



Washcoated Pd/Al₂O₃ monoliths for the liquid phase hydrodechlorination of dioxins

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ARTICLE INFO

Article history:

Received 27 June 2012

Received in revised form 2 August 2012

Accepted 8 August 2012

Available online 16 August 2012

Keywords:

Pd/Al₂O₃ catalyst

Washcoated monoliths

Catalyst deactivation

Dioxins

Fly ash

ABSTRACT

The catalytic activity and durability of 2 wt.% Pd/Al₂O₃ in powder and washcoated on cordierite monoliths were examined for the liquid phase hydrodechlorination (LPHDC) of polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs), also known as dioxins. NaOH was employed as a neutralizing agent, and 2-propanol was used as a hydrogen donor and a solvent. Fresh and spent powder and monolith samples were characterized by elemental analysis, surface area, hydrogen chemisorption, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), and transmission electron microscopy/energy dispersive X-ray spectroscopy (TEM/EDX). Three reactor configurations were compared including the slurry and monolith batch reactors as well as the bubble loop column resulting in 100, 70, and 72% sample toxicity reduction, respectively, after 5 h of reaction. However, the slurry and monolith batch reactors lead to catalyst sample loss via a filtration process (slurry) and washcoat erosion (monolith batch), as well as rapid deactivation of the powder catalyst samples. The monolith employed in the bubble loop column remained stable and active after four reaction runs. Three preemptive regeneration methods were evaluated on spent monolith catalyst including 2-propanol washing, oxidation/reduction, and reduction. All three procedures reactivated the spent catalyst samples, but the combustion methods proved to be more efficient at eliminating the more stable poisons.

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1. Introduction

Catalytic hydrodechlorination (HDC) over noble metal supported catalysts is one of the most promising methods for the degradation of chlorinated wastes from gas and liquid phases [1]. Among the noble metals, Pd exhibits high activity and poisoning resistance [2,3]. Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs), which are also known as dioxins, are a group of highly toxic compounds generated from a wide range of anthropogenic sources in the gas, liquid, and solid phases [4]. Fly ash produced in solid waste incinerators contains one of the highest amounts of dioxin waste, and the extraction of the dioxins with organic solvents for further treatment has been recently investigated. Liquid phase hydrodechlorination (LPHDC) of dioxins over 2 wt.% Pd/γ-Al₂O₃ using 2-propanol as a hydrogen donor and solvent has been successfully accomplished in a slurry reactor under mild conditions [5,6]. This reaction involves the

interaction between the liquid phase where the organic compound is dissolved, the hydrogen gas phase, which is produced in situ by 2-propanol decomposition, and the catalyst solid phase. Good mixing of the involved phases will reduce the mass and heat transfer limitations resulting in a proper heterogeneous catalytic reaction. This goal can be achieved either in slurry or in fixed bed reactors [7]. However, these configurations are affected by catalyst separation, reuse, presence of mass and heat transfer artifacts, pressure drop, and over costs in industrial scale implementation [8].

Although the most widely used catalytic systems for environmental applications with gas-phase reactions are monolithic materials [9], multiphase gas–liquid reactions using monolith catalysts have recently become of interest to the academic and industrial community. The first large-scale application was the production of hydrogen peroxide via the anthraquinone process developed by Akzo Nobel, which illustrated the potential for monolith reactors to replace other conventional reactor types in certain applications [10–12]. In addition, washcoated monoliths have been employed in reactor devices, such as the gradientless Berty reactor for the selective hydrogenation of benzaldehyde over Ni/Al₂O₃ [13], the monolithic stirred reactor for styrene hydrogenation over Pd/SiO₂ [14] and sunflower oil hydrogenation over Pd/Al₂O₃ [15],

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