Platinum catalysts on various substrates

Ph.D. Pinchuk O.A.[1], Ph.D. Bryuhanov A.IU.[2],
Yasenko E.A. [2], , Chelibanov I.V. [2]

[1] Faculty of Cryogenic Engineering, ITMO University,
St.- Petersburg, Russia
[2] JSC “OPTEC”, St.- Petersburg, Russia

April 2021

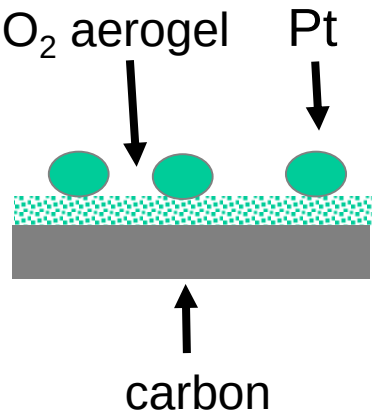
Preparation of Pt/(C–SiO2) catalysts

Pt catalysts → metallic platinum
Pt catalysts → nanoparticles

Pt catalysts are widely used in various industries and scientific fields.

Improvement of thermal stability in Pt/C catalysts

Use of silica for
- Protection of carbon support
- Prevent Pt nanoparticle growth / aggregation



1 Pinchuk O.A. Aubuchon S.R., Marks C., Dominey R., Dundar F., Deniz O.F., Ata A., Wynne K.J. // Fuel cells. 2009. V. 9. № 5. P. 554–561.

2 Pinchuk O.A. Dundar F., Ata A., Wynne K.J. // International Journal of Hydrogen Energy. V. 37. Issue 3. February 2012. P. 2111–2120

Sol-gel deposition of SiO_x

Two step process:

- Deposition of SiO_x on carbon

$$\equiv Si–OCH_3 + H_2O \rightarrow \equiv Si–OH + CH_3OH$$
$$\equiv Si–OCH_3 + \equiv Si–OH \rightarrow \equiv Si–O–Si\equiv + CH_3OH$$
$$\equiv Si–OH + HO–Si\equiv \rightarrow \equiv Si–O–Si\equiv + H_2O$$

Sol-gel deposition of SiO_x

- Carbon (Vulcan XC-72)
- CH_3OH / H_2O
- Sonication, 1 h

↓

Stirring / TMOS

↓

Silica Deposition (4 days)

↓

Filtering, washing, drying (60°C, in vacuum)

↓

Powdering

- Carbon (Vulcan XC-72)
- CH_3OH / H_2O
- pH ≅ 2 (CH_3COOH-H_2O, HCl-H_2O)
- Sonication, 1 h

↓

Stirring / TMOS Hydrolyzes (3 h)

↓

pH ≅ 7 (NH_4OH-H_2O) Polycondensation (4 h)

↓

Filtering, washing, drying (60°C, in vacuum)

↓

Powdering ← Deposition - 9 h

Sol-gel method provides:

- homogeneous C-SiO_2 network
- controlled amount of SiO_2

Deposition of Pt on various support

- **Pt nanoparticles prepared from reduction of H_2PtCl_6**
- **$NaBH_4$ as a reducing agent**
- **Pt nanoparticles adsorption on various substrates**

- Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H. R.; Hyde, E. K. *Journal of the American Chemical Society* **1953**, *75*, 215.
- F. T. Awadalla et al., U.S. Pat. 5,304,233 (1994)

Deposition of Pt on ($C–SiO_2$)

Impregnation method

- Carbon / SiO_2
- $H_2PtCl_6 – H_2O$ (sonication)

↓

$NaBH_4$(aq) reduction

↓

Filtering, washing, drying (60 - 70°C)

↓

Drying at reduced pressure for 2 h, 60°C

↓

Powdering

↓

TEM, SEM

Colloidal method

- $H_2PtCl_6 – H_2O$
- $NaBH_4 – H_2O$

Reduction of Pt

→ DLS

↓

Carbon / SiO_2 , stirring, keeping 1 h

↓

Filtering, washing, drying (60 - 70°C)

