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The Effect of NaOH on the Liquid-Phase Hydrodechlorination of Dioxins over Pd/γ-Al_2O_3

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The effect of sodium hydroxide on the-liquid phase hydrodechlorination (LPHDC) of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/Fs) over 2% Pd/γ-Al_2O_3 was evaluated. Reactions were carried out using 2-propanol both as a hydrogen donor and as a solvent. Fresh and used catalyst samples were characterized by BET, hydrogen chemisorption, TEM/EDS, XPS, and TPR. When the reaction mixture contained no NaOH, active-phase leaching and Pd−C formation were observed even after 10 min of reaction. Therefore, sodium hydroxide appears to be required to maintain surface metal clusters on the support and avoid binding of carbon species to the active metal. On the other hand, excess NaOH in the reaction mixture led to deposition of organic and inorganic solid residues on the catalyst surface, blocking the active sites. Under the conditions of this study, the addition of 30 mg of NaOH maintained the basicity of the system and diminished deposition of solid residues on the catalyst samples, and almost 100% detoxification was reached after a 3 h reaction.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans, currently known as dioxins, are a group of 210 chlorinated compounds that have received a lot of attention, primarily because of their toxicity at very low concentrations.[1–4] Congeners chlorinated at 2,3,7,8-possitions are considered the most toxic, being 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3.7,8-TCDD) cataloged as a human carcinogen by the World Health Organization (WHO).[5] As unintentional byproducts of combustion, dioxin emissions are expected in all countries; therefore, they are included in the dirty dozen of persistent organic pollutants (POPs) of the Stockholm Convention.[6,7] During waste combustion, the highest dioxin burden is adsorbed mainly on fly ashes, turning them to highly toxic materials.[8,9] Currently, fly ashes are disposed of in landfills, leading to water and soil contamination.[10,11] For example, most incineration plants in Colombia generate fly ash containing dioxin levels over 100 ng of I-TEQ/g. Thus, treatment and disposal of fly ash has to be efficient enough to ensure that it is suitably made inert.

Among the approaches to degrade dioxins, liquid-phase hydrodechlorination (LPHDC) under mild reaction conditions has been accomplished on fly ash extracts, allowing the rapid and efficient degradation of these compounds.[12–15] However, LPHDC reactions generally must be conducted in the presence of a base in order to neutralize hydrogen chloride released from the chlorine−hydrogen replacement process.[16–19] Some authors have reported that HCl is a catalyst poison acting in different ways, such as promoting active-phase leaching, competitive adsorption between HCl and the substrate, the formation of Pd−Cl, support degradation,[16] active-phase oxidation,[20] and the formation of chlorinated carbonaceous residues.[21] Important effects of pH on the amphoteric characteristics of catalyst surface and catalyst/reactant interactions in aqueous media have been reported.[18,19] Ukisu et al.[22] found a positive and direct association between conversion and base addition on the LPHDC of 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD). However, other studies have reported better hydrodechlorination (HDC) results without base addition since basic media might promote partial oxidation of the active metal.[16,20] Moreover, most studies agree that an excess of base can negatively affect catalyst performance.[13,18] In this way, the addition of base to the reaction system is a very important parameter for HDC reaction. In this contribution, the effect of sodium hydroxide addition and reaction efficiency were studied using extracts of fly ash samples containing very high concentrations of PCDD/Fs. 2-Propanol was used as the solvent and hydrogen donor, and 2 wt % Pd/γ-Al_2O_3 was used as the catalyst. Fresh and used catalyst samples were characterized by chemical analysis, BET surface area, hydrogen chemisorption, XPS, TEM-EDS, and TPR.

2. Experimental Methods

2.1. Materials. Catalysts were prepared by incipient wetness impregnation of palladium acetylacetonate (99%, Aldrich Chemical Co., U.S.A.) on γ-alumina (99.97%, Alfa Aesar, U.S.A.). All solvents used for catalytic tests and dioxin extraction, clean up, and analysis were Ultimar grade from Mallinckrodt Baker (U.S.A.). Silica, florisil, and alumina adsorbents for clean up were from Merck, Germany. EPA-1613CVS (CS1 to CS5) calibration solutions, EPA-1613LCS extraction standards, and EPA-1613ISS syringing standard, for PCDD/Fs determination were obtained from Wellington Laboratories (Canada). All ultrahigh purity gases were purchased from AGA, Colombia.

2.2. Catalyst Preparation. Pd/γ-Al_2O_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 the γ-alumina support under continuous stirring at 40 °C, allowing acetone evaporation. This material oven-dried at 100 °C for 12 h is denoted as PA-fresh. For catalyst activation, samples were

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heated at 2 °C/min to 400 °C in 50 mL/min of flowing air. Then, they were reduced by heating at 2 °C/min to 300 °C, maintaining this temperature for 1 h in 50 mL/min of flowing 10% H_2/N_2. Then, samples were cooled down to room temperature in flowing nitrogen. Activated (calcined and reduced) catalyst samples are denoted as (PA-act).

