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Liquid phase dioxin hydrodechlorination over Pd/γ–Al_2O_3

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Abstract

Liquid phase hydrodechlorination of dioxins and furans over Pd/Al_2O_3 was studied at 75 °C under nitrogen and air environments, using 2-propanol as solvent as well as hydrogen donor. The pH of reaction was maintained by addition of NaOH. More chlorinated congeners readily transformed into less chlorinated ones during the first minutes of reaction, so less chlorinated congeners took a larger time for their complete degradation. Under air atmosphere, initial hydrodechlorination reaction rates were slower than under inert conditions since oxygen competes with chlorinated compounds for hydrogen. However, 99.9% conversion was achieved after about 3 h and toxicity decreased to 98.5% under both inert and air atmospheres. Fresh and used catalyst samples were characterized by elemental analysis, nitrogen adsorption, hydrogen chemisorption, XRD and TPR. No clear evidence of Pd leaching was obtained. However, BET surface area and Pd dispersion decreased on used samples.
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Keywords: Hydrodechlorination; Dioxins; Furans; Pd/γ-Al_2O_3 catalyst

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) currently known as dioxins are a family of 210 stable lipophilic aromatic chemicals, highly persistent in the environment, comprising 75 PCDDs and 135 PCDFs. However, only 17 congeners (7 PCDDs and 10 PCDFs) with chlorine atoms in the 2, 3, 7 and 8 positions are considered to be of toxicological significance due to their affinity with intracellular Ah receptor [1]. These compounds have toxic effects as well as immune suppression, skin alterations (chloracne), sperm count reduction and body weight loss in studied animals and humans. Furthermore, 2,3,7,8-TCDD was classified as a human carcinogen by the World Health Organization (WHO), the International Agency for Research of Cancer (IARC) and the US Environmental Protection Agency (EPA) [2,3].

Since the seventies, incineration has been identified as an important source of dioxins [4,5]. Consequently, a stringent limiting value of 0.1 ng (I-TEQ)/Nm^3 (i.e., International Toxicity Equivalents per Nm^3) for PCDD/F emissions have been set in several European countries and Japan [6]. Colombian authorities, based on regulations well-implemented in developed countries also set a limit value of 0.1 ng I-TEQ/Nm^3 to be accomplished in 2012 [7]. In order to achieve this goal, incineration facilities have been installing a variety of air pollution control devices (APCDs) including cyclones, electrostatic precipitators, bag filters, scrubbers and activated carbon. Notwithstanding, many of these systems generate large amounts of solid waste containing high dioxin levels [8,9]. Currently, these solids are disposed of in landfills and in most cases they are not included in dioxin inventories [6,9]. The problem becomes more difficult in developing countries like Colombia where landfills are not well-controlled, leading to water and soil contamination. In this way, dioxins might travel through the food chain and finally ingested, as diet has become the main source of dioxins in human beings [10]. PCDD/Fs degradation process in solids and/or liquid samples has been studied at laboratory scale [6,11–14] aiming at obtaining an efficient and economical technique for detoxifying these residues.

Degradation studies of PCDD/Fs have been performed in solid phase and in fly ash extracts. Supercritical fluid processes, where high temperature and pressure are commonly required, have been used for solid treatment [6]. Weber et al. studied the dechlorination and destruction of dioxins in fly

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ashes using a mixture of hydrogen/inert gas at 260 °C. A complete degradation of octa-, hepta- and hexa-chlorinated congeners was reached [14]. Liquid phase degradation has been much more studied than solid phase reactions, since higher reactivity has been found under mild conditions. Photocatalytic, biotechnological, chemical and catalytic processes have been studied in order to obtain detoxified matrices. Photocatalytic processes use UV, sunlight or γ-rays irradiation for degradation, but long exposure times are necessary to decrease sample toxicity [15,16]. Also, biotechnological processes take long reaction times. Chemical studies have been successfully accomplished for both solid and liquid matrices using reactants as polyethylene glycol and potassium hydroxide, or Fe^{3+}–H_2O mixed reagent in liquid phase. However, reactant recovery is not possible [17,18]. Catalytic hydrodechlorination has emerged as a promising detoxification technology since high conversions have been achieved under mild conditions at laboratory scale. Tundo et al. used metal supported catalysts and hydrogen in a multiphase reaction system [12], Ukisu et al., studied liquid reaction systems using 5 wt.% Pd/Al_2O_3-supported catalyst and 2-propanol (as hydrogen source and solvent). Almost total conversion of PCDD/Fs under inert atmosphere was reported [13]. Hydrogen gas replacement is a significant improvement due to handling costs and safety problems manipulating hydrogen. However, the effect of the reaction atmosphere, the conversion profiles for each congener and catalyst characterization are missing in the above study [13]. In the present contribution we extend the work of Ukisu et al, so commercial and synthesized Pd/γ–Al_2O_3-supported catalyst samples have been evaluated for PCDD/Fs hydrodechlorination (HDC) of fly ash extracts under both inert and air atmospheres, determining the conversion for each congener. Catalysts have been characterized before and after reaction by TPR, chemisorption, TEM, nitrogen adsorption, DRX and chemical analysis. 2-Propanol was used as solvent and hydrogen donor. Toxic and non-toxic 2, 3, 7, 8-chlorinated PCDD/Fs concentration vs. time profiles were obtained under inert and air atmospheres in the absence of mass transfer limitations.

2. Experimental

2.1. Materials

Commercial 5 wt.% Pd/Al_2O_3 catalyst was purchased from Aldrich Chemical Co. (USA). Synthesized catalysts were prepared by incipient wetness impregnation of palladium acetylacetonate (99%, Aldrich Chem. Co., USA) on γ-alumina (99.97%, Alfa Aesar, USA). 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 clean up were from Merck, Germany. EPA-1613CVS (CS1–CS5) calibration solutions, EPA-1613LCS extraction standard and EPA-1613ISS syringing standard were obtained from Wellington Laboratories (Canada). All ultra-high purity gases were purchased from AGA, Colombia.

2.2. Catalyst preparation

Pd/γ–Al_2O_3 samples were prepared by wetness impregnation of γ-Al_2O_3 to obtain 2, 5 and 7 wt.% Pd loadings. Catalysts were coded PA(2), PA(5) and PA(7), respectively. The amount of palladium acetylacetonate necessary to obtain the required Pd loading was dissolved in 10–20 mL of acetone. This mixture was slowly added to γ-Al_2O_3 support under continuous stirring at 40 °C, allowing acetone to evaporate. Then, catalyst samples were dried at 100 °C during 12 h. Two pretreatments were tested in order to eliminate organic residues from precursor: (i) heating at 2 °C/min until 300 °C in static air for 2 h, PA(5)-300 (ii) heating at 2 °C/min until 400 °C in 50 mL/min flowing air, PA(5)-400. Both, commercial (PdAldrich) and synthesized catalysts were reduced before reaction in 50 mL/min flowing 10% H_2/N_2, heating at 2 °C/min to 300 °C, maintaining this temperature for 1 h, and cooling down in flowing nitrogen to room temperature.

