

Spatially resolved UV-Vis micro-spectroscopy: A physicochemical study on the preparation of metal-ion supported catalysts

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Introduction

The elemental steps of impregnation and drying in the preparation of different hydrogenation catalysts containing Ni²⁺, Cu²⁺, Pd^{II} and Pt^{IV} were under study. To do so, a newly developed technique was applied, UV-Vis micro-spectroscopy, which is able to monitor the physico-chemical processes involved during the preparation of mm-sized supported catalysts with both spatial and time resolution.

Materials and Methods

UV-Vis micro-spectroscopy enables monitoring the metal-ion speciation along the cross section of bisected catalyst bodies in the UV-visible-NIR region (250-1100 nm) with a spatial resolution of around 200 μm . Measurements can be done both in the wet and in the dry stage of the preparation process thanks to the measuring cell. The set-up (shown in Figure 1) consists of a UV-Vis probe containing 7 optical fibres ($\varnothing=100 \mu\text{m}$), six of them connected to a light source and the other one to a detector. A step motor allows the movement of the measuring cell (x, y directions) and the probe (z direction) [1].

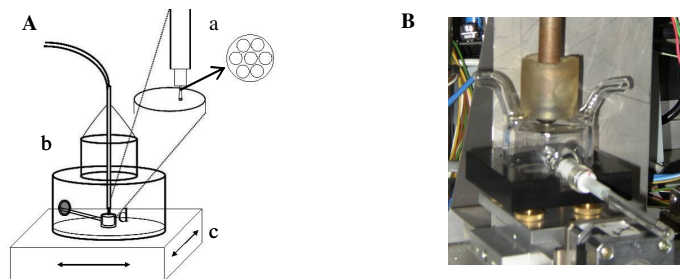


Figure 1. UV-Vis micro-spectrometer. (A) Scheme of the set-up: (a) UV-Vis probe, (b) measuring cell, (c) movable platform, (d) sample holder. UV-Vis probe formed by one collecting fiber in the center and six illuminating fibers around. (B) Illustration of the set-up.

Results and Discussion

The impregnation step was monitored for Pd^{II}/Al₂O₃ catalysts. The ligand-to-metal-charge-transfer transition at 280 nm and the Pd^{II} d-d band at 474 nm of [PdCl₄]²⁻ complexes were measured. Immediately after contact between the solution and the support, the latter band shifted to shorter wavelengths. This shift continued with aging time, indicating a change in the coordination sphere of the metal ion. Moreover, both bands were only present in the outer rim

of the pellet. Pd^{II} distribution could be modified by adding excess of NaCl to the impregnation solution giving a Pd^{II} egg-yolk distribution after 4 days of aging. The impregnation step in Pt^{IV}/Al₂O₃ catalysts was monitored as well. Pt^{IV} d-d bands at 353 and 453 nm were measured at all times after impregnation in the outer ring of the pellets (egg-shell distribution). However, it was observed that pretreating the extrudates with HCl enabled a deeper penetration of Pt^{IV} complexes inside the pellets, obtaining a uniform distribution of the metal-ion [2].

The influence of the drying temperature was studied on [Ni(en)₃]²⁺ and [Cu(en)₂]²⁺/Al₂O₃ pellets. For Ni²⁺/Al₂O₃ catalysts, UV-Vis spectra collected after drying at room temperature, showed two Ni²⁺ d-d transitions bands at 549 and 890 nm, present in all the positions inside the pellet. These bands indicated a uniform distribution of [Ni(en)₃]²⁺ (Figure 2a). Drying at 60 °C yielded a shift of the bands to longer wavelengths from the edge to the core of the pellets (Figure 2b). The shift of the bands showed that a gradual change in the coordination sphere of Ni²⁺ occurred from the outer part of the pellet to the core, in which ethylenediamine groups were partly substituted probably for hydroxyl ligands from the support. A similar behaviour was observed for [Cu(en)₂]²⁺/Al₂O₃ catalysts.

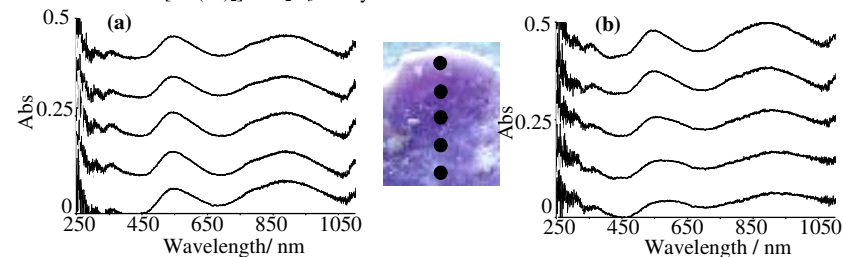


Figure 2. UV-Vis spectra collected along the cross-section of an impregnated pellet with 0.5 M [Ni(en)₃]²⁺, after 2 h of aging followed by drying at room temperature (a) and at 60 °C (b).

Significance

Spatially resolved UV-Vis micro-spectroscopy enables studying the physicochemical processes involved during catalyst preparation. It allows monitoring the wet and dry steps, giving information of the metal ion complexes present and their distribution. In addition, how the experimental conditions affect both properties can be measured. The nature and macrodistribution of the active component are decisive properties in the catalyst efficiency since they can determine the final metal dispersion and phases [3, 4]. Therefore, controlling them will enable designing catalysts for specific purposes.

References

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