

Pre-treatment effect on Pt/CeO₂ catalysts in the selective hydrodechlorination of trichloroethylene

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Introduction

The emission of chloro compounds into the environment is now stringently regulated, due to the associated adverse health effects and ecological damage. Therefore, the conversion of by-products of industrial processes such as chlorocarbons into more useful or environmentally benign products is of great interest. Noble metals are the main catalytic phase for hydrodechlorination due to their high reactivity for transformation of chlorinated organic compounds into fully hydrogenated products which is much less useful from an industrial point of view compared with unsaturated compounds. Previous work demonstrated that Pt-CeO₂ catalysts have high activity and selectivity in the selective hydrodechlorination reaction of trichloroethylene to obtain ethylene with the activity and selectivity dependent on the preparation method of the catalyst. Several studies have reported that CeO₂ exhibits different kinds of interaction with the noble metals affecting the catalytic activities, depending on, for example, the method of synthesis and catalyst pre-treatment[1]. In order to study how the interaction of noble metal with the support affects the catalytic behaviour with Pt/CeO₂ catalysts in hydrodechlorination reactions, the surface species and reactivity/selectivity were examined as a function of the pre-treatment conditions and noble metal precursor salts used in the preparation.

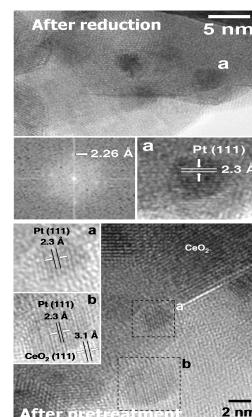
Experimental

Two procedures were used for the Pt/CeO₂ preparation namely, impregnation (IMP) and solution co-combustion (COC) described in detail elsewhere [2]. Two platinum salts were employed, H₂PtCl₆ in the case of chloride precursor (WCl), and Pt(acac)₄ for chloride free samples(NCl). The catalysts were either pretreated under atmospheric air up to 300 °C and then reduced under flowing pure hydrogen at 14 cm³ min⁻¹ for 15 min (denoted as pretreatment) or heated to 300°C under flowing hydrogen at which temperature the catalyst was maintained for 30min (denoted as reduced).

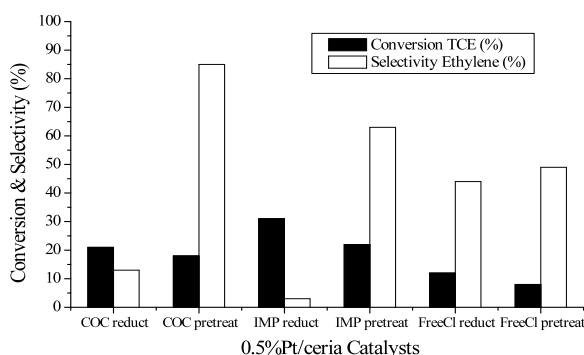
Results and discussion

Surface changes are observed depending on the treatment applied to the catalyst. After pre-treating Pt/CeO₂, HRTEM reveals that there is an increase in Pt particle size and no deposition of CeO_x on platinum particles.

IR spectroscopy shows the different nature of carbonates formed upon CO adsorption, thus denoting changes in the ceria surface sites. These differences are not observed when chloride-free Pt precursors are employed. The surface changes are therefore related to the presence of chloride species. XPS results show higher percentage of chloride species in the reduced samples than in the pre-treated ones. These results are consistent with the formation of CeOCl showed by Kepinski et al. [3]. A CeOCl



phase made with a chloride precursor synthesis decomposes in an oxidizing atmosphere (pre-treatment), leading to the formation of vacancies. This could facilitate the creation of a dechlorination step in the vacancies, thus producing ethylene. TCE adsorption studies were performed by DRIFTS. Whereas on WCl sample mono-chloro species are observed, on NCL ones TCE decomposed to di-chloro species. In this case where bigger particles of Pt are presented (lower energy surface), the reaction does not go to complete hydrogenation of the chlorinated alkene. The pretreatment leads to decomposition of CeClO to CeO₂ reducing the chloride present on the surface, assembling the NCl samples. Although, when a chloride-free precursor is employed bigger particle size and worse dispersion is obtained. In this way it is necessary to prepare the catalyst using chloride precursor in order to obtain small particle size well dispersed and then apply a pre-treatment to clean the surface of chloride species.



In the TCE hydrodechlorination reaction, the main changes were observed in the selectivity, depending on the treatment applied. 0.5%Pt/CeO₂ after reduction exhibits 13% selectivity toward ethylene, however after pre-treatment the selectivity increased to 85%, keeping the activity around 20%. This influence is only observed when a chloride-containing precursor is used for preparation.

Conclusions

By changing the synthesis and treatment applied to Pt/ceria catalyst it is possible to increase the selectivity toward ethylene in the TCE hydrodechlorination process.

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References

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