

Hydrodechlorination of PCDD/Fs and dl-PCBs over molybdenum supported catalysts

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Introduction

Catalytic hydrodechlorination is an effective method for the removal of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls, similar to dioxins (dl-PCBs) due to the moderate operating conditions required and the relatively low operating costs. However, the catalyst to be used must be resistant to poisoning by hydrochloric acid formed during the reaction. The PCDD/Fs and dl-PCBs are a group of structurally related chemicals that persist in the environment, they are bioaccumulated in the chain food and are unintentionally generated in combustion processes, where they are present in its gaseous emissions and solid wastes, such as fly ashes¹. In catalytic hydrodechlorination of organochlorine compounds, although Pd is considered as the most active and selective metal^{2,3}, it has been found that this catalyst is fastly deactivated^{4,5}. The aim of this work is to evaluate the catalytic hydrodechlorination of extracts of PCDD/Fs and dl-PCBs using Mo supported, by wet incipient impregnation⁵, on γ -alumina (γ -Al₂O₃), silica (SiO₂) and activated carbon (AC); catalysts were characterized using BET, XRD, NH₃-TPD and UV-vis spectroscopy.

Materials and methods

Extraction from fly ashes: fly ashes were collected from bag filters of a solid waste incinerator located in Medellín (Colombia). The sample was acid digested with 1 M HCl during 2 h, for releasing PCDD/Fs, water washed and dried for 12 h. Afterwards, sample was soxhlet extracted with toluene during 48 h, roto-evaporated and cleaned-up by liquid-solid adsorption chromatography at atmospheric pressure using glass columns filled with acidic/basic silica gel, florisil and basic alumina as adsorbents. The liquid extract was cleaned up and analyzed following the EPA1613 method⁶.

Catalysts synthesis: molybdenum catalysts were supported on γ -Al₂O₃, SiO₂ and AC. γ -Al₂O₃ support was prepared using the sol-gel method reported by Mizukami et al.⁷, the SiO₂ support was obtained by precipitation of commercial sodium metasilicate⁸ and the commercial AC support (Merck) was pretreated⁹ with HCl (J.T. Baker) and H₂SO₄ (Merck). The catalysts were then obtained by incipient wetness impregnation^{5,10} of a solution of ammonium heptamolybdate tetrahydrate (J.T. Baker) to get catalysts with 1 wt.% molybdenum loading. The catalysts were aged for 12 h at room temperature and dried overnight under air atmosphere at 100°C. The materials were activated under static air at 700°C (Mo/ γ -Al₂O₃), or at 450°C (Mo/SiO₂) or under a stream of N₂ flow at 500°C (Mo/AC) for 2 h and then the materials were reduced in flowing H₂/Ar 5% at 600°C for 2 h.

Catalyst characterization: bulk molybdenum content was determined by atomic absorption spectroscopy, Thermo Elemental brand, model S4 Solaar. The X-ray diffraction (XRD) patterns were obtained in a Siemens D500 diffractometer, using CuK α radiation, with a scan step size of 0.020415° and 38.4 seconds. The surface area (S_{BET}) and the pore volume (V_{pore}) were measured by physical adsorption of N₂ in a Micromeritics AutoChem II 2920. UV-vis diffuse reflectance spectra were obtained on a Cary Series UV-Vis-NIR spectrometer 5000 (Agilent Technologies). Temperature-programmed desorption of ammonia was recorded using a thermal conductivity detector at a Micromeritics AutoChem II 2920 at atmospheric pressure. Temperature Programmed Reduction (H₂-TPR) experiments were carried out in an AutoChem II 2920 Micromeritics instrument equipped with a TCD detector in a Micromeritics AutoChem II 2920 at atmospheric pressure.

Catalytic tests: hydrodechlorination reactions in liquid phase were performed in a three-mouth round-bottom flask equipped with a septum, a thermowell, and a condenser. PCDD/Fs and dl-PCBs extract from fly ashes was mixed with 2-propanol as solvent and reducing agent, catalyst and sodium hydroxide as neutralizing agent. The resulting reaction system was magnetically stirred at 2300 rpm to avoid external mass-transport limitations, at 75 °C for 5 h. After reaction, catalyst samples were recovered by centrifugation and filtration, washed with toluene, and dried at 100 °C for 24 h. Liquid samples were spiked with EPA1613-LCS standard and cleaned up.

