduction to bromate removal in the presence of catalysts (especially for Pd₁-In₄/Al₂O₃) was attributed to the increase of electron transfer to the adsorbed bromate due to the unique property of Pd metal in trapping electrons and the promoting effect of In within the catalyst. Since dissolved oxygen (DO) could compete with target pollutants for the reaction sites and then suppress the removal efficiency toward pollutants,³⁸ DO in the reaction system was removed by N₂ sparging, and its concentration was reduced from 7.42 to 0.80 mg/L. As shown in Figure 7, the bromate reduction efficiency

Figure 7. Effect of DO on electrochemical reduction of bromate in the reactor with Pd₁-In₄/Al₂O₃ catalyst (catalyst dosage = 1.0 g/L, initial bromate concentration = 100 μg/L, 2 mM Na₂SO₄, pH = 7.0, current density = 0.9 mA/cm²).

was greatly enhanced when DO was removed, and the reaction constant was 3 times higher than that in the presence of DO (0.3709 min⁻¹ vs 0.1275 min⁻¹). This indicated the competition effects with oxygen for reactive sites on the catalyst by consuming both the electrons and atomic H^{*}. As shown in Figure S3, a reaction mechanism for bromate reduction over Pd₁-In₄/Al₂O₃ was proposed based on all the experimental results. Bromate was first adsorbed on Pd₁-In₄/Al₂O₃, and after the addition of applied current, electrons and atomic H^{*} were both generated in the reaction system. The direct reduction of bromate by electrons played a more important role in bromate removal in the presence of Pd₁-In₄/Al₂O₃ catalyst, probably due to the enhancement of electron transfer by Pd-In within the catalyst. Compared to the other catalysts such as Pd-Cu, Pd-Sn, and Pd-Bi, the higher activity of Pd₁-In₄/Al₂O₃ toward bromate reduction may be due to two aspects: (i) the improved adsorption of bromate on the catalyst and (ii) the enhanced transfer of electrons and atomic H^{*} from catalyst to bromate.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02822.

Additional experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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