

## Strategies for minimizing catalyst deactivation in the aqueous-phase hydrodechlorination of chlorinated pollutants

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### Introduction

Industrial wastewaters containing organochlorinated pollutants are an important environmental and toxicological hazard. Catalytic hydrodechlorination (HDC) should be considered as an alternative for the treatment of these wastewaters, since it is clean, relatively cheap, and efficient technique, being possible the treatment even at ambient temperatures. The most usual catalysts used for HDC reactions are noble metals on alumina supports or on carbonaceous supports<sup>1</sup>. The main problem in the use of these catalysts is the catalytic deactivation, specially caused by leaching of the active phase promoted by the chlorides and protons produced in the reaction<sup>2</sup>. Most of the works found in the literature considering these effects are devoted to polluted groundwater, with very low concentration of chlorinated pollutants (about 1-10 ppm)<sup>3,4</sup>. However, this problem becomes more important in industrial wastewaters, with concentrations of chlorinated compounds close to the saturation (1100 ppm in the case of trichloroethylene, the chlorinated pollutant most often found in these wastes).

This work is focused on the study of the stability of the catalyst for the treatment of these wastewaters. Specifically, the effect of the support, as well as the effect of the addition of external chlorides, bases (NaOH) and alkalinity (addition of Na<sub>2</sub>CO<sub>3</sub>) on the catalyst performance, for the hydrodechlorination of trichloroethylene (TCE) has been studied.

### Materials and Methods

Two commercially available catalysts (ESCAT 16 and ESCAT 18; 0.5 % of Pd over activated carbon and  $\gamma$ -alumina, respectively, supplied by Engelhard) have been used in this work. Catalysts performance was evaluated in a fixed bed reactor, feeding different solutions of trichloroethylene in water (100 -1000 ppm of TCE concentration). Liquid feed was previously saturated with hydrogen at 0.25 MPa and room temperature, in order to ensure that hydrogen is not the limiting reactant. Typically, experiments were carried out at 300 K and 0.25 MPa with a WHSV of 0.6 h<sup>-1</sup>, and 60 h of TOS. The absence of mass transfer limitations has been experimentally checked by carrying out experiments changing particle diameter and fluid velocity. Samples were periodically taken and analysed in a GC-ECD apparatus (Shimadzu GC-17A). Analyses were carried out after extraction with diethylether of the samples. Chloride electrochemical analysis (CRISON 9652) of the treated water was also carried out in order to check the closure of the chlorine mass-balance.

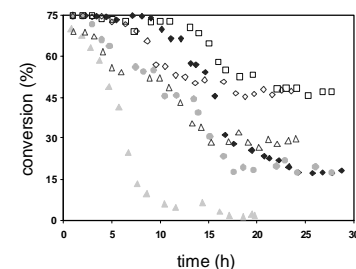
Used catalysts were characterised using TEM, XPS and chemical analysis of the chlorine content of the catalysts (ICP-MS).

### Results and Discussion

Direct comparison of the performance of the carbon- and alumina-supported catalysts reveal that the alumina-supported catalyst presents lower activity but is less prone to deactivation than carbon-supported catalysts. This different behavior (in spite of their similar composition and metal dispersion) suggests that carbon support enhances the activity for the

main reaction, but is not able to adsorb the chloride ions generated during the reaction, as the alumina support does.

Further experiments were carried out with these catalysts adding external chlorides (five times higher than the stoichiometric amount of chlorine released during the reaction), sodium hydroxide, sodium carbonate, and pH buffers (pH=7). Results, shown in the Fig. 1 for the Pd/C catalyst, show that both the decrease of the pH and the presence of chlorides lead to catalyst deactivation. At this point, characterization of the aged catalysts by XPS reveals an increase of the Pd<sup>2+</sup> species, whereas their chemical analysis reveal decreases in the Pd content of up to a 20 % (for the catalyst treated in excess of chlorine ions). The addition of bases improves the catalyst performance, especially if the base is added as carbonate (i.e. addition of alkalinity instead of direct addition of OH<sup>-</sup>). This differential behavior is caused by the formation of palladium hydroxide in the later case, whereas the addition of carbonates ensures the scavenging of the protons without adding hydroxide ions to the medium.



**Figure 1.** Stability of the Pd/C catalyst for the hydrodechlorination of trichloroethylene (1.8 mM) in distilled water (◆); water with 25 mM of Cl<sup>-</sup> as NaCl (▲); water with 25 mM of Cl<sup>-</sup> and 40 mM of Na<sub>2</sub>CO<sub>3</sub> (●); water buffered at pH=8 (◇); water with 40 mM of Na<sub>2</sub>CO<sub>3</sub> (□); and 40 mM of NaOH (Δ)

Regeneration procedures, keeping the deactivated catalysts under distilled water flows for more than twenty hours, lead to important recoveries of the catalyst activity (up to 80 % in the case of the catalyst aged in presence of external chloride, and up to 100% for the catalysts aged in presence of Na<sub>2</sub>CO<sub>3</sub>). This result indicates that the deactivation caused by chlorine poisoning is completely reversible, being possible to operate without irreversible deactivation when an alkalinity source is added to the feed. By contrast, if the protons released during the reaction are not removed they lead to active phase leaching and consequently irreversible deactivation of the catalyst.

### Significance

This work provides better understanding on the deactivation of palladium catalysts used for the liquid-phase hydrodechlorination, suggesting that it is possible to operate without irreversible deactivation just by adding controlled amounts of alkalinity (for example Na<sub>2</sub>CO<sub>3</sub>) to the water.

### References

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