

## The effect of NaOH on dioxin hydrodechlorination over Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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### Introduction

Polychlorodibenzo-p-dioxins and polychlorodibenzofurans, 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. Congeners chlorinated at 2,3,7,8-positions are considered the most toxic. As unintentional by-products of combustion dioxin emissions are expected to take place in all countries, so they are included in Stockholm Convention dirty dozen persistent organic pollutants (POPs) [1]. During waste combustion the highest burden is adsorbed on fly ashes [2] so they are very toxic materials. Currently, fly ashes are generally disposed in landfills leading to water and soil contamination. Among the approaches to degrade dioxins, liquid phase hydrodechlorination (LPHDC) at mild reaction conditions [3] has been accomplished on fly ash extracts allowing the rapid and efficient hydrodehalogenation of these compounds. However, LPHDC reactions must be conducted in the presence of a base in order to neutralize hydrogen chloride released from the chlorine-hydrogen replacement process [4, 5]. HCl may be catalyst poison by Pd-Cl formation and may promote active phase leaching [4]. Moreover, excess base can negatively affect catalyst performance [3, 5]. In this contribution LPHDC of PCDD/Fs fly ash extracts has been studied varying NaOH addition (0 to 150 mg). 2-propanol was used as solvent and hydrogen donor and 2 wt-% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as catalyst.

### Materials and Methods

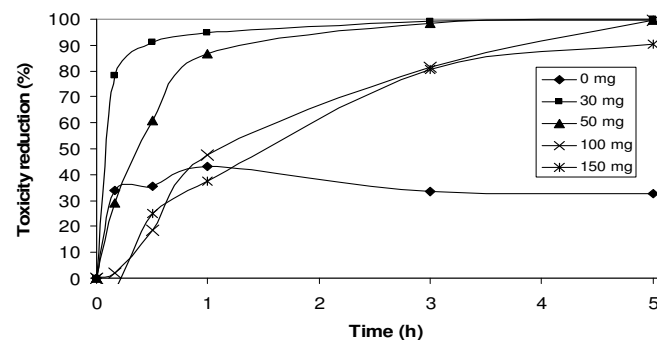
2 wt-% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by wetness impregnation of commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (99.97%, Alfa Aesar, USA) using palladium acetylacetonate (Aldrich Chemical Co., USA) as metal precursor. After drying at 100°C during 12 h, it was calcined for 2 h at 400 °C in 50 mLmin<sup>-1</sup> flowing air and reduced during 1 h at 300 °C in 25 mLmin<sup>-1</sup> flowing 10 % H<sub>2</sub>/N<sub>2</sub>. Heating ramp was 2 °C min<sup>-1</sup> for all runs.

LPHDC reactions were performed in a three mouth round bottom flask equipped with a septum, a thermowell and a condenser. Approximately, 3.5 ng I-TEQ/mL of PCDD/Fs extracts from fly ashes in 2-propanol (20 mL) was added to 100 mg of 2 wt-% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and different amounts of sodium hydroxide. The resulting system was magnetically stirred at 2300 rpm and zero-time reaction was recorded once the mixture boiled, 75°C ( $\pm$ 1°C). Tests were carried out at 10, 30, 60, 180 and 300 minutes. After reaction, catalyst was recovery by filtration, washed with 100 mL of toluene and dried at 100°C during 24 hours. Liquid samples were analyzed following EPA1613 method.

### Results and Discussion

Figure 1 shows the profiles of Toxic Equivalent Quantitated (TEQ) reduction for different sodium hydroxide amounts. Without addition of NaOH, catalyst deactivates after 30

minutes reaction. When 30 mg of sodium hydroxide was added, samples are 100% detoxified after three hours. Larger amounts of NaOH decrease catalytic activity. This negative effect has been associated by other authors [6] with obstruction or partial destruction of alumina structure by excess NaOH. Catalyst characterization of fresh and used samples indicates 50 % reduction of BET surface area in all cases after 1 hour of reaction. Clear differences in metal dispersion have been observed. In general, Pd dispersion (20-25% in fresh catalysts) is drastically diminished to 2-3% after one hour reaction when 30 and 50 mg of NaOH are added but, there are larger decreases (to about 0.6-0.7%) when 100 and 150 mg of NaOH are added and to 0.2% in the absence of NaOH. Also, TPR of catalyst used in large excess of base showed that leftover sodium hydroxide was deposited over the catalyst, obstructing active sites.



**Figure 1.** TEQ toxicity reduction of PCDD/Fs contaminated samples over 2 wt-% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: 70.35 ng I-TEQ, 100 mg of catalyst, 20 mL 2-propanol, 75°C.

### Significance

Sodium hydroxide affects the performance of 2 wt-% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during degradation of PCDD/Fs contaminated fly ash samples. The absence of NaOH leads to palladium sintering and poisoning. Large excess of NaOH also causes sintering and catalyst obstruction. An optimum amount of sodium hydroxide is necessary to efficiently degrade dioxin extracts from fly ashes at short reaction times.

### References

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