Kinetics of chloroform hydrodechlorination over Pd/TiO_2 washcoated cordierite minimonoliths

Carlos A. González[1]* and Consuelo Montes de Correa[1]
[1]*Environmental Catalysis Research Group,Universidad de Antioquia, Sede de Investigación Universitaria-SIU, A.A 1226, Calle 62#52-59, Medellín (Colombia)*
*ecags989@udea.edu.co

Introduction

Chlorinated organic compounds are widely used in several industrial applications even though the release of these compounds into the environment has a negative impact in public health and ecology. Once in the environment, they may be transformed to other dangerous chlorinated compounds [1,2]. Chloroform is among the light chlorinated hydrocarbons mainly found in Colombian industrial emissions [1]. Besides it is included in the list of the 17 highly dangerous chemicals targeted in the 33/50 emission reduction program of the US Environmental Protection Agency [3]. Palladium catalysts have proved to be well suited for promoting hydrodehalogenation reactions in the gas phase as well as in the aqueous phase: $CH_mX_n + nH_2 \rightarrow CH_{m+n} + nH_x$ [2,4]. Numerous hydrodechlorination studies have been performed using powder catalysts. Nevertheless, for practical applications the use honeycomb monoliths is desirable because of the low pressure drop, good mass transfer, and ease of product separation [5,6]. In this work the kinetics of chloroform hydrodechlorination over Pd/TiO_2 washcoated cordierite minimonoliths was examined under integral conditions to obtain empirical reaction orders and rate constants. Diffusional limitations were determined by means of the Thiele module applied to minimonoliths, taking into consideration the washcoating thickness [7]. Additionally, the specific kinetic reaction rates were compared with the corresponding mass transfer coefficients.

Materials and Methods

Commercial TiO_2 Hombikat uv-100 powder samples were impregnated with the required amount of palladium acetylacetonate to obtain a 0.8 wt-% palladium loading. Then, they were washcoated over previously calcined cordierite minimonoliths at 400 ºC in air. The slurry was prepared by mixing the catalyst powder samples in excess water (1:2.3) and milling for 36 hours at room temperature. In order to increase washcoating adherence, alumina sol binder was used. Minimonoliths (1cm x 1cm x 1.2 cm) were dipped into the slurry, excess liquid removed by blowing air and coated minimonoliths dryed in a microwave oven. This operation was repeated until 15 wt-% washcoating loading was reached. Washcoated minimonoliths were calcined at 400 ºC in air. Kinetics studies were performed by using a ratio of hydrogen:chloroform=10, chloroform concentrations in the range 300-1000 ppm and keeping an excess of toluene ($C_6H_5CH_3/CHCl_3=10$) as solvent. GHSV was 0.48 g cat*min/L and temperatures were between 120-200º C. A FTIR gas analyzer (Temet) equipped with a 2 L cell, optical step of 240 cm and operated at 120 ºC was used to monitor reactants and products. Fresh and used catalyst samples were characterized by XRD, BET, AAS, SEM, chemisorption, TPR and TPD on-line-coupled quadruple mass spectrometer.

Results and Discussion

As listed in table 1, the effectiveness factor is close to one. Also the estimation of the kinetic mass transfer by means of Sherwood and Schmidt numbers under the reaction conditions used gives much higher values than those obtained for the specific kinetic constant, confirming the absence of diffusional problems. The empiric kinetic parameters for chloroform hydrodechlorination correspond to a first reaction order and a specific reaction constant of 1916 mL/gcat.min.[8]. The TPR characterization results evidenced the presence of metallic palladium as the main catalytic phase for the reaction, while TPD coupled to the mass spectrometer indicated desorption of different hydrocarbons which can be removed by means of air at the calcination conditions described.

Table 1. Parameters evaluated during catalytic hydrodechlorination of $CHCl_3$ at 200ºC

Parameter	Value
Reaction order	1.0
TOF (s^{-1})	0.018
Specific constant (mL/gcat.min)	1916
Thiele module	0.51
Effectiveness factor	0.98
Mass transfer constant (mL/gcat.min)	$6.17x10^9$

Significance

There are not many works dealing with the catalytic hydrodechlorination of chloroform even thought it has been detected in industrial emissions. We used Pd/TiO_2 washcoated cordierite minimonoliths which have been little tested for this reaction. The results showed at high activity in the catalytic hydrodechlorination when they are compared with those found with other similar organochlorinated compounds [8].

References

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