Catalyst Surface modification by Ion-beam sputtering

Ruairi O'Donnell,[a] Salvatore Scaglione[b], Nancy Artioli [a]*

[a]*Queen's University Belfast, Belfast, BT9 5AG, U.K.*

[b]*ENEA CR Casaccia, Rome,00123, Italy*

**Corresponding author: n.artioli@qub.ac.uk*

Interface science is at the forefront in the development of new materials for advanced technological applications. In this study, Ion irradiation is proven to be an effective and innovative method for the controlled surface modification of several solid catalytic materials which microstructure can be tailored to significantly enhance their catalytic activity, stability and resistance to ageing. The feasibility of this method is thoroughly investigated here on Pt/$Ce_{0.7}Zr_{0.3}O_2$ and Pd/$Ce_{0.5}Zr_{0.5}O_2$ catalysts, which are extensively applied in the reduction of the impact of the emissions from mobile sources. Different techniques have been applied to relate the properties of the materials with their reactivity and modelling of low energy ion sputtering was introduced to describe the erosion phenomena on the catalytic surface with different type of ion, doses and current density.

1. Scope

Surface modification is leading the development of new advanced materials. Recently has gained a lot of interest the application ion beam methods for the preparation and characterization of heterogeneous catalysts *[1]*. Nevertheless, the applications of ion beam sputtering can give a significant contribution also in the *post-synthesis* modification of solid catalysts. In this study we show the effectiveness of this novel technique on the enhancement of catalytic properties of Pt(1%w/w) /$Ce_{0.7}Zr_{0.3}O_2$ and Pd(1%w/w) /$Ce_{0.5}Zr_{0.5}O_2$, which plays an important role in automotive exhaust control applications, among others[2].

2. Results and discussion

Commercial samples of Pt(1%w/w) /$Ce_{0.7}Zr_{0.3}O_2$ and Pd(1%w/w) /$Ce_{0.5}Zr_{0.5}O_2$ catalysts were bombarded with N^+ ion beams, with an ion energy of 1.2keV and a current density of 10μA/cm^2. The incident angle was 40˚ for Pt samples and 30˚for Pd samples. Each catalyst was exposed to multiple bombardment regimes, varying the number of ion passages and exposure time. In order to investigate the differences in term of reducibility after ion bombardment, TPR (Temperature Programed Reduction) experiments were carried out on Pt/$Ce_{0.7}Zr_{0.3}O_2$ and Pd/$Ce_{0.5}Zr_{0.5}O_2$ before and after the ion treatment using H_2 as the reactant.

The results are reported as Fig. 1 for Pt/$Ce_{0.7}Zr_{0.3}O_2$ and Fig. 2 for Pd/$Ce_{0.5}Zr_{0.5}O_2$, in terms of H_2 consumption as a function of temperature. It is observed that for both Pt and Pd-based catalysts, the samples treated with ion irradiation presents a remarkably higher reducibility respect to the unmodified catalyst.

As a result, for the Pt-based catalysts (Fig.1) the peak of H_2 consumption was measured at 405K, 427K and 418K respectively for samples A, B and C. These reduction temperatures are all lower than the max peak temperature measured on the untreated Pt/$Ce_{0.7}Zr_{0.3}O_2$ (Fresh, 445K). This shows that surface modification by ion bombardment can improve the reducibility of the Pt catalyst on a $Ce_{0.7}Zr_{0.3}O_2$ support and the decrement of the maximum reduction temperature is proportional to the number of ion doses. For instance, the most significant reduction of the temperature (40 K), respect to the fresh catalyst, is observed on sample A which has been exposed to the highest number of doses (16 doses, 15 min). Analogous results have been obtained from TPR experiments performed on Pd/$Ce_{0.5}Zr_{0.5}O_2$ samples treated with the same ion bombardment protocol (Fig.2). Both bombarded samples (B and C), were reduced at a lower temperature than untreated catalyst that shows the maximum peak of H_2 consumption at 337K. It is worth to note that the samples B and C have been exposed to the same ion doses and they show similar reduction profiles, indicating a good reproducibility of the treatment. The difference in the reduction temperatures before and after the ion surface treatment measured on Pd/$Ce_{0.5}Zr_{0.5}O_2$ system are less significant than those observed on

Pt/Ce$_{0.7}$Zr$_{0.3}$O$_2$, suggesting a different effect of the ion bombardment on the metals and metal-support interaction.

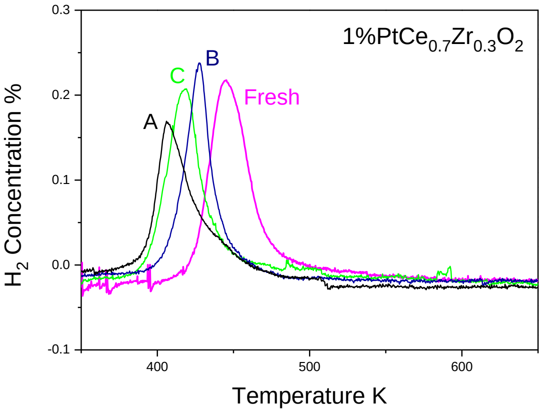

Figure 1 H$_2$ consumption as a function of temperature measured on TPR experiments on untreated (fresh) Pt/Ce$_{0.7}$ Zr$_{0.3}$O$_2$ and treated samples. (Sample A – 15 min dose x16. Sample B – 15 min dose x4. Sample C – 60 min dose x4)

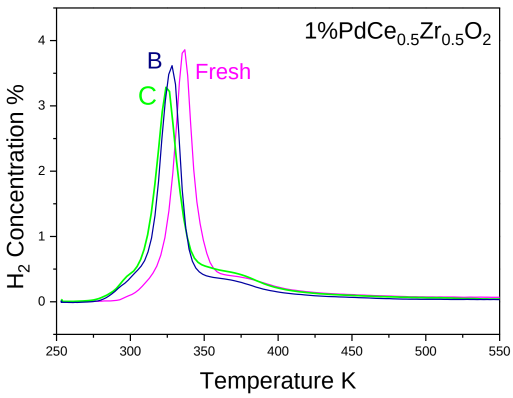

Figure 2 H$_2$ consumption as a function of temperature measured on TPR experiments untreated (fresh) Pd/Ce$_{0.5}$Zr$_{0.5}$O$_2$ and treated samples. (Sample B and C – 60 min doses x4)

The enhanced reducibility of Pt/Ce$_{0.7}$Zr$_{0.3}$O$_2$ and Pd/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalysts is strictly related to a higher catalytic activity evaluated in TPO (Temperature Programmed Oxidation) experiments performed in the presence of exhaust gases (CO, CH_4, C_3H_6, C_6H_{14}, O_2) in the range 293-823 K. The results on catalyst reactivity are in line with the morphological modification observed on the catalysts upon bombardment [4]. The treated materials, which have been characterized by HRTEM and XPS analysis, show a uniform distribution of nanoparticles on the catalytic surface, as well as the formation of atom vacancies and incomplete terraces, and the creation of local charges**.**

3. Conclusions

The results from this study show that the catalytic activity of Pt/Ce$_{0.7}$Zr$_{0.3}$O$_2$ and Pd/Ce$_{0.5}$Zr$_{0.5}$O$_2$ can be enhanced through ion bombardment post-synthesis surface treatment. It indicates that ion sputtering is an effective method to tailor the reactivity of the catalyst and enhance its stability. It opens up the concept of using ion bombardment as a new tool for the rational design of nanodispersed catalysts and their applications in heterogeneous catalytic processes.

References

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