2.3. Catalyst Characterization. Fresh and used samples of 2 wt % Pd/Al_2O_3 were characterized by different techniques. Elemental analysis was performed by atomic absorption in a Philips PU9200 apparatus. Single-point BET surface area, pulse chemisorption, and TPR experiments were carried out in an AutoChem II 2920 Micromeritics instrument equipped with a TCD detector. For BET surface area experiments, samples were previously outgassed at 150 °C in a helium stream for 1 h to remove impurities. Then, a mixture of 30% N_2/He was allowed to flow through the sample previously immersed in a liquid nitrogen bath at −182 °C. Both the amount of adsorbed and desorbed N_2 were recorded. The amount of desorbed nitrogen was used to calculate the total surface area. Experiments were repeated twice, and surface areas were reproducible within ±5%. Pulse chemisoption was used to determine the percent Pd dispersion and average active particle size by applying measured doses of 10% H_2/Ar to catalyst samples. Between 50−100 mg of fresh and used catalyst samples were reduced by flowing 10% H_2/Ar while increasing the temperature until 300 °C. Chemisorption was performed at 100 °C to make sure that β-PdH desorption was reached.[23,24] H_2/Pd stoichiometry was established by oxygen titration in four consecutive experiments. TPR runs were carried out to determine reducible species in catalyst samples. Fresh catalyst samples were previously oxidized in a flowing O_2/Ar stream (25 mL/min), heating at 10 °C/min to 300 °C. Used catalyst samples were degassed in a 25 mL/min Ar stream at 150 °C before TPR experiments in order to diminish catalyst changes after reaction. Then, fresh and used catalyst samples were cooled down to −20 °C in flowing Ar using an ethanol−ice bath. Carrier gas was replaced by H_2/Ar (25 mL/min), and after removing the ethanol−ice bath, the TPR sample was heated at 5 °C/min until 1000 °C.

Transmission electron microscopy (TEM) experiments were carried out in a JEOL JEM-2010 microscope operating at 200 kV. The microscope was coupled to an X-ray energy dispersion spectroscope (EDS), OXFORD instruments model INCA Energy TEM100, with a Si (Li) detector with a 30 mm^2 detection area and resolution of 142 eV. Samples were dispersed in ethanol by ultrasonic vibration and dropped on a copper grid coated with carbon film. At least 200 individual Pd particles were counted for each catalyst sample, and the mean Pd particle size was quoted as the surface-area-weighted average size ($\bar{d}Pd$):[17,25]

$$\bar{d}Pd = \sum_i \frac{n_i d_i^3}{n_i d_i^2} \qquad (1)$$

where n_i is the number of particles of diameter d_i and $\Sigma_i n_i > 200$. Sigma Scan Pro 5 Software was used for particle size measurement in TEM images.

The XPS spectra of C1s, O1s, Al2p, Pd3d, Na1s, and Cl2p were scanned on fresh, activated, and used catalyst samples with a VG-Microtech Multilab electron spectrometer, by using the Mg /K//α/ (1253.6 eV) radiation of the twin anode in the constant analyzer energy mode with a pass energy of 50 eV. The pressure of the analysis chamber was maintained at 5×10^{-10} mbar. The binding energy scale was regulated by setting the C1s transition at 284.6 eV. The accuracy of the binding energy (BE) values was ±0.2 eV. The BE values were obtained by using the peak-fit program implemented in the control software of the spectrometer.

TABLE 1: Pd Loading, BET Surface Area, And Metal Dispersion of Fresh and Used 2 wt % Pd/Al_2O_3 Catalyst Samples

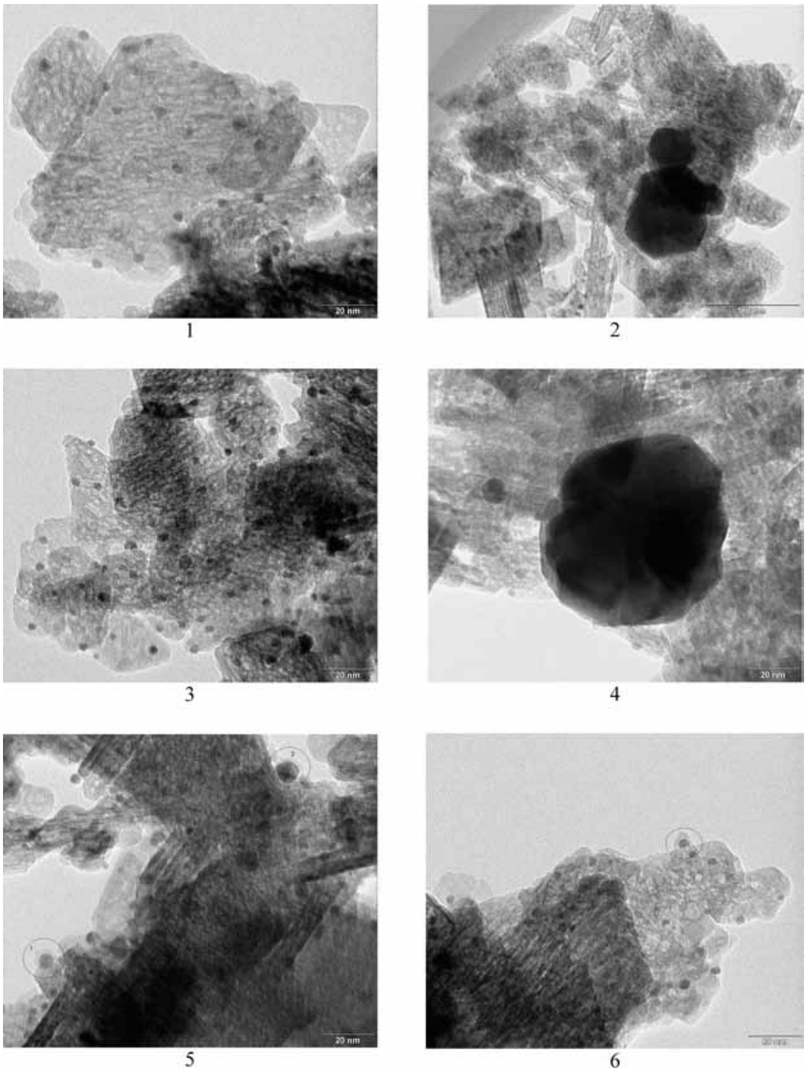
	catalyst sample				
reaction time (min)	PA-0	PA-30	PA-50	PA-100	PA-150
			Pd Loading (%)		
0	2.41	2.52	1.94	2.52	2.52
30	2.26	2.50	1.77	2.24	2.44
180	2.06				
300	1.23	2.40	1.65	2.24	2.37
			BET Surface Area, m^2/g		
0	85.9	89.1	96.6	89.1	89.1
10	54.9	44.9		44.1	44.5
60	57.2	43.6	41.8	49.4	39.7
180	46.4	43.2		45.0	33.4
			Pd Dispersion, %		
0	22.8	21.3	23.0	21.3	21.3
10	0.9	4.6	4.7	0.9	1.4
60	0.3	2.0	2.7	0.6	0.6
180	0.4	1.9		0.7	0.6

