Effect of the reducing agent on the hydrodechlorination of dioxins over 2 wt.% Pd/γ-Al$_2$O$_3$

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A B S T R A C T

2-Propanol and molecular H$_2$ (in methanol (MeOH) and MeOH–water) were examined as reducing agents for the liquid phase hydrodechlorination (HDC) of dioxins over 2 wt.% Pd/γ-Al$_2$O$_3$. Different amounts of NaOH were added to the reaction mixtures. The 2-propanol and H$_2$(g)/MeOH systems presented similar HDC activity. Notwithstanding, Pd sintering and graphitic carbon directly bonded to Pd on catalyst surface was observed on samples used with H$_2$(g)/MeOH. The addition of water to H$_2$(g)/MeOH decreased Pd sintering and favored dissolution of sodium compounds. However, dioxin degradation efficiency diminished. By contrast, 2-propanol acting both as reducing agent and solvent provided hydrogen to the HDC reaction, avoided metal sintering and Pd–C formation. Besides, almost complete dioxin degradation under mild reaction conditions was obtained. Kinetic experiments of dioxin HDC with 2-propanol showed a maximum net reaction rate and turnover frequency (TOF) for a given initial concentration of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). After that value, both reaction rate and TOF decreased. On the other hand, reaction rates and TOFs of dioxin-like polychlorinated biphenyls (DL-PCBs) linearly increased with concentration.

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of structurally related chemicals which persist in the environment, bioaccumulate in the food chain and are toxic. These compounds have similar mechanisms of toxicity so they are grouped together when considering potential risks [1]. Congeners containing chlorine at 2,3,7,8 positions have been identified as more toxic to exposed organisms. So, target substances are reduced to 7 PCDDs and 10 PCDFs. Nevertheless, not all 2,3,7,8 chlorinated PCDDs/PCDFs have the same toxicity. The most toxic is considered to be 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) [1]. Although there are far fewer data on the other sixteen 2,3,7,8-substituted compounds, dioxins are found in the environment as complex mixtures, and it is necessary to have some way of assessing the toxicity of such mixtures. The World Health Organization (WHO) defined the toxic equivalence factors (TEF) to measure the concentration of dioxins and furans in terms of the overall toxicity of the mixture [2]. The concentration of either compound is multiplied by its corresponding TEF giving the toxic equivalent concentration (TEQ). The sum of all TEQs provides the amount of 2,3,7,8-TCDD that gives the same overall toxic effect. The close toxicological similarity of coplanar polychlorinated biphenyls (PCBs) to dioxins has led to the extension of the TEF system to some of the coplanar PCB compounds, the dioxin-like PCBs, and for the TEQ of an environmental sample to include contributions from dioxins, furans and dioxin-like PCBs. In 1997, the WHO system of TEFs includes TEF values for 12 non-ortho- and mono-ortho-PCBs that have demonstrated dioxin-like toxicity [2].

Waste incineration is an important source of dioxins, furans and dioxin-like PCBs which are mainly concentrated in the solid residues of gas cleaning systems [1,3,4]. Actions for suitable treatment and inertization of solid waste, in particular fly ash, are of primary concern because improper disposition of this waste can lead to severe environmental pollution [5]. HDC is one of the most promising methods for detoxifying chlorinated organic waste [6]. As a non-destructive approach, HDC represents a complement to the traditional landfill disposal of solid waste because it can reduce sample toxicity under mild conditions avoiding future environmental contamination. Nevertheless, a large variety of chlorinated compounds with different toxicity and degradation pathways make HDC of real fly ash samples a complex technique affected by several parameters. Particularly, PCDD/Fs degradation is the main target in fly ash HDC studies, due to their important contribution to total sample toxicity, stable chemical structure, trace concentration in

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environmental samples, and interference with other coexistent halogenated pollutants at higher concentrations [5]. Additionally, dioxin degradation might indicate destruction of other chlorinated hydrocarbons from fly ash.

The source of hydrogen for HDC can be either molecular hydrogen or a hydrogen donor [7]. HDC of PCDD/Fs fly ash extracts with molecular hydrogen over a supported metal catalyst (Pt/C or Pd/C) was successfully accomplished in a multiphase reaction system (isooctane–water) [8]. PCDD/Fs and DL-PCBs from fly ash samples collected from a commercial solid-waste incinerator were HDC at 355 K over 5 wt.% Pd/Al$_2$O$_3$ using 2-propanol as solvent and hydrogen source [9]. Comparable results were obtained over 2 wt.% Pd/γ-Al$_2$O$_3$ [10]. Dioxin HDC reactions over Pd/C have been recently reported by Yang et al. [5] using a 2-propanol/water solution and by Zhang et al. [11] using a H$_2$(g)/ethanol/water mixture. These systems provided complete dioxin degradation at temperatures below 323 K. Additionally, methanol/water and ethanol/water mixtures demonstrated superior efficiency compared to pure methanol or ethanol for the HDC of tetrachloroethylene [12,13], chlorophenols [14], and aromatic halides [15] over Pd/C. In this work, 2-propanol and molecular H$_2$ (in MeOH and MeOH/water) were examined as reducing agents for the HDC of dioxins over 2 wt.% Pd/Al$_2$O$_3$. Reactions were carried at the solvent boiling points and different NaOH amounts were added. Fresh and used catalyst samples were characterized by TEM-EDS, XPS, XRD and TGA/DTA. Also, the effect of the initial concentration on the HDC rate of dioxins was evaluated in the 2-propanol/2 wt.% Pd/γ-Al$_2$O$_3$/NaOH system.

