Ion beam surface engineering for highly active nanocatalysts

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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 Ce0.7Zr0.3O2 and the supported noble metal catalyst Pt/Ce0.7Zr0.3O2, which plays an important role in automotive exhaust control applications, among others. The effect on the catalytic properties is discussed from Temperature Programmed Oxidation (TPO) and Reduction (TPR) measurement, together with the results of microstructural (TEM) and IR spectrometric analyses.

Materials and Methods

Industrial catalysts Ce0.7Zr0.3O2 and Pt (1%w/w) /Ce0.7Zr0.3O2 were bombarded with N2 ions using a ion beam working at 52.5 keV with partial pressure in a vacuum chamber of 10−3 mbar, which gives a current density of 3.75 μA/cm². The incident angle of N2 ions was 0° from surface normal. Catalytic measurements, such as TPO and TPR experiments, were carried out on wafers (50-60 m2 kg⁻¹) in a flow infrared cell (293-823 K, 2000 ppm CO, CH4, C2H6, C3H8, H2 and 10% O2). An infrared spectrometer (Nicolet 6700) and a quadrupole mass spectrometer (OmniStar, Pfeiffer) were used to detect adsorbates and gas species. High Resolution Transmission Electron Microscopy (HRTEM, TECNAI 3062) was used to observe the microstructures of the catalysts.

Results and Discussion

The reducibility of Ce0.7Zr0.3O2 and Pt/Ce0.7Zr0.3O2 catalysts before and after ion bombardment was investigated by TPR experiments using H2 as a reductant. The results are reported in term of H2 consumption in function of temperature in Fig.1 for both catalysts. It was observed that Ce0.7Zr0.3O2 catalyst treated with Ion irradiation presents a remarkably higher reducibility respect to the non bombarded catalyst. As a result, the peak of H2 consumption was measured at 585 K, a temperature roughly 100 K lower than that reported for the correspondent unmodified 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 in correspondence of the maximum of the reduction peak to 340 K.

The higher reducibility of both Ce0.7Zr0.3O2 and Pt/Ce0.7Zr0.3O2 bombarded catalysts was also confirmed by FTIR study of H2 reduction between 373 and 773 K. The evolution of surface hydroxyl species vibrational modes (vOH) was used as probe of the surface oxidation state [3]. In particular, the band assigned to the hydroxyl group coordinated to two cations in proximity of 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 correspondent untreated ones. The results are in line with HRTEM analysis (Fig.2) which revealed that the sample, after ion bombardment, is characterized by an uniform distribution of nanoparticles on the catalytic surface, as well as by the formation of atom vacancies and incomplete terraces.

References