2.3. Catalyst characterization

Chemical analysis was done by atomic absorption in a Philips PU9200 apparatus. X-ray diffraction was performed in an AXS Bruker diffractometer with Kα radiation (1.5406 Å), $2\theta = 2$–$80°$. 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 to remove impurities at 300 °C in a helium stream during 1 h. Then, a mixture of 30% N_2/He was allowed to flow through the sample previously immersed in a liquid nitrogen bath at 77.36 K (−195.8 °C). Both adsorbed and desorbed N_2 were recorded. The amount of desorbed nitrogen was used to calculate total surface area. Experiments were repeated twice or until surface areas were reproducible within ±5%. Pulse chemisorption was used to determine percent Pd dispersion and average active particle size by applying measured doses of 10% H_2/Ar to catalyst samples. Almost 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, in order to avoid bulk hydride formation [19,20]. The hydrogen–oxygen titration method was used for measuring metal surface area. Titration values were within 1% deviation. The stoichiometric equations [21] are shown in Fig. 1. TPR runs were performed to determine the nature of Pd

$$2Pd_s + H_2 \rightarrow 2\overset{H}{\overset{/}{Pd_s}}$$

$$\frac{4}{3}Pd_sH + O_2 \rightarrow \frac{4}{3}\overset{O}{\overset{/}{Pd_s}} + \frac{2}{3}H_2O$$

$$\frac{2}{3}Pd_sO + H_2 \rightarrow \frac{2}{3}\overset{H}{\overset{/}{Pd_s}} + \frac{2}{3}H_2O$$

Fig. 1. H_2–O_2–H_2 titration–stoichiometric equations [21].

Table 1
Operation conditions of hazardous waste incinerator

Location	Medellin, Colombia
Fuel	Natural gas
Capacity (kg/h)	40–70
Combustion T (°C)	700
Post-combustion T (°C)	950
Stack gas T (°C)	73
Control system	Heat exchanger, scrubber, cyclone, bag filter and activated carbon

species present in catalyst samples. Fresh and used catalyst samples were previously oxidized in a flowing O_2/Ar stream (25 mL/min) heating to 300 °C at 10 °C/min then cooled down to −20 °C in flowing Ar using an ethanol-ice bath. Carrier gas was replaced by 10% H_2/Ar flow (25 mL/min) and after removing the ethanol-ice bath, TPR recording began by heating at 5 °C/min until 1000 °C. Transmission electron microscopy (TEM) experiments were carried out in a Philips CM2000 microscope operating at 200 kV. Samples were dispersed in ethanol by sonication and dropped on a copper grid coated with carbon film.

2.4. Catalytic tests

Fly ash was collected from bag filters of a hazardous waste incinerator located in Medellín, Colombia. Operation conditions of said incinerator are listed in Table 1. Solid samples were soxhlet extracted with toluene during 48 h and liquid extracts were transferred to graduated vials to obtain an exact volume. One fraction of this sample was spiked with EPA1613-LCS standard containing a known quantity of ^{13}C-PCDD/Fs mixture and cleaned up by liquid–solid adsorption chromatography at atmospheric pressure using H_2SO_4, NaOH and $AgNO_3$ modified silica, florisil and basic alumina columns, respectively. Finally, EPA1613-ISS standard was added to purified samples before GC/MS analysis.

Catalytic tests were conducted at a sufficiently high stirring velocity (2300 rpm) to avoid external mass transport problems [22,23]. Koros–Nowak (KN) criterion was used for evaluation of mass and heat transfer limitations. KN test [22,24,25] was carried out in the same reaction system as described below, evaluating conversion of two samples (PA(2) and PA(7)) with different metal loading and the same dispersion. Catalyst amount in the two experiments was calculated by Eq. (1) [24]:

$$w_2 = w_1\left(\frac{f_{m1}}{f_{m2}}\right) \quad (1)$$

where f_m is surface moles of active material per unit weight of catalyst.

Hydrodechlorination reactions were performed in a round bottom flask equipped with a septum, a thermowell and a condenser. Approximately, 3.5 ng I-TEQ/mL of PCDD/Fs mixture in 2-propanol (20 mL) was added to different amounts of Pd/γ-Al_2O_3 catalyst samples and 50 mg of sodium hydroxide. The system was magnetically stirred at 2300 rpm and starting reaction time was recorded once the mixture boiled at 75 °C (±1 °C). Reactions were carried out under air and inert atmospheres at 10, 30, 60, 180, 300 and 420 min. After reaction, samples were filtered, washed with 100 mL of toluene and dried at 100 °C during 24 h. Liquid samples were spiked with EPA1613-LCS standard and cleaned up as mentioned above. Initial and final concentrations of each PCDD/F congener were determined and used to calculate conversion by congener, conversion (Eq. (2)) and percent toxicity reduction (Eq. (3)). GC/MS detection limit was established at 2 pg/μL for each congener.

$$\text{conversion}\ (\%) = \frac{\sum_1^{17}\left[\text{PCDD/Fs}\right]_{\text{initial}} - \sum_1^{17}\left[\text{PCDD/Fs}\right]_{\text{final}}}{\sum_1^{17}\left[\text{PCDD/Fs}\right]_{\text{initial}}} \times 100 \quad (2)$$

Table 2
Characterization of fresh and used Pd/Al_2O_3 samples

Catalyst	Reaction time (min)	Palladium contents[a] (% Pd)	BET surface area[b] (m^2/g)	Pd dispersion[c] (%)	Active particle diameter[c] (nm)
2.6 wt.% PA(2)	0 (fresh)	2.1	159	23.0	4.6
	180	2.7	97	3.6	33.6
7.0 wt.% PA(7)	0 (fresh)	4.8	157	23.0	7.9
	180	5.1	74	2.4	46.7
5.0 wt.% PdAldrich	0 (fresh)	3.8	116	25.6	4.4
5.0 wt.% PA(5)	0 (fresh)	4.5	134	23.1, 23.2[d]	4.8, 4.8[d]
	30	4.4	63	6.3	17.9
	180	4.4	–	4.7	24.1
	420	4.1	–	3.2	34.9

Used samples were analyzed after a 3 h-reaction.
[a] Chemical analysis by atomic adsorption.
[b] N_2 adsorption at 77 K.
[c] H_2 chemisorption.
[d] Duplicate experiments.

$$\text{toxicity reduction } (\%) = \frac{(\text{ng TEQ})_{\text{initial}} - (\text{ng TEQ})_{\text{final}}}{(\text{ng TEQ})_{\text{initial}}} \times 100 \quad (3)$$

After a 3 h-reaction, 29% and 24% conversions (toxicity reductions of 69% and 70%) were obtained over PA(2) and PA(7) samples, respectively. Then, the KN criterion was obeyed and the system was free from mass and heat transfer effects [24].

