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Reductive dechlorination of trichloroacetic acid (TCAA) by electrochemical process over Pd-In/Al_2O_3 catalyst

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ABSTRACT

Electrochemical reduction treatment was found to be a promising method for dechlorination of Trichloroacetic acid (TCAA), and acceleration of electron transfer or enhancement of the concentration of atomic H* significantly improve the electrochemical dechlorination process. Bimetallic Pd-based catalysts have the unique property of simultaneously catalyzing the production of atomic H* and reducing target pollutants. Herein, a bimetallic Pd–In electrocatalyst with atomic ratio of 1:1 was evenly deposited on an Al_2O_3 substrate, and the bimetallic Pd-In structure was confirmed via X-ray photoelectron spectroscopy (XPS). Electrochemical removal of trichloroacetic acid (TCAA) by the Pd-In/Al_2O_3 catalyst was performed in a three-dimensional reactor. 94% of TCAA with the initial concentration of 500 $\mu g\,L^{-1}$ could be degraded within 30 min under a relatively low current density (0.9 $mA\,cm^{-2}$). In contrast to the presence of refractory intermediates (dichloroacetic acid (DCAA)) found in the Pd/Al_2O_3 system, TCAA could be thoroughly reduced to monochloroacetic acid (MCAA) using Pd-In/Al_2O_3 catalysts. According to scavenger experiments, an electron transfer process and atomic H* formation function both existed in the TCAA reduction process, and the enhanced indirect atomic H* reduction process (confirmed by ESR signals) played a chief role in the TCAA removal. Moreover, the synergistic effects of Pd and In were proven to be able to enhance both direct electron transfer and indirect atomic H* formation, indicating a promising prospect for bimetallic electrochemical reduction treatment.

1. Introduction

Trichloroacetic acid (TCAA) is one of the largest fractions of chloroacetic acids (CAAs) that always exists in chlorinated water [1–3]. TCAA has been proven to be carcinogenic and poses potential risks to human health [4,5], and a 0.1 mg/L standard for TCAA in drinking water has already been promulgated. To meet this limitation, numerous treatment methods, including biodegradation, photocatalysis, advanced oxidation, and Fenton reaction, have recently been explored [6–8]. Among these removal approaches, catalytic hydrogenation has been proven to be an efficient method to remove TCAA [9]. Zhou et al. [10] found that CAAs could be completely dechlorinated to acetic acid over supported Pd catalysts on ZrO_2, which could convert H_2 to atomic H*. However, liquid-phase catalytic hydrogenation requires constant H_2 supplementation, causing hidden danger for storage and transportation. Alternatively, the electrochemical treatment of TCAA was found to be more promising as it ensures the selective removal of chlorine atoms from TCAA, while no toxic byproducts are produced [11–14]. Two main steps, namely, direct dechlorination by electron transfer and an indirect process induced by atomic H*, take place during the electrocatalytic reduction process [15]. Generally, in contrast to the low reduction efficiency of electron transfer, the catalytically produced atomic H* plays a predominant role in dechlorination. Li et al. [13] studied the electrochemical dechlorination activity of CAAs with electrodeposited Fe- and Pd/Fe-modified carbon paper as cathodes. The results showed that while only 58% of TCAA could be removed within 30 min at pH 7.0 with the bias potential of

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−1.5 V using a Fe-C electrode through the direct electron transfer process, 96% of TCAA could be removed using a Pd/Fe-C electrode under the same experimental conditions where atomic H* were formed. Thus, the fabrication of suitable catalysts that can produce higher amounts of atomic H* has great potential for practical applications.

Palladium catalysts have been proven to have the unique property of activating H_2 and catalyzing the electrochemical reduction of H^+ or H_2O to produce adsorbed atomic H*, which is a much stronger reducing agent than H_2 in catalytic reduction reactions [16]. Some studies found that coupling two metals with different oxidizing abilities could enhance the generation of electrons [17], and some chemical reactions were reported to show better activity and selectivity when using bimetallic and trimetallic catalysts compared with monometallic Pd catalysts [18–20]. The chemical environment of Pd could be modified by a second metal addition [21,22], and the second metal, such as Au, Cu, Bi, Sn etc. [18–20,23], acts as a promoter for the Pd-based catalysts. For instance, the polymer-protected Au/Pd bimetal alloy, with an Au core structure, exhibited a higher catalytic activity for selective hydrogenation of 1,3-cyclooctadiene than that of monometallic Au or Pd catalyst [20]. In addition, the reduction efficiency of nitrates by Pd/SnO_2 was greatly enhanced after Sn addition [24]. Notably, nitrates and *N*-Nitrosodimethylamine could be effectively removed after indium was added to Pd/Al_2O_3, owing to the formation of Pd-In intermetallic compounds [25,26]. However, studies on the electrochemical reduction of TCAA by Pd-In suspended electrodes are still rare.

In this study, Pd-In mixtures with different atomic ratios were evenly deposited on Al_2O_3 substrates via coprecipitation followed by H_2 reduction, and their reduction efficiency toward TCAA was evaluated in a three-dimensional electrochemical reactor having better electroreduction efficiency compared to the particle-free system. TEM, XRD, XPS, BET and Zeta potential analysis were carried out to study the synergistic effect between Pd and In. Then, the effects of applied current density, catalyst dosage, initial TCAA concentration and solution pH on TCAA reduction over Pd-In/Al_2O_3 were also studied in detail. Moreover, scavenger and DO impact experiments on the TCAA direct electron transfer and indirect atomic H* process were studied. On the basis of the experimental results, we proposed a reaction mechanism for TCAA reduction using Pd-In/Al_2O_3.

2. Materials and methods

2.1. Preparation of Pd-In/Al_2O_3 particle electrodes

The particle electrodes were prepared by a coprecipitation method. γ-Al_2O_3 was immersed in a 0.1 M hydrochloric acid solution containing a certain content of $PdCl_2$ and $InCl_3 \cdot 4H_2O$, then the mixture was ultrasonically treated (360 min) and left to stand overnight. After drying at 120 °C, the obtained samples were further calcined at 300 °C (120 min), followed by reduction in H_2 atmosphere (200 °C; 300 min; 100 mL/min flow rate). For all the catalysts, the initial palladium loading amount was 3 wt. %, and the final obtained Pd-In catalyst with the initial palladium-to-indium atomic ratio of 1:1 was denoted as Pd-In/Al_2O_3, while others were recorded as Pd_x-In_y/Al_2O_3 (x: y refers to palladium-to-indium ratio). Pd/Al_2O_3 and In/Al_2O_3 with 3 wt. % metal loading amounts were also prepared under the same conditions.

2.2. Particle electrode characterization

X-ray powder diffraction (XRD) patterns were measured using Ni-filtered Cu K_α irradiation from 5° to 90° (in 2θ) on an X'Pert PRO Powder diffractometer (PANalytical Co.). Transmission Electron Microscope (TEM) images and Energy Dispersive Spectrometer (EDS) images were obtained with a Transmission Electron Microscope (JEM-2100F Field Emission Electron Microscope, JEOL Ltd.). The specific surface area (BET), pore diameter, and pore volume were measured by the nitrogen adsorption method with a surface area analyzer, model ASAP 2020 HD88 (Micromeritics Co.). Surface potential was characterized with a Nano Particle Sizing & Zeta Potential Analyzer (DelsaNano C, Beckman Coulter Ltd.). The X-ray photoelectron spectroscopy (XPS) data for particle electrodes were collected with a PHI Quantera SXM™ Scanning X-ray Microprobe™ (Φ ULVAC-PHI. INC.).

