STUDIES OF THE INTERACTION OF H₂PtCl₆ WITH γ-Al₂O₃ BY DIFFUSE REFLECTANCE SPECTROSCOPY

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Anchoring of [PtCl₆]²⁻ on γ-Al₂O₃ follows an ion exchange mechanism without altering the ligand environment. Drying catalysts at elevated temperatures leads to chemical conversions of the adsorbed complex to form oxygen-containing Pt(IV) complexes due to the substitution of Cl ligands by surface groups of the support.

Studies of the interaction of metal compounds with a carrier during impregnation and its further chemical conversions at heating are important in scientific approaches to synthesis of supported catalysts.

According to Ref. [1], for the [PtCl₆]²⁻ - γ-Al₂O₃ system the anchoring occurs through the substitution of Cl ligands in [PtCl₆]²⁻ by surface OH groups of the support. In Refs [2-3], however, it is suggested that in this case the ion exchange mechanism is followed.

Several studies of γ-Al₂O₃-supported Pt compounds by the

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complete diffuse reflectance (CDR) technique have been reported recently [4, 5, 8]. For samples obtained by impregnation of γ-Al₂O₃ with an HCl and H₂PtCl₆ solution and drying at 120 °C it is suggested [4] that the fixation of Pt complex follows a mechanism of ion exchange with the surface OH-groups without altering the ligand environment, which is only getting distorted. The authors, however [4], do not take into account the difference in sorption kinetics of chlorine- and platinate ions. Due to high diffusion coefficients, the sorption front of chlorine ions under impregnation goes ahead that of [PtCl₆]²⁻. In this case the interaction of the complex with preadsorbed chlorine ions is likely to follow the ligand substitution mechanism rather than that of ion exchange.

In the present study we have made an attempt to examine the composition of the surface Pt compounds on γ-Al₂O₃ impregnated with an aqueous solution of H₂PtCl₆ and to test further conversions of supported complexes upon drying.

The support used was γ-Al₂O₃ with S_BET = 240 m²/g. The initial aqueous solution of H₂PtCl₆ was prepared from crystalline H₂PtCl₆·6H₂O and then stored several hours to attain equilibrium in the complex hydrolysis.

Catalysts were prepared as follows. The necessary amount of the H₂PtCl₆ solution is slowly (for 30 min) added to a suspension of γ-Al₂O₃ (2 g) in water (20 cm³) with stirring. Then the residual solution is removed and the support is washed with water. The samples obtained are dried in vacuum at ambient temperature for 3 h or at 120 °C for 2 h. For comparison, in preparing some samples, γ-Al₂O₃ pretreated with HCl (2 wt.% of Cl) was also used.

To identify surface compounds, some samples were prepared by supporting Pt on the carrier from a solution of K₂[PtCl₄(OH)₂]. CDR spectra were recorded on a Specord M-40 instrument.

H₂[PtCl₆] and K₂[PtCl₄(OH)₂] were used as model complexes to interpret spectra. Spectra of an aqueous solution of H₂PtCl₆ exhibit charge transfer (CT) bands at 263 nm and d-d-transitions at 380 and 483 nm with extinction coefficients of 24500, 450 and 90, respectively. Spectra of the K₂[PtCl₄(OH)₂] solution exhibit CT