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 $Ce_{0.7}Zr_{0.3}O_2$ 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. 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 $Ce_{0.7}Zr_{0.3}O_2$ and Pt (1%w/w) /$Ce_{0.7}Zr_{0.3}O_2$ were bombarded with N^+ ions using a ion beam working at 52,5 keV with partial pressure in a vacuum chamber of 10^{-5} mbar, which gives a current density of 3,75 µA/cm^2. The incident angle of N^+ ions was 0° from surface normal. Catalytic measurements, such as TPO and TPR experiments, were carried out on wafers (50-60 m^3 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). An infrared spectrometer (Nicolet 6700) and a quadrupole mass spectrometer (Omnistar, Pfeiffer) were used to detect adsorbates and gas species. High Resolution Trasmission Electron Microscopy (HRTEM, TECNAI 30G2) was used to observe the microstructures of the catalysts.

Results and Discussion

The reducibility of $Ce_{0.7}Zr_{0.3}O_2$ and $Pt/Ce_{0.7}Zr_{0.3}O_2$ catalysts before and after ion bombardment was investigated by TPR experiments using H_2 as a reductant. The results are reported in term of H_2 consumption in function of temperature in Fig.1 for both catalysts. 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 non bombarded 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 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 $Ce_{0.7}Zr_{0.3}O_2$ 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 prossimity 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.

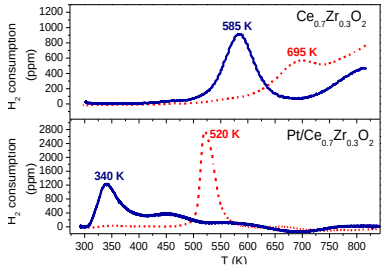

Fig.1 H_2 consumption in function of temperature measured on TPR experiments on $Ce_{0.7}Zr_{0.3}O_2$ and $Pt/Ce_{0.7}Zr_{0.3}O_2$ catalysts before (dash line) and after (solid line) ion bombardment

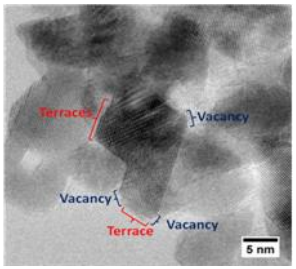

Fig.2 HRTEM characterization of Pt nanoparticles supported on $Ce_{0.7}Zr_{0.3}O_2$

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 temperature programmed oxidation experiments (293-823 K) of 2000 ppm CO, CH_4, C_3H_6, C_6H_{14} in 10 % O_2. 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 (T_{50}) which were roughly 20 K lower than the correspondent T_{50} values measured before ion bombardment. The $Pt/Ce_{0.7}Zr_{0.3}O_2$ catalytic system showed 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 T_{50} values of about 40 K. TPO experiments were repeated several time on the same catalyst in order to study the variation of the catalytic activity with time. Both $Ce_{0.7}Zr_{0.3}O_2$ and $Pt/Ce_{0.7}Zr_{0.3}O_2$ after ion irradiaton were more stable and resistant to aging respect to the non treated catalysts. 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.

Significance

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.

References

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