2.3. Three-dimensional electrochemical reactor and batch experiment

The electrochemical dechlorination of TCAA by Pd-In/Al_2O_3 was carried out in a three-dimensional electrochemical batch reactor, where a proton-exchange membrane (Nafion 117, Dupont) divided the reactor into a cathode cell and anode cell. A 50 mL aqueous solution composed of a certain content of TCAA (500 μg/L, unless otherwise specified) was added to the cathode cell, and 50 mL Na_2SO_4 solution (2 mM) was added into the anode cell correspondingly. Solution pH was adjusted with diluted H_2SO_4 and NaOH solutions (guaranteed grade) before each batch experiment. 0.9 mA/cm^2 current density (with a 6.8 V potential) was applied to the reactor which was powered by a DC power supply source (AMERLLPS302A, Dahua instrument corporation of Beijing). RuO_2/Ti electrodes with the same effective geometric surface area (10 cm^2) and 2 cm separation were employed as the cathode and anode, and a certain quantity of Pd_x-In_y/Al_2O_3 (1.0 g/L unless emphasized) was added into the cathode cell as the particle electrode (stirring rate: 800 rpm, room temperature). Pure Nitrogen/oxygen was purged to modify the DO concentration (0.2 and 30 mg/L, 7.42 mg/L "air saturated solution"). Heating bath method was applied to control the reaction temperature (303.15 K and 273.15 K, room temperature ranged from 288.15 to 291.15 K).

2.4. Analysis method

The concentrations of TCAA, dichloroacetic acid (DCAA) and monochloroacetic acid (MCAA) were measured by an ion chromatograph (IC) (Dionex 2000) equipped with an IonPac AS-19 anion-exchange analytical column and an IonPac AG19 guard column. The mobile phase eluent of the IC was KOH solution. The chromatograms of TCAA, DCAA and MCAA were collected under gradient elution conditions (0.0-30.0 min: 10.0 mM KOH; 30.1-37.0 min: 35.0 mM KOH; 37.1-43.0 min: 10.0 mM KOH, flow rate: 1.0 mL/min).

Atomic H* was trapped by 5,5′-dimethyl-1-pirroline-N-oxide (DMPO), and the signals were further detected by a Bruker model 300E electron spin resonance (ESR) spectrometer, using a quanta-Ray Nd:YAG laser system for the irradiation source.

3. Results and discussion

3.1. Characterization of Pd-In/γ-Al_2O_3 particle electrodes

As shown in Fig. 1(a), diffraction peaks at 40.1°, 46.7° and 68.1° assigned to the face centered cubic (fcc) crystallographic structure of metallic Pd were observed for the Pd/Al_2O_3 catalyst [27,28], and the peak at 40.1° shifts slightly to lower angle at 39.2° for Pd-In/Al_2O_3 catalysts, related to the formation of the Pd-In bimetallic alloy [29]. The dark spots in the TEM picture (Fig. 1(b)) were denoted as Pd or In particles with atomic numbers. Though it was difficult to distinguish whether the Pd, In particles was just located between the Al_2O_3 multi-layers or scattered in the inner channels of Al_2O_3, the EDS images (Fig. 1(c)) indicated that Pd and In

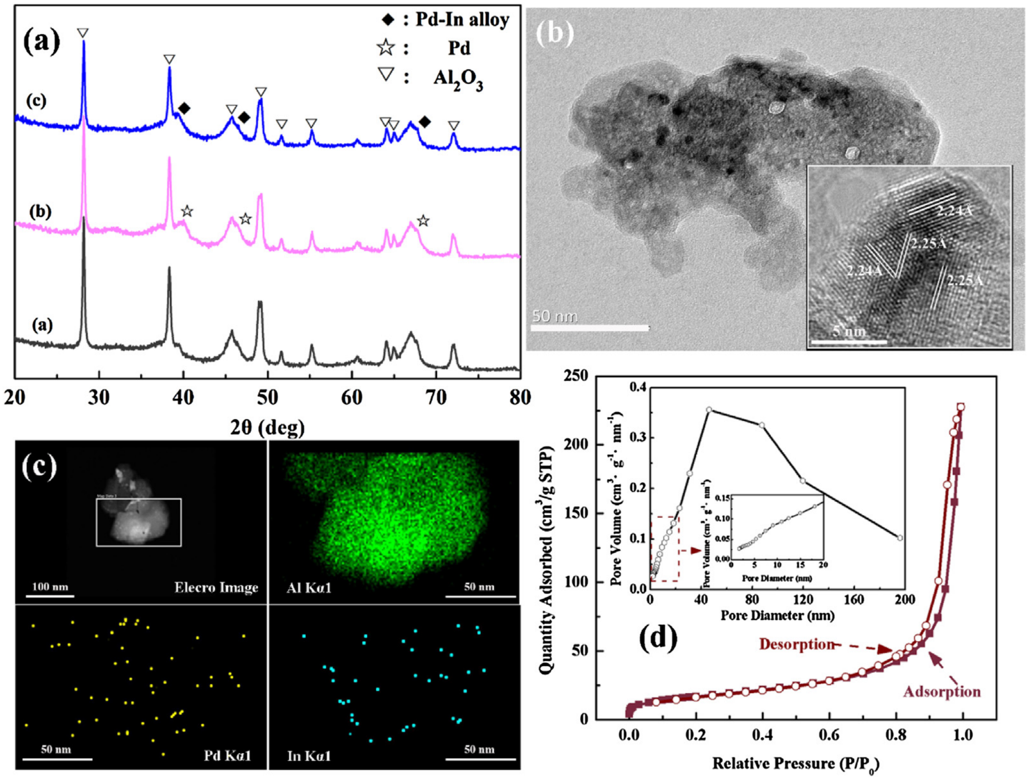

Fig. 1. (a) X-ray diffractograms for Al_2O_3, Pd/Al_2O_3, and Pd_x-In_y/Al_2O_3; (b) TEM image of Pd-In/Al_2O_3; (c) EDS images for Pd-In/Al_2O_3 element mapping; (d) BET analysis of Pd-In/Al_2O_3.

particles were dispersed uniformly on the surface of Al_2O_3. As shown in inset Fig. 1(b), a distinct lattice structure with a lattice spacing around 2.2 Å was observed, which may derive from the (111) plane of the Pd-In bimetallic alloy (the lattice spacings for Pd and In are 2.2458 Å [27] and 2.25680 Å [30] respectively); besides, some of In particles cover the same sites as Pd particles (shown in Fig. S1), further confirmed the potential of Pd-In alloy formation. BET analyses of the catalysts are listed in Table S1. The specific surface area of the catalysts decreases with increasing Pd-In loading amount, while the pore diameter increases correspondingly. The pore volume of Al_2O_3 and Pd-In/Al_2O_3 were both around 0.3 cm^3/g, it was reasonable to speculate that the decreased specific surface area (71.61 vs 60.77 m^2/g) was probably resulted from the increased pore diameter (from 16.72 to 23.16 nm). The increased pore diameter in the Al_2O_3 substrate had much more opportunities to be entered by those nano-seized metallic Pd and

