



Reductive removal of chloroacetic acids by catalytic hydrodechlorination over Pd/ZrO₂ catalysts

Juan Zhou^a, Yuxiang Han^a, Wenjuan Wang^a, Zhaoyi Xu^a, Haiqin Wan^a, Daqiang Yin^b, Shourong Zheng^{a,*}, Dongqiang Zhu^a

^a State Key Laboratory of Pollution Control and Resource Reuse, Jiangsu Key Laboratory of Vehicle Emissions Control, School of the Environment, Nanjing University, Nanjing 210093, China

^b Key Laboratory of Yangtze River Water Environment of Ministry of Education, Tongji University, Shanghai 200092, China

ARTICLE INFO

Article history:

Received 14 October 2012

Received in revised form

21 December 2012

Accepted 4 January 2013

Available online 18 January 2013

Keywords:

Chloroacetic acids

Catalytic hydrodechlorination

Supported Pd catalyst

Metal–support interaction

ABSTRACT

Chloroacetic acids are common disinfection byproducts in drinking water and are of significant concern due to their strong carcinogenic, mutagenic and hepatotoxic effects. In the present study, the catalytic hydrodechlorination of chloroacetic acids (monochloroacetic acid, dichloroacetic acid and trichloroacetic acid) was investigated over supported Pd catalysts on SiO₂, ZrO₂, and activated carbon (AC) prepared by the impregnation method (denoted as *im*-Pd/support) and/or the deposition-precipitation method (denoted as *dp*-Pd/support). The catalysts were characterized by X-ray diffraction, transmission electron microscopy, measurement of point of zero charge, N₂ adsorption–desorption isotherm, H₂ chemisorption, and X-ray photoelectron spectroscopy. Characterization results showed that the points of zero charge of the supports varied. In contrast to *im*-Pd/ZrO₂, strong metal–support interaction was identified in *dp*-Pd/ZrO₂. Accordingly, *im*-Pd/ZrO₂ was found to be more active than *im*-Pd/AC and *im*-Pd/SiO₂, and *dp*-Pd/ZrO₂ exhibited higher catalytic activity than *im*-Pd/ZrO₂. Complete dechlorination of chloroacetic acids to acetic acid could be achieved on *dp*-Pd/ZrO₂ within 120 min of hydrodechlorination. The hydrodechlorination rate constants of trichloroacetic acid, dichloroacetic acid, and monochloroacetic acid over *dp*-Pd(1.74)/ZrO₂ were 0.22, 0.16, and 0.044 min⁻¹, respectively, reflecting an increase in dechlorination activity with increasing number of chlorine atoms in chloroacetic acids. It was further demonstrated that the catalytic hydrodechlorination was accomplished via a combined stepwise and concerted pathway for both trichloroacetic acid and dichloroacetic acid.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

As an effective, simple and cost-competitive disinfection method, chlorination has been widely adopted in drinking water supply [1,2]. However, chlorination inevitably leads to the formation of disinfection byproducts (DBPs) by a series of substitution, addition and oxidation reactions between the disinfection agent and dissolved organic compounds that are ubiquitous in the drinking water source [3,4]. Among the DBPs, chloroacetic acids (CAAs), including mono-, bi- and tri-chloroacetic acids, are of significant concern due to their strong carcinogenic, mutagenic and hepatotoxic effects [5,6]. Toxicity test results showed that the lowest concentrations of monochloroacetic acid (MCAA), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) for significant toxic effects were 0.25, 2.0, and 0.4 mM, respectively,

reflecting a toxic order of MCAA > TCAA > DCAA [7,8]. Additionally, CAAs were frequently detected at μg l⁻¹ level in drinking water [9,10]. Therefore, development of effective treatment methods to eliminate CAAs in drinking water is highly demanded for assuring safe drinking water supplies.

Reductive dechlorination has been considered as an attractive option to remove CAAs in water. For example, Hozalski et al. [11] studied the reduction of haloacetic acids by zero-valent iron and found that polyhaloacetic acids were readily reduced via a sequential hydrogenolysis mechanism; however, the dechlorination by zero-valent iron was not complete and MCAA was very recalcitrant toward the reduction. Due to the strong capability for H₂ activation, metallic Pd can be added to zero-valent iron to enhance the reduction of CAAs. Wang et al. [12] investigated the dechlorination of CAAs on Pd/Fe nanoparticles and concluded that MCAA could be effectively dechlorinated into acetic acid and the reaction activities of Pd/Fe nanoparticles were strongly dependent on the preparation method. Consistently, Li et al. [13] studied the electrocatalytic dechlorination of CAAs and found that effective dechlorination of MCAA into acetic acid could only be achieved on Pd-carbon and Pd/Fe-carbon electrodes.

