

STATE OF SUPPORTED COMPONENTS
IN (Pb + Pt)/SiO₂ CATALYSTS PREPARED VIA DECOMPOSITION
OF ANCHORED COMPLEXES

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IR spectroscopy, ESCA and RAD studies indicate that in contrast to impregnation catalysts, platinum and lead in the anchored, reduced (Pb + Pt)/SiO₂ catalysts interact, thus decreasing the electron density on Pt.

Методами ИКС, РФЭС и РРА показано, что состояние платины и свинца в закрепленных восстановленных катализаторах (Pb + Pt)/SiO₂, в отличие от пропиточных имеется взаимодействие между Pb и Pt, приводящее к снижению электронной плотности на платине.

In platinum catalysts prepared via decomposition of metal complexes anchored to the surface of SiO₂, ultradisperse Pt particles do not agglomerate up to 600 °C in the presence of low-valent ions Re, W, Mo and Sn bonded to the support /1/. According to electron microscopy data, similar stabilization of disperse metal particles is also observed for Pt-Pb catalysts prepared via supporting platinum on silica, modified by lead ions. The aim of the present study was to obtain data on the electronic state of Pt and Pb in (Pb + Pt)/SiO₂ catalysts prepared by various methods.

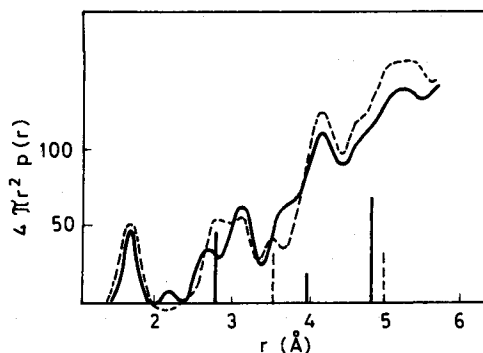


Fig. 1. RAD curves of a (Pb + Pt)/SiO₂ catalyst reduced by hydrogen at 600 °C, prepared via interacting Pb(CH₃COO)₄ and Pt(C₄H₇)₂ with SiO₂ surface (dotted line) and SiO₂ (solid line). Vertical lines illustrate coordination peaks of platinum (—) and lead (---)

RAD Data. The RAD curve of the (Pb + Pt)/SiO₂ catalyst reduced at 600 °C (Fig. 1) demonstrates an increased (compared with the support) electron density at interatomic distances of the face-centered cubic structure (FCC) of platinum ($r = 2.78, 3.92$ and 4.82 \AA) and at distances which can be attributed to the Pb-Pt bonds in the FCC structure of metallic lead or in the structure of Pb-O ($r = 3.50$ and 4.95 \AA). In addition, the peak intensity corresponding to the first coordination sphere of platinum, contributes an interatomic distance of $r = 2.9 \text{ \AA}$, which can be attributed to the Pt-Pb bond in the Pt₃Pb particles. A comparison between experimental and theoretical areas under the coordination peaks indicates that the size of metal particles is about 10 \AA and the content of particles of metallic or lead oxide forms is no more than 30% of its total content in the catalyst.

XPS Data. The electronic state of platinum or lead is determined by the method of (Pb + Pt)/SiO₂ preparation. In the catalyst reduced at 600 °C and prepared via SiO₂ impregnation by an aqueous solution of H₂PtCl₆ and Pb(NO₃)₂, the bond energy (E_b) of Pt 4f_{7/2} is 71.2 eV (Fig. 2), which is close to the value obtained for metallic platinum [2]. The E_b of Pb 4f_{7/2} slightly changes upon reduction, hence