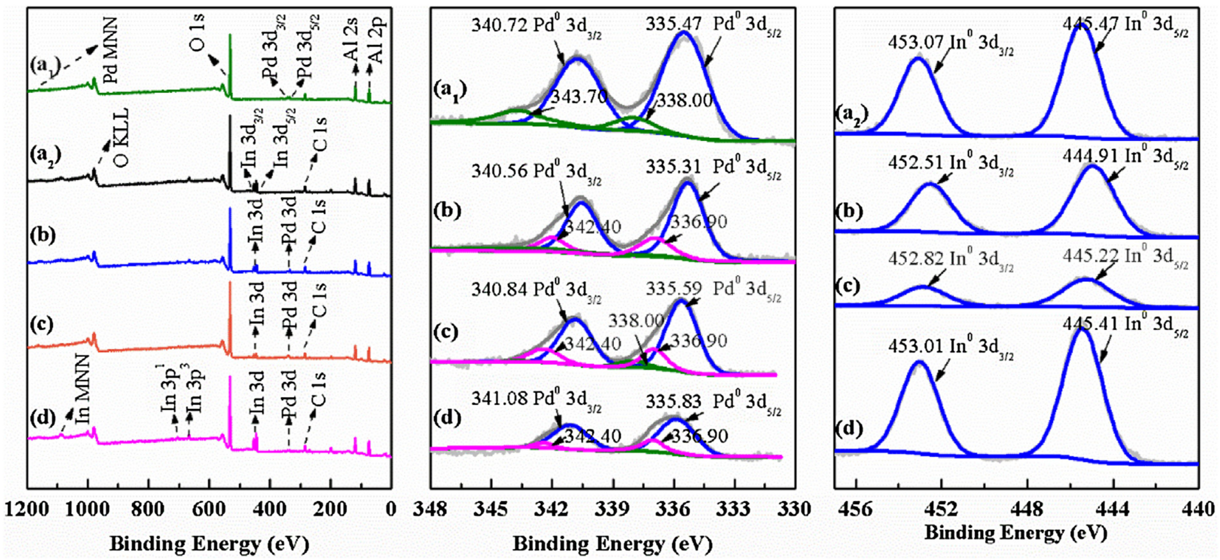

Fig. 2. XPS survey spectrum for (a_1) Pd/Al_2O_3, (a_2) In/Al_2O_3, (b) Pd-In/Al_2O_3, (c) Pd_1-$In_{0.5}$/Al_2O_3, (d) Pd_1-In_2/Al_2O_3; and XPS spectra of Pd in (a) Pd/Al_2O_3, (b) Pd-In/Al_2O_3, (c) Pd_1-$In_{0.5}$/Al_2O_3, (d) Pd_1-In_2/Al_2O_3; and XPS spectra of In in (a) In/Al_2O_3, (b) Pd-In/Al_2O_3, (c) Pd_1-$In_{0.5}$/Al_2O_3, (d) Pd_1-In_2/Al_2O_3.

In, so that the inner channels were readily to be blocked, decreasing in the specific surface area of the catalysts. As shown in Fig. 1(d), Pd-In/Al_2O_3 has a mesoporous structure with 60.77 m^2/g BET area and 17.56 nm average pore size, giving a type-IV isotherm with a type-H3 loop.

In addition, XPS analyses were carried out to study the influence of In introduction on the Pd valence state, and calibration of XPS spectra was performed referencing to C1s peak at 284.8 eV from the adventitious carbon. As shown in Fig. 2, Pd and In were detected in all the Pd-In catalysts. The Pd 3d spectra exhibit a spin-orbit doublet at 335.47 eV ($3d_{5/2}$) and 340.72 eV ($3d_{3/2}$), indicting the formation of metallic Pd in Pd/Al_2O_3 [31]; Compared with the Pd/Al_2O_3 catalyst, the Pd $3d_{5/2}$ spectrum shifted towards a lower value (335.31 eV) for Pd-In/Al_2O_3, while an opposite shift was observed for Pd_1-$In_{0.5}$/Al_2O_3 and Pd_1-In_2/Al_2O_3. The low binding energy of the Pd $3d_{5/2}$ peaks for the Pd-In/Al_2O_3 catalyst indicated that metallic Pd existed in a more electron-rich state, which was beneficial for atomic H^* formation; meanwhile, a decrease in the indium $3d_{5/2}$ binding energy was detected, indicating that a Pd-In bimetallic alloy was formed in the Pd-In/Al_2O_3 catalysts [32,33]. Moreover, the $PdCl_2$ remaining in Pd/Al_2O_3 changed into PdO for all the Pd-In/Al_2O_3 catalysts, showing that In could change the chemical environment of Pd [34].

3.2. Efficient electroreduction of TCAA by Pd-In/Al_2O_3 with different In to Pd atomic ratios

As the amount of the promoter metal would greatly influence the activity of Pd-based bimetallic catalysts [35], the effect of the In to Pd atomic ratio on TCAA electroreduction was optimized first. As shown in Fig. 3(a), the removal efficiency of TCAA by Pd-based catalysts was increased to a maximum value, and then decreased with increasing atomic ratio of In to Pd. While In/Al_2O_3 showed almost no activity for TCAA reduction, 94% of TCAA could be reduced in 30 min by Pd-In/Al_2O_3, which had the highest electrochemical activity towards TCAA removal. All the reduction processes were shown to follow pseudo-first order kinetics. The reaction rate constants of the catalysts followed the order In/Al_2O_3 < Pd_1-In_2/Al_2O_3 < Pd/Al_2O_3 < Pd_1-$In_{0.5}$/Al_2O_3 < Pd-In/Al_2O_3, and the catalyst activity increased from 114.29, 672.28, 839.33, 840.28 to 931.34 $\mu g\, gCat^{-1}\, h^{-1}$ respectively, as shown in Fig. 3(b). This result indicated that the reduction ability of Pd-based catalysts could be enhanced by adding a proper amount of In, while excess addition of In would restrain the catalyst activity. As In itself did not have the ability for TCAA reduction, an excessive In concentration would decrease the isolated Pd sites [36] and block the channels of the Al_2O_3 substrate (confirmed by BET analysis), thus reducing the TCAA removal efficiency.

The reduction products of TCAA over different particle electrodes were further studied. As shown in Fig. 4, 40.0% of TCAA could be reduced to DCAA in 30 min without using any catalysts. The TCAA reduction efficiency increased to 67.0%, 84.0% and 93.2% after addition of Al_2O_3, Pd/Al_2O_3 and Pd-In/Al_2O_3 particle electrodes respectively. Notably, MCAA was detected during the electrochemical process when Pd-In/Al_2O_3 was used as the particle electrode, and around 42% DCAA and 16% TCAA were detected in the 30 min batch experiment. However, no MCAA was formed when using Al_2O_3 or Pd/Al_2O_3 under the same experimental conditions. As In/Al_2O_3 had no effect on TCAA reduction (Fig. 3), we could reasonably infer that In acts as a “promoter” metal for Pd-based catalysts [25,37] and the 1:1 initial Pd to In atomic ratio produces the most pronounced synergistic effect between metallic Pd and In on TCAA electroreduction. According to the XPS analysis, metallic Pd existed in a more electron-rich state for Pd-In/Al_2O_3 than in the other catalysts due to the modification by In, and the electron-rich state was beneficial for atomic H^* formation. So, Pd-In/Al_2O_3 was shown to be a promising catalyst for the electrochemical removal of TCAA.

