Stabilisation of Palladium Metal Function of Oxide Supported Palladium Catalyst during the Hydrogenolysis of Chlorofluorocarbons

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Relative to Pd/C or Pd/γ-Al_2O_2 systems, γ-alumina supported Pd/ZnO catalyst exhibits enhanced catalytic activity and stability towards deactivation by halogen adsorption, during the hydrogenolysis of 1,1,2-trichlorotrifluorethane.

The hydrogenolysis of chlorofluorocarbons is an important process for the conversion of chlorofluorocarbons to hydrofluoroalkanes. The hydrogenolysis step is performed at elevated temperatures using platinum or palladium supported catalysts.[1–4] Pd/AlF_3 or Pd black catalysts offer some resistance to deactivation, but Pd/γ-Al_2O_3 and Pd/C catalysts are prone to substantial deactivation, the conversion of CF_2Cl_2 substrate decreasing at *ca.* 1.5–2.5% h^{-1}.[5]

Deactivation of the metal function for the γ-alumina supported Pd catalyst occurs by diffusion of chlorine and fluorine into the bulk of the Pd crystallites during the hydrogenolysis of the chlorofluorocarbon.[6] This change in the metal composition is compounded by halogenation of the oxide support, resulting in an accelerated passivation of the γ-alumina supported Pd catalyst.[5] A search for a metal cocatalyst that will stabilise the Pd^0 function has led to the discovery of a novel zinc(II) oxide supported palladium catalyst that is active towards the hydrogenolysis of 1,1,2-trichlorotrifluoroethane (CFC-113), giving up to 96% conversion of the feedstock CFC, with a fourfold increase in catalyst lifetime relative to the Pd/C system.

Catalysts with varying Pd/ZnO ratios (Pd/ZnO = 0.25, 0.5, 1.0 and 2.0 respectively) were tested. Each catalyst was prepared by the wet coimpregnation of γ-alumina (Degussa 'C' surface area 110 ± 1.5 $m^2\ g^{-1}$) with palladium(II) nitrate hydrate (5% m/m) and the appropriate stoichiometric equivalent of zinc(II) oxide (purity > 99.999%, BDH Chemicals). The dried cake was passed through a sieve (240 μm mesh), loaded into a grade 316 stainless steel reactor (charge = 1.0 g) where the catalyst was calcined under oxygen flow at 623 K (O_2 flow-rate = 30 $cm^3\ min^{-1}$; 2 h), followed with reduction by 10% hydrogen in oxygen free nitrogen (flow-rate 50 $cm^3\ min^{-1}$) at 573 K over an 8 h period. Finally the reactor temperature was increased to 673 K prior to the addition of the CFC feedstock vapour (flow-rate 43 μl min^{-1}) in N_2 carrier to give a reactor space velocity of 1875 h^{-1}. Reactor eluent was sampled using on-line gas chromatography. Product R_f values were compared with those obtained from authentic samples. The conversions and rates of deactivation for the Pd/ZnO/γ-Al_2O_3 catalysts were compared with those obtained under identical reaction conditions for Pd/C and Pd/γ-Al_2O_3 systems. The Pd/C and Pd/γ-Al_2O_3 catalysts gave conversions of 11 and 14%, respectively, for the hydrogenolysis of CFC-113, with a loss in activity of 2.4 and 1.7% h^{-1}, respectively.

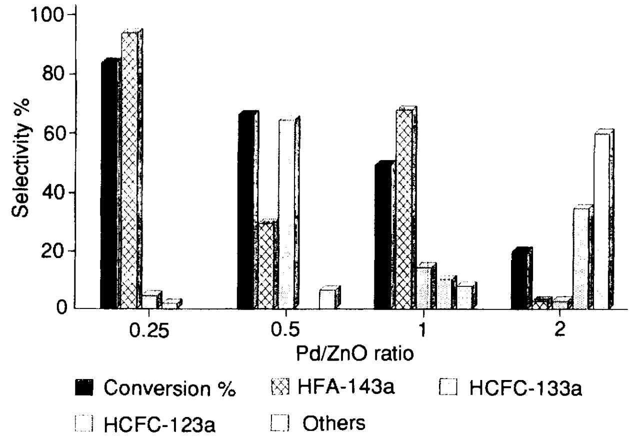

Fig. 1 Hydrogenolysis of 1,1,2-trichlorotrifluoroethane at 673 K as a function of Pd/ZnO ratio

Investigation of the hydrogenolysis of CFC-113 as a function of temperature on the Pd/ZnO/γ-Al_2O_3 catalyst, shows that the optimum reaction temperature of 623 K gives conversions of *ca.* 90% of CFC-113 to hydrogenated products. Time dependent studies show that reaction equilibrium is obtained after 2 h, hence samples of reactor eluent were analysed after the initial catalyst conditioning period. Results from the hydrogenolysis of CFC-113 at 673 K as a function of Pd/ZnO ratio are presented in Fig. 1. The results show that conversions of 82% with selectivity to $MeCF_3$ of 94% are obtained with the Pd/ZnO ratio of 0.25. The products from the hydrogenolysis reaction are 1,1,1-trifluoroethane (HFA-143a), 1-chloro-2,2,2-trifluoroethane (HCFC-133a) and 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123a). Other volatile materials from the reaction were gaseous HX (X = chlorine, fluorine), methane, fluoroform and chloroform. Passivation of the Pd/ZnO catalyst (Pd/ZnO = 0.25) occurs with decreasing conversion of 0.6% h^{-1}. Increasing the Pd content of the catalyst has an adverse effect on the conversion and selectivity of the catalyst (Fig. 1). As the Pd/ZnO ratio is increased to 0.5, a corresponding decrease in the conversion of the catalyst to 66.14% is observed, together with a decrease in the extent of dechlorination. Selectivity to CH_2ClCF_3 is found at 64.2%. The rate of deactivation for the Pd/ZnO catalyst (Pd/ZnO = 0.5) is 0.75% h^{-1}. The catalyst containing a Pd/ZnO ratio of 1 : 1 exhibits a further decrease in conversion of CFC-113 relative to the Pd/ZnO ratio 0.5 (Fig. 1). An increase in the rate of deactivation to 0.9% h^{-1} also occurs. However, the catalyst gives good selectivity to $MeCF_3$ (67%). The final Pd/ZnO system to be investigated (ratio = 2 : 1), produces a further decrease in hydrogenolysis activity, exhibiting conversion of the CFC feedstock of 20%. Passivation of this catalyst occurs with a decrease in CFC-113 conversion of 2.5% h^{-1}. Removal of the Pd phase to give the ZnO/γ-Al_2O_3 system results in elution of a mixture of zinc halides from the reactor at *ca.* 433 K in the presence of the feedstock mixture, hence no hydrogenolysis of CFC-113 was obtained.

The results suggest a synergistic relationship existing where the presence of Pd in the catalyst formulation stabilises the zinc oxide function against halogenation, and the presence of zinc oxide stabilises the Pd function against oxidation in the presence of gaseous hydrogen fluoride and hydrogen chloride at high reaction temperatures. Hydrogen turnover data indicate that the Pd function maintains its metallic character over an extended period relative to Pd systems where the ZnO is absent. The catalytic activity and selectivity of the Pd/ZnO catalyst towards complete dechlorination of the chlorofluorocarbon substrate is dependent upon an optimum stoichiometric ratio of these two catalyst components.

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