2.4. Catalytic Tests. Fly ash was collected from bag filters of an incinerator located in Medellín, Colombia,[15] and Soxhlet extracted with toluene for 48 h. One fraction of the liquid extract was cleaned up and analyzed following the EPA1613 method, as previously described.[15,26] LPHDC reactions were performed in a three mouth round-bottom flask equipped with a septum, a thermowell, and a condenser. Approximately 3.5 ng of I-TEQ/mL of PCDD/Fs extract from fly ash was mixed with 20 mL of 2-propanol (the initial concentration of the toxic PCDD/Fs congeners was about 0.5 ppm.) Then, 100 mg of 2 wt % Pd/γ-Al_2O_3 and different amounts of pure sodium hydroxide (0, 10, 30, 50, 100, and 150 mg) were added. The resulting reaction system was magnetically stirred at 2300 rpm to avoid external mass-transport limitations. The reaction started at the mixture boiling point, 75 °C (±1 °C). Tests were carried out for 10, 30, 60, 180, and 300 min. After reaction, catalyst samples were recovered by filtration, washed with 100 mL of toluene, and dried at 100 °C for 24 h. Used catalyst samples were coded PA-X, where X denotes the NaOH amount added to the reaction mixture. Liquid samples were spiked with EPA1613-LCS standard and cleaned up as reported.[15,26] Initial and final concentrations of each PCDD/F congener were determined and used to calculate the conversion by congener, the total conversion, and the % toxicity reduction.[15]

2.5. Dioxin Analyses. Dioxin samples were analyzed before and after reaction by high-resolution gas chromatography coupled to ion-trap low-resolution mass spectrometry (HRGC-QITMS/MS) in a CP-3800 GC coupled to a Saturn 2000 ion-trap spectrometer (Varian, Walnut Creck, CA, U.S.A.) equipped with a CP-8400 automated sampling device and a DB-5-MS low-bleed/MS (60 m, 0.25 mm ID, 0.25 μm film thickness) capillary column (J&W Scientific, CA, U.S.A.). EPA 1613 standard solutions in nonane (CS1 to CS5) were used for instrument calibration and quantification, according to the EPA1613 method.[15,26]

3. Results and Discussion

3.1. Catalyst Characterization. ***3.1.1. Metal Loading.*** Metal loading of fresh and used catalyst samples are shown in Table 1. Pd loading of used samples was analyzed after 30 and 300 min of reaction. For further verification, an analysis was



1 2 3 4 5 6

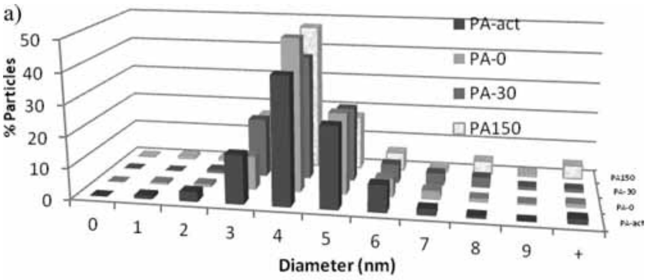
Figure 1. TEM images of 2 wt % Pd/Al_2O_3 samples PA-act (1 and 2), PA-0 (3 and 4), PA-30 (5), and PA-150 (6).