↓

Drying at reduced pressure for 2 h, 60°C

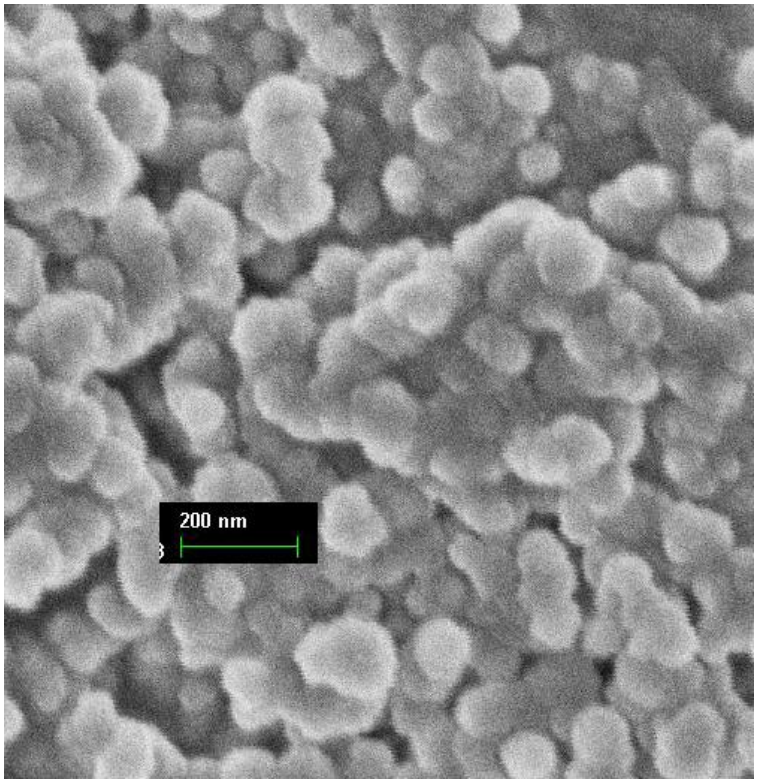
↓

Powdering

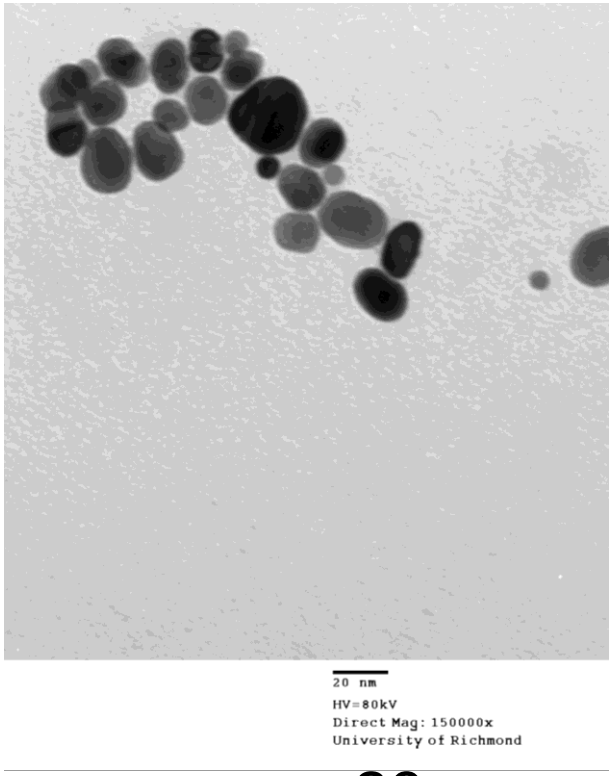
↓

TEM, SEM

Micrographs for SiO_2 aerogel and (SiO_2 aerogel + Pt)



