Effect Of Zr On The Oxidation State Of Pd And Catalytic Activity Of The Sol-Gel Prepared Pd/Al₂O₃-ZrO₂ Catalysts

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Introduction
The palladium-only three-way catalyst has been developed by the catalytic industry to achieve better elimination of the cars exhaust gases, especially during the cold-start [1]. This type of catalysts has substituted advantageously to the Pt-Rh or Pd-Rh catalysts in the catalytic converters, since it has been found that under close-loop operation conditions palladium can meet the properties of the bi or three-metallic catalysts. Some challenges remain in the optimization of these catalysts, as, diminishing the concentration of palladium, improving the thermo-stability, reducing NOₓ in presence of oxygen excess, improving the selectivity to nitrogen, etc. With the aim of design improved palladium-only catalysts, we started a study of preparation of mixed oxides of Al₂O₃ with additives of La₂O₃ [2], ZrO₂ [3] and CeO₂ [4] using the sol-gel technique. In this work the effect of zirconia over the properties of the catalysts of Pd supported in Al₂O₃ will be addressed.

Materials and Methods
Mixed Al₂O₃-ZrO₂ supports were prepared with different ZrO₂ concentrations (1.6, 4.7, 8.0, 12.2, 20.8 and 44 wt %), using the sol-gel method. The solids were calcined at 650 C, and then impregnated with a palladium chloride solution to give a concentration of 0.3 wt% of palladium. The surface areas were determined by N₂ adsorption, finding a maximum area for the catalyst containing 4.7 wt% of ZrO₂. CO adsorption monitored by infrared spectroscopy was one of the techniques used to characterize the properties of the Pd surface. It was observed that different species of CO adsorbed are formed both on the support and on the palladium, depending on the ZrO₂ concentration and the pretreatment conditions.

Results and Discussion
Mixed Al₂O₃-ZrO₂ supports were prepared with different ZrO₂ concentrations (1.6, 4.7, 8.0, 12.2, 20.8 and 44 wt %), using the sol-gel method. The solids were calcined at 650 C, and then impregnated with a palladium chloride solution to give a concentration of 0.3 wt% of palladium. The surface areas were determined by N₂ adsorption, finding a maximum area for the catalyst containing 4.7 wt% of ZrO₂. CO adsorption monitored by infrared spectroscopy was one of the techniques used to characterize the properties of the Pd surface. It was observed that different species of CO adsorbed are formed both on the support and on the palladium, depending on the ZrO₂ concentration and the pretreatment conditions.

CO oxidation was used as a model reaction. The comparison of the different catalysts was done by ramping the temperature up and down. A typical set of curves is shown in the figure 2 for the catalyst 0, 8 and 44 wt % ZrO₂. It is seen an activity increase for the 8 wt % sample, compared to the 0 % sample. Then for high zirconia contents, 44 wt %, the activity goes down significantly. The above results can be explained by the combination of chemical and physical changes induced by the addition of zirconia to support, changes including average Pd particle size and its oxidation state.

Significance
It is known that the catalytic activity of the supported palladium depends strongly on the properties of the support. This work is part of a systematic study to understand influence of zirconia on the palladium properties to optimize the composition of a prototype of an industrial catalyst for automotive emission control.

Figure 1. IR spectra of Pd/Al₂O₃-ZrO₂ samples pretreated in O₂ at 550 C. CO adsorbed at -120 C.
Figure 2. CO oxidation curves for Pd/Al2O3-ZrO2(0, 8 and 44).

References