

Metal-Support Interactions in Supported Pt Catalysts: A Combined *In Situ* IR and Raman Spectroscopy Study under Reverse Water Gas Shift Reaction Conditions

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Introduction

Platinum supported on ceria and alumina is widely used as heterogeneous catalyst in reactions related to fuel reforming and automotive emission control [1-4]. For the supported Pt/CeO₂ catalytic system, strong support effect through electronic interaction and/or geometric decorations were found play an important role in determining its performance. The CeO₂ support has also been reported to improve Pt dispersion and, thus, increase the number of exposed catalytic active sites. In addition, Pt poisoning by CO chemisorption under reducing conditions is suppressed by preferential CO oxidation by oxygen supplied by the CeO₂ support. The most widely used spectroscopic techniques to reveal the nature of the Pt-CeO₂ interactions are IR CO chemisorption and TEM. Very recent studies have demonstrated *in situ* Raman spectroscopy, a complementary vibrational spectroscopy technique to IR spectroscopy, as an easy and effective tool to monitor the state of Pt on various metal oxide support under reaction conditions. Furthermore, the complementary vibrational selection rules of IR and Raman spectroscopy presents an ideal approach to providing a complete molecular level understanding of the Pt-support interactions for supported Pt/CeO₂, Pt/Al₂O₃ and Pt/SiO₂ catalysts under reaction conditions.

The reverse water gas shift (RWGS) reaction is a model reaction taking place during many catalytic fuel production reactions and catalytic automotive exhaust reduction. The present investigation aims to employ combined *in situ* Raman and IR spectroscopy to investigate metal-support interactions of supported Pt catalysts during the RWGS reaction.

Materials and Methods

Pt was loaded onto CeO₂, Al₂O₃ and SiO₂, at 1.0 wt% Pt, by the incipient wetness impregnation method using a chlorine-free platinum precursor (Pt(NH₃)₄(NO₃)₂). The Pt particle size distribution and morphology were examined with high resolution TEM. The combined *in situ* Raman and IR spectroscopy study was performed with the Horiba-Jobin Yvon LabRam-IR HR spectrometer. The reactor cell was a modified Harrick cell with CaF₂ windows to allow simultaneously collection of the Raman and IR spectra in different reaction environments. The typical RWGS reaction feed contained 1 % CO₂, 4 % H₂ and 95% He.

Results and Discussion

The calcined supported Pt/SiO₂ catalyst gives rise to the crystalline PtO₂ Raman band (~550 cm⁻¹) reflecting the weak interaction of Pt with the SiO₂ support. The calcined

supported Pt/Al₂O₃ catalyst, however, exhibits a broad Raman band at ~610 cm⁻¹ reflecting the presence of distorted PtO_x nanoparticles (NPs). For the calcined supported Pt/CeO₂ catalyst, Raman gives rise to a well-defined band at ~675 cm⁻¹ characteristic of two-dimensional surface PtO_x species (see Raman spectra in Figure 1). These PtO_x Raman signals are stable until 700 °C under oxidizing conditions. Under the reducing H₂/CO₂ conditions, the supported PtO_x phases on SiO₂ and Al₂O₃ are easily reduced to metallic Pt at 50 °C (loss of PtO_x Raman signal) and RWGS reaction is initiated at ~150 °C, as indicated by the IR band of chemisorbed CO on Pt (see IR spectra in Figure 1). Reduction of PtO_x/CeO₂ under the reducing H₂/CO₂ conditions, however, is retarded and only initiates at ~280 °C, which reflects the stronger interaction with the CeO₂ support. Interestingly, IR reveals that CO chemisorbs at both bridged and atop sites on Pt/CeO₂ (see Figure 1) and only atop positions on Pt/Al₂O₃ and Pt/SiO₂ catalysts. Furthermore, reoxidation of Pt/CeO₂ with ¹⁸O₂ resulted in the appearance of Pt¹⁶O reflecting the supply of oxygen from the CeO₂ support rather than the gas phase. Thus, the Pt-support interactions determine the (i) dispersion of the supported PtO_x phase, (ii) molecular structure of the supported PtO_x phase under oxidizing conditions, (iii) ease of reduction of the supported PtO_x phase, (iv) nature of exposed metallic Pt sites for CO chemisorption and (v) reoxidation mechanism for supported Pt. The TEM characterization studies of Pt dispersion and morphology are current being performed and will also be presented.

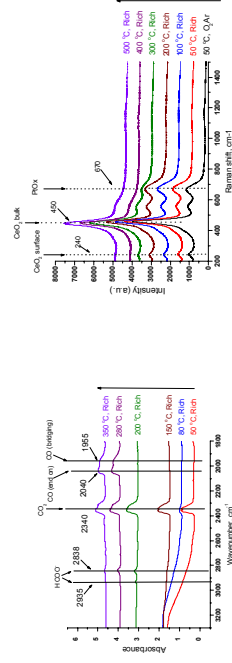


Figure 1. *In situ* IR (a-left) and Raman (b-right) spectroscopy of initially calcined supported Pt/CeO₂ catalysts under RWGS reaction conditions.

Summary

The combined *in situ* Raman and IR spectroscopy studies of supported Pt catalysts have provided the *first direct* fundamental insights into metal-support interactions in different reactive environments.

References

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