2. Experimental

2.1. Materials

Palladium acetylacetonate (99%, Aldrich Chem. Co., USA) was used as Pd precursor and γ-alumina (99.97%, Alfa Aesar, USA) as support material. All solvents used for catalytic tests and PCDD/Fs extraction, clean up and analysis were Ultimar Grade from Mallinckrodt Baker (USA). Silica, florisil and alumina adsorbents for cleaning up were from Merck, Germany. EPA-1613CVS (CS1–CS5) calibration solutions, EPA-1613LCS extraction standard and EPA-1613ISS syringing standard for PCDD/Fs determination were obtained from Wellington Laboratories (Canada). All ultra-high purity gases were purchased from AGA, Colombia.

2.2. Catalyst preparation

2 wt.% Pd/γ-Al$_2$O$_3$ was prepared by wetness impregnation. The amount of palladium acetylacetonate necessary to obtain 2 wt.% Pd loading was dissolved in 10–20 mL of acetone. This mixture was slowly added to γ-alumina under continuous stirring at 313 K allowing acetone evaporation. The resulting solid was oven dried at 373 K during 12 h. The catalyst was pretreated at 2 K min^{-1} up to 673 K for 1 h in flowing 50 mL min^{-1} air and reduced at 2 K min^{-1} up to 573 K in 50 mL min^{-1} flowing 10% H$_2$/N$_2$. The samples were maintained at this temperature for 1 h. Finally, they were cooled down to room temperature in flowing nitrogen. Calcined and reduced catalyst samples were coded as PA-act. Pd dispersion of the PA-act samples was 21.3% as previously reported [16].

2.3. Catalytic tests

Fly ash samples were taken from a container filled with accumulated bag filter fly ash from several incineration batches of an incinerator located in Medellin, Colombia. Solid samples were soxhlet extracted with toluene during 48 h. One fraction of the liquid extract was cleaned up and analyzed following EPA1613

method as described previously [10,18]. Briefly, fly ash extract samples were spiked with EPA1613-LCS standard and cleaned up. Cleaned samples were analyzed by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry (HRGC-QITMS/MS) in a Varian CP-3800 GC coupled to a Saturn 2000 ion-trap spectrometer equipped with an 8400 auto sampler and a DB-5MS column (60 m × 0.25 mm I.D., 0.25 μm film thickness). Quantification of dioxins, furans and DL-PCBs were performed by the isotope dilution method. Relative response factors (RRFs) were determined using calibration standards for PCDD/Fs and DL-PCBs analysis (EP1613-CS and WP-CS solutions from Wellington Labs, Canada). Toxic equivalents (WHO-TEQ) were determined using WHO-TEF factors [10,18]. The detection limit of 2378-TCDD was 8.22E−12 g.

HDC reactions were performed in three mouth round bottom flasks equipped with a septum, a thermowell and a condenser. When 2-propanol was the reducing agent, reaction mixtures consisted of 400–600 μL of fly ash extracts dissolved in toluene at different initial dioxin concentrations, 100 mg of 2 wt.% Pd/γ-Al$_2$O$_3$ and different amounts of NaOH dissolved in 20 mL of 2-propanol. The fly ash extract samples were coded as S10, S50, S75, S150 and S250 depending on the initial ng TEQ added to the reaction mixture, i.e. S10 corresponds to the addition of 10 ng TEQ. On the other hand, when molecular hydrogen was the reducing agent MeOH and 20–80% MeOH–water mixtures were used as solvents. 75 ng TEQ (S75) was used in these experiments. At the beginning of the reaction molecular hydrogen was injected several times into the system through a septum and kept at a slightly higher pressure than atmospheric. Then, the reaction mixture was heated to the desired temperature. The reaction temperature varied depending on the solvent boiling point, i.e. 333 K for MeOH or 348 K for 2-propanol.

As we previously reported [10], the absence of mass transfer limitations was confirmed using different catalyst particle diameters and checking the compliance to Koros–Nowak criterion at 2300 rpm stirring velocity [19,20]. The sieve fraction used was lower than 37 μm (400 mesh). After a 3-h reaction, the catalyst was recovered by filtration, washed with 100 mL of toluene and dried at 373 K during 24 h. Used catalyst samples were coded as PA-X-Y, where X denotes the reducing agent, i.e., 2P for 2-propanol and H$_2$ for molecular hydrogen and Y denotes the reaction temperature in Kelvin.

The HDC over 2 wt.% Pd/γ-Al$_2$O$_3$ of toxic compounds, i.e. 7 dioxins, 10 furans and 12 PCBs, was determined by calculating the conversion of either toxic compound from its concentration in the sample before and after reaction. Also, total conversion (TC %) was figured out by summing up the conversion of all toxic compounds before and after reaction (Eq. (1)) and the percent toxicity reduction (TR %) was obtained from the initial and final ng TEQ of each sample (Eq. (2)) [10].

$$TC(\%) = \frac{\sum_1^{29}[\text{PCDD/PCDF/PCB}]_{initial} - \sum_1^{29}[\text{PCDD/PCDF/PCB}]_{final}}{\sum_1^{29}[\text{PCDD/PCDF/PCB}]_{initial}}$$
(1)

$$TR(\%) = \frac{(\text{ng TEQ})_{initial} - (\text{ng TEQ})_{final}}{(\text{ng TEQ})_{initial}}$$
(2)

When 2-propanol was used as reductant, the turnover frequency (TOF) was calculated taking Pd dispersion as 21.3% [19] and the Pd loading listed in Table 2. The production of hydrogen was estimated from the amount of acetone generated in the reaction mixture after 30-min reactions at different temperatures, in the presence and in the absence of dioxin extracts. From stoichiometry 1 mol of 2-propanol produces 1 mol of acetone and 1 mol of H$_2$ [21,22]. After reaction, the sample was cooled down to room