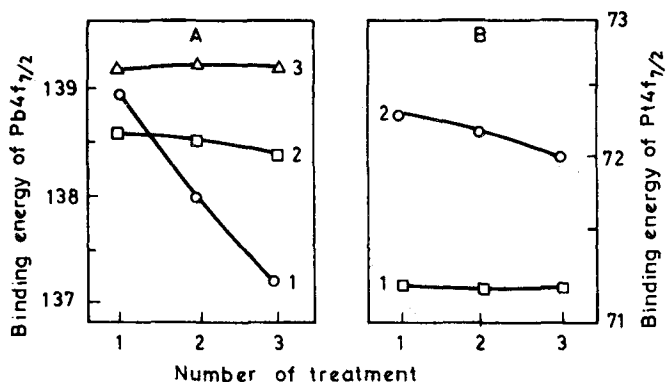


Fig. 2. Binding energies of Pb 4f_{7/2} (A) and Pt 4f_{7/2} (B) after various treatments of the catalysts. A: 1 - sample prepared through Pb(OOCCH₃)₄ and Pt(C₄H₇)₂, 2 - through Pb(NO₃)₂ and H₂PtCl₆, 3 - through Pb(OOCCH₃)₄, B: 1 - sample prepared through Pb(OOCCH₃)₄ and Pt(C₄H₇)₂, 2 - through Pb(NO₃)₂ and H₂PtCl₆. Treatments of the catalysts: 1 - unreduced samples, 2-3 - samples heated in H₂ at 300 and 600 °C, respectively

the lead in the impregnation catalyst (Pb + Pt)/SiO₂ treated with hydrogen at 600 °C is in an oxidized state, and probably does not interact with the supported platinum, in contrast to the platinum-lead catalyst prepared via decomposition of SiO₂ - supported platinum and lead complexes (Fig. 2). Hydrogen treatment of this catalyst decreases the E_b of Pb 4f_{7/2} to the value typical for metallic lead (137 eV /3/), and its platinum is in an electron-deficient state (E_b Pt 4f_{7/2} = 72.0 eV). It should be noted that without platinum (Pb/SiO₂ prepared via interaction between Pb(CH₃COO)₄ and SiO₂ surface) E_b Pb 4f_{7/2} changes slightly after reduction.

In discussing the possible mechanism for the action of lead in the catalysts prepared via decomposition of supported Pt and Pb complexes, one should take into account the following experimental results:

1. The presence of ultradisperse metal particles in the reduced catalyst (according to electron microscopic data, their predominant size is 6-9 Å.

2. Preservation of the chemical bond between part of the bonded lead ions and the SiO_2 surface after catalyst reduction (IR spectroscopy).

3. Variations in the electronic state of Pt and Pb in the reduced $(\text{Pb} + \text{Pt})/\text{SiO}_2$ catalyst, as compared with Pt/SiO_2 and Pb/SiO_2 (XPS data).

4. The presence of interatomic distances typical for Pt-Pt, Pb-Pt and Pb-Pb in the RAD curve.

The data obtained can be interpreted in terms of a model involving stabilization of Pt and Pb atoms on Pb(II) ions bonded to the SiO_2 surface, with the formation of ultradisperse Pt, Pb and Pt-Pb particles.

A chemical bond in these surface formations between metal atoms and lead ions bonded to the support is a possible reason for the stability increase of the supported metal against sintering.

The state of Pt and Pb in reduced $(\text{Pb} + \text{Pt})/\text{SiO}_2$ catalysts prepared via bonding of metal complexes significantly differs from their state in impregnation catalysts. Catalysts of a similar composition prepared via SiO_2 impregnation by aqueous solutions of inorganic metal compounds, may contain particles of metallic platinum and lead oxide (XPS data) and coarse particles of Pt-Pb alloys /4/.

As a result of interaction with lead, the adsorptive and catalytic properties of platinum change. Thus the amount of hydrogen desorbed in the temperature range of 30 to 600 °C decreases from 0.7 H/Pt to 0.15 H/Pt, upon going from Pt/SiO_2 to $(\text{Pb} + \text{Pt})/\text{SiO}_2$, though the latter has the highest dispersity. The nature of change in the catalytic properties of Pt in platinum-lead systems prepared by bonding metal complexes, is in many ways similar to that observed for Pt-Sn systems, wherein platinum is stabilized by interaction with tin surface ions /5/. In the presence of lead, the sensitivity of platinum to the poisoning effect of the reaction medium and the hydrogenolysis of C-C bonds in hydrocarbons decreases.

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