TABLE 2: Atomic Concentration (%) of Elements in TEM Images

catalyst sample	image	Al	O	Pd	C[a]	Na
PA-act	1	55.720	43.510	0.780	N.D.	N.D.
	2	16.000	9.840	74.150	N.D.	N.D.
PA-0	3	44.990	54.430	0.570	N.D.	N.D.
	4	12.670	15.770	71.560	2.340	N.D.
PA-30	5	31.520	39.350	22.710	4.800	1.630
PA-150	6	21.990	30.130	47.880	3.215	2.063

[a] N.D.: Not detected.

done after 180 min of reaction on a catalyst sample, PA-0 (no NaOH). Pd losses were observed after 30 min of reaction in all catalyst samples. Nevertheless, these losses were more pronounced after 300 min of reaction (about 49 wt % Pd) in the PA-0 sample. This behavior is ascribed to the HCl increase during reaction and the subsequent corrosion effect leading to leaching of the active phase from the support. Yang and Keane[17] also found similar active metal loss without NaOH addition for HDC of 2,4-dichlorophenol after 120 min of reaction (5 wt % loss with NaOH and 11 wt % loss without NaOH). For the other catalyst samples, Pd losses were lower than 0.30 wt % Pd, revealing that base addition is necessary for catalyst stability.



b)

Catalyst Sample	$\bar{d}_{Pd}$
PA-act	4.83
PA-0	4.87
PA-30	5.12
PA150	5.06

Figure 2. (a) Particle size distribution of 2 wt % Pd/Al_2O_3. (b) Pd surface area weighted average size.

3.1.2. BET Surface Area and Metal Dispersion. BET surface area and metal dispersion of fresh and used catalyst samples are shown in Table 1. In all used catalyst samples, both parameters show drastic reduction from the beginning of the reaction. The BET surface area decreases as the reaction time increases and with the addition of NaOH. It can be attributed to inorganic (NaOH and NaCl) and organic residue deposition on the catalyst, leading to pore blocking.[21,27] As the reaction progresses, more solid is deposited, and the surface area diminishes. Without NaOH addition, the decrease in surface area

TABLE 3: Binding Energies (eV) and Atomic Ratios of C/Al, Pd/Al, and Na/Al Determined by XPS

	binding energies (eV)			atomic ratio		
catalyst sample	C1s	Pd $3d_{5/2}$	Na1s	C/Al	Pd/Al	Na/Al
PA-fresh	284.6; 286.7	336.2; 337.9	N.D.	0.38	0.026	0
PA-act	284.6; 286.6	334.2	N.D.	0.29	0.009	0
PA-0	283.1; 284.5	334.7	N.D.	0.75	0.010	0
PA-10	284.2; 285.3	334.5	1071.5	0.55	0.008	0.04
PA-30	284.0; 285.1	335.0	1071.1	0.72	0.009	0.13
PA-100	284.1; 285.3	335.0	1071.6	0.52	0.009	0.39
PA-150	284.5	334.6	1070.7	0.27	0.007	0.50

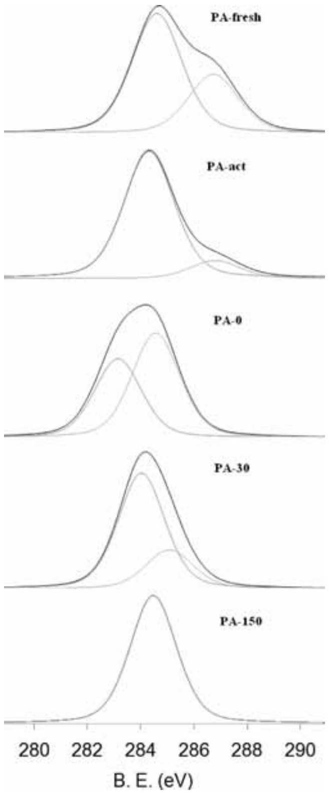


Figure 3. C1s XPS spectra of 2 wt % Pd/Al_2O_3 fresh, activated by calcination and reduction and used in reaction mixtures containing different amounts of NaOH.

is lower and may be associated with carbonaceous deposits.[21,27] From chemisorption analysis (Table 1), fresh catalyst samples exhibited about 22% palladium dispersion with active particle diameters between 4 and 5 nm. Used samples showed lower dispersion. The drop in the dispersion has been attributed to the blockage of the pore system by deposits, which submerge Pd into the bulk of the catalyst.[28] Therefore, it is likely that the chemisorption probe (H_2) could not reach the palladium in closed pores, and the actual dispersion calculations bare a significant error.

3.1.3. TEM/EDS. In order to determine the real cluster particle size, TEM/EDS analysis of fresh and used catalyst samples was carried out. TEM images are shown in Figure 1. The active phase is dispersed in faceted Pd particles, suggesting strong metal−support interaction, which can be attributed to electron transfer from the alumina.[17] Also, fresh and used catalyst samples exhibit isolated particles with diameters between 70 and 80 nm possibly formed during catalyst preparation. EDS gives a qualitative detection of different compounds over selected catalyst zones. The elements detected in Figure 1 are listed in Table 2. In the activated catalyst (PA-act), only Al, O, and Pd were detected, confirming the presence of primary Pd in large black particles (images 2 and 4) with more than 70 atom % Pd loading. Used catalyst samples in the presence of NaOH presented a core over Pd particles clearly observed in images 5 and 6 (marked with a circle). EDS analysis in this zone indicates the presence of Na compounds. Additionally, carbon was detected in all used catalyst samples. The particle size distributions of catalyst samples are presented in Figure 2. Smooth differences in the Pd size distribution were detected in fresh and used catalyst samples. PA-0 and PA-150 showed particles within 4−5 nm of diameter, while more contribution of particles larger than 9 nm was observed in PA-150. Major mobility of the active phase with increasing of the Pd particle size has been reported for HDC reactions in acid media and has been attributed to possible formation of Pd−Cl species.[29,30] This behavior was not observed in the PA-0 sample, which has a similar Pd particle size as the other used catalyst samples. Moreover, the Pd−Cl species was not detected by XPS, vide infra.