3.3. Effect of different parameters on electrochemical removal of TCAA by Pd-In/Al_2O_3

The influences of current density, catalyst dosage, initial concentration, solution pH and dissolved oxygen (DO) on the electrochemical reduction of Pd-In/Al_2O_3 were further investigated. As shown in Fig. 5(a), the TCAA removal rate increased greatly with the current density from 0.3 to 0.9 mA/cm^2, and then increased slightly when the current density further increased to 1.2 mA/cm^2. With the increase of current density, more electrons were available for H^* formation and TCAA reduction [38], thus enhancing the TCAA removal efficiency. However, the removal efficiency of TCAA did not change much in the first ten minutes when the current density rose above 0.9 mA/cm^2. This can be explained by the formation of profuse hydrogen bubbles at the electrode surface. Although the presence of bubbles did not damage the electrode, they could still interfere with TCAA diffusion to the catalyst [39]. In addition, as active Pd-In sites are vital for

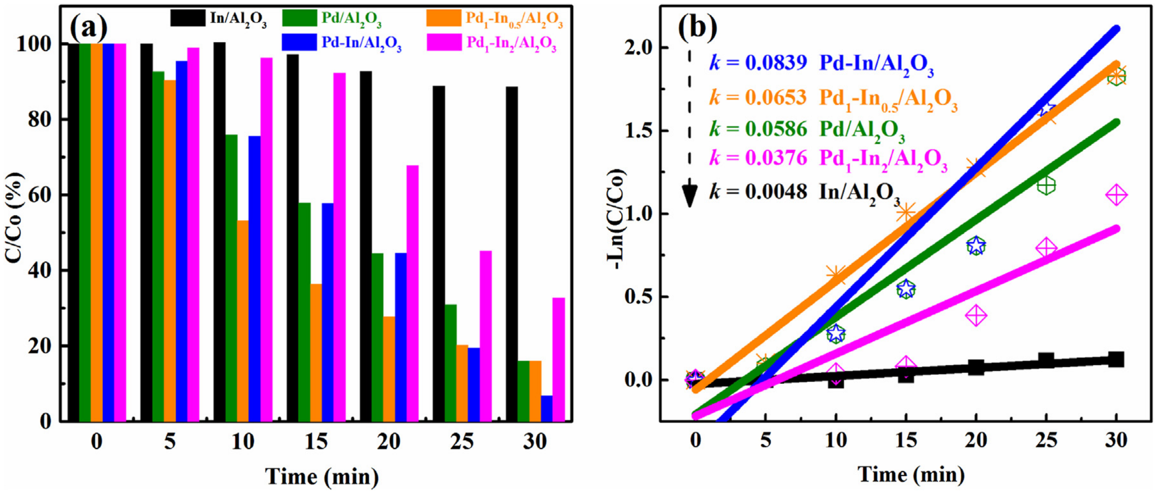

Fig. 3. (a) Effect of atomic ratio of palladium and indium on the removal of TCAA (catalyst dosage = 1.0 g/L, initial TCAA concentration = 500 μg/L, current density = 0.9 mA/cm^2, initial pH = 7.0, 2 mM Na_2SO_4, room temperature); (b) the pseudo-first-order kinetics equations of the catalysts.

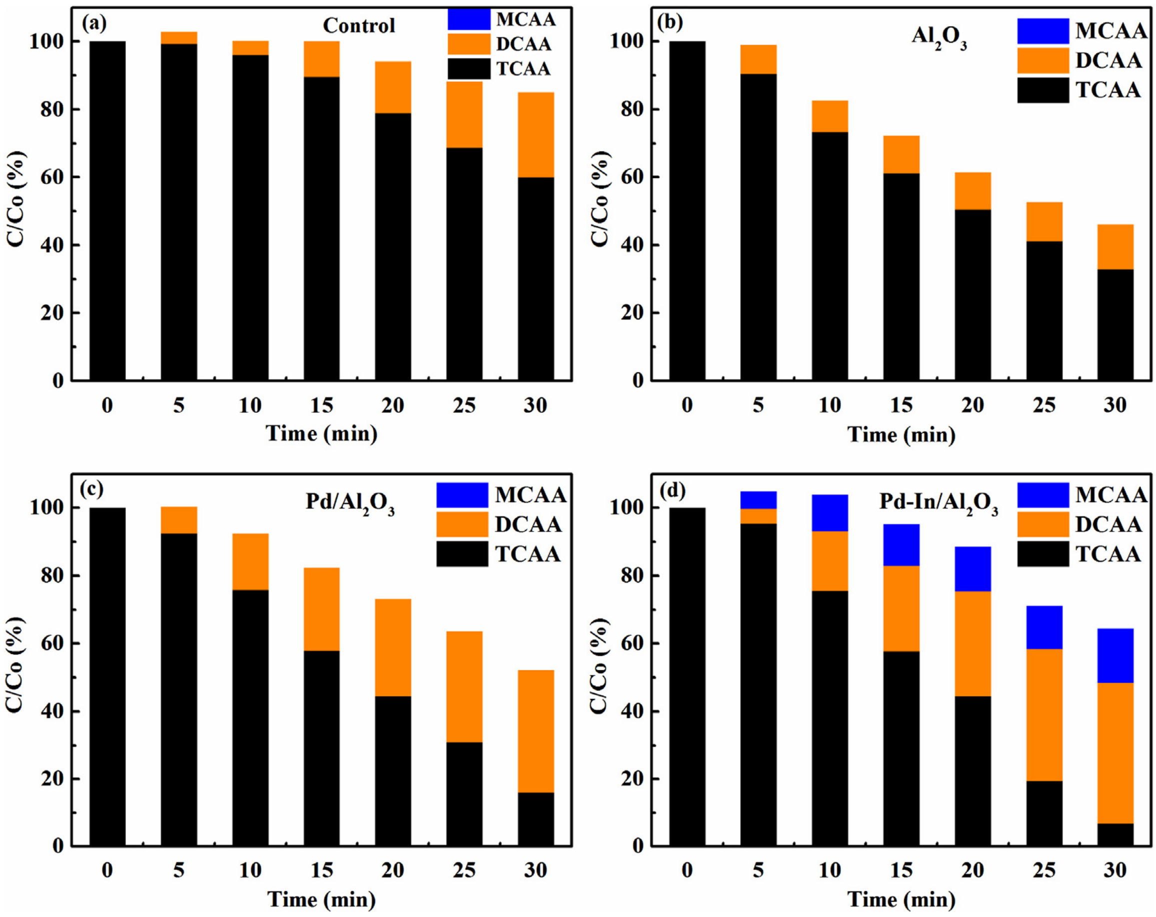

Fig. 4. Intermediates and final products of reductive dechlorination of TCAA through (a) control (without catalyst); (b) Al_2O_3; (c) Pd/Al_2O_3; and (d) $Pd\text{-}In/Al_2O_3$ catalyst (catalyst dosage = 1.0 g/L, initial TCAA concentration = 500 μg/L, current density = 0.9 mA/cm^2, initial pH = 7.0, 2 mM Na_2SO_4, room temperature).

TCAA removal [40], the TCAA electrochemical removal rate was observed to increase gradually as the $Pd\text{-}In/Al_2O_3$ dosage increased from 0.2 g/L to 1.0 g/L (Fig. 5(b)), and the removal rate achieved a relatively stable value when more catalyst (1.5 g/L) was used, where the current density restricted the further enhancement of TCAA reduction.

