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Hydrodechlorination of dichloromethane with mono- and bimetallic Pd–Pt on sulfated and tungstated zirconia catalysts

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ABSTRACT

Monometallic (Pt or Pd) and bimetallic (Pt–Pd) catalysts supported on zirconia promoted with sulfate (SZ) or tungsten oxide (WZ) were prepared and tested in the gas-phase hydrodechlorination of dichloromethane. The catalysts showed a high selectivity to non-chlorinated products (between 80% and 90% at 250 °C) being methane the main reaction product. As a general trend, the WZ catalysts yielded significantly higher dichloromethane conversion than the SZ ones, yielding all the catalysts initial conversions higher than 80% at a reaction temperature of 250 °C. However, the former showed a very poor stability regardless of the metallic active phase. On the other hand, the presence of palladium in the sulfated zirconia catalyst avoids deactivation as proved in long-term experiments (80-h time on stream). XPS and elemental analyses of the used catalysts suggest that adsorption of organochlorinated species is a cause of deactivation by blocking the active sites. In the monometallic SZ Pt catalyst, deactivation occurs also by poisoning of the Pt sites by the H_2S resulting from sulfate reduction under the hydrogen-rich gas atmosphere. The metal particle size appears to be a critical point with regard to stability of the catalysts. The one with the highest dispersion showed the highest stability with no signs of deactivation after more than 80 h on stream.

1. Introduction

The emission of chlorinated volatile organic compounds (CVOCs) to the atmosphere contributes to ozone depletion, photochemical smog formation, and global warming [1–3]. In particular, dichloromethane (DCM) is used as solvent in the chemical and pharmaceutical industries in the synthesis of different chemical compounds and polymers and for paint stripping and degreasing operations. Among the different removal techniques, catalytic hydrodechlorination (HDC) shows potential economic and environmental advantages when compared with other techniques.

In the last years, much effort has been focused in the study of the catalytic hydrodechlorination of CVOCs by catalysts based on different metals and supports. However, in the studies analyzing the gas-phase deep hydrodechlorination of chloroform and dichloromethane with supported metallic catalysts, either a rapid deactivation has been reported or simply long-term experiments were not performed [4–13]. The stability of the hydrodechlorination catalysts is a key feature for industrial applications. Deactivation has been attributed to poisoning by HCl and chlorinated organic species, coke formation (in some cases including chlorine in its composition), loss of metal through the formation of volatile compounds and metal sintering, changes in the metallic oxidation state and metal migration [10,14–20]. The support plays a significant role in the activity and the stability of the catalysts [4–21], its surface acidity seems to play a key role in deactivation.

Our research group has previously investigated the gas-phase hydrodechlorination of dichloromethane and chloroform using Pd on activated carbon (Pd/C) catalysts, which showed high activity and high selectivity to non-chlorinated products [22–26]. However, these catalysts underwent significant deactivation due to the irreversible chemisorption of reactants and/or reaction products on the active sites. A comparative study [23] on the behavior of Pd, Ru, Pt, and Rh catalysts supported on activated carbon in the hydrodechlorination of DCM showed that Pd/C and Rh/C were the most active catalysts but Pt/C showed the highest stability with no sign of deactivation after 65 h on stream. More recently [27], a Pt/C catalyst prepared in our lab showed a very high stability with no significant loss of activity after 26 days on stream, which had not been previously reported. It seems that a high Pt^0/Pt^{n+} ratio favors the stability of the catalyst since Pt^0 appears to be more resistant than Pt^{n+} to poisoning by organochlorinated compounds. The Pt^0/Pt^{n+} ratio can be controlled with the reduction temperature. Higher reduction temperatures lead to a higher proportion of zerovalent platinum, although at reduction temperatures higher than around 250 °C, an agglomeration of the metal particles can take place with

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the consequent decrease in dispersion. Based on preliminary studies [28], we have selected a proper reduction temperature in order to obtain catalysts with a high Pt^0/Pt^{n+} ratio and with low metal particle sizes. On the other hand, re-dispersion of metal particles was observed in the Pt/C catalyst [27] leading to non-agglomerated small particles well distributed on the support, which contribute to increase the concentration of H_2 in the vicinity of the active sites and its spillover in the catalytic surface. This appears to favor the reaction of H_2 with the adsorbed chlorinated hydrocarbons, thus inhibiting the poisoning of the catalyst [27]. Therefore, the high resistance of Pt/C to poisoning by these compounds when compared to other catalysts reported in the literature can be attributed to redispersion of Pt during the reaction leading to much smaller metal particles with a very homogeneous size distribution, showing very little agglomeration and being well distributed over the support. It is proposed that these factors would inhibit the formation and stabilization of hydrocarbons other than CH_4 at the active centers.

In order to confirm the role of the metallic particle size and distribution over de support in the stability of the catalysts in the HDC of chloromethanes, in this work, the performance of catalysts prepared from supports with a very different nature than that of carbon, but allowing a wide range of dispersions of the active phase, is investigated. This may contribute to improve rational design of future catalysts.

Taking into account the key role of the acidity of the support in the dispersion of the metallic phase and the deactivation of the catalysts, it is of interest to investigate the development of catalysts with a good balance between the metallic and acidic functions. The objective of this work is to analyze the activity, selectivity, and stability of different mono- and bimetallic Pd–Pt catalysts based on acidic supports, like sulfated (SZ) and tungstated (WZ) zirconia, in the hydrodechlorination of dichloromethane. The selection of metals was made by considering the great stability of Pt and the high activity of Pd [23,27]. Moreover, the use of bimetallic catalysts often results in an increase in the metallic dispersion. In fact, the novel catalytic system SZ Pt–Pd reported in this study shows the same stability and selectivity that our previous Pt/C catalysts [27] but with a significant increase in activity.