3.1.4. XPS. Binding energies of C1s, Pd3d, and Na1s are listed in Table 3. XPS spectra of C1s and Pd3d core levels of catalyst samples that are fresh, activated by calcination and reduction, and used in reaction mixtures containing different amounts of NaOH are shown in Figures 3 and 4. C1s presents peaks in the range of 283.1−286.7 eV. The carbon oxidation state increases with binding energy.[31] More oxidized carbon species in fresh and activated catalyst samples are present around 286.6 eV. This peak can be ascribed to C−O species[32] from a metal precursor (palladium acetylacetonate). The size of this peak is reduced when the catalyst is activated (PA-act) due to the combustion of carbonaceous residues occurring during activation. Peaks between 284.0 and 284.7 eV present in all catalyst samples have been attributed to adventitious carbon (AC), corresponding to adsorbed species typically present in samples exposed to ambient air.[32–34] This AC is one of the least desired, but it is the most persistent of nearly every surface study in XPS and corresponds to the presence of carbon deposits, which are difficult to remove and even more difficult to keep off.[31] Peaks at about 285 eV due to C−OH species[34] are observed in used catalyst samples when 10, 30, 50, and 100 mg of NaOH are added to the reaction mixture. The intensity of this peak can be linked with catalyst activity and might correspond to reaction products in the presence of NaOH. The catalyst sample used under acid conditions (PA-0) presents one peak at 283.1 eV attributed to more crystalline and negatively charged carbon species directly bonded to palladium.[34] This species was found to form a graphitic structure over the active-phase blocking substrate interaction. The presence of this Pd−carbide species has been well observed in gas-phase hydrogenolysis reactions, where HCl in the media cannot be avoided.[28,34]Therefore, PdC species can be reduced or avoided by NaOH addition to the reaction mixture.

$Pd3d_{5/2}$ of a PA-fresh sample (Figure 4) shows two peaks ascribed to oxidized species. The peak at 336.2 eV has been attributed to the presence of PdO particles, and the peak at 337.9 eV is attributed to Pd−C binding from the precursor salt.[28,32–34] The latter species was not detected in C1s spectra probably due to the low contribution to the total carbon in the fresh catalyst. Oxidized species disappeared after the activation process, and a completely reduced catalyst sample was obtained with a unique peak at 334.2 eV. All used catalyst samples presented only a peak with a binding energy between 334 and 335 eV ascribed to the Pd^0 species. These results revealed no important changes in the active phase after reaction. Padmasri et al.[35] and Ordoñez et al.[36] found no changes in the Pd oxidation state after gas-

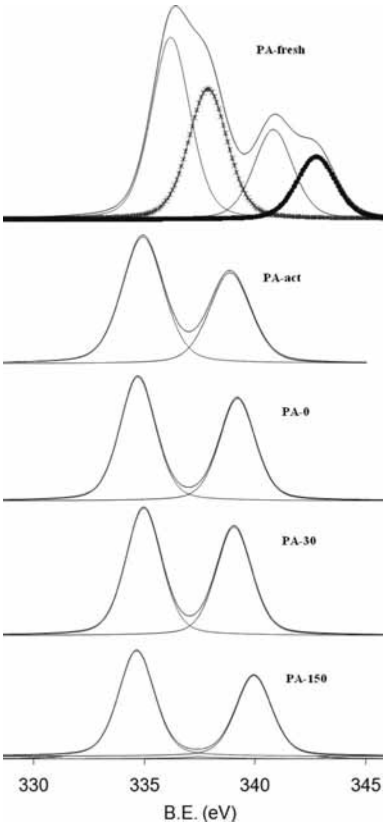


Figure 4. Pd3d XPS spectra of 2 wt % Pd/Al_2O_3 fresh, activated by calcination and reduction and used in reaction mixtures containing different amounts of NaOH.