2.5. PCDD/Fs analysis

Dioxin samples were analyzed before and after reaction by high-resolution gas chromatography coupled to ion-trap low-resolution mass spectrometry–mass spectrometry (HRGC–QITMS/MS) in a CP-3800 GC coupled to a Saturn 2000 ion-trap spectrometer (Varian, Walnut Creck, CA, USA), equipped with a CP-8400 automated sampling device and a DB5-MS low bleed/MS (60 m, 0.25 mm i.d., 0.25 μm film thickness) capillary column (J&W Scientific, CA, USA). EPA 1613 standard solutions in nonane (CS1–CS5) were used for instrument calibration and quantification, according to EPA 1613 [26]. System control, data logging and data handling were all performed using Varian Saturn GC/MS Workstation version 6.41 software. A 2 μL sample was introduced using the injector in splitless mode, with the split vent being opened 0.01 min after injection at a split ratio of 25:1, closed until 1.50 min and

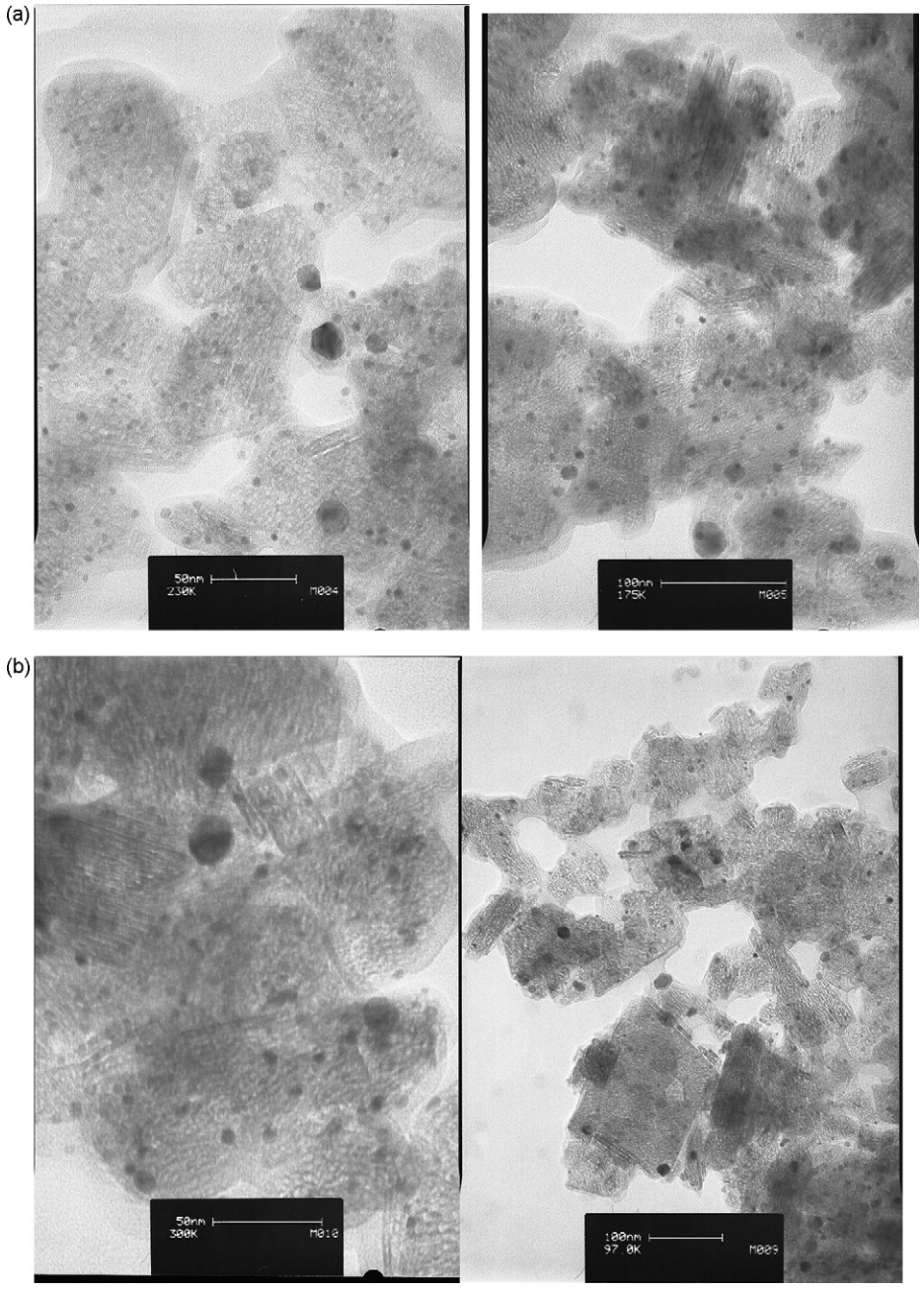

Fig. 2. TEM images of PA(5) samples (a) fresh and (b) used.

remaining open at a split ratio of 50:1 until the next injection, to continually flush the injector of any remaining solvent or other contaminants. The injector oven was maintained at 300 °C; the transfer line to the ion trap from the column oven was kept at 280 °C and the manifold at 80 °C. The ion trap oven was set to 220 °C. The carrier gas was helium at a constant flow rate of 1 mol/min. The column oven program, was as follows: initial temperature 130 °C, held for 1.5 min, ramp at 20 °C min^{-1} to 200 °C, held for 1.30 min, ramp at 1.0 °C min^{-1} to 230 °C, held for 7.0 min, ramp at 10.0 °C min^{-1} to 290 °C, held for 20.70 min. Electron impact ionization with automatic gain control and multiple reaction monitoring (MRM) were employed. The filament current was set to 70 μA. Resonant collision-induced dissociation (CID) was used to create daughter ions. PCDD/Fs concentrations were calculated using isotopic dilution method, from Relative Response Factor (RRFs) determined from CS1 to CS5 injections and area comparison with ^{13}C-labeled internal standard compounds [27,28].

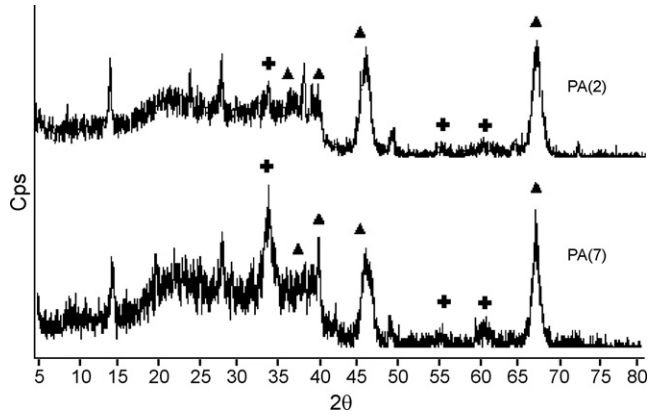

Fig. 3. X-ray diffraction profiles of unreduced PA(2) and PA(7) catalyst samples. PdO (✚), γ-Al_2O_3 (▲).