SiO_2 aerogel



20 nm

SiO_2 aerogel + Pt

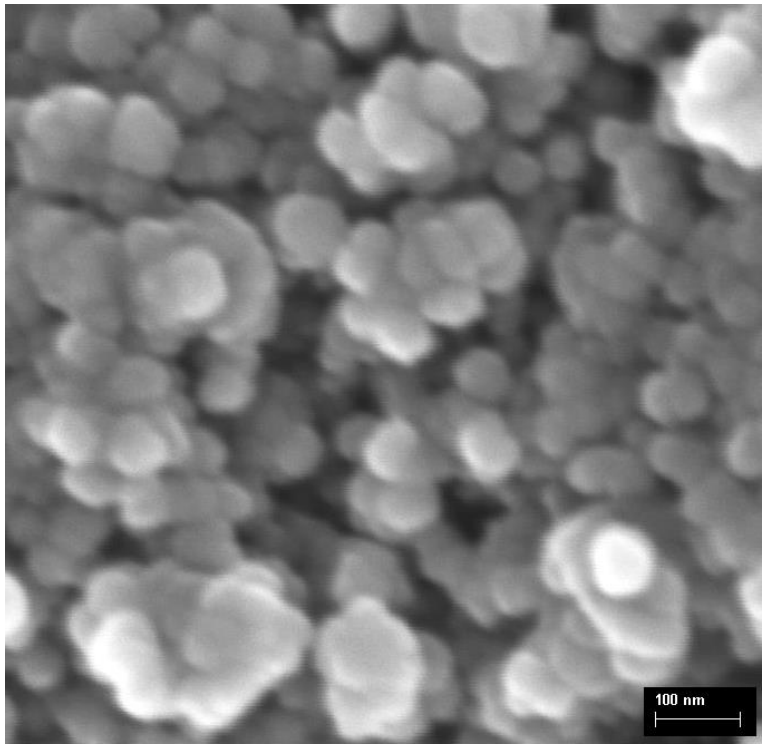
SEM (Zeiss Supra 55)

Deposition of Pt on TiO_2

- Pt nanoparticles prepared from reduction of H_2PtCl_6
- Deposition of platinum on TiO_2

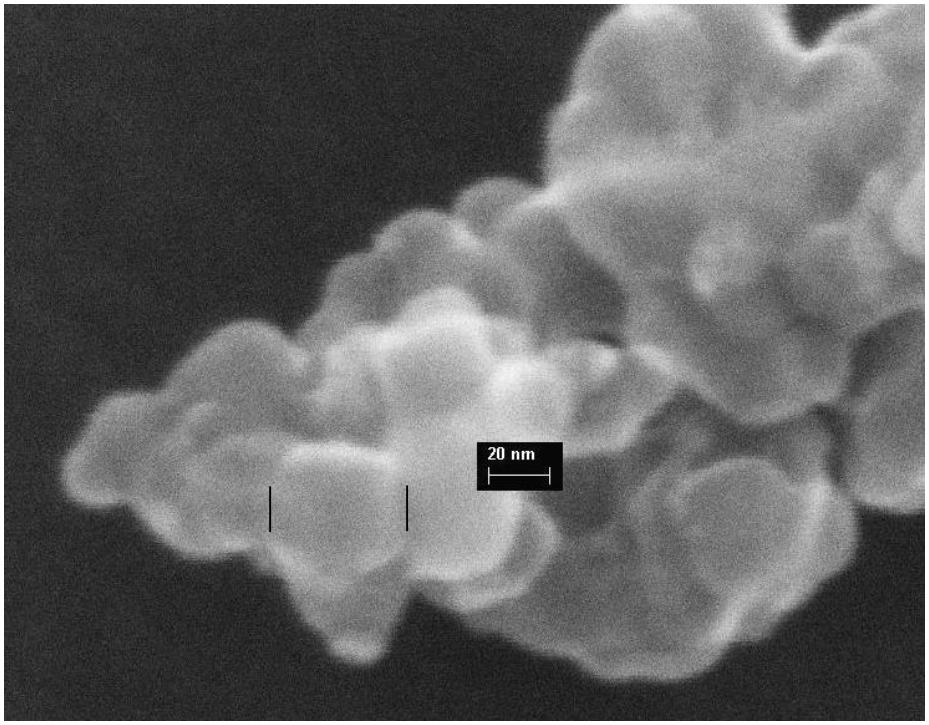
The Raman spectra of TiO_2 and (TiO_2-Pt) showed that the spectrum of the composite (TiO_2–Pt) does not contain bands characteristic of TiO_2, which indicates a uniform coating of the surface of the TiO_2 particles with Pt nanoparticles.

Micrographs for TiO_2 and (TiO_2 + Pt)



TiO_2 (Degussa Company)

