



Gas-phase hydrodechlorination of mixtures of chloromethanes with activated carbon-supported platinum catalysts



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ABSTRACT

Platinum catalysts supported on activated carbon (Pt/C) at different metal loadings (0.5–2% Pt) have been tested in the gas-phase hydrodechlorination (HDC) of mixtures of dichloromethane (DCM) and chloroform (TCM), with a total feed concentration of 1000 ppm_v. Almost complete dechlorination was achieved at 250 °C, 1 kg h mol⁻¹ space time and a H₂/CM molar ratio of 25 with the 2% Pt catalyst. At a reaction temperature of 250 °C, scarce inhibition in the conversion of both compounds was observed compared to the HDC of the individual chloromethanes. The TOF values for DCM increase with the Pt content, which can be attributed to the higher proportion of the zero-valent species. The selectivity to reaction products suggests a parallel reactions scheme. The catalysts showed a high stability, demonstrated by the unchanged conversion of both chloromethanes upon time on stream in long-term experiments carried out at up to 26 h.

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1. Introduction

The release of chloromethanes to the atmosphere represents a serious environmental problem. Chloromethanes (CMs) are chlorinated volatile organic compounds which are commonly used as solvents and reactants in numerous processes. They are also employed in the manufacture of aerosols, adhesives, and for dry cleaning [1]. The main problem of these compounds is their high toxicity and carcinogenic character. In addition to this, their emission contributes to the depletion of the ozone layer, global warming and the formation of photochemical smog [2–4]. In particular, dichloromethane (DCM) and chloroform (TCM) are included in the list of the 17 highly dangerous chemicals targeted in the emissions reduction effort of the US Environmental Protection Agency (EPA). In consequence, their emissions have been progressively submitted to more stringent regulations. This leads to the need of developing effective technologies for the treatment of residual streams contaminated with those species. Catalytic hydrodechlorination (HDC) is a suitable technology for this purpose since it can operate under

ambient pressure and relative low temperature, the selectivity to reaction products can be modified, the reaction products are less dangerous than those obtained by other techniques and is applicable over a wide range of pollutant concentrations [5–7].

Several studies focused on the HDC of DCM or TCM have been published in the last years. However, in many cases, these CMs appear together in off-gas streams (for example in chloromethanes production plants [8]), and the application of HDC technology requires catalysts capable of working efficiently in those conditions [9]. There is scarce literature dealing with the HDC of mixtures of chlorinated compounds and the few studies available show reciprocal inhibitory effects which reduce the efficiency of the process compared with that found when working with each individual species. The main novelty of the current work lies on the study of HDC of mixtures of chloromethanes. Ordoñez et al. [10] analyzed the kinetics and the activity of a commercial Pd/Al₂O₃ catalyst in the simultaneous HDC of mixtures of tetrachloroethylene (TTCE), trichloroethylene (TCE) and 1,1-dichloroethylene (DCE). They found important inhibition phenomena since all of the organochlorinated compounds were adsorbed on the same active sites of the catalyst, as it was evidenced by the fitting to the kinetic models proposed. Gonzalez et al. [11] studied the HDC of mixtures of DCM, TCM and TTCE with Pd/TiO₂ catalysts, and observed much lower conversions than the obtained with the individual compounds. Furthermore, the catalysts showed deactivation by coke deposition and HCl poisoning. They also investigated the HDC of TCM and TTCE with DCM traces using palladium catalysts supported on alumina and titania [12], and found faster catalyst

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deactivation when working with mixtures of the three compounds. The metallic active phase plays an important role in HDC. In previous studies [1,13–16], we have investigated the HDC of individual chloromethanes (mainly DCM and TCM) using catalysts based on Pd, Pt, Rh and Ru supported on activated carbon. The catalysts were found to be effective in the HDC of DCM and TCM individually. However the efficiency of the process has not yet been proved with mixtures of both species where some possible inhibitory effects may occur. Although all the above mentioned metals showed effective in the HDC of the chloromethanes, significant differences were found in both, activity and selectivity. In all cases, high selectivities to non-chlorinated products (>80%) were obtained, but the Pt/C catalyst showed much higher stability. Alvarez-Montero et al. [15] confirmed the exceptional stability of that catalyst with no loss of activity after 26 days on stream in the HDC of DCM. This was attributed to the different oxidation state of metallic particles on the catalytic surface and the smaller metal particle size. In contrast with other catalysts, in Pt/C the zero-valent species (Pt^0) predominated at the surface, which is more resistant to poisoning by chloromethane adsorption than the electro-deficient species (Pt^{nt}). On the other hand, re-dispersion of the active phase during the reaction was found, leading to much smaller metal particles, with a very homogeneous size distribution, well distributed over the support with very little agglomeration. The catalyst showed high conversion values (up to 95% conversion for DCM and 100% for TCM) and was highly selective to methane, which was the only non-chlorinated product (selectivities of up to 85% for HDC of DCM and 93% for HDC of TCM). Metal dispersion appeared to be a determining issue for the performance of these catalysts and usually it is modified depending on the metallic content. Moreover, the metal loading and dispersion are important factors to be considered. The effect of Pt loading in the HDC of these chloromethanes has not been previously studied.