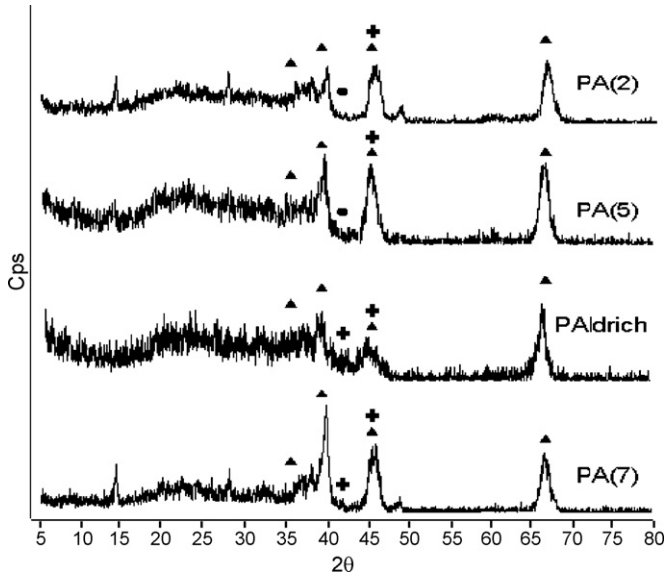

Fig. 4. X-ray diffraction patterns of reduced PA(2), PA(5), PdAldrich and PA(7) samples. Pd (●), γ-Al_2O_3 (▲).

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Chemisorption, BET and chemical analyses

Table 2 lists palladium loading, BET surface area and Pd dispersion of fresh and used commercial and synthesized catalysts. PA(2) and PA(7) catalyst samples with different Pd loadings but identical palladium dispersion, 23%, were used to check Koros–Nowak (KN). Fresh PA(5) and PdAldrich exhibit similar Pd dispersion and BET surface area. Small differences may be ascribed to textural characteristics and preparation method of each alumina batch. In order to discard possible sintering by H_2/Ar degasification prior to chemisorption experiments, two consecutive runs were carried out with fresh PA(5) samples at 300 °C. Dispersions were close to each other (23.1 and 23.2), suggesting that the reduction program until 300 °C does not significantly affect surface palladium.

Table 2 lists characteristics of PA(2), PA(5) and PA(7) used samples. There is no evidence of active phase leaching during reaction, suggesting strong Pd–Al_2O_3 interaction. Catalyst surface area decreases after 180 min around 50% in all analyzed samples. H_2 chemisorption results indicate that, Pd particle size increased about eight times after reaction. The fact that BET surface area of PA(5) decreased by 50% after just

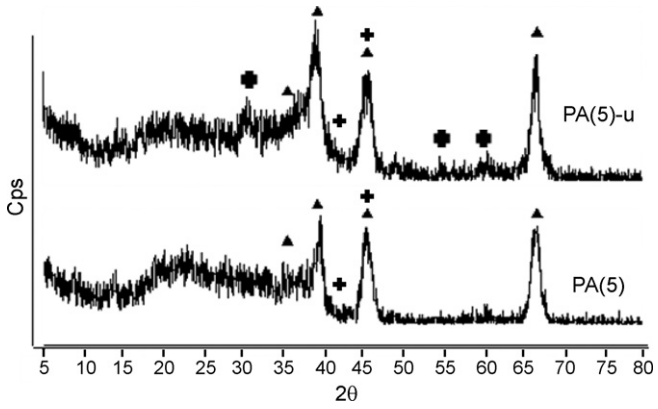

Fig. 5. X-ray diffraction patterns of fresh, PA(5) and used, PA(5)-u, samples. PdO (●), Pd (✚), γ-Al_2O_3 (▲).

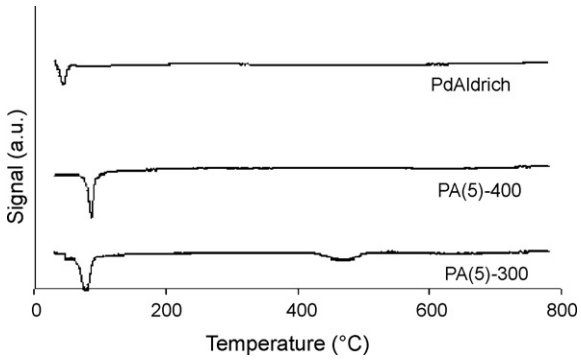

Fig. 6. TPR profiles of 5 wt.% Pd/γ-Al_2O_3 samples. (PdAldrich) and PA(5)-400 samples were calcined in flowing air at 400 °C and PA(5)-300 sample calcined in a muffle furnace at 300 °C.

30 min reaction suggests that this phenomenon occurs as the catalyst contacts the reactant mixture. Support pore occlusion and partial destruction of alumina structure due to the harsh basic environment have been reported as possible reasons for surface area decrease [29,30] and agglomeration of Pd particles [30].

3.1.2. Transmission electron microscopy (TEM)

TEM images of PA(5) samples are shown in Fig. 2(a). Small spherical particles with diameters in the range of 2–3 nm are observed. The mean active particle diameter in this sample calculated from H_2 chemisorption is 4.8 nm (see Table 2). Similar particle sizes of Pd/γ–Al_2O_3 catalysts have been reported by other authors [22,31,32]. However, larger particles with diameter between 10 and 15 nm are observed indicating that Pd particles are not homogeneous. TEM pictures of a PA(5)-u sample after a 3 h-reaction are shown in Fig. 2(b). Some particles with diameters between 18 and 20 nm which were not observed in fresh catalyst samples can be distinguished. Also, smaller particles (5–10 nm diameters) appear to be present. These observations indicate that the increase of palladium particle size is not homogeneous.

3.1.3. X-ray diffraction (XRD)

Fig. 3 shows XRD patterns of PA(2) and PA(7) catalyst samples before reduction. Peaks corresponding to γ-Al_2O_3 phase can be seen in both catalyst samples at 2θ values of 36.7, 40.0, 45.7 and 66.7 [33–36]. Peaks at 2θ values of 33.7, 54.9 and 59.9 correspond to PdO. These peaks are stronger in high Pd-loaded samples. Metallic Pd is not detected in these samples (they were not treated in hydrogen). As shown in Fig. 4, XRD patterns of reduced catalyst samples exhibit more defined peaks than unreduced catalysts. This can be ascribed to the presence of crystalline alumina caused by thermal treatment during reduction. Commercial alumina samples (PdAldrich) are less crystalline than synthesized samples. PdO peaks have disappeared due to reduction and peaks corresponding to Pd^0 at 2θ = 39.7 and 46.2 appear very close to γ-Al_2O_3 peaks [33]. Peak at 2θ = 46.2 increases with Pd content except in amorphous PdAldrich. PA(7) shows higher and more defined peaks confirming the presence of large reduced palladium particles. Fig. 5 compares XRD patterns of fresh (PA(5)) and used (PA(5)-u) catalyst samples. Profiles are similar, no phase degradation of γ-Al_2O_3 can be detected, but small peaks due to PdO can be observed. Therefore in our working catalysts there are mostly metallic Pd particles, although some of them might be oxidized by contact with air (no special care was taken during sample manipulation).