Moreover, the catalytic activity of $Pd\text{-}In/Al_2O_3$ catalysts for TCAA removal was more than doubled when the initial TCAA concentration increased from 200 to 500 μg/L (298.9, 451.5, 544.4 and 752.9 μg gCat^{-1} h^{-1} for TCAA with the initial concentration of 200, 300, 400 and 500 μg/L, Fig. S2), attributed to the positive correlation between the TCAA removal rate and the surface coverage of adsorbed TCAA [41]. The corresponding pseudo-first order kinetics reaction rate constant increased gradually from 0.0540, 0.0550, and 0.0561 to 0.0613 min^{-1}.

Furthermore, the effect of initial solution pH on TCAA removal was not significant, and the pseudo-first order kinetics reaction rate constant of $Pd\text{-}In/Al_2O_3$ for 20 min of reaction was 0.04 min^{-1} at all studied pH values from 3.0 to 9.0 (Fig. S3). As shown in Fig. S4, the $Pd\text{-}In/Al_2O_3$ catalyst was positively charged when pH was lower than 9.0 and the surface zeta potential changed only slightly when pH ranged from 3.0 to 9.0. Therefore, the adsorption of TCAA would not change much with changing pH, weaken the impact of the pH influence. As more than 80% of TCAA was removed after reaction for 30 min, TCAA could be effectively removed by $Pd\text{-}In/Al_2O_3$ over a wide pH range.

The effect of temperature to TCAA removal efficiency was further investigated. As shown in Fig. S5, 80.28%, 94.01% and 95.23% of TCAA could be reduced within 30 min under 273.15, 289.15 (room temperature) and 303.15 K respectively, exhibiting a positive correlation to the temperatures.

In addition, as DO is a ubiquitous kind of oxidant that can compete with TCAA in consuming reducing agents such as electrons and atomic H*, thus suppressing the removal efficiency of TCAA [42], the electrochemical reduction of TCAA by $Pd\text{-}In/Al_2O_3$ was also investigated as a function of DO content. As shown in Fig. 5(d), the TCAA reduction efficiency was highly dependent on the DO content. When the DO concentration was reduced from 7.42 to less than 0.20 mg/L, the TCAA concentration decreased sharply in the first 5 min and was totally removed in just 15 min, and the reaction constant increased 6-fold compared to that in the presence of DO of 7.42 mg/L. Comparatively, when the DO content was above 30 mg/L, almost no TCAA was removed in the 30 min batch experiment, while the reaction constant decreased 31-fold compared to that with the DO concentration of 7.42 mg/L (0.5802, 0.0026 and 0.0839 min^{-1} for DO concentrations of 0.20, 7.42 and 30 mg/L respectively). That is to say, DO is a strong competitor for TCAA in this three-dimensional electrochemical reactor.

As the important indicator for the efficient catalyst, the reusability of $Pd\text{-}In/Al_2O_3$ was also evaluated. The used $Pd\text{-}In/Al_2O_3$ catalysts was recovered by centrifuging followed by drying at 80 °C. After reduction in H_2 atmosphere at 200 °C for 300 min, the regenerated $Pd\text{-}In/Al_2O_3$ was applied to reduce TCAA. After three cycles, more than 80% of TCAA with the initial concentration of 0.5 mg/L could be reduced in 30 min, so that the TCAA was decreased below the standard (0.1 mg/L) (Fig. S6). The stability of $Pd\text{-}In/Al_2O_3$ is essential for reducing the cost in the practical applications.

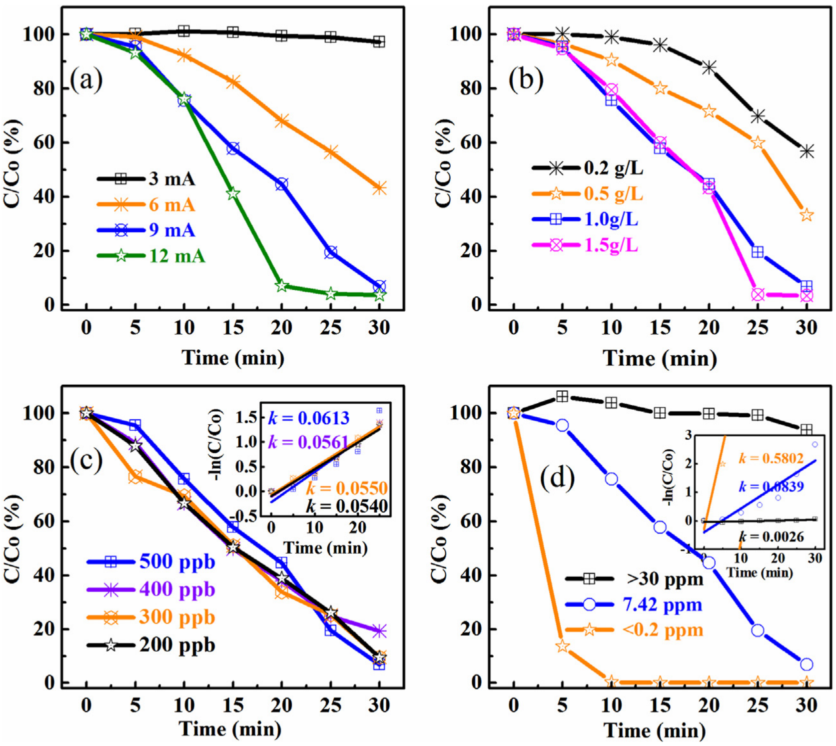

Fig. 5. Effect of (a) current density, (b) dosage, (c) initial concentration, (d) DO concentration on the electrochemical removal of TCAA (catalyst dosage = 1.0 g/L, initial TCAA concentration = 500 µg/L, current density = 0.9 mA/cm^2, initial pH = 7.0, 2 mM Na_2SO_4 unless emphasized); inset shows (c) the reaction rate constant of Pd-In/Al_2O_3 under different initial TCAA concentration; (d) the reaction rate constant of Pd-In/Al_2O_3 under different DO concentration.

3.4. Proposed mechanisms of TCAA electroreduction on Pd-In/Al_2O_3

The adsorption efficiency of TCAA by different catalysts was tested without electricity. No TCAA was adsorbed by Al_2O_3 and In/Al_2O_3, and 3.0% and 2.3% of TCAA could be adsorbed by Pd/Al_2O_3 and Pd-In/Al_2O_3 respectively (shown in Fig. S7). This result agreed with the zeta potential analysis (Fig. S4), where all the catalysts were positively charged and differed slightly at neutral pH, but the potentials still followed the order Al_2O_3 < Pd-In/Al_2O_3 < Pd/Al_2O_3. DCAA and MCAA adsorption by Pd-In/Al_2O_3 was also detected. As shown in Fig. S8, no adsorption of DCAA and MCAA was observed in the 30 min batch experiment. After adding 0.9 mA/cm^2 current density, the TCAA was dechlorinated to DCAA or further to MCAA (Pd-In/Al_2O_3 only, Fig. 4). However, a decrease in the summed concentration of MCAA, DCAA and TCAA along the batch experiments was detected for all the catalysts. For instance, the sum of MCAA (16%), DCAA (42%) and TCAA (6%) accounted for 64% of the total CAAs at 30 min for Pd-In/Al_2O_3, and since little of the CAAs could be adsorbed by Pd-In/Al_2O_3, the decrease of CAA concentration was due to the formation of other intermediates like $Cl_2\dot{C}COOH$ and $Cl\dot{C}HCOOH$.