* Corresponding author at: State Key Laboratory of Pollution Control and Resource Reuse, Jiangsu Key Laboratory of Vehicle Emissions Control, School of the Environment, Nanjing University, Nanjing 210093, China. Tel.: +86 25 89680373; fax: +86 25 89680596.

E-mail address: srzheng@nju.edu.cn (S. Zheng).

Liquid phase catalytic hydrogenation is a promising method to selectively remove inorganic and organic pollutants in water under ambient pressure and temperature conditions. For example, Vorlop and Tacke [14] first explored the liquid phase catalytic hydrogenation for the selective reduction of nitrate in water. Chen et al. [15,16] found that Cr(VI) and bromate in water could be readily reduced using the catalytic hydrogenation method. Schüth and Reinhard [17] verified the feasibility of the catalytic hydrodechlorination (HDC) of chlorinated aromatic compounds in hydrogen-saturated water. Additionally, some research groups systematically studied the catalytic HDC of chlorophenols on supported noble metal catalysts [18–24]. Hence, we hypothesized that effective removal of CAAs in water could be achieved by the liquid phase catalytic HDC over supported noble catalysts under ambient conditions. To the best of our knowledge, relevant study has not been reported thus far.

In the present study, supported Pd catalysts on different supports were prepared by the impregnation and/or deposition-precipitation method, and the liquid phase catalytic HDC of selected CAAs on the catalysts was investigated. The results showed that the CAAs could be readily reduced into acetic acid over the synthesized catalysts, reflecting the potential of liquid phase HDC as an effective option to remove CAAs in drinking water.

2. Experimental

2.1. Catalyst preparation

Bituminous coal-based activated carbon (Filtrisorb-300) with a Brunauer–Emmett–Teller (BET) surface area of $981 \text{ m}^2 \text{ g}^{-1}$ was purchased from Calgon Carbon Co., USA. SiO_2 (BET surface area of $132 \text{ m}^2 \text{ g}^{-1}$) were purchased from Shanghai Chem. Co. (Shanghai, China).

ZrO_2 support was prepared by the precipitation method. Briefly, under vigorous stirring 150 ml of 2.0 M aqueous ammonia solution was added slowly to 400 ml of 0.5 M aqueous ZrOCl_2 solution. After aging at room temperature for 2 h, the resulting precipitant was recovered by filtration, followed by washing with distilled water and drying at 105°C for 6 h. ZrO_2 support was obtained by calcining the ZrO_2 precipitant in the air at 500°C for 4 h.

Supported Pd catalysts with different supports (SiO_2 , AC and ZrO_2) but similar Pd loading amounts were prepared by the impregnation method, and ZrO_2 supported Pd catalysts with varied Pd loading amounts were further prepared using the deposition-precipitation method. For the impregnation method, the support was impregnated by PdCl_2 solution under stirring for 2 h, followed by drying at 105°C for 6 h, calcining in air at 300°C for 4 h and reducing at 300°C under a H_2 stream (40 ml min^{-1}) for 2 h. The resulting catalyst with ZrO_2 as the support is denoted as *im-Pd(x)/ZrO₂*, where *x* is the Pd loading amount (wt.%). As for the deposition-precipitation method, ZrO_2 support was suspended in PdCl_2 solution under stirring for 2 h. Then, 1.0 M Na_2CO_3 solution was added slowly to the suspension until pH 10.5. The resulting solid was recovered by filtration, washed thoroughly with distilled water, dried at 105°C for 6 h, and reduced under a H_2 stream (40 ml min^{-1}) at 300°C for 2 h. The obtained catalyst is denoted as *dp-Pd(x)/ZrO₂*, where *x* is the Pd content (wt.%). Prior to catalytic activity test, all catalysts were ground to pass through a 400-mesh sieve ($<37 \mu\text{m}$) to avoid possible intraparticle diffusion [25,26].

