Highly active nanocatalysts by ion beam surface modification

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1 Introduction

Interface science is at the forefront in the development of new materials for advanced technological applications [1]. In particular, surface properties strongly influence catalysis which is essentially a surface phenomenon. One of the novel applications of ion beam irradiation includes the modification of the catalytic activity of solid catalysts [2]. In this study we evaluated the effect of ion irradiation on the catalytic properties of $Ce_{0.7}Zr_{0.3}O_2$ and the supported noble metal catalyst Pt/ $Ce_{0.7}Zr_{0.3}O_2$, which plays an important role in automotive exhaust control applications, among others.

2 Experimental/methodology

Industrial catalysts $Ce_{0.7}Zr_{0.3}O_2$ and Pt (1%w/w) /$Ce_{0.7}Zr_{0.3}O_2$ were bombarded with N^+ ions with a current density of 3.75 μA/cm^2. The effect on the catalytic properties is analyzed by Temperature Programmed Oxidation (TPO) and Reduction (TPR) experiments which were carried out on catalyst wafers (50-60 m3 kg^{-1}h^{-1}) in a flow infrared cell (293-823 K, 2000 ppm CO, CH_4, C_3H_6, C_6H_{14}, H_2 and 10% v/v O_2) connected to a quadrupole mass spectrometer (Omnistar, Pfeiffer) to detect both the adsorbed and gas species. High Resolution Transmission Electron Microscopy (HRTEM, TECNAI 30G^2) and X-Ray Photoelectron Spectroscopy (XPS, k-alpha ThermoScientific) were used for microstructural analyses.

3 Results and discussion

The differences in the catalytic activity of $Ce_{0.7}Zr_{0.3}O_2$ and Pt/ $Ce_{0.7}Zr_{0.3}O_2$ before and after the ion irradiation were evaluated performing TPO experiments of 2000 ppm CO, CH_4, C_3H_6, C_6H_{14} in 10 % O_2 in the range 293-823 K. It was noticed that $Ce_{0.7}Zr_{0.3}O_2$ bombarded catalyst achieved the 50% of conversion of the different species at temperatures (T50) which were roughly 20 K lower than the correspondent T50 values measured before ion bombardment. The Pt/ $Ce_{0.7}Zr_{0.3}O_2$ catalytic system showed as expected higher activity respect to the unmodified $Ce_{0.7}Zr_{0.3}O_2$ with significantly lower T_{50} values (70-90 K) due to the presence of the noble metal. The ion bombardment induced a further decrement of the T50 values of about 40 K. The T_{50} values of the representative pollutants are reported in details in Table 1 for both catalysts.

The higher catalytic activity of $Ce_{0.7}Zr_{0.3}O_2$ and Pt/$Ce_{0.7}Zr_{0.3}O_2$ catalysts after ion bombardment is strictly related to their enhanced reducibility, as shown by TPR experiments carried out using H_2 as a reductant. It was observed that $Ce_{0.7}Zr_{0.3}O_2$ catalyst treated with ion irradiation presents a remarkably higher reducibility respect to the unmodified catalyst. As a

result, the peak of H_2 consumption was measured at 585 K, a temperature roughly 100 K lower than that reported for the corresponding non bombarded catalyst. In the presence of Pt, the reduction was achieved at lower temperature (520 K) than on the bare support and the ion bombardment lead to a further decrement of the temperature linked with the maximum of the reduction peak to 340 K.

Table1 T_{50} values of representative pollutants combustion measurements

	$Ce_{0.7}Zr_{0.3}O_2$		$Pt/Ce_{0.7}Zr_{0.3}O_2$	
	non treated	bombarded	non treated	bombarded
T_{50} CO (K)	739	696	640	579
T_{50} C_3H_6 (K)	756	738	682	645
T_{50} C_6H_{14} (K)	764	754	693	660

The higher reducibility of both $Ce_{0.7}Zr_{0.3}O_2$ and Pt/ $Ce_{0.7}Zr_{0.3}O_2$ bombarded catalysts was also confirmed by FTIR study of H_2 reduction between 373 and 773 K. The evolution of surface hydroxyl species vibrational modes ν(OH) was used as probe of the surface oxidation state [3]. In particular, the band assigned to the hydroxyl group coordinated to two cations in close proximity with an oxygen vacancy (~3630 cm^{-1}) was observed to increase in intensity with the reduction temperature until 673 K and to be always more intense for the bombarded catalysts respect to the corresponding untreated ones. The results are in line with HRTEM analysis (Fig. 1) which revealed that the sample, after ion bombardment, is characterized by a uniform distribution of nanoparticles on the catalytic surface, as well as by the formation of atom vacancies and incomplete terraces. XPS clearly shows that the spectra, thus the associated microstructures, are modified after the bombardment. Local charges seem to be created, in line with the enhanced catalytic properties.

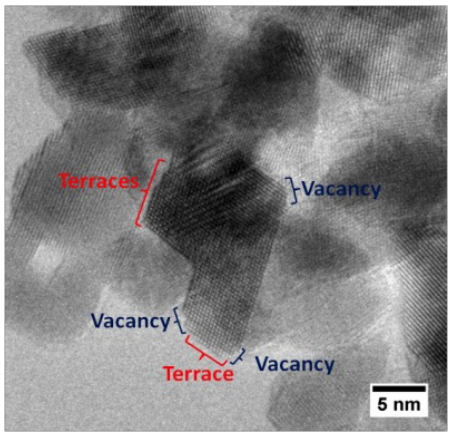

Fig.1 HRTEM characterization of Pt nanoparticles supported on $Ce_{0.7}Zr_{0.3}O_2$

Analogous results have been obtained from the study of alternative catalytic systems such as Pd/Al_2O_3 treated with the same ion bombardment protocol, which provokes a remarkable change in the particle morphology, as highlighted by both XPS and IR studies.

4 Conclusions

The present study revealed that ion irradiation significantly enhanced the catalytic activity and the stability of both $Ce_{0.7}Zr_{0.3}O_2$ and the $Pt/Ce_{0.7}Zr_{0.32}O_2$ catalysts and it suggests the feasibility of this method for the effective and controlled surface modification of several catalytic materials.

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