Evaluation of Pd/TiO_2 washcoated cordierite monoliths for dichloromethane hydrodechlorination

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Introduction

Catalytic hydrodechlorination (HDC) of chlorocarbons is being considered as a safe alternative for the treatment of chlorinated organic wastes, due to its potential economic and environmental advantages over conventional treatments such as thermal incineration [1-3]. Numerous HDC studies have been performed using powder catalysts. Nevertheless, for practical applications it is desirable to use honeycomb monoliths characterized by thin walls, high geometric surface area, low pressure drop, good mass transfer, and ease of product separation [4,5]. However, conventional procedures for preparing catalysts cannot be simply applied to monoliths and different procedures must be tried to obtain acceptable washcoats [6]. In this study the kinetics of dichloromethane hydrodechlorination over Pd/TiO_2 washcoated cordierite minimonoliths prepared by different methods and different binders is reported. Tests were performed under differential conditions to obtain empirical reaction rates, reaction orders and rate constants.

Materials and Methods

Palladium was incorporated over TiO_2 supports (sol-gel or Hombikat uv-100) both on powder and minimonoliths by wetness impregnation using palladium acetyl acetonate solution as Pd precursor. Several slurry solutions were prepared by mixing catalyst powders in water excess (1:2.3) and milled for 36 hours at room temperature. In order to increase washcoat adherence, 5 wt-% binder (alumina or titania sol or commercial titania, Aldrich) was used in some cases. Minimonoliths (1cm x 1cm x 1.2 cm) were dipped into slurry, excess liquid removed by blowing air, drying performed using a microwave oven, and calcination conducted at 400 ºC. The coating cohesive resistance was assessed by ultrasonic vibration, thermal shocks and abrasion proofs were done in flowing air under stronger conditions than those used during catalytic runs. Kinetics studies were performed by varying dichloromethane, hydrogen, methane and hydrogen chloride concentrations from 300 to 1000 ppm, keeping an excess of toluene ($C_6H_5CH_3/CH_2Cl_2$=10) as solvent, GHSV was 0.48 g cat*min/L and temperatures between 100-235º 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 catalysts were characterized by XRD, BET, AAS, SEM, chemisorption, TPR and TPD.

Results and Discussion

Resistance tests indicated lower weight losses when alumina sol was used as binder. Table 1 shows the best adherence results obtained. Before catalytic tests the absence of mass transfer limitations was confirmed using different catalysts particle diameters and checking the compliance to Koros-Nowak criterion. The highest reaction rate values ($3x10^{-3}$ mmol/gcat*min at 235 ºC) were obtained over samples in which Pd was impregnated on titania before preparing the slurry. Pd/titania Hombikat uv-100 with sol-alumina as binder exhibited the best hydrodechlorination activity. So, kinetic parameters were determined for minimonolith samples washcoated with Pd/TiO_2 Hombikat uv-100 with sol-alumina as binder. Rate constants were between 0.082 (135 ºC)-15.95 (235 ºC) mmol/gcat*min. The activation energy was 21.46 kcal/mol and overall reaction order was 0.85. Dichloromethane hydrodechlorination increased by increasing the concentration of both dichlorometane and hydrogen and decreased with hydrogen chloride concentrations while methane did have any effect on reaction rate.
BET surface areas for catalysts supported over titania hombikat were about 196 m^2/g. Nitrogen adsorption - desorption isotherms exhibited type I hysteresis, characteristic of mesoporous materials with cylindrical channels, uniform pore size and shape, and narrow pore size distribution. Isotherms did no significantly change with palladium loading. The anatase phase was the only phase identified by X-ray diffraction. SEM micrographs showed no structural changes of catalyst samples after resistance tests and hydrodechlorination reactions. Besides, the binder did not affect anatase phase and palladium loading kept constant during all catalytic tests. On the other hand, TPR characteristics of spent samples did not deviate significantly from profiles associated with fresh samples. However, Pd dispersion was lower for used catalysts. TPD of aged catalysts shows HCl desorption at temperatures higher than 750 ºC. This has been mainly related with adsorbed chlorine on support [7].

Table 1 Weight loss of different minimonolith washcoats

Washcoat	Weight loss (%)
[1]Pd/TiO_2 hombikat, sol-Al_2O_3 binder	0.30
[1]Pd/TiO_2 sol-gel, sol-Al_2O_3 binder	1.18
Pd/TiO_2 hombikat, no binder	3.00
Pd/TiO_2 sol-gel, no binder	4.00
TiO_2 without milling	8.20
[2]TiO_2 Aldrich (binder) + TiO_2 hombikat	7.20
[2]TiO_2 sol-gel (binder) + TiO_2 hombikat	15.80

[1] Binder added to slurry.
[2] Monoliths were washcoated with binder before dipping into slurry.

Significance

This work attempts to fill out the of lack kinetic studies of the gas phase hydrodechlorination of dichloromethane using cordierite honeycomb washcoated with Pd/TiO_2 catalyst.

References

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