

Following the Reduction of Pt/Al₂O₃ catalysts using UV-Vis Spectroscopy

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Introduction

In spite of the industrial importance of low-loaded supported metal catalysts, such as those used in naphtha reforming [1], there are few tools, if any, for the direct analysis of these materials as they are reduced under practical conditions. Such analysis has been limited by the low sensitivity of some spectroscopic techniques, or by the need to use high vacuum during the analysis. Ultraviolet-Visible spectroscopy (UV-Vis) is a sensitive technique that provides direct information about the HOMO-LUMO electronic transitions in molecular structures, or the interband transitions when studying extended materials. It has been used primarily in studies concerning the oxidation-calcination steps in synthesis [2-6], but to our knowledge, there are no thorough spectroscopic studies of reduction steps. In this work we show that it is possible to follow the reduction process of supported Pt using UV-Vis spectroscopy, and that this opens an interesting alternative for studying other reduced supported metals.

Materials and Methods

Pt/ γ -Al₂O₃ samples (0.37, 1 and 3 wt% Pt) were prepared by impregnation of H₂PtCl₆ (Aldrich) on γ -Al₂O₃ (Ketjen) followed by drying at 110°C for 24 h. Each sample was placed in a diffuse reflectance stainless-steel flow cell equipped with a heater (Harrick) which was mounted onto the UV-Vis spectrometer (Cary 5E, Varian). Calcination and reduction of the samples were made in-situ with chromatographic air and H₂ (Infra-Air Products) in a 0.2 ml/s flow, respectively. Thermal treatment of the samples (50 mg) was from 100 to 500°C and the UV-Vis spectra were recorded at 25°C after each thermal treatment step. The scan range was from 200 to 2500 nm with a 0.5 nm interval.

Results and Discussion

UV-vis spectra of the 0.37 wt% Pt sample calcined in the 150-500°C range showed three bands located at 287, 374 and 465 nm (Figure 1). The first was a ligand-to-metal charge-transfer (CT) absorption band assigned to [PtCl₆]²⁻ [3]. The next two bands were attributed to the d-d transitions of Pt⁴⁺ from [PtCl₆]²⁻ and [PtCl₅(OH)]²⁻ [3,4]. Both 1 and 3 wt% Pt samples showed the first two bands and the band at 465 nm disappeared. In these samples, a new band at 640 nm appeared which is being studied.

Reduction of the Pt catalysts caused significant changes in the UV-Vis spectra, as shown in Figure 2 for the 0.37 wt% sample. Those changes correlate with TPR results, which show reduction bands below 100°C, at roughly 200°C, and above 400°C. In particular, besides bands at 308, 380 and 470 nm, that appear to correspond to d-d transitions, upon reduction there is a

large broad band that first appears upon reduction, and that increases with reduction temperature. This band is responsible for the darkening of the catalysts and is linked to the so-called colour centers [7], and with the appearance of free electron conduction in the reduced crystallites. We discuss further the structural and electronic information provided by our results, and their extension to other supported metal systems.

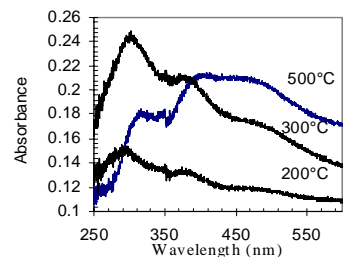


Figure 1. UV-vis spectra of the 0.37 wt%Pt/Al₂O₃ catalyst calcined at several temperatures.

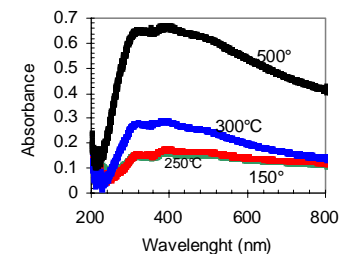


Figure 2. UV-vis spectra of the 0.37wt % Pt/ Al₂O₃ catalyst after reduction in hydrogen.

Significance

We introduce for the first time the use of UV-Vis spectroscopy as a tool for analyzing low-loaded supported Pt/Al₂O₃ catalysts in the *reduced* state. This type of catalysts, of large industrial relevance, cannot be analyzed properly using other spectroscopic techniques.

References

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