PCDD/Fs and dl-PCBs analysis: dioxin samples were analyzed before and after reaction using high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC-HRMS) in a equipped with a CTC Analytics AG automated sampling device and a DB-5-MS fused-silica capillary column (60 m x 0.25 mm x 0.25 μm). EPA 1613 standard solutions in nonane (CS1 to CS5) were used for instrument calibration and quantification, according to the EPA1613 method. The injector oven was maintained at 290 $^{\circ}\text{C}$; the transfer line to the ion trap from the column oven was kept at 280 $^{\circ}\text{C}$ and the manifold at 80 $^{\circ}\text{C}$. The ion trap oven was set to 220 $^{\circ}\text{C}$. The carrier gas was helium at a constant flow rate of 1.1 $\text{mL}\cdot\text{min}^{-1}$.

Results and discussion:

Characterization of the catalysts: Table 1 summarizes the results of molybdenum content, porous structure (S_{BET} and V_{pore}) and acidity. The BET surface areas of supported catalysts show that deposition of Mo on the support had no obvious effects on its surface area.

Table 1. Molybdenum content, porous structure (S_{BET} and V_{pore}) and acidity

Catalyst	Molybdenum content (wt.%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{m}^3 \text{g}^{-1}$)	Acidity (%)		
				Weak (< 250 $^{\circ}\text{C}$)	Medium (250-400 $^{\circ}\text{C}$)	Strong (> 400 $^{\circ}\text{C}$)
$\gamma\text{-Al}_2\text{O}_3$	0.00	356	0.17	69	31	0
Mo/ $\gamma\text{-Al}_2\text{O}_3$	1.32	276	0.13	69	31	0
SiO_2	0.00	100	0.047	54	0	46
Mo/ SiO_2	1.22	101	0.048	46	0	54
AC	0.00	713	0.34	0	0	100
Mo/AC	1.75	638	0.30	25	0	75

Table 1 shows the acidity obtained from *NH₃-TPD analysis*. $\gamma\text{-Al}_2\text{O}_3$ and Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalysts shows two desorption peaks at around 114 $^{\circ}\text{C}$ and 397 $^{\circ}\text{C}$, indicating weak and intermediate acid sites, respectively; SiO_2 and Mo/ SiO_2 catalysts show two desorption peaks at around 101 $^{\circ}\text{C}$ and 425 $^{\circ}\text{C}$, indicating weak and strong acid sites, respectively; Mo/AC catalyst shows two desorption peaks at around 118 $^{\circ}\text{C}$ and 412 $^{\circ}\text{C}$, indicating weak and strong acid sites, respectively; while activated carbon support only shows one desorption peak at around 406 $^{\circ}\text{C}$, indicating a strong acidic sites.

The *XRD patterns* of the catalyst Mo/ $\gamma\text{-Al}_2\text{O}_3$, Figure 1, presents a single phase at $2\theta = 19^{\circ}$, 37° , 46° and 67° , which corresponds to the pattern of the support $\gamma\text{-Al}_2\text{O}_3$. The catalyst Mo/ SiO_2 shows a single phase at $2\theta = 22^{\circ}$, which corresponds to the pattern of SiO_2 . The absence of diffraction peaks associated with phases of metal oxides, MoO_3 ($2\theta = 13^{\circ}$, 24° , 26° , 28° y 40°)¹¹ suggests the high dispersion of species containing these metals. The XRD peaks of Mo/AC at $2\theta = 26^{\circ}$, 37° , 53° , 60° and 67° are associated to MoO_2 formed because ammonium heptamolybdate decomposition and reduction.

The *UV-vis absorption* bands of the catalyst Mo/ $\gamma\text{-Al}_2\text{O}_3$, Figure 2, appear around 220-240 nm and 260-300 nm, which are assigned to the charge transfer O^{2-} to Mo^{6+} . The spectra exhibit no absorption at wavelengths greater than 340 nm because of the presence of MoO_3 , indicating no aggregates of these species, but only scattered Mo oxides.¹² UV-vis spectra of the catalyst Mo/ SiO_2 shows weak bands at around 200-300 nm due to transitions between ligands and strong broad absorption band around 300-400 nm due to charge transfer ligand to transition metal ($\text{O}^{2-} \rightarrow \text{Mo}^{6+}$).¹³ The species corresponded to MoO_3 and moieties with structures equivalent ($[\text{MoO}_4]^{2-}$, $[\text{Mo}_2\text{O}_7]^{2-}$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$)¹¹.