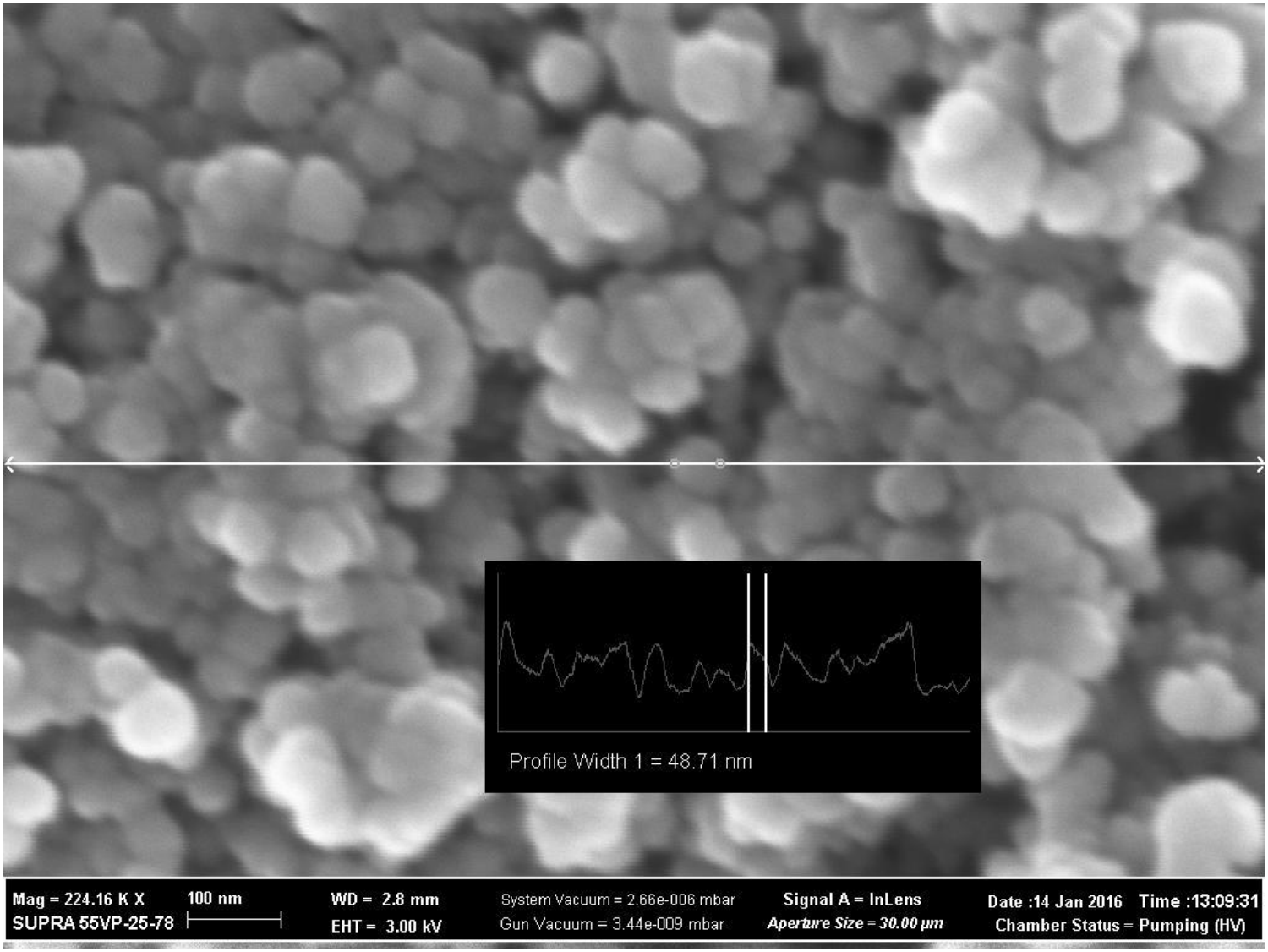
SEM



48 nm

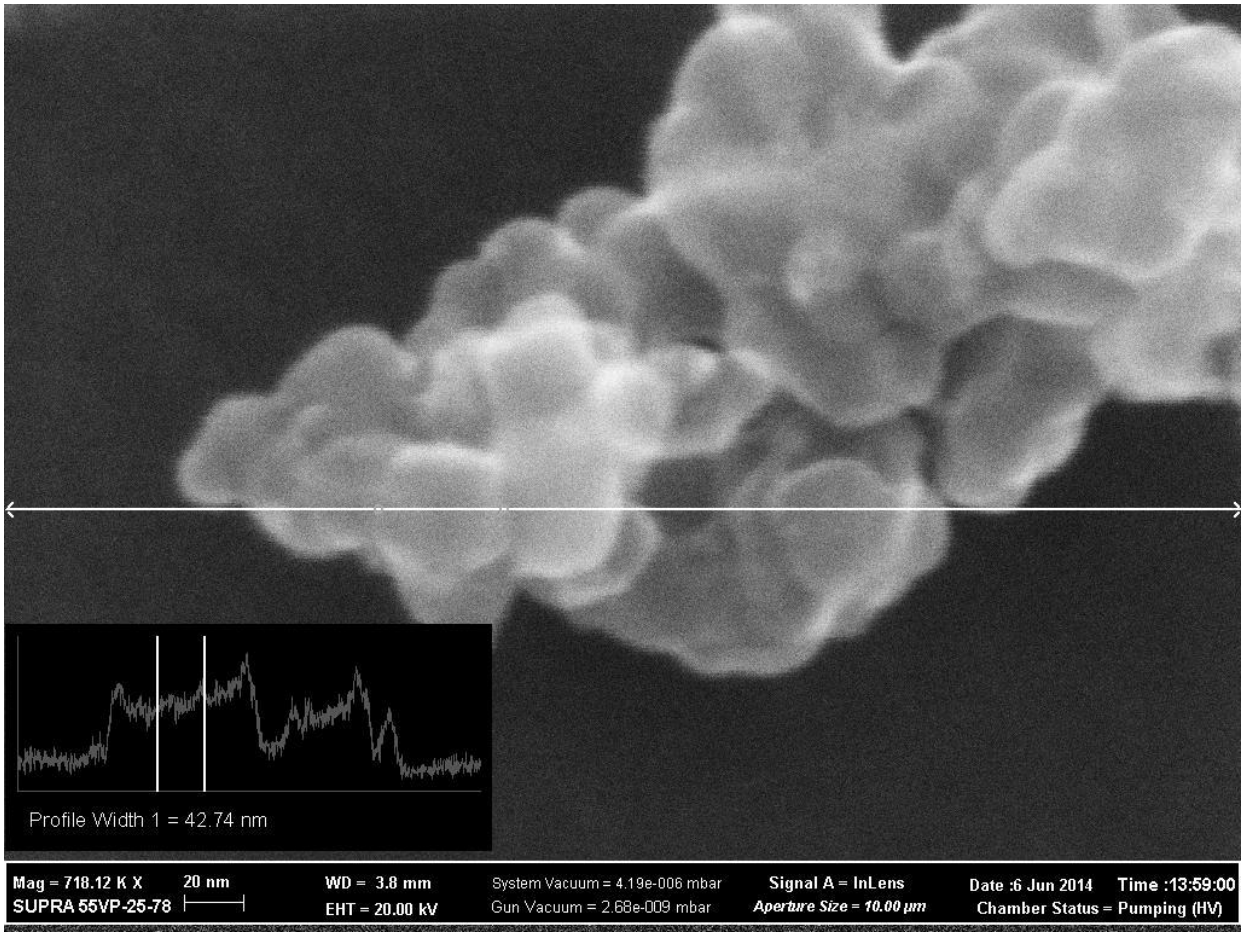
TiO_2 +Pt

SEM


Profile Width 1 = 48.71 nm
Mag = 224.16 K X
SUPRA 55VP-25-78
100 nm
WD = 2.8 mm
EHT = 3.00 kV
System Vacuum = 2.66e-006 mbar
Gun Vacuum = 3.44e-009 mbar
Signal A = InLens
Aperture Size = 30.00 µm
Date :14 Jan 2016 Time :13:09:31