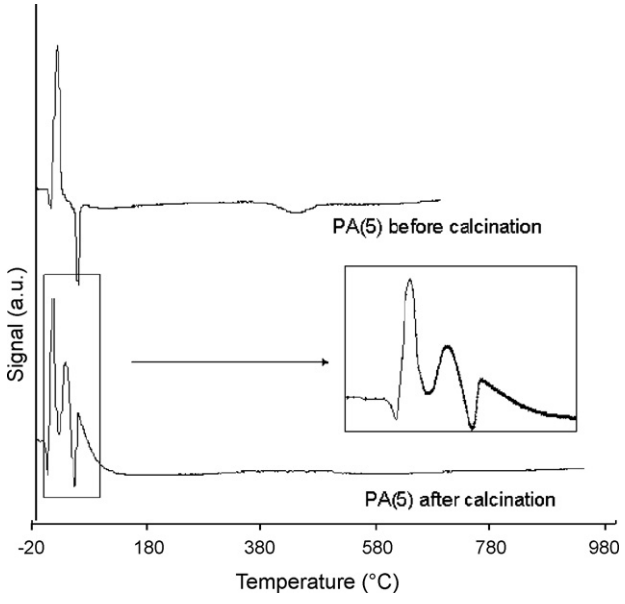

Fig. 7. TPR profile of a PA(5) catalyst sample before and after calcination in 50 mL/min flowing air at 400 °C.

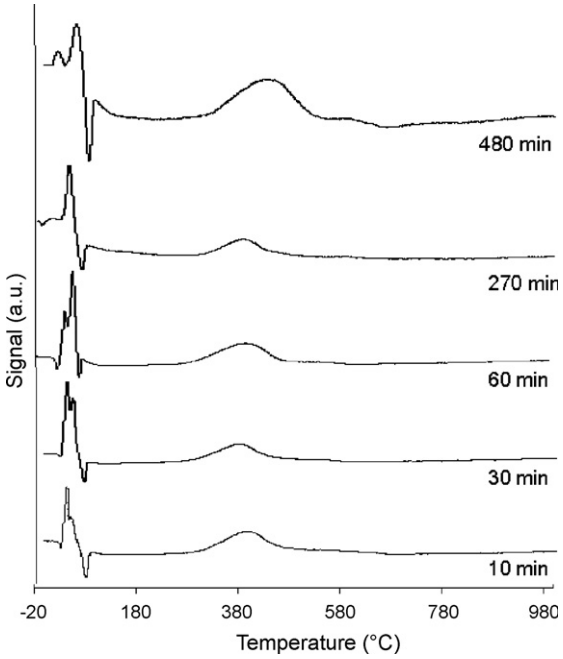

Fig. 8. TPR profiles of 5 wt.% Pd/γ-Al_2O_3 samples after different reaction times.

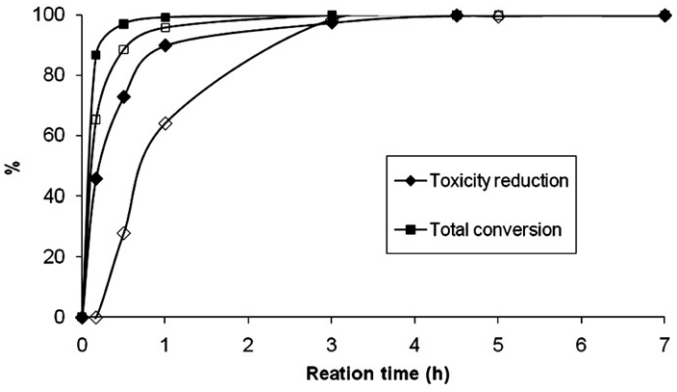

Fig. 9. PCDD/Fs total conversion and toxicity reduction over PA(5) sample under N_2 (close symbols) and air (open symbols) atmospheres. Reaction conditions: 70.30 ng I-TEQ, 50 mg of NaOH, 100 mg of PA(5) sample, 20 mL 2-propanol, 75 °C.

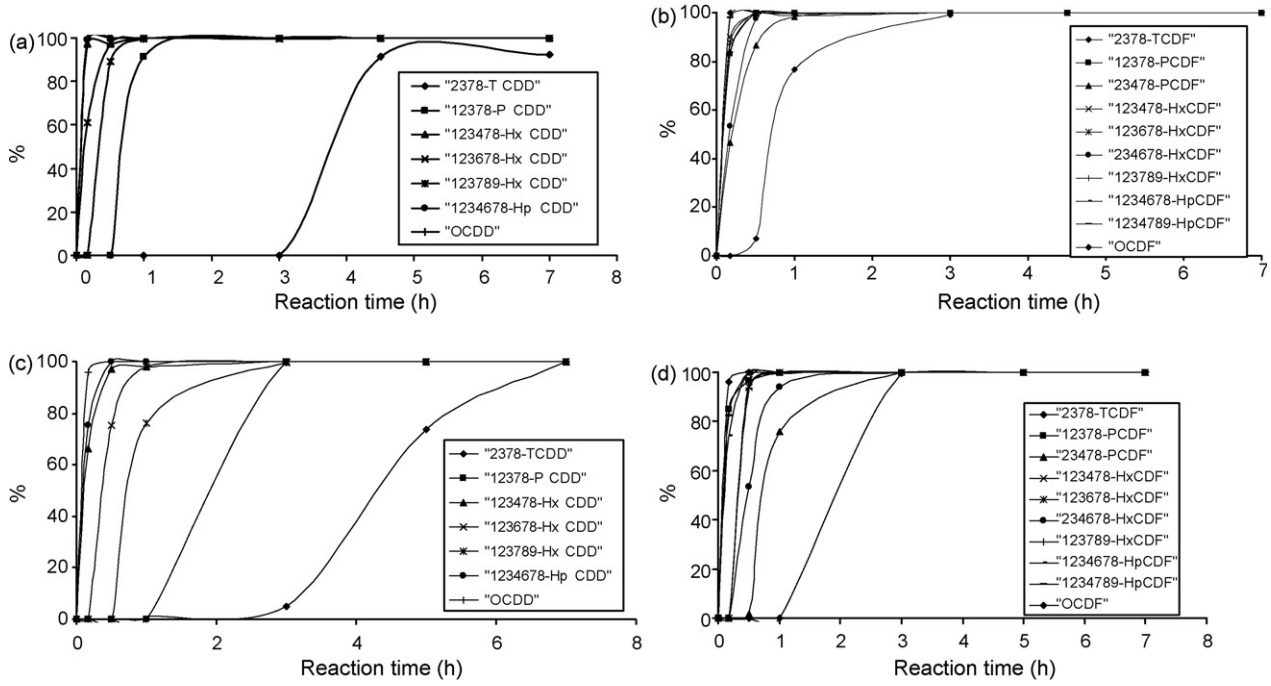

Fig. 10. Conversion over a PA(5) catalyst sample: (a) PCDD and (b) PCDF under N2 atmosphere; (c) PCDD and (d) PCDF under air atmosphere. Reaction conditions:70.30 ng I-TEQ, 50 mg of NaOH, 100 mg catalyst, 20 mL of 2-propanol, 75 °C.