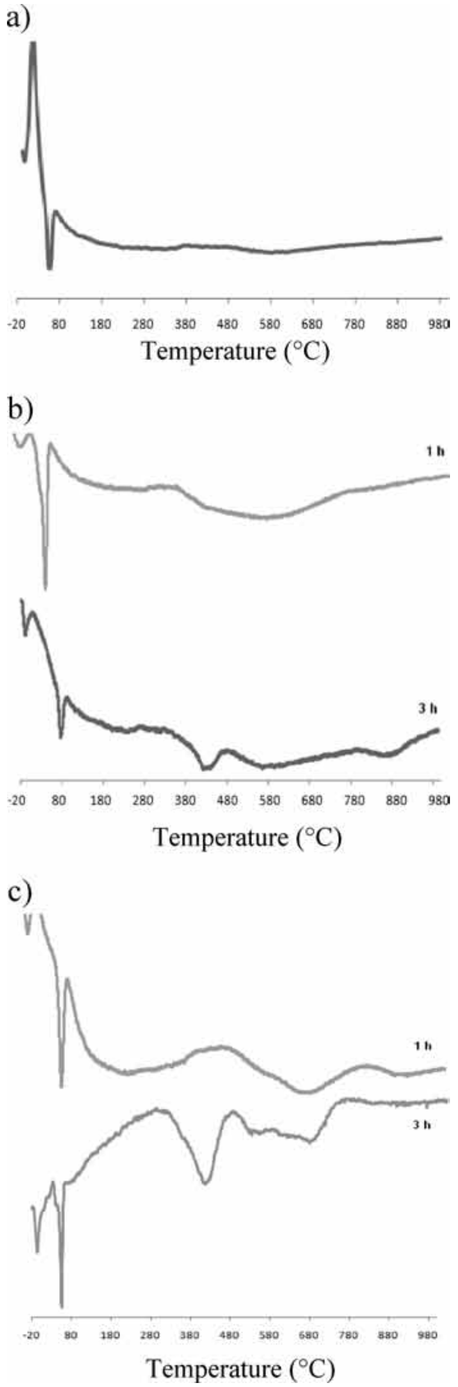


Figure 5. TPR profiles of 2 wt % Pd/Al_2O_3 samples taken at different reaction times: (a) PA-act, (b) PA-10, and (c) PA-30.

phase HDC of $CClF_2$ over Pd/Al_2O_3 prepared by wet impregnation and in the gas-phase HDC of tetrachloroethylene (TTCE) over commercial Pd/Al_2O_3 catalyst. In contrast, other studies have reported Pd^{n+} species after HDC. Babu et al.[37] found this change after gas-phase HDC of chlorobenzene. They attributed the new Pd state to an electron transfer from Pd to Al_2O_3 facilitated by the deposition precipitation method used for catalyst preparation and to $PdCl_2$ formation during reaction. On the other hand, Ahn et al.[34] attributed these species to Pd$-$C formation in the gas-phase HDC of CF_2Cl_2 over Pd/Al_2O_3 prepared by impregnation from $PdCl_2$ as a precursor. Gómez-Saneiro et al.[38] observed this change in the Pd/C catalyst after LPHDC of CCl_4 under acid conditions. It was ascribed to a chlorine Pd precursor that can create an electronegative environment which oxidizes the active phase. In this way, variation in the chemical state of Pd during the HDC reaction seems to be significantly affected by the catalyst precursor and preparation method, where a chlorine Pd precursor can oxidize the active phase[38] and the deposition precipitation method allows Pd to acquire a positive charge, forming cationic species.[37] In the present study, Pd/Al_2O_3 catalyst was prepared by wet impregnation from a free chlorine organic salt, as reported by Padmasi et al.[35] and Ordoñez et al.[36] Therefore, a Pd^0 stable phase was achieved which is not oxidized in the reaction media. Also, the added base neutralizes the HCl formed and keeps the catalytic metal in a reduced state, free from halide ions[39] and contributing to stabilize the active phase during reaction.

Na1s atoms were detected in used catalyst samples in the presence of NaOH (Table 3). As can be observed in Table 3, NaOH (1070.7 eV) and NaCl (about 1071.4 eV) species are present. A lower binding energy ascribed to NaOH was observed in PA-150, but the NaCl binding energy was detected in catalyst samples used with lower NaOH concentrations. Chlorine atoms were not detected in these samples.

The atomic ratios (C/Al, Pd/Al, and Na/Al) show surface enrichment of different elements on catalyst samples (Table 3). Reduction of the carbon concentration after the activation process is observed in fresh and activated catalysts. PA-0 presented high carbon concentration due to Pd$-$C residues. A maximum of carbon in PA-30 used catalyst samples may be related to C$-$OH species formation. The Pd/Al ratio shows a similar metal surface concentration for all catalyst samples, except for the high value corresponding to PA-fresh, where Pd can be completely exposed to the surface. Finally, the Na/Al increased with base addition.

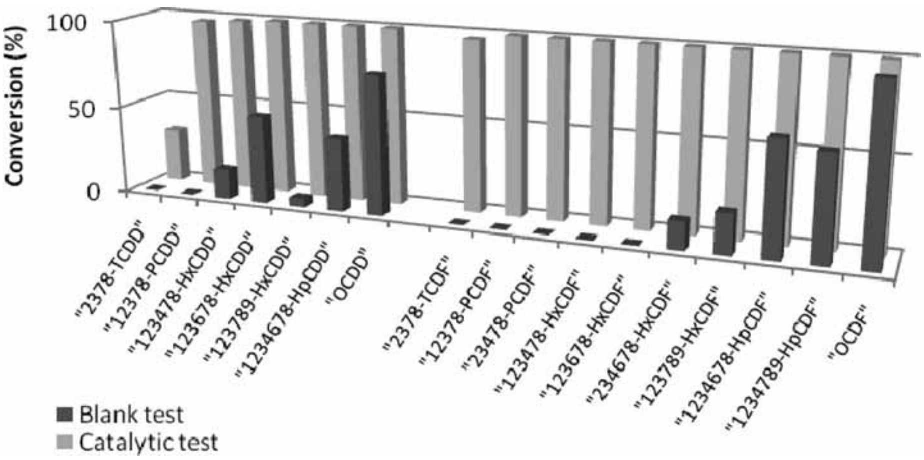


Figure 6. Conversions of 2,3,7,8-chlorosubstituted PCDD/Fs congeners in the absence (blank test) and in the presence (catalytic test) of 100 mg of 2 wt % Pd/Al_2O_3 catalyst. Reaction conditions: 50 mg of NaOH, 77.35 ng of I-TEQ, 20 mL of 2-propanol, 75 °C, 3 h reaction.