Chamber Status = Pumping (HV)

TiO2

TiO2 +Pt

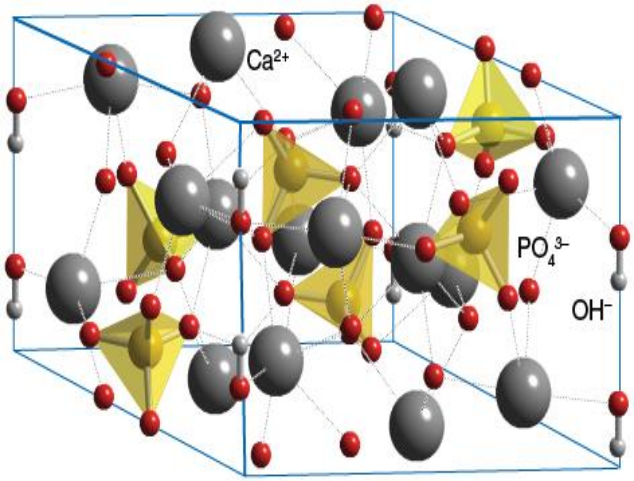

Profile Width 1 = 42.74 nm
Mag = 718.12 K X
20 nm
SUPRA 55VP-25-78
WD = 3.8 mm
EHT = 20.00 kV
System Vacuum = 4.19e-006 mbar
Gun Vacuum = 2.68e-009 mbar
Signal A = InLens
Aperture Size = 10.00 µm
Date :6 Jun 2014
Time :13:59:00
Chamber Status = Pumping (HV)