The aim of this work is to analyze the performance of Pt/C catalysts with different Pt content (0.5–2%) in the gas phase HDC of mixtures of DCM and TCM.

2. Experimental

2.1. Catalysts preparation

Different platinum-containing catalysts supported on a commercial activated carbon (Merck Carbon) were prepared by incipient wetness impregnation, using aqueous solutions of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (supplied by Sigma–Aldrich) of appropriate concentration to obtain nominal Pt loadings in the range of 0.5–2.0 wt%. The activated carbon was used with a particle size of 0.25–0.50 mm. The catalysts were dried overnight at room temperature and heated up to 100 °C at a rate of 20 °C h⁻¹, maintaining the final temperature for 2 h. Finally, the activation of the catalysts was carried out by reduction under a continuous flow of H_2 (supplied by Praxair with a minimum purity of 99.999%) at 300 °C for 2 h. A heating rate of 10 °C min⁻¹ was used to reach the activation temperature.

2.2. Catalyst characterization

The porous structure of the catalysts was characterized by N_2 adsorption–desorption at –196 °C (Tristar II 3020, Micromeritics). The samples were previously outgassed for 12 h at 150 °C at a residual pressure of 10⁻³ Torr (VacPrep 061, Micromeritics). The surface areas were calculated by the BET equation and the t-method was used to obtain the micropore volume and the external or non-microporous surface area.

The bulk platinum content was determined via inductively coupled plasma-mass spectroscopy (ICP-MS) in an Elan 6000

PerkinElmer Sciex system, equipped with an autosampler AS-91. The samples were previously digested for 15 min with a strongly acidic mixture in a microwave oven (Milestone ETHOS PLUS) at 180 °C.

The surface composition of the reduced catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) (5700 C Multitechnique System, Physical Electronics), using $\text{MgK}\alpha$ radiation ($h\nu = 1253.6$ eV). General spectra were recorded for the samples by scanning the binding energy (BE) from 0 to 1200 eV. The BE of the Pt 4f core level and full width at half maximum (FWHM) values were used to assess the chemical state of Pt. The chlorine content of the catalysts was also measured, considering BE values between 198 and 199 and 200–202 eV for inorganic and organic chlorine, respectively. BE values were corrected for the effects of sample charging by taking the C1s peak (284.6 eV) as an internal standard. The data analysis procedure involved smoothing, a Shirley background subtraction, and curve fitting using mixed Gaussian–Lorentzian functions by a least-squares method. The atomic ratios of the elements were calculated from the relative peak areas of the respective core level lines using Wagner sensitivity factors. The reduction of the catalysts was carried out in a separate reactor prior to the XPS measurements.

Metal dispersion on the reduced and used catalysts was determined by CO chemisorption at room temperature (PulseChemiSorb 2705, Micromeritics). Several pulses of CO were introduced until saturation of the catalyst surface. The number of exposed platinum atoms (Pt_s) was calculated from the CO chemisorption data (CO_{ads}). The stoichiometry of the adsorption of CO on platinum atoms ($\text{Pt}_s/\text{CO}_{\text{ads}}$) was assumed to be 1 [17–21].

Transmission electron microscopy (TEM) of the samples was carried out using a JEOL JEM-2100F microscope operating at 200 kV. The apparatus had a point resolution of 0.25 nm and was equipped with a STEM unit with a bright field detector, and a CCD ORIUS SC1000 camera. The samples were previously dispersed in ethanol and dropped onto holey carbon-coated Cu grids. Particle size distributions were obtained by counting between 100 and 200 particles on each sample. From the size distribution, it was determined the average diameter: $d_n = \sum n_i d_i / \sum n_i$, where n_i is the number of particles with diameter d_i .

The crystalline structure of the catalysts was analyzed by X-ray diffraction (XRD) (X'Pert PRO Panalytical Diffractometer). The powdered samples were scanned using $\text{CuK}\alpha$ monochromatic radiation ($\lambda = 0.15406$ nm) and a Ge mono filter. A scanning range of $2\theta = 20$ –75° and scan step size of 0.020° with 5 s collection time were used.

XRD, TEM, XPS, CO chemisorption and –196 °C N_2 adsorption–desorption were performed with the catalysts after reduction under a continuous hydrogen flow of 50 $\text{Ncm}^3 \text{min}^{-1}$ at 300 °C for 2 h and then cooled to room temperature under helium flow.

2.3. Catalytic activity experiments

The HDC experiments were conducted in a continuous flow reaction system described elsewhere [1], consisting in a quartz fixed bed micro-reactor coupled to a gas-chromatograph with a FID detector to analyze the reaction products. The chromatographic column was made of silica (Plot Fused Silica 60 m x 0.53 mm ID, Bruker).

The operation conditions in those HDC experiments were: Atmospheric pressure, a total gas flow rate of 100 $\text{Ncm}^3 \text{min}^{-1}$ and a total chloromethane (CM) inlet concentration of 1000 ppmv (TCM plus DCM). The catalysts weight, the reaction temperature and the H_2/CM molar ratio were adjusted to the desired values in each run. Space-times (τ) in the range of 0.04–1.73 kg h mol^{-1} , reaction temperatures of 100–250 °C and H_2/CM molar ratio of 10–100 were

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