As TCAA could be electroreduced both by electrons and atomic H* [43,44], the electroreduction mechanism of TCAA reduction by Pd-In/Al_2O_3 was investigated further. As Fig. 6(a) shows, the nine characteristic peaks of DMPO-H for atomic H* [39] were detected, and the peak intensities followed the order Pd-In/Al_2O_3 > Pd/Al_2O_3, while no such signal was detected when Al_2O_3 or no catalyst was used. This result confirmed the formation of atomic H* in the TCAA electroreduction process in the three-dimension electrochemistry system using Pd-based catalysts as the particle electrode. The atomic H* reduction of TCAA could be further enhanced by introducing In into Pd-based catalysts, further confirming that a synergistic effect between Pd and In occurred in the catalyst. In addition, scavenger experiments using *Tert*-BuOH to quench atomic H* were carried out to further study the TCAA reduction process (shown in Fig. 6(b) and (c)). Blending *Tert*-BuOH (10 mM) into the TCAA reduction system inhibited the TCAA removal significantly. While the TCAA removal rate was 69.0% and 80.5% for Pd/Al_2O_3 and Pd-In/Al_2O_3 at 25 min respectively without *Tert*-BuOH, the electroreduction efficiency decreased by 49.2% and 51.2% for Pd/Al_2O_3 and Pd-In/Al_2O_3 respectively, accounting for nearly 2/3 (71.3% and 63.6% respectively) of TCAA removal without *Tert*-BuOH. Meanwhile, 16.7% inhibition was also detected for the control experiment (no particle electrodes). It can be speculated that the indirect atomic H* process played a more dominant role than direct electron transfer in TCAA reduction by Pd-In/Al_2O_3 catalysts, and was found to be more prominent for Pd/Al_2O_3. As introducing In into Pd-based catalysts could enhance the atomic H* formation, this may explain why the TCAA removal efficiency was higher for Pd-In/Al_2O_3 than Pd/Al_2O_3. Comparatively, 28.7% of TCAA could be reduced by Pd/Al_2O_3 after atomic H* was inhibited, lower than the value of 36.4% for Pd-In/Al_2O_3. That is to say, the direct electron reduction of TCAA was enhanced after In addition, indicating that the direct electron transfer was also promoted by the introduction of In into the Pd-based catalyst.

Furthermore, we investigated the intermediates and final products of the electroreduction of TCAA by Pd-In/Al_2O_3 after elimination of DO from the system, since DO is a strong competitor for TCAA, which would hinder both the direct electron transfer and indirect atomic H* process for the electroreduction of TCAA as discussed above. As shown in Fig. 6(d), TCAA decreased rapidly while DCAA as the dechlorination intermediate increased initially, and then decreased slightly along the course of reaction; meanwhile the MCAA concentration increased along with the reduction of TCAA. As only DCAA was formed without the Pd-In catalyst (Fig. 4), the detected MCAA was formed via the indirect

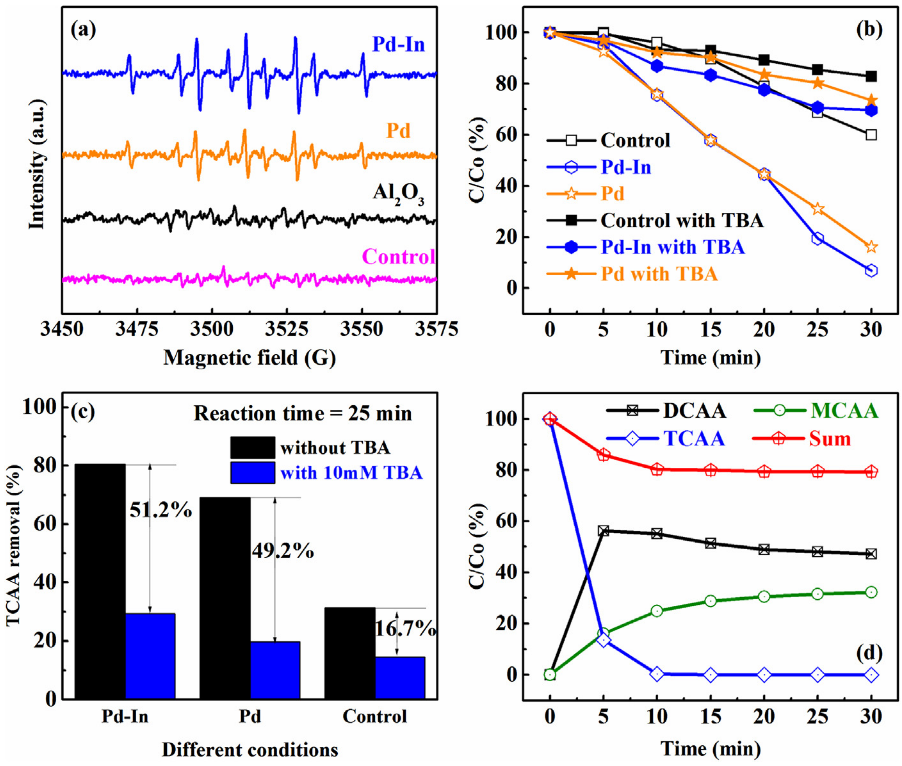

Fig. 6. (a) the DMPO spin-trapping ESR spectra with different catalysts at the current density of 0.9 mA/cm^2; (b) electrochemical reduction of TCAA in different systems with and without $C_4H_{10}O$; (c) TCAA removal under different $C_4H_{10}O$ concentrations at the reaction time of 25 min; (d) intermediates and final products of reductive dechlorination of TCAA by Pd-In/Al_2O_3 without DO (catalyst dosage = 1.0 g/L, initial TCAA concentration = 500 µg/L, current density = 0.9 mA/cm^2, initial pH = 7.0, 2 mM Na_2SO_4, room temperature).

atomic H* function, while DCAA could also be formed via direct electron transfer. As shown in the schematic diagram (Fig. 7), the direct electroreduction may follow the pathway:

$$Cl_3CCOOH + e^- \rightarrow Cl_2\dot{C}COOH + Cl^- \qquad (1)$$

$$Cl_2\dot{C}COOH + H^+ + e^- \rightarrow Cl_2CHCOOH \qquad (2)$$

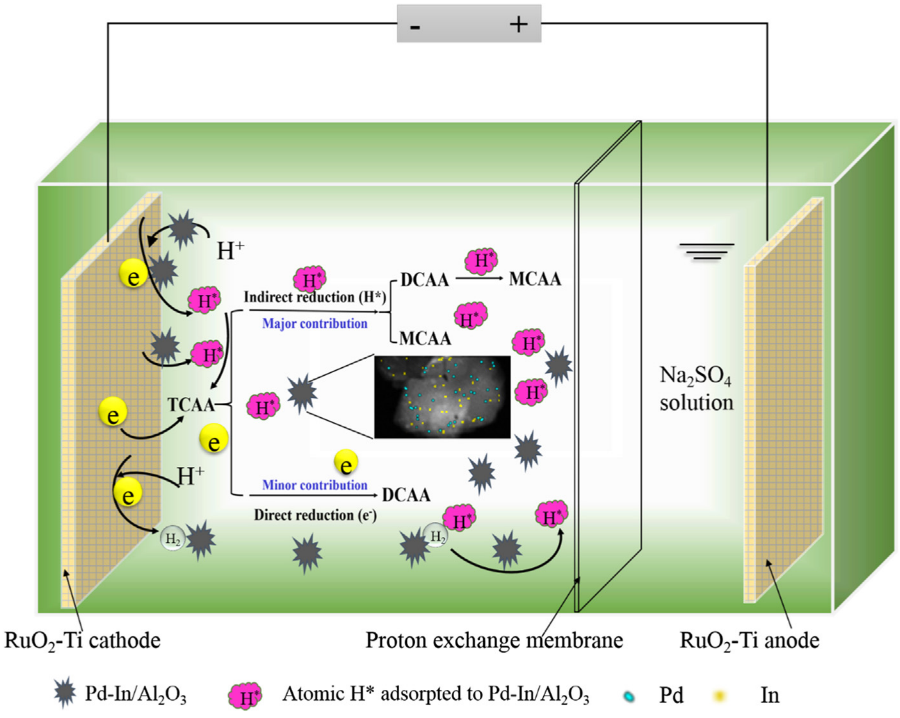

Fig. 7. Schematic diagram: reaction mechanism for TCAA reduction over Pd-In/Al_2O_3.

While the indirect electroreduction of TCAA by $Pd\text{-}In/Al_2O_3$ can be described as:

$$In \sim Pd + H^+ + e^- \rightarrow In \sim PdH^* \tag{3}$$

$$Cl_3CCOOH^* + In \sim PdH^* \rightarrow Cl_2CHCOOH + Cl^- \tag{4}$$

$$Cl_2CCOOH^* + In \sim PdH^* \rightarrow ClCH_2COOH + Cl^- \tag{5}$$

$$Cl_3CCOOH^* + 2In \sim PdH^* \rightarrow ClCH_2COOH + 2Cl^- \tag{6}$$

The indirect atomic H^* played a major contribution to TCAA reduction, while direct electron transfer had a minor impact on TCAA removal by $Pd\text{-}In/Al_2O_3$.

4. Conclusion

In conclusion, $Pd\text{-}In/Al_2O_3$ was proven to have the highest reduction efficiency in the electrochemical reduction of TCAA in the three-dimensional electrochemical reactor, and was able to reuse in the catalyst process. The reduction process followed pseudo-first-order kinetics. Physical and chemical characterization analyses indicated that after In addition, metallic Pd existed in a more electron-rich state, which was beneficial for atomic H^* formation for the $Pd\text{-}In/Al_2O_3$ catalyst, and the formation of Pd-In bimetallic alloy also had a positive effect on TCAA removal. The synergistic effect of Pd and In enhanced both the direct electron transfer and indirect atomic H^* function for TCAA reduction, and the enhanced indirect atomic H^* process played a major contribution to TCAA removal. While DCAA cannot be converted using the Pd/Al_2O_3 catalyst, MCAA was further produced when using $Pd\text{-}In/Al_2O_3$ under the same experimental conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2017.02.071.

References

[1] E. Malliarou, C. Collins, N. Graham, M.J. Nieuwenhuijsen, Haloacetic acids in drinking water in the United Kingdom, Water Res. 39 (2005) 2722–2730.

[2] J.G. Pressman, S.D. Richardson, T.F. Speth, R.J. Miltner, M.G. Narotsky, I.I.I.E.S. Hunter, G.E. Rice, L.K. Teuschler, A. McDonald, S. Parvez, S.W. Krasner, H.S. Weinberg, A.B. McKague, C.J. Parrett, N. Bodin, R. Chinn, C.-F.T. Lee, J.E. Simmons, Concentration, chlorination, and chemical analysis of drinking water for disinfection byproduct mixtures health effects research: U.S. EPA's four lab study, Environ. Sci. Technol. 44 (2010) 7184–7192.

[3] H. Zhou, X.J. Zhang, Occurrence of haloacetic acids in drinking water in certain cities of China, Biomed. Environ. Sci. 17 (2004) 299–308.

[4] G. Hua, J. Kim, D.A. Reckhow, Disinfection byproduct formation from lignin precursors, Water Res. 63 (2014) 285–295.

[5] M.J. Cardador, M. Gallego, Haloacetic acids in swimming pools: swimmer and worker exposure, Environ. Sci. Technol. 45 (2011) 5783–5790.

[6] B.M. Mcrae, T.M. Lapara, R.M. Hozalski, Biodegradation of haloacetic acids by bacterial enrichment cultures, Chemosphere 55 (2004) 915–925.

[7] A. Matilainen, M. Sillanpää, Removal of natural organic matter from drinking water by advanced oxidation processes, Chemosphere 80 (2010) 351–365.

[8] B. Zhao, X. Wang, H. Shang, X. Li, W. Li, J. Li, W. Xia, L. Zhou, C. Zhao, Degradation of trichloroacetic acid with an efficient Fenton assisted TiO_2 photocatalytic hybrid process: reaction kinetics, byproducts and mechanism, Chem. Eng. J. 289 (2016) 319–329.

[9] J. Zhou, K. Wu, W. Wang, Y. Han, Z. Xu, H. Wan, S. Zheng, D. Zhu, Simultaneous removal of monochloroacetic acid and bromate by liquid phase catalytic hydrogenation over $Pd/Ce_{1\text{-}x}Zr_xO_2$, Appl. Catal. B. Environ. 162 (2015) 85–92.

[10] J. Zhou, Y. Han, W. Wang, Z. Xu, H. Wan, D. Yin, S. Zheng, D. Zhu, Reductive removal of chloroacetic acids by catalytic hydrodechlorination over Pd/ZrO_2 catalysts, Appl. Catal. B. Environ. 134–135 (2013) 222–230.

[11] L. Yu-Ping, C. Hong-Bin, Z. Yi, Reductive dehalogenation of haloacetic acids by hemoglobin-loaded carbon nanotube electrode, Water Res. 41 (2007) 197–205.

[12] G.V. Korshin, M.D. Jensen, Electrochemical reduction of haloacetic acids and exploration of their removal by electrochemical treatment, Electrochim. Acta. 47 (2001) 747–751.

[13] A. Li, X. Zhao, Y. Hou, H. Liu, L. Wu, J. Qu, The electrocatalytic dechlorination of chloroacetic acids at electrodeposited Pd/Fe-modified carbon paper electrode, Appl. Catal. B. Environ. 111–112 (2012) 628–635.

[14] X. Zhao, A. Li, R. Mao, H. Liu, J. Qu, Electrochemical removal of haloacetic acids in a three-dimensional electrochemical reactor with Pd-GAC particles as fixed filler and Pd-modified carbon paper as cathode, Water Res. 51 (2014) 134–143.

[15] R. Mao, N. Li, H. Lan, X. Zhao, H. Liu, J. Qu, M. Sun, Dechlorination of trichloroacetic acid using a noble metal-free graphene–Cu foam electrode via direct cathodic reduction and atomic H^*, Environ. Sci. Technol. 50 (2016) 3829–3837.

[16] B.P. Chaplin, M. Reinhard, W.F. Schneider, C. Schuth, J.R. Shapley, T.J. Strathmann, C.J. Werth, Critical review of Pd-based catalytic treatment of priority contaminants in water, Environ Sci Technol 46 (2012) 3655–3670.

[17] H. Choi, S.R. Al-Abed, S. Agarwal, D.D. Dionysiou, Synthesis of reactive nano-Fe/Pd bimetallic system-impregnated activated carbon for the simultaneous adsorption and dechlorination of PCBs, Chem. Mater. 20 (2008) 3649–3655.

[18] D. Fang, W. Li, J. Zhao, S. Liu, X. Ma, J. Xu, C. Xia, Catalytic hydrodechlorination of 4-chlorophenol over a series of Pd-Cu/gamma-Al_2O_3 bimetallic catalysts, Rsc Adv. 4 (2014) 59204–59210.

[19] I. Witońska, A. Królak, S. Karski, Bi modified Pd/support (SiO_2 Al_2O_3) catalysts for hydrodechlorination of 2, 4-dichlorophenol, J. Mol. Catal. A. Chem. 331 (2010) 21–28.

[20] N. Toshima, M. Harada, Y. Yamazaki, K. Asakura, Catalytic activity and structural analysis of polymer-protected gold-palladium bimetallic clusters prepared by the simultaneous reduction of hydrogen tetrachloroaurate and palladium dichloride, J. Phys. Chem. 96 (1992) 9927–9933.

[21] J.A. Rodriguez, M. Kuhn, Interaction of zinc with transition-metal surfaces: electronic and chemical perturbations induced by bimetallic bonding, J. Phys. Chem. 100 (1996) 381–389.

[22] R.C. Budhani, A. Banerjee, T.C. Goel, K.L. Chopra, XPS study of glassy $Pd_{80}Ge_{20}$, J. Non-Cryst. Solid. 55 (1983) 93–102.

[23] E.P. Alves Rocha, F.B. Passos, F.C. Peixoto, Modeling of hydrogenation of nitrate in water on Pd-Sn/Al_2O_3 Catalyst: estimation of microkinetic parameters and transport phenomena properties, Ind. Eng. Chem. Res. 53 (2014) 8726–8734.

[24] R. Gavagnin, L. Biasetto, F. Pinna, G. Strukul, Nitrate removal in drinking waters: the effect of tin oxides in the catalytic hydrogenation of nitrate by Pd/SnO_2 catalysts, Appl. Catal. B. Environ. 38 (2002) 91–99.

[25] I. Witońska, S. Karski, J. Rogowski, N. Krawczyk, The influence of interaction between palladium and indium on the activity of Pd–In/Al_2O_3 catalysts in reduction of nitrates and nitrites, J. Mol. Catal. A. Chem. 287 (2008) 87–94.

[26] M.G. Davie, K. Shih, F.A. Pacheco, J.O. Leckie, M. Reinhard, Palladium-indium catalyzed reduction of n-nitrosodimethylamine: indium as a promoter metal, Environ. Sci. Technol. 42 (2008) 3040–3046.

[27] H.E. Swanson, T. E, Standard x-ray diffraction powder patterns, National Bureau of Standards (U.S.), 1953.

[28] H. Chen, Z. Xu, H. Wan, J. Zheng, D. Yin, S. Zheng, Aqueous bromate reduction by catalytic hydrogenation over Pd/Al_2O_3 catalysts, Appl. Catal. B. Environ. 96 (2010) 307–313.

[29] I.R. Harris, M. Norman, A.W. Bryant, A study of some palladium-indium platinum-indium and platinum-tin alloys, J.the Less Common Metals. 16 (1968) 427–440.

[30] K. Takemura, H. Fujihisa, High-pressure structural phase transition in indium, Phys. Rev. B. Solid State. 47 (1993) 8465–8470.

[31] A.K.-V. Alexander, V. Naumkin, Stephen W. Gaarenstroom, Cedric J. Powell, NIST X-ray photoelectron spectroscopy database, NIST Standard Reference Database 20, (2000) http://srdata.nist.gov/xps/Default.aspx.

[32] T. Hirano, Y. Ozawa, T. Sekido, T. Ogino, T. Miyao, S. Naito, The role of additives in the catalytic reduction of NO by CO over Pd-In/SiO_2 and Pd-Pb/SiO_2 catalysts, Appl. Catal. A. Gen. 320 (2007) 91–97.

[33] I.A. Witońska, M.J. Walock, P. Dziugan, S. Karski, A.V. Stanishevsky, The structure of Pd–M supported catalysts used in the hydrogen transfer reactions (M = In, Bi and Te), Appl. Surf. Sci. 273 (2013) 330–342.

[34] F.A. Marchesini, S. Irusta, C. Querini, E. Miró, Spectroscopic and catalytic characterization of Pd–In and Pt–In supported on Al_2O_3 and SiO_2, active catalysts for nitrate hydrogenation, Appl. Catal. A. Gen. 348 (2008) 60–70.

[35] J. Zhao, W. Li, D. Fang, Effect of indium-modified palladium catalysts on the hydrodechlorination of 4-chlorophenol, Rsc Adv. 5 (2015) 42861–42868.

[36] F.A. Marchesini, L.B. Gutierrez, C.A. Querini, E.E. Miró, Pt, In and Pd, In catalysts for the hydrogenation of nitrates and nitrites in water. FTIR characterization and reaction studies, Chem. Eng. J. 159 (2010) 203–211.

[37] H. Lan, R. Mao, Y. Tong, Y. Liu, H. Liu, X. An, R. Liu, Enhanced electroreductive removal of bromate by a supported Pd-In bimetallic catalyst: kinetics and mechanism investigation, Environ. Sci. Technol. 50 (2016) 11872–11878.

[38] X. Wang, P. Ning, H. Liu, J. Ma, Dechlorination of chloroacetic acids by Pd/Fe nanoparticles: Effect of drying method on metallic activity and the parameter optimization, Appl. Catal. B. Environ. 94 (2010) 55–63.

[39] R. Mao, X. Zhao, H. Lan, H. Liu, J. Qu, Graphene-modified Pd/C cathode and Pd/GAC particles for enhanced electrocatalytic removal of bromate in a continuous three-dimensional electrochemical reactor, Water Res. 77 (2015) 1–12.

[40] R. Mao, X. Zhao, J. Qu, Electrochemical reduction of bromate by a Pd modified carbon fiber electrode: kinetics and mechanism, Electrochim. Acta. 132 (2014) 151–157.

[41] J. Lipkowski, P.N. Ross, Electrocatalysis, Wiley-VCH, New York, 1998.

[42] W. Xie, S. Yuan, X. Mao, W. Hu, P. Liao, M. Tong, A.N. Alshawabkeh, Electrocatalytic activity of Pd-loaded Ti/TiO_2 nanotubes cathode for TCE reduction in groundwater, Water Res. 47 (2013) 3573–3582.

[43] R. Mao, X. Zhao, H. Lan, H. Liu, J. Qu, Efficient electrochemical reduction of bromate by a Pd/rGO/CFP electrode with low applied potentials, Appl. Catal. B. Environ. 160–161 (2014) 179–187.

[44] J. Farrell, N. Melitas, M. Kason, T. Li, Electrochemical and column investigation of iron-mediated reductive dechlorination of trichloroethylene and perchloroethylene, Environ. Sci. Technol. 34 (2000) 2549–2556.