Deposition of Pt on HA

Synthesis of Hydroxyapatite (HA)

$$10Ca(NO_3)_2+6(NH_4)_2HPO_4+8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2+20NH_4NO_3+6H_2O$$

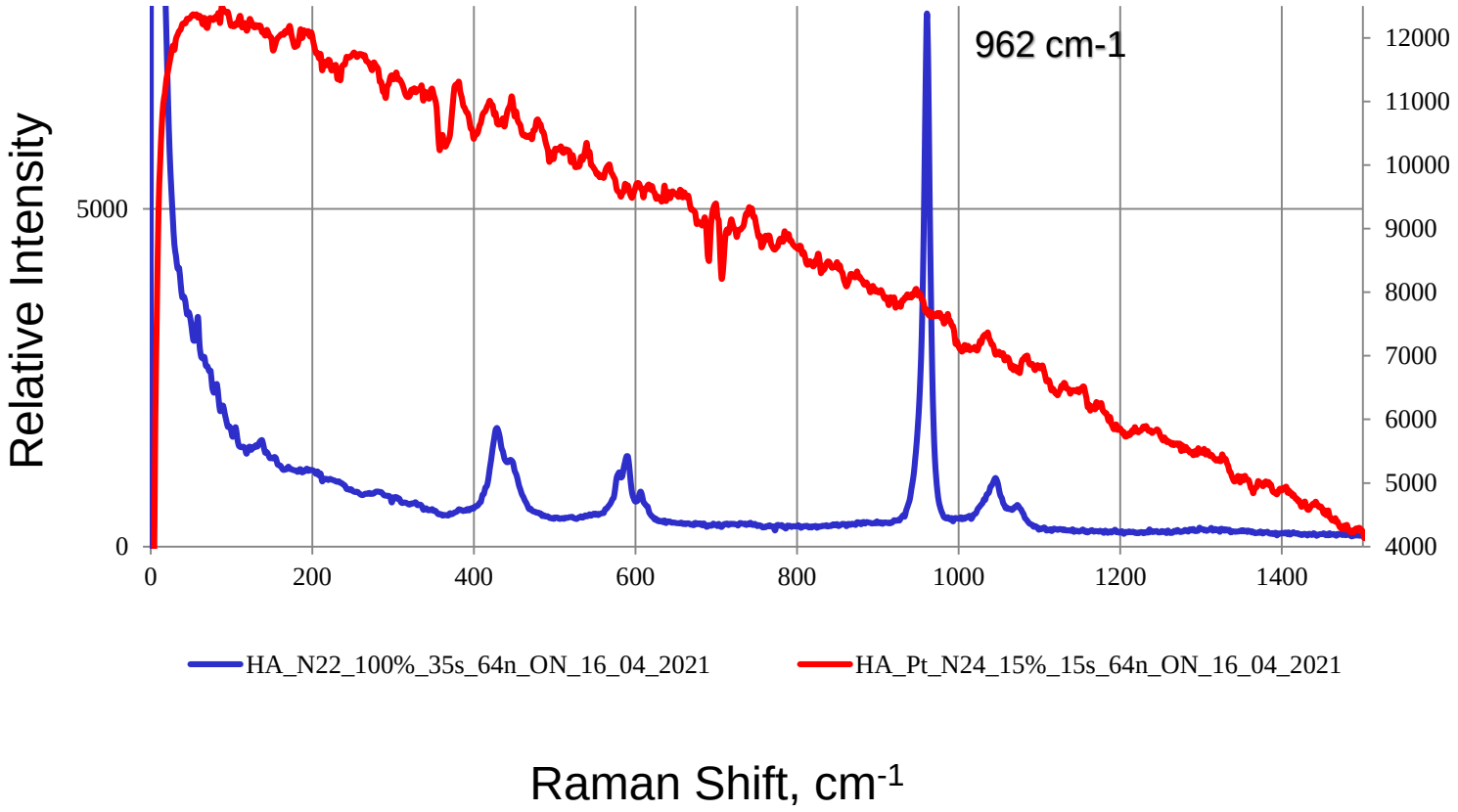
Solid phase — fine suspension