3.1.4. Temperature-programmed reduction (TPR)

Fig. 6 compares TPR profiles of catalyst samples calcined in 50 mL/min flowing air at different temperatures. PA(5)-300 is a typical profile of samples calcined in a muffle furnace until 300 °C. A negative feature about 470 °C is attributed to carbonaceous residues from palladium precursor. This feature is not observed in TPR profiles of samples calcined at 400 °C in flowing air. A low-temperature peak observed in Fig. 6 corresponds to desorption of β-Pd hydride [19,36–38]. β-Pd hydride peaks appear at 80 °C and 87 °C, in TPR of PA(5)-300

Table 3
Hydrodechlorination reaction without catalyst

Compound	Initial (pg)	Run		Run	
		1	2	1	2
		Final (pg)	Final (pg)	Conversion (%)	Conversion (%)
Dioxins					
"2378-TCDD"	1434.53441	2442.40499	2459.146696	0.00	0.00
"12378-PCDD"	13651.6005	17239.722	55694.86377	0.00	0.00
"123478-HxCDD"	4934.11618	4101.97687	6746.119062	16.87	0.00
"123678-HxCDD"	22765.2061	11400.9249	15761.81877	49.92	30.76
"123789-HxCDD"	13111.0582	12460.7667	15387.52015	4.96	0.00
"1234678-HpCDD"	48679.1626	28641.6144	51260.78159	41.16	0.00
"OCDD"	28873.2955	6124.51953	4363.575675	78.79	84.89
Furans					
"2378-TCDF"	12593.9652	18580.3444	20365.72668	0.00	0.00
"12378-PCDF"	44287.1907	51197.6845	70809.9263	0.00	0.00
"23478-PCDF"	62776.3536	106676.741	110032.7949	0.00	0.00
"123478-HxCDF"	60410.7076	90029.852	52924.4922	0.00	12.39
"123678-HxCDF"	66798.3143	95674.0161	84027.43273	0.00	0.00
"234678-HxCDF"	65890.7148	55798.3926	82282.80129	15.32	0.00
"123789-HxCDF"	13292.6072	10330.3341	8445.840244	22.29	36.46
"1234678-HpCDF"	847388.747	316191.246	23836.30011	62.69	97.19
"1234789-HpCDF"	47672.1529	19990.5172	400.3226674	58.07	99.16
"OCDF"	40171.7149	1687.51365	48.60610831	95.80	99.88
Total (pg)	1394731.44	848568.571	604848.069	39.16	59.46
Total (pg I-TEQ)	77.3538323	100.454227	98.49069028	0.00[a]	0.00[a]

[a] Toxicity reduction percent calculated from Eq. (3).

and PA(5)-400, respectively but, at a lower temperature in TPR of PdAldrich catalyst sample (50 °C). These differences are ascribed to different Pd-support interactions associated with the method of preparation and to the presence of a PdO core, in synthesized catalyst samples, affecting the rate of hydrogen absorption [37,38].

Fig. 7 shows TPR profiles of 5 wt.% Pd/Al_2O_3 catalyst samples, PA(5), before and after calcination. Before calcination, 5 wt.% Pd/Al_2O_3 sample shows a positive peak at 27 °C and a negative feature at 62 °C while calcined samples in flowing air show another positive peak at 48 °C. A peak around 25 °C has been attributed to hydrogen uptake due to formation of massive PdHx phases and the one at 48 °C, to the presence of large PdO particles [37,39]. Two different species of palladium oxide have been reported: low-temperature reducible crystalline PdO (formed by contact with air at high temperature) and a more stable phase strongly interacting with the support. However, the stable PdO phase species was not observed in TPR of fresh catalyst which suggests that PdO detected by XRD of unreduced catalyst may correspond to weak PdO species. From these results, reduction at 300 °C was satisfactory to transform palladium oxide to Pd^0. A negative peak at 446 °C in TPR of PA(5) sample before calcination is again ascribed to carbonaceous residues from Pd precursor which can be eliminated by heating in flowing air [40].

Fig. 8 shows TPR profiles of catalyst samples after different reaction times. Four peaks can be observed. A peak close to 25 °C is associated to β-PdH formation, a peak around 40 °C has been attributed to reduction of large PdO particles, a negative peak at 65 °C is ascribed to hydrogen release from PdH formation and a peak at c.a. 400 °C is ascribed to reduction of more stable oxidized palladium species [39,41].

3.2. Catalytic tests

3.2.1. The effect of reaction atmosphere

Conversion and toxicity reduction of dioxin extracts under N_2 and air environments are shown in Fig. 9. In both cases, percent toxicity reduction is lower than conversion, but both parameters reached almost 100% after 4 h. Observed differences during the first three-hour reaction are due to dechlorination of more chlorinated compounds which transform to less chlorinated ones increasing sample toxicity. However, dechlorination formation ratio increases with time for less chlorinated compounds until dechlorination of all PCDD/Fs congeners. Initially, dechlorination rate is faster under inert