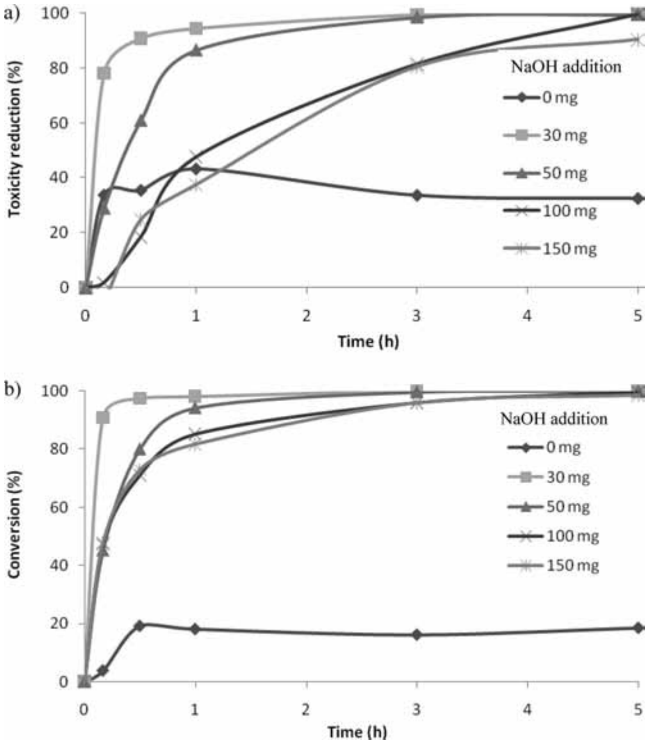


Figure 7. Toxicity reduction (a) and PCDD/Fs total conversion (b) over 2 wt % Pd/Al_2O_3 in reaction mixtures containing different NaOH amounts. Reaction conditions: 77.35 ng of I-TEQ, 100 mg of 5 catalyst, 20 mL of 2-propanol, 75 °C.

3.1.5. TPR. Organic deposits were also observed by TPR analysis. Figure 5 shows TPR profiles for fresh and used catalyst samples in reaction mixtures containing various NaOH amounts and different reaction times. Figure 5a shows TPR of a fresh 2 wt % Pd/Al_2O_3 sample (PA-act). The first peak at 10 °C corresponds to hydrogen absorption over a metallic Pd surface producing β-Pd hydride species at ambient temperature.[40–43] This complex is desorbed at higher temperature, showing a negative peak at 62 °C.[15] TPRs of used catalyst samples PA-10 and PA-30 after reaction times of 1 and 3 h are shown in Figure 5b and c, respectively. Formation and desorption of β-Pd hydride species can be observed between −20 and 80 °C. Negative peaks at higher temperature correspond to desorption of organic residues from the catalyst. The intensity of these peaks increases with time and NaOH addition, showing that the amount of organic residues increases with time since they are formed during reaction.

Summarizing, before the HDC reaction catalyst samples contained Pd reduced (Pd^0) over the alumina support. In the absence of NaOH, there was partial leaching of Pd^0 and graphitic carbon deposits, while C−OH, NaCl, and NaOH species were detected on the catalyst surface in the presence of NaOH. The amount of adsorbed NaOH was proportional to its initial concentration in the reaction mixture. No changes in the oxidation state of Pd were detected in all used catalyst samples.

3.2. The Effect of the Catalyst and NaOH during Dioxin LPHDC. Conversions of 2,3,7,8-chlorosubstutited PCDD/Fs congeners in the absence of catalyst (blank test) were compared with those obtained over 100 mg of 2 wt % Pd/Al_2O_3 (catalytic test).[15] Results are shown in Figure 6. When no catalyst was present in the reaction mixture (50 mg of NaOH, 77.35 ng of I-TEQ, 20 mL of 2-propanol, 75 °C) after a 3 h reaction, octa isomers reacted almost completely; some hepta and hexa congeners were partially converted, but the concentration of more toxic congeners increased, leading to an increase in sample toxicity from 77.35 to 100.45 ng of I-TEQ. In the presence of catalyst, the sample toxicity decreased by 98.55%. These results confirm that the catalyst is necessary to degrade more stable and toxic PCDD/Fs congeners and diminish the toxicity of the sample.

The catalytic activity versus reaction time when 0, 30, 50, 100, and 150 mg of NaOH were added to the reaction mixture is plotted in Figure 7 in terms of toxicity reduction (Figure 7a) and total conversion (Figure 7b). Without base addition (0 mg), the catalyst deactivates after 30 min of reaction, reaching conversions of around 20% and reducing the sample toxicity only by 40%. The presence of HCl showed significant inhibitory effects on the initial HDC reaction. At 30 min, PA-0 showed 6% loss of the active phase (Table 1), but a large amount of Pd−C species are probably formed from the beginning of the reaction, poisoning the active metal and rapidly reducing catalytic activity. Lopez et al.[21] also reported porous occlusion by carbonaceous residues favored by HCl formed during reaction at high temperature and poisoning their catalyst samples in gas-phase tetrachloroethylene HDC. Although the BET surface area was higher in the PA-0 catalyst, the nature of occlusive species plays a key role in catalyst deactivation. Carbonaceous deposition over used catalyst samples in the presence of NaOH presented a higher oxidation state and less graphitic structure. However, highly crystalline carbon bonded