2. Experimental

2.1. Catalyst preparation

Monometallic (Pd or Pt) and bimetallic (Pd and Pt) catalysts were supported on sulfated and tungstated-promoted zirconia. The SO_4^{2-}–ZrO_2 support (SZ) was obtained from commercial material in the form of a powdered sulfate-doped hydroxide gel (SZOH) (Grade XZO 1249/01, 7.6 wt.% S on ZrO_2 basis) and the WO_3–ZrO_2 support (WZ) was obtained from commercial material in the form of a powdered tungstated-doped hydroxide gel (WZOH) (Grade XZO 1251/01, 16 wt.% W on ZrO_2 basis). Both commercial materials were supplied by MEL Chemicals. These supports were first pressed and shaped into cylindrical pellets using a hydraulic press (8 Ton cm^{-2}). Then, the pellets were ground and sieved to 35–80 meshes. Samples were taken and subjected to calcination in a muffle furnace in static air for 3 h at 600 °C in the case of SZOH and at 800 °C in the case of WZOH, temperatures that were confirmed in previous studies as optimal for obtaining a crystalline tetragonal zirconia with a proper amount of acidic sites [29,30]. In each calcination treatment, the catalyst was first heated from room temperature to 180 °C at 2 °C min^{-1} in air and this temperature was held for 1 h. Then, the temperature was increased at a heating rate of 5 °C min^{-1} up to 600 °C or 800 °C and held for another 3 h. The sample was then cooled down to room temperature.

The resulting crystalline solids (SZ and WZ, for sulfated and tungstated zirconia supports, respectively) were then impregnated at room temperature with chloroplatinic acid ($H_2Cl_6Pt{\cdot}6H_2O$, Sigma–Aldrich, <99.9%, CAS Number: 26023-84-7) and/or palladium chloride (Cl_2Pd, Sigma–Aldrich, <99.9%, CAS Number: 7647-10-1) aqueous solutions by the incipient wetness method. The amount of solution was regulated to obtain nominal 0.5% Pt or Pd in the final catalyst. Once impregnated, the samples were maintained 24 h at room temperature and then dried slowly in a stove. The temperature was raised slowly from ambient to 110 °C in order to prevent the solvent carrying over the metal precursor to the pore mouths. The samples obtained were denoted as SZ Pd and SZ Pt for the palladium and platinum sulfated zirconia, respectively, and WZ Pd and WZ Pt for the palladium and platinum tungstated zirconia, respectively. In the case of the bimetallic catalysts, the supports (SZ and WZ) were impregnated first with a chloroplatinic acid solution by the incipient wetness method.

Then, the impregnated samples were maintained 24 h at room temperature, subsequently dried at 120 °C and finally calcined in air for 1 h at 500 °C to assure the removal of water and the decomposition of the metallic precursor. Afterward, incipient wetness impregnation was accomplished with palladium chloride solution. Once again, the impregnated samples were maintained 24 h at room temperature, subsequently dried at 120 °C and finally calcined in air for 1 h at 500 °C to assure the removal of water and the decomposition of palladium chloride. The concentrations of Pt and Pd in the impregnation solution were adjusted in order to get a nominal 0.325% Pt and 0.175% Pd in the final catalyst. These weight percentages yield a Pt/Pd atomic ratio of 1:1. The samples obtained were named SZ Pd–Pt and WZ Pd–Pt, for the bimetallic catalysts supported on sulfated and tungstated zirconia, respectively.

2.2. Catalyst characterization

The pore structure of the catalysts fresh and once used in the HDC reaction was characterized from 77 K N_2 adsorption–desorption using a Micromeritics TriStar apparatus. The samples were previously outgassed for at least 8 h at 150 °C at a residual pressure of 10^{-3} Torr. From the N_2 adsorption–desorption isotherms, the apparent surface area (A_{BET}) was determined applying the BET equation [31] and the total pore volume was calculated from the amount of nitrogen adsorbed (as liquid) up to a relative pressure of 0.95.

The X-ray diffraction (XRD) patterns of the catalysts and supports were obtained in a X'Pert PRO Panalytical Diffractometer. The powdered sample was scanned using Cu Kα 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.

The elemental analyses of the samples were performed in a Leco CHNS-932 system. The chemical analysis of Pt and Pd content of the solids was determined by atomic emission spectroscopy (ICP-AES) using an ARL model 3410 equipment. The solids were dissolved in a digestive pump with a mixture of 1 mL sulphuric acid, 3 mL hydrochloric acid, and 1 mL nitric acid. The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with a Physical Electronics 5700C Multitechnique System, using Mg Kα radiation ($h\upsilon = 1253.6$ eV). To determine all the elements present on the catalyst surface, general spectra were recorded for the samples by scanning the binding energy (BE) from 0 to 1200 eV. Binding energy values were corrected for the effects of sample charging by taking the C 1s peak (284.6 eV) as an internal standard. The accuracy of the BE scale was ±0.1 eV. The deconvolution procedure involved smoothing, a Shirley background subtraction, and curve fitting using mixed Gaussian–Lorentzian functions