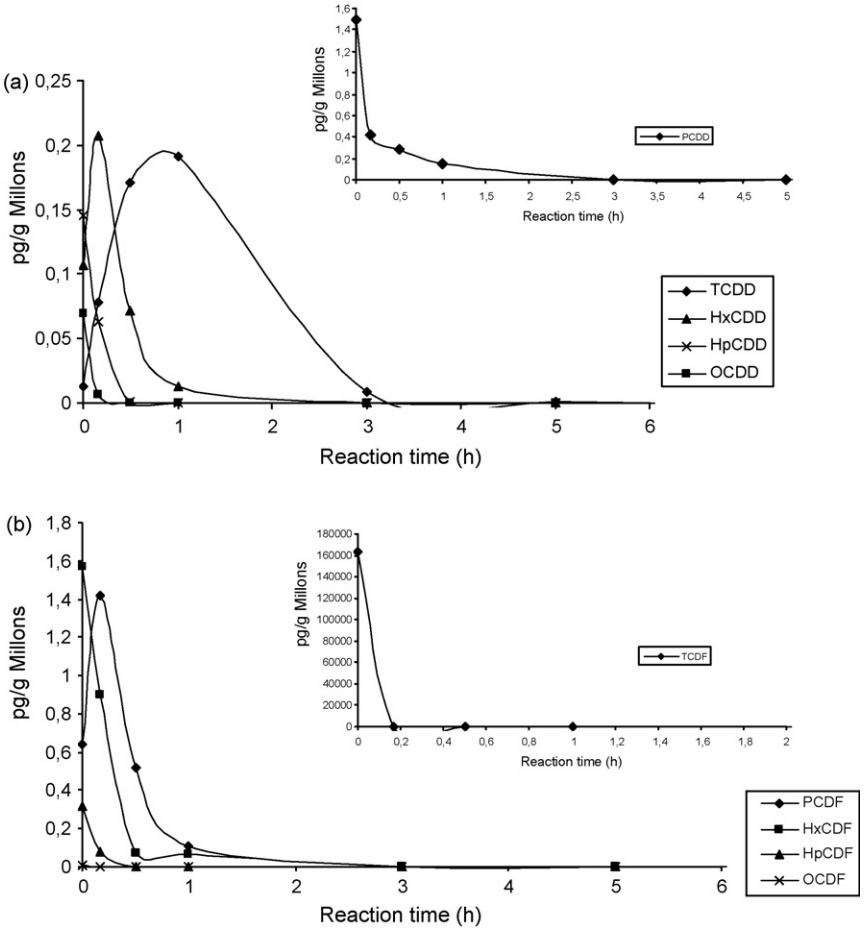

Fig. 11. Total tetra through octa-chlorinated PCDD/Fs concentration vs. reaction time (a) dioxins and (b) furans. Reaction conditions: 70.30 ng I-TEQ, 50 mg NaOH, 100 mg 5 wt.% $Pd/\gamma\text{-}Al_2O_3$ catalyst, 20 mL of 2-propanol, 75 °C. Reaction atmosphere: air.

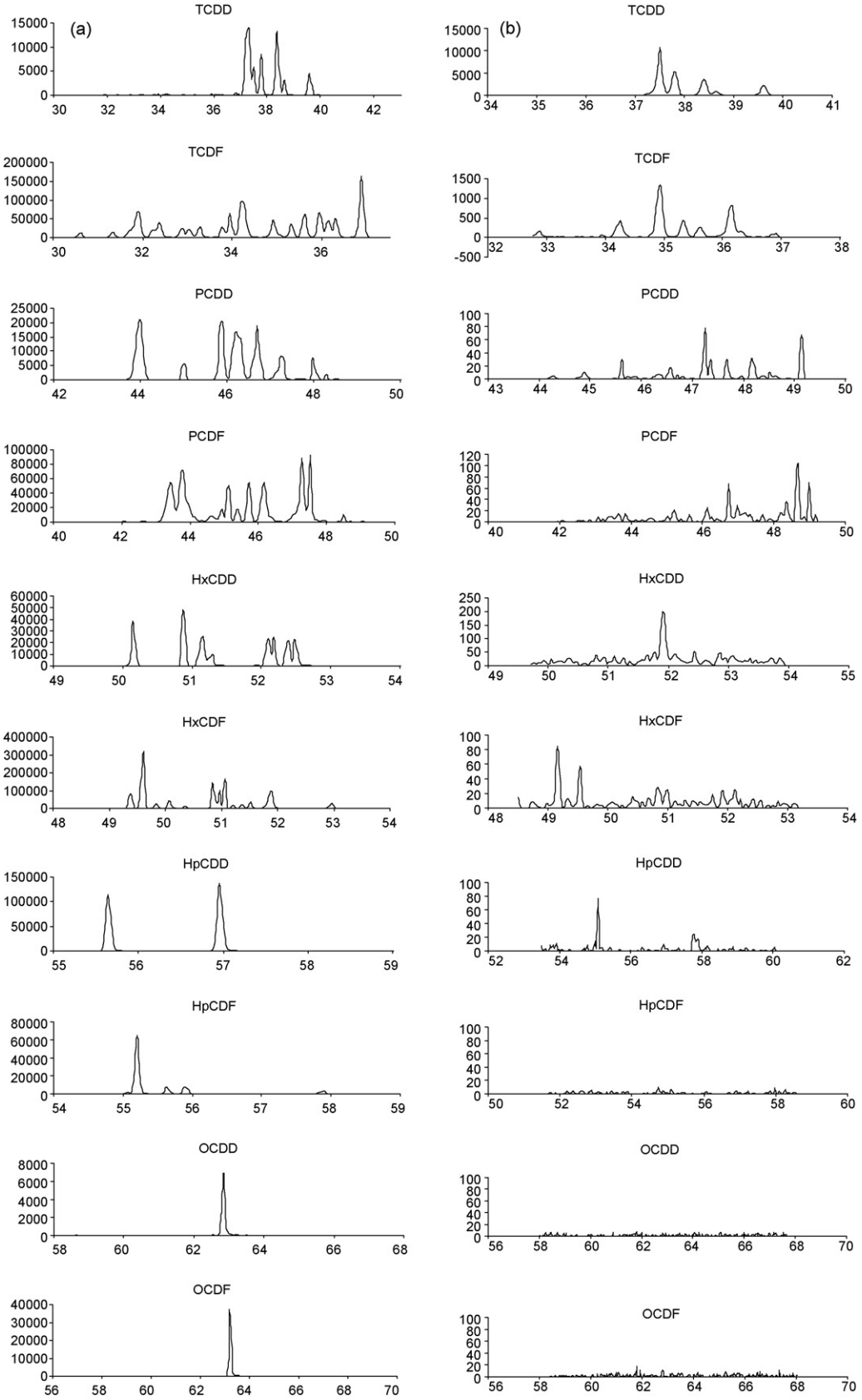

Fig. 12. HRGC (DB5-MS)–MS–MS (EI)–SIR chromatograms of (a) fly ash original extract and (b) fly ash extract after 3 h reaction over a PA(5) catalyst sample.

atmosphere, but almost total dechlorination is reached in both systems. Inert atmosphere has been recommended when 2-propanol is used as H_2-donor since it can react with oxygen to produce 2-propanone and water [13,42]. When reaction is carried out without oxygen, all compounds, readily react (see Fig. 10). The presence of oxygen slows hydrodechlorination reaction rate at the beginning, but sample degradation is completely reached after about 4 h. Fig. 10 shows that less chlorinated congeners take more time for complete degradation in air than in nitrogen. In fact, TCDD congener took additional 90 min for total degradation in air compared to total degradation in nitrogen. However, after about 4 h, differences in conversion under inert and air atmospheres are not so remarkable and the latter system can be more attractive at industrial level. Fig. 10 also shows that furans react faster than dioxins in both environments. After 3 h, all furans have been dechlorinated but 2,3,7,8-TCDD is already present. High reactivity of furans compared to dioxins is ascribed to their higher initial concentration [43,44], and also to stability differences between dioxins and furans since hexagonal structure formed by two benzene rings and oxygen could give more resonance and stability to the dioxin molecule than to the pentagonal furan structure.