TABLE 4: I-TEQ of 2,3,7,8-Chlorinated PCDD/Fs over 2 wt % Pd/Al_2O_3 after a 1 h Reaction using Different NaOH Amounts

		NaOH amount (mg)					
dioxins	initial	0	10	30	50	100	150
2378-TCDD	4396.46	4010.24	6389.40	3653.36	6580.33	18996.89	17583.41
12378-PCDD	17958.70	16520.67	4486.80	4400.88	4144.90	26878.04	28001.26
123478-HxCDD	2182.23	2228.29	44.56	60.42	91.47	0.00	80.99
123678-HxCDD	2813.26	2327.13	40.68	161.51	278.95	246.03	254.47
123789-HxCDD	3188.11	3545.50	108.33	193.86	1148.76	1619.50	1824.28
1234678-HpCDD	1179.84	1215.32	1.00	3.19	3.13	N.D.	0.65
OCDD	96.79	106.32	0.22	0.17	N.D.	N.D.	N.D.
furans							
2378-TCDF	2929.72	3061.55	810.12	650.40	1936.41	4647.82	5171.81
12378-PCDF	4288.73	4091.52	7.51	218.84	220.51	702.27	1042.17
23478-PCDF	66981.74	66606.68	2595.89	2743.31	20902.74	40684.18	57426.09
123478-HxCDF	15971.23	13441.44	10.20	17.83	106.98	17.88	41.25
123678-HxCDF	19730.60	15914.96	12.46	12.87	112.80	80.57	191.63
234678-HxCDF	14497.70	15778.21	113.04	15.16	1521.94	1425.12	2015.80
123789-HxCDF	3346.69	3729.38	4.11	13.07	64.23	N.D.	29.17
1234678-HpCDF	5219.58	4183.22	N.D.	7.20	3.70	N.D.	11.77
1234789-HpCDF	519.37	333.94	1.91	7.81	N.D.	N.D.	N.D.
OCDF	95.93	89.73	0.05	0.05	N.D.	N.D.	N.D.
total I-TEQ (pg/g)	165396.65	157184.10	14626.27	12159.91	37116.85	95298.31	113674.74

to Pd on PA-0 covered the catalytic surface, affecting the HDC activity much more. In this way, catalyst deactivation under acid conditions can be ascribed to active-phase blocking by Pd−C species formation and high Pd leaching by a corrosive environment.

Higher catalytic activity was obtained when 30 mg of sodium hydroxide was added to the reaction mixture, reaching 97% conversion after 30 min, and detoxification was ∼100% after 3 h (Figure 7). NaOH preserved HDC activity, limiting HCl inhibition. I-TEQ values are presented in Table 4 for different base amounts after a 1 h reaction. NaOH amounts larger than 30 mg decreased the catalytic activity (Table 4 and Figure 7). This negative effect can be associated with active site obstruction due to excess base making reactant diffusion to Pd sites difficult and taking more time for complete degradation, as observed by TEM/EDS analysis. Ten mg of NaOH (Table 4) showed a slightly higher final I-TEQ concentration than did 30 mg.

It can be observed in Table 4 that furans and more chlorinated congeners are more reactive than dioxins and less chlorinated ones.[13–15] Also, complete dechlorination of more chlorinated congeners was faster when increasing the amount of sodium hydroxide added to the reaction mixture. However, the process was slow, and active site occlusion increased, avoiding the complete dioxin dechlorination. Therefore, 30 mg of NaOH added to the reaction system allowed a complete degradation of PCDD/Fs from very contaminated fly ash over 2 wt % Pd/Al_2O_3 using 2-propanol as the hydrogen source and without carrying out the reaction under inert conditions.

It is important to remark that the initial concentration of toxic PCDD/Fs congeners in the reaction mixture was around 0.5 ppm. These compounds contain between four and eight chlorine atoms. Additionally, other chlorinated compounds not quantified, such as PCBs, PCNs, PCPs, and nontoxic PCDD/F, were more likely present and might have dechlorinated. All of these chlorinated precursors might have increased the HCl concentration during reaction, affecting the catalyst surface. In the absence of NaOH, active-phase leaching was experimentally observed. Besides, differences in the nature of carbonaceous deposits found by XPS over the catalyst may be an indication of the HCl effect on the catalyst surface. Highly crystalline carbon bonded to Pd covered the catalytic surface when no NaOH was added to the reaction mixture. However, more oxidized and less graphitic carbon was deposited over used catalyst samples in the presence of NaOH.

4. Conclusions

Sodium hydroxide affects the performance of 2 wt % Pd/γ-Al_2O_3 during degradation of PCDD/Fs extracts from fly ash samples. Free chlorine organic salt used as a metal precursor leads to a catalyst with an active phase resistant to oxidation even under acid conditions. However, in the absence of NaOH, palladium poisoning occurs due to formation of Pd−C species and leaching due to the corrosive environment. NaOH addition avoids active-phase loss from the support and graphitic carbon species formation. In the presence of NaOH, C−OH species were deposited on the catalytic surface. A large excess of NaOH causes catalyst obstruction due to formation of a Na core over Pd particles. An optimum amount of sodium hydroxide is necessary to efficiently degrade dioxin extracts from fly ash at short reaction times to avoid poisoning and leaching of Pd and to reduce Na deposition over the active phase.

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