Hydrodechlorination of trichloroethylene on noble metal promoted 
Cu-hydrotalcite-derived catalysts

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Introduction
The emission of chlorocompounds into the environment is now strictly regulated, due to the severe influence on health and ecological damage. Catalytic hydrodechlorination is an alternative low-energy, non-destructive method, which enables the conversion of industrial by-products to valuable chemical feedstock or environmentally friendly products. Noble metals catalysts are very active for the hydrodechlorination of chlorinated organic compounds producing fully hydrogenated products [1]. Whereas, the modification of supported Pt or Pd catalysts by addition of a second metal dramatically changes the catalytic performance with respect to vicinal chlorocarbon dechlorination; the catalysts become highly selective towards olefins [2]. The main drawbacks are the low activity when bimetallic catalysts are employed and the deactivation during the process. In this way, the aim of this work was to investigate the catalytic properties of catalysts prepared from hydrotalcite-like materials containing Cu and Mg, as well as the effect of the addition of noble metals like Pt and Pd for the gas-phase hydrodechlorination of trichloroethylene (TCE), in order to improve the catalyst stability and selectivity to ethene. By changing the preparation procedure and the interaction between Cu and noble metal a different catalytic behaviour has been observed and studied in detail.

Experimental
MgCuAl hydrotalcites were prepared by a standard co-precipitation procedure [3]. Two different protocols were employed to introduce the noble metal. In the first protocol (labelled as "-R") the materials were reduced under hydrogen for 3 hours at 350°C before the introduction of the noble metal, whereas in the second synthesis protocol ("-WR") the reduction step was omitted. The catalysts were tested for the hydrodechlorination of trichloroethylene (TCE) using a continuous fixed-bed glass reactor at 100°C - 300°C and atmospheric pressure [3].

Results and discussion
Characterization results show the formation of an alloy between Pt, Pd and copper (Cu0.4Ptx0.6 and Cu0.25Pd0.75) when the first synthesis protocol (R) is followed, with high dispersion and small particle size (1.4nm for Pt catalysts and 2.6nm for Pd ones). Besides, when the second protocol (WR) is applied, no alloy formation is obtained leading to higher particles size (4-8nm for Pt catalysts and 1-15nm for Pd ones).

In the hydrodechlorination of trichloroethylene at 300°C and at stoichiometric conditions the -R catalysts present practically total conversion (98%) of TCE with high selectivity to ethylene (94%).

Figure 1. HRTEM of 0Pt-CuHT (R)
remaining constant during the investigated reaction time (180 min). However, on WR catalysts the performance was different under the same reaction conditions. Constant activity is observed with time on stream, whereas the selectivity toward ethylene decreases from 90% to 20% after 380 min. The different catalytic behaviour obtained for the catalysts prepared by the two different protocols could be explained considering a different interaction between the noble metal (Pt or Pd) and Cu.

A reaction scheme that involves adsorption of TCE on the Cu phase leading to dechlorination reaction producing ethylene is proposed. The main role of the noble metal forming the alloy is the regeneration of the Cu-Cl x species by spillover of hydrogen. On the alloyed particles a high selectivity to ethylene is obtained. However, on catalysts containing copper and the noble metal in separate form the dehalogenation reaction occurs on the copper surface whereas on the surface of the noble metal a deep hydrogenation to ethane is taking place. To test this assumption, after three hours on stream the catalyst (WR) was reactivated for two hours in hydrogen/helium mixture without the presence of TCE. During this process HCl species were probably removed from the surface of the catalyst. Then, the reaction was started again restoring the initial high selectivity to ethene (see Fig. 2).

Conclusions
Pt,Pd-Cu hydrotalcites catalysts present high activity in TCE removal with high selectivity toward the valuable compound ethylene. The alloy formation determined the mechanism and the stability of these catalysts in the hydrodechlorination process.

Acknowledgements
MEC Spain (CTQ2006-08196, HU2006-0026 and ENE2006-06925); (Acciones Integradas, ES 05/2009) and Hochschuljubiläumsstiftung (Gemeinde Wien, Project H-979/2004).

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