SORPTION MECHANISM FOR Pt-Sn COMPLEXES ON γ-Al₂O₃ MODIFIED WITH HCl

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The sorption mechanism for Pt(SnCl₃)₅⁻ complex on γ-Al₂O₃ pretreated with HCl has been examined using ¹⁹⁵Pt and ¹¹⁹Sn NMR. The anchoring of the complex on the support surface has been found to follow the ligand substitution mechanism with changing the number of ligands in the inner coordination sphere of the complex.

Alumina supported Pt-Sn catalytic systems have been extensively used in hydrocarbon conversion processes. One of the methods to obtain such catalysts is the adsorption of Pt-Sn complexes on the appropriate supports [1]. The composition of the surface compounds produced is suggested to correspond to that of the initial material.

The aim of the present study was to examine the sorption mechanisms of Pt(SnCl₃)₅⁻ (noted as PtSn₅) on γ-Al₂O₃ modified with HCl using ¹⁹⁵Pt and ¹¹⁹Sn NMR.
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EXPERIMENTAL

γ-Al₂O₃ (S=240 m²/g) used as support was treated with 1N HCl till the complete saturation of its surface with Cl⁻ ions. Then the support was washed with water and dried in air at room temperature. The surface concentration of Cl⁻ was 2x10⁻³ mg-eq/m².

PtSn₅ was synthesized either in water or in alcohol (isopropanol) media with the atomic ratio Pt:Sn=1:5. To 135.6 mg of SnCl₂·2H₂O, 0.53 mol of concentrated HCl and 1.11 ml of H₂PtCl₄ solution (Pt=20.6 mg/ml) were added. Then the solution volume was increased up to 6 ml by adding a solvent.

After a 10 min contact of 4 ml of the initial solution with 2 g of γ-Al₂O₃, the solution containing the unadsorbed complex (a residual solution) was poured out and γ-Al₂O₃ was treated with a fresh solvent (water or isopropanol). The surface concentration of the sorbed complex on the support was about 0.3 wt% with respect to platinum. The sorbed surface compounds were then desorbed with 8N HClO₄. The extent of desorption was above 90%. After desorption, the solutions were analyzed using ¹⁹⁵Pt and ¹¹⁹Sn NMR on a CXP-300 Bruker spectrometer. Chemical shifts were measured relative to 3M H₂PtCl₆ solution in 3N HCl and tetramethylin as external standards.

RESULTS AND DISCUSSION

The behavior of PtSn₅ and PtSn₂ complexes in homogeneous media has been examined previously [2,3]. Since these compounds decompose with different rates in different media, we have examined their sorption mechanisms from water and alcohol solutions.

PtSn₅ sorption in isopropanol.

¹⁹⁵Pt and ¹¹⁹Sn spectra for the initial impregnation solution exhibit peaks whose parameters are typical for PtSn₅ [2,3]. 1.5 h later bands of PtSn₂ and Sn(IV) appear and after 4 h the solution contains PtSn₅, PtSn₂ and Sn(IV) in the ratio: 0.25: 0.55: 0.20 (atomic % Sn). After a 10 min contact of the initial solution with γ-Al₂O₃, the NMR spectra of the residual solution