

Liquid phase degradation of dioxins over Pd/Al₂O₃

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Introduction

Liquid phase hydrodechlorination (LPHDC) over Pd-supported catalysts is a promising technique for dioxin degradation. However, reaction parameters such as initial concentration, reductant agent, reaction temperature and pH can drastically affect catalyst performance [1]. In this contribution we assess the LPHDC of dioxins over 2 wt-% Pd/Al₂O₃ in a slurry reactor using 2-propanol, H₂/methanol and formic acid as reducing agents. Moreover, due to difficulties associated with the slurry reactor such as catalyst separation and reuse [2] cordierite minimonoliths were washcoated with 2 wt-% Pd/Al₂O₃ and tested for the LPHDC of dioxins using 2-propanol as reductant. Powder and minimonolith catalyst samples were characterized by chemical analysis, H₂ chemisorption, TPR, XRD, SEM, TEM, XPS and TGA before and after reaction.

Materials and Methods

Powder 2 wt-% Pd/Al₂O₃ samples were synthesized by wetness impregnation of commercial γ -alumina (Alfa Aesar, USA). Square cordierite minimonoliths (Corning Inc., USA) were washcoated by the dip-coating method using a 2 wt-% Pd/Al₂O₃ slurry with 23 wt-% solids and neutral pH [3]. Samples of 100 mg of 2 wt-% Pd/Al₂O₃ either in powder or washcoated minimonoliths were introduced into reaction mixtures consisting of: 77.35 ng I-TEQ of PCDD/Fs fly ash extract, 0-50 mg NaOH in 20 mL of 2-propanol, methanol or formic acid solution. Only 2-propanol was used with washcoated minimonolith samples. Three different regeneration methods of used washcoated minimonolith samples were tested: (1) calcination at 400°C followed by reduction at 300°C, (2) reduction at 300°C and (3) reflux washing with 2-propanol at 75°C during 24 h.

Results and Discussion

Toxicity reductions obtained after 3-h under the best reaction conditions with each reducing agent are listed in Table 1. With formic acid, the overall conversion was less than 20%. By TEM and XPS it was observed that the acid environment contributed to Pd sintering and carbon obstruction limiting formic acid decomposition and further degradation of chlorinated compounds. On the other hand, Pd sintering, sodium depositions and graphitic carbon on used catalyst in the H₂/MeOH system diminished the degradation efficiency. The presence of water in this system reduced the catalytic activity due to the diminishing in the catalyst-substrate interaction. 2-propanol appears to be the most efficient reducing agent under the conditions of this study due to the low stability of carbonaceous residues detected by TGA on spent catalyst samples.

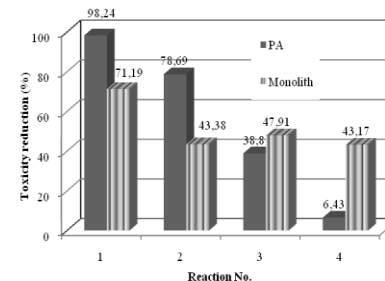
Figure 1a compares toxicity reduction after a 5-h reaction over powder (PA) and washcoated minimonolith (Monolith) 2 wt-% Pd/Al₂O₃ samples using 2-propanol as reducing

agent. The high initial reactivity of powder samples significantly decreased in further runs and the initial amount of PCDD/Fs decreased due catalyst loss during successive filtrations. By contrast, minimonolith samples maintained their reactivity in several runs and no catalyst was lost after each reaction. This behavior may be due to the homogeneous washcoat thin layer where the active sites are more accessible and the negative impact of deposits on the catalyst is diminished. As shown in Figure 1b the three regeneration methods tested are comparable for recovering the reactivity of used washcoated minimonolith samples. Nevertheless, combustion methods proved to be more efficient for the elimination of more stable poisons.

Table 1. Toxicity reduction in the LPHDC of PCDD/Fs with different reducing agents over 2 wt-%Pd/Al₂O₃ after 3-h

Reducing agent	Reaction conditions		Toxicity reduction (%)
	Temperature (°C)	NaOH (mg)	
Formic acid	75	50	37.17
H ₂ /MeOH	60	30	87.02
2-propanol	75	30	99.59

a)



b)

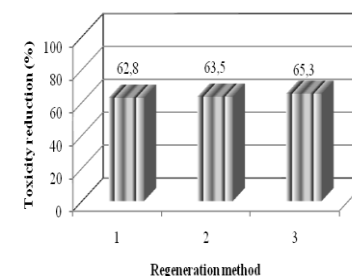


Figure 1. (a) Reactivity of 2 wt % Pd/Al₂O₃ over powder (PA) and minimonolith (Monolith) samples for PCDD/Fs LPHDC and (b) reactivity of washcoated minimonolith samples after regeneration. Reaction conditions: 30 mg NaOH, 20 mL 2-propanol, 75°C, 5 h.

Significance

Washcoated minimonoliths present several advantages for degradation of dioxins using 2-propanol as reductant. The negative effect of carbonaceous deposits is diminished. Besides, though reactivity of minimonolith samples is lower than powdered ones, it is compensated by an easier reusability and larger resistance to deactivation of washcoated minimonoliths.

References

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