According to the literature, the *reduction profiles* for MoO_3 show two peaks in the range of 570-760 $^{\circ}\text{C}$ and another at $> 760^{\circ}\text{C}$. The first peak is assigned to the reduction of Mo^{6+} to Mo^{4+} ($\text{MoO}_3 \rightarrow \text{MoO}_2$), which consists in the reduction of small crystallites of MoO_3 (570-670 $^{\circ}\text{C}$), the second peak is assigned to the reduction of larger crystals of MoO_3 (670-760 $^{\circ}\text{C}$). The third peak at higher temperatures ($> 760^{\circ}\text{C}$) is attributed to the reduction of Mo^{4+} to Mo^0 ($\text{MoO}_2 \rightarrow \text{Mo}$)¹⁴, including highly dispersed tetrahedral species¹⁵. Figure 3 shows that the three catalysts have these three described peaks. In the Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, these temperatures correspond to 508 $^{\circ}\text{C}$, 588 $^{\circ}\text{C}$ and 930 $^{\circ}\text{C}$; the first two peaks are displaced to the left, probably because these species are not strongly interacting with the support. It could be concluded that the fraction of the Mo^{4+} oxide species was totally reduced in the support, according to the observation that the TPR signal has returned to the initial baseline at higher temperatures¹⁶.

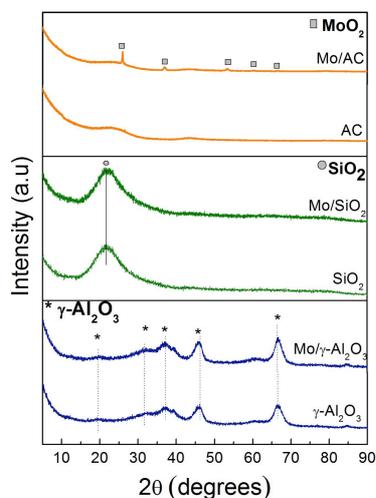


Figure 1. XRD patterns of catalysts

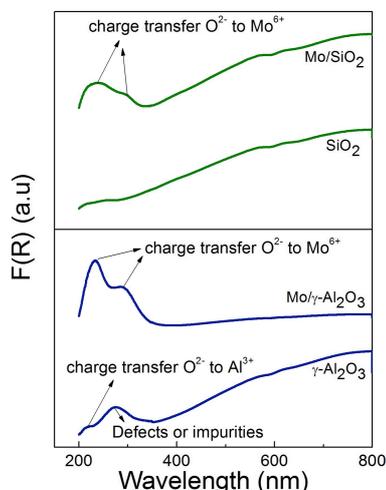


Figure 2. UV-Vis spectra of catalysts

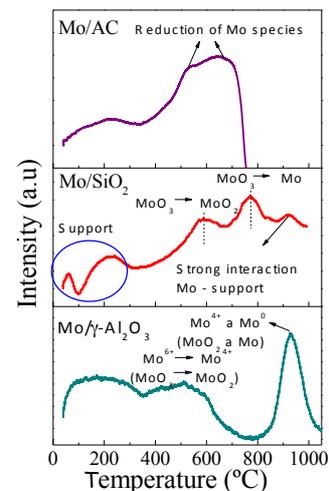


Figure 3. H₂-TPR of catalysts

MoSiO₂ catalyst showed the first two reduction peaks at approximately 587 °C and 770 °C, which correspond to the two stages of reduction of molybdenum oxide: MoO₃ → MoO₂ and MoO₂ → Mo(0), respectively. The third peak appeared at around 920 °C and according to the literature¹⁷, highly dispersed tetrahedral Mo species strongly interact with the support are usually reduced to relatively high temperatures. MoCA catalyst, showed three main peaks: two positive peaks at temperatures around 440 and 720 °C and the third is the negative peak around 850 °C. Small peaks at 530 °C and 690 °C could indicate the reduction of molybdenum species. The negative peak at 850 °C, that is reported in literature, is not observed in this catalysts, although the plot begins to descend at approximately 760 °C, which could indicate the presence of that peak at a higher temperature than 1000 °C¹⁸. A maximum of hydrogen consumption at around 695 °C is also observed, which has been attributed to the interaction of H₂ with the reactive sites of the carbon surface created by the decomposition of the functional groups.

PCDD/Fs and dl-PCBs analysis in the extract: the initial total concentration of the furans almost doubled the initial total concentration of the dioxins and exceeded by more than 40 times the initial total concentration of the dl-PCBs, Figure 4. The congener that had the highest initial concentration (7971 pg/mL), among the group of furans, was 2,3,4,7,8-PeCDF that has assigned the highest toxic equivalence factor; therefore, it has a large contribution to the total toxicity of this group (51%). The congener that had the highest initial concentration (3685 pg/mL) among the group of dioxins was 1,2,3,4,6,7,8-HpCDD (1.9%); however, it does not have a high toxic equivalence factor. The congener 1,2,3,7,8-PeCDD has the main contribution (61%), with a concentration of 1203 pg/mL. The congener of the group of dl-PCBs that contributed the most was PCB 126 (1002.33 pg/mL), which has the highest toxic equivalence factor, with a large toxicity contribution (89%). In general, the contribution to the toxicity of furans was 69.1%, dioxins 29.2% and dl-PCBS 1.7%.

Catalytic tests: Figure 5 shows that the reduction in toxicity was slightly higher in dioxins than in furans over the tested catalysts. The catalyst that most reduced the congener with the highest toxicity was MoA (302.77 pg/mL). The order of activity of the catalysts for all the PCDD/Fs congeners was MoA > MoCA > MoSiO₂ and for the dl-PCBs congeners was MoA > MoSiO₂ > MoCA. In the literature¹⁹, the efficiency of palladium in the HDC of PCDD/Fs and dl-PCBs has been reported; however, the main problem associated with supported Pd catalysts is the deactivation of the catalyst due to coke deposition, surface metal halide formation or metal sintering. The catalytic activity of Mo supported on γ-Al₂O₃, Figure 5, for hydrodechlorination, is comparable with the value reported in the literature (71 - 99%)²⁰.

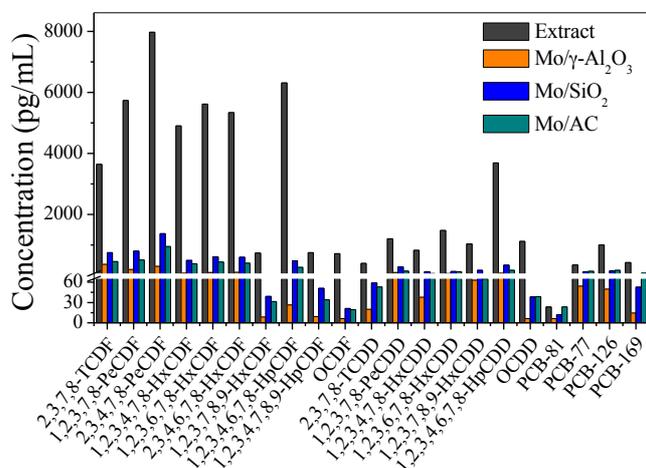


Figure 4. Initial and final concentration of PCDD/Fs and dl-PCBs in extract of fly ash over Mo catalyst

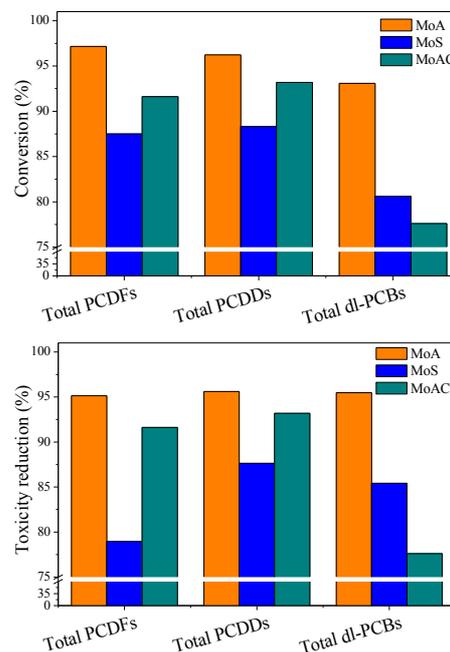


Figure 5. Conversion and toxicity reduction of PCDD/Fs and dl-PCBs using catalysts of Mo

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