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were collected in a range of $10\text{--}70^\circ$ with a Rigaku D/max-RA powder diffraction-meter using $\text{Cu K}\alpha$ radiation (Rigaku, Tokyo, Japan). Transmission

electron microscopy (TEM) images of the samples were obtained on a JEM-2100 transmission electron microscope (JEM-2100, JEOL, Japan). N_2 adsorption–desorption isotherms were measured at -196°C (77 K) on a Micromeritics ASAP 2020 instrument (Micromeritics Instrument Co., Norcross, GA, USA). The specific surface areas of the samples were calculated according to the BET method ($0.05 < P/P_0 < 0.25$). Prior to the measurement the samples were pre-treated at 300°C under vacuum (1.33 Pa) for 1 h. Pd contents of the catalysts were determined using an inductive coupled plasma emission spectrometer (ICP) (J-A1100, Jarrell-Ash, USA). The X-ray photoelectron spectroscopy (XPS) analysis was performed with a PHI5000 VersaProbe equipped with a monochromatized Al K α excitation source ($h\nu = 1486.6 \text{ eV}$) (ULVAC-PHI, Japan). The C 1s peak (284.6 eV) was used for the calibration of binding energy.

The points of zero charge (PZCs) of the supports were measured using the potentiometric mass titration method [27,28]. Typically, 0.5 g of the support was suspended in 50 ml of 0.03 M KNO_3 solution at 25.0°C , which was continuously bubbled with a N_2 flow (50 ml min^{-1}) under stirring. 0.2 ml of 1.0 M KOH solution was added to the suspension, and the mixture was equilibrated for 20 h to reach a stable pH. Then, the mixture was titrated by a 0.5 M HNO_3 solution, and the pH was monitored intermittently. The blank solution (without support) was also titrated by the same procedure.

Metallic Pd dispersion of the catalyst was measured using the H_2 chemisorption method. Briefly, 100 mg of the reduced catalyst was pressed into wafers, broken into small platelets, and loaded in a U-shaped quartz tube, in which the catalyst was activated in a H_2 flow (40 ml min^{-1}) at 300°C for 1 h. After purging with an Ar flow (30 ml min^{-1}) for 1 h, the catalyst was cooled down to room temperature. The H_2 chemisorption was performed using the pulse titration model with H_2 partial pressure below 0.011 atm. The H_2 contents in the pulses were monitored by a thermal conductivity detector (TCD).

2.3. Liquid phase catalytic HDC of CAAs

The liquid phase catalytic HDC of CAAs was conducted under atmospheric pressure of hydrogen using a 250 ml of four-necked flask reactor with a sample port, pH-stat, H_2 inlet and condenser. The reaction temperature was stabilized at $25 \pm 0.5^\circ\text{C}$ with a water-bath (SDC-6, Scientz Co., China). Typically, 30 mg of catalyst was suspended in 200 ml of 0.16 mM chloroacetic acid solution with pH pre-adjusted to 5.6. The suspension was purging with a N_2 flow (50 ml min^{-1}) under stirring (1400 rpm) for 30 min, and then the N_2 flow was switched into a H_2 flow (250 ml min^{-1}) during the reaction process. Samples were taken at selected time intervals and the catalyst particles were removed by fast filtration. The filtrate was analyzed using an Ion Chromatography (ICS1000, Dionex) with a mobile phase of 20 mM KOH solution. Catalyst activity was evaluated using the initial activity defined as the specific removal rate of chloroacetic acid within the initial 6 min. The results of two separate runs of the catalytic HDC of MCAA on *dp-Pd(1.74)/ZrO₂* indicated a high data reproducibility (see Fig. 1S, supporting information).

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the supported catalysts are compiled in Fig. 2S and 3S, supporting information. For the catalysts with AC and SiO_2 as the supports, diffraction peaks assigned to metallic Pd with a face centered cubic (fcc) crystallographic structure were observed at 40.2° and 46.7° [29,30]. However, diffraction peaks characteristic of metallic Pd were not identified in ZrO_2 supported Pd catalysts,

Download English Version:

<https://daneshyari.com/en/article/45786>

Download Persian Version:

<https://daneshyari.com/article/45786>

[Daneshyari.com](https://daneshyari.com)