

In-situ XAS studies of Pt/CeO₂ catalysts for indoor air quality

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Introduction

Indoor air cleaning catalysts are especially demanding since they have to perform at room temperature and varying humidity. A thorough understanding of the mechanisms governing the catalytic activity is probably the most reliable pathway to develop improved catalysts. Recent discussion on the oxidation state of noble metal oxidation catalysts¹ and the possibility to improve catalytic activity by doping of the support^{2,3} motivated us to study in detail the structure-reactivity relationship of platinum-cerium oxide catalysts with room temperature activity for CO oxidation and formaldehyde mineralization. A set of catalysts with varying oxidation state and microstructure was analyzed by means of in-situ XAS measurements. For the most active catalyst, we find a specific Ce-Pt-O bond at the surface of the catalyst under working conditions.

Materials and Methods

Two sets of platinum-cerium oxide catalysts were prepared. The first one denoted as Pt/CeO₂ was prepared by wet impregnation of high-surface area CeO₂ using Pt(NO₃)₂. The second series denoted as Pt-CeO₂ was prepared in a one-step synthesis by controlled decomposition of the precursors. The catalysts were analyzed using XRD, XPS, N₂-sorption, HRTEM, HAADF-STEM analysis and XAS. The catalysts were pretreated under hydrogen at 300°C and 500°C. Catalytic tests were run in a fixed bed continuous flow reactor. CO oxidation was conducted at an O/CO = 1.6, a GHSV = 50,000 h⁻¹ in a temperature range between room temperature and 300°C. Formaldehyde mineralization conditions were 1000 ppbv formaldehyde, 40% humidity, air flow 300ml/min and room temperature.

Results and Discussion

The light off curves for CO oxidation for the impregnated and one-step synthesized catalysts are given in Fig. 1a. The impregnated catalyst treated at 300°C shows the best activity, even though the platinum is not completely reduced at this stage, as seen by XANES and XPS measurements (results not shown here). Increase in the pretreatment temperature decreases the catalyst activity. Room temperature activity is also seen for the complete mineralization of formaldehyde (Fig. 1b). HAADF-STEM analysis shows that the two sets of catalyst are inherently different (Fig. 1c and 1d). Platinum nanoparticles below 2 nm in size are found on the impregnated catalyst, while the one-step synthesized one shows no Pt nanoparticles, even after H₂-treatment at 300°C; suggesting successful integration of platinum in the cerium oxide lattice. In-situ XAS studies were done to elucidate the structure-reactivity relationship. Pt/CeO₂ catalysts reveal the presence of unique Pt-O-Ce bonds with a

characteristic bond length of 2.1 Å. (see Fig 1e). The presence of this bond seems to be crucial for the superior activity of this catalyst.

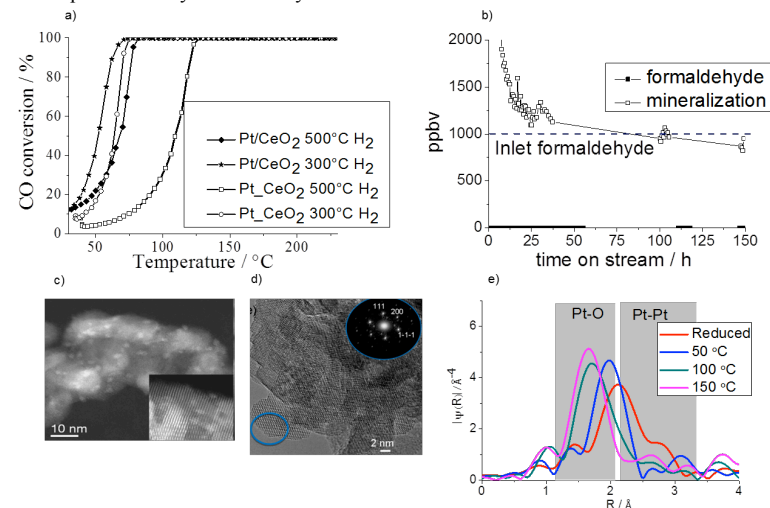


Figure 1 a) CO conversion versus temperature curves for impregnated and one-step synthesized samples b) Formaldehyde mineralization at room temperature c) and d) HRTEM and HAADF-STEM images of impregnated (c) and one-step sample (d) e) Fourier Transform of EXAFS during CO oxidation

Significance

We are studying in detail the mechanisms governing the catalytic activity of platinum nanoparticles deposited on cerium oxide. Factors such as oxidation state, doping of cerium oxide with Pt-atoms and interaction of platinum with cerium oxide are taken into consideration. EXAFS results show that the best performing catalyst forms Pt-O-Ce bonds on the surface of cerium oxide with a characteristic bond length of 2.1 Å. This bond length has been predicted by DFT simulations,³ but to the best of our knowledge has not been observed experimentally.

References

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