The most chlorinated congeners reacted nearly instantaneously (Fig. 10). In fact, in the absence of catalyst (blank tests) these compounds exhibited some reactivity. Table 3 shows results of duplicate blank tests after 3 h at 75 °C. Some hepta and hexa congeners are partially converted and octa isomers react almost completely. More toxic congeners increased leading to an increase in sample toxicity. Therefore, it is evident that a catalyst is necessary to degrade more stable and toxic PCDD/Fs congeners.

3.2.2. Toxic and non-toxic PCDD/Fs

Just 17 congeners, out of a total of 210 dioxin and furans, chlorinated in 2, 3, 7 ,8 positions are the most toxic. However, there are 138 tetra- through octa-chlorinated congeners that can co-elute with other toxic and non-toxic isomers and it has been established that this co-elution can vary from each chromatographic column [28,45–47]. Non-toxic congeners were identified, quantified and analyzed in SIR-chromatograms. Ukisu and Miyadera reported hydrodechlorination not only of PCDD/Fs but also coplanar PCBs at similar conditions [13]. Fig. 11 shows concentration vs. reaction time for total PCDD/Fs homologue groups in air atmosphere. Profiles corresponding to inert atmosphere showed similar behavior. As can be observed in Fig. 11 furans are more reactive than dioxins, in line with results of Fig. 10. Almost total degradation of all compounds is observed after 4 h. PCDD and TCDF homologue groups are more concentrated than other groups and they are shown in a separated plot. TCDF group reacts almost instantaneously. TCDD, HxCDD and PCDF groups took more time for degradation. SIR-chromatograms of original fly ash extract and samples taken after a 3 h-reaction are compared in Fig. 12. It is important to point out that *y*-axis scale in Figs. 12(a) and (b) are different. After reaction, not only peak areas decrease but also, the number of peaks, due to differences in the reaction rate

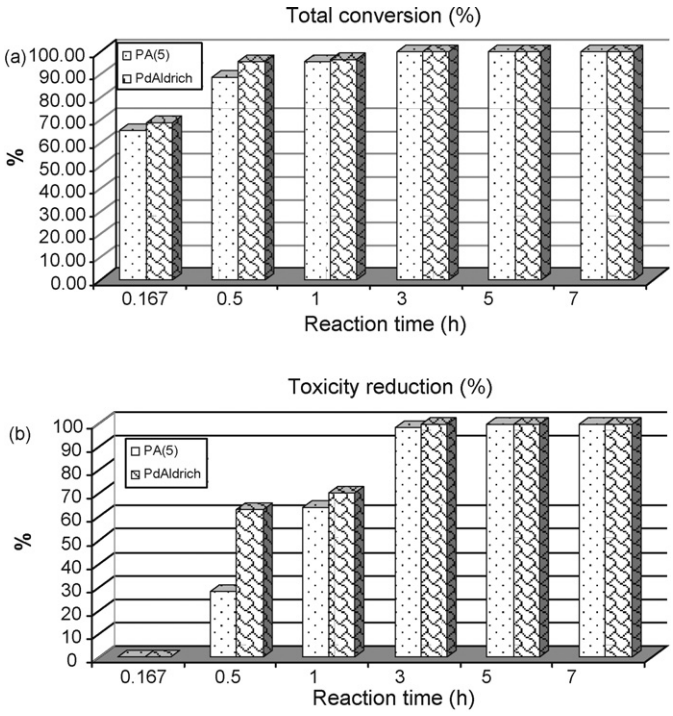

Fig. 13. (a) Toxicity reduction and (b) total conversion vs. time of PCDD/Fs over (PA(5)) and commercial (PdAldrich) catalyst samples. Reaction conditions: 70.30 ng I-TEQ, 50 mg of NaOH, 100 mg of catalyst, 20 mL of 2-propanol, 75 °C. Reaction atmosphere: air.

of each congener. Analysis of chlorine loss from all 138 compounds was done by searching strongest and weakest C–Cl bonds, but it was not possible to establish a sequence, suggesting that this process can occur randomly in the same homologue group. However, from these results it is again demonstrated that HDC process occurs by successive degradation of more chlorinated to less chlorinated compounds as observed by Ukisu and Miyadera [48].

3.2.3. Comparison of commercial and synthesized catalysts

Commercial catalyst from Aldrich was tested in hydrodechlorination reaction in order to compare its behavior against catalyst synthesized in our laboratory. Both catalysts were tested in nitrogen and air atmospheres. Fig. 13(a) compares conversion as a function of time over synthesized and commercial catalyst samples in air atmosphere. Although a slightly higher initial activity is observed over PdAldrich catalyst samples, after 1 h both catalysts exhibited the same conversion. However, as shown in Fig. 13(b) toxicity reductions are different for both catalysts especially during the first three

Table 4
Hydrodechlorination reactivity[a] of synthesized and commercial catalysts

Catalyst	PA(5)		PdAldrich	
Run	1	2	1	2
Toxicity reduction (%)	99.65	99.66	96.62	99.79
Total conversion (%)	99.30	99.32	99.31	99.32

[a]Reactions conditions: 70.30 ng I-TEQ of PCDD/Fs at 75 °C, 3 h, 100 mg of catalyst, 50 mg of NaOH, 20 mL of 2-propanol, nitrogen atmosphere.

hours of reaction. Table 4 lists reaction conditions and results after 3 h under N_2 atmosphere indicating that after this time, both commercial and synthesized catalysts show similar toxicity reduction and total conversion.

4. Summary and conclusions

Dechlorination reactions of PCDD/Fs were carried over Pd/γ–Al_2O_3 catalyst samples. During reaction, Pd particle size increased due to cluster formation or partial destruction of alumina structure.

Furans were more reactive than dioxins. Hydrodechlorination follows an established sequence from most to less chlorinated dioxins and furans congeners. Non-toxic tetra- to octa-chlorinated PCDD/Fs exhibited similar behavior to toxic congeners, following the same dechlorination pattern. However, it was not possible to establish isomer selectivity, suggesting no preference in a given kind of C–Cl bond. PCDD/F degradation under inert atmosphere is faster than in air, since oxygen competes with dioxins for H_2 released from 2-propanol. However, this undesired reaction proceeds until oxygen is consumed and total sample detoxification is achieved at almost the same time as when performed under inert atmosphere. More than 99% dioxin dechlorination and sample toxicity reduction were achieved after 4 h under N_2 atmosphere or air, on both commercial and synthesized 5 wt.% Pd/γ–Al_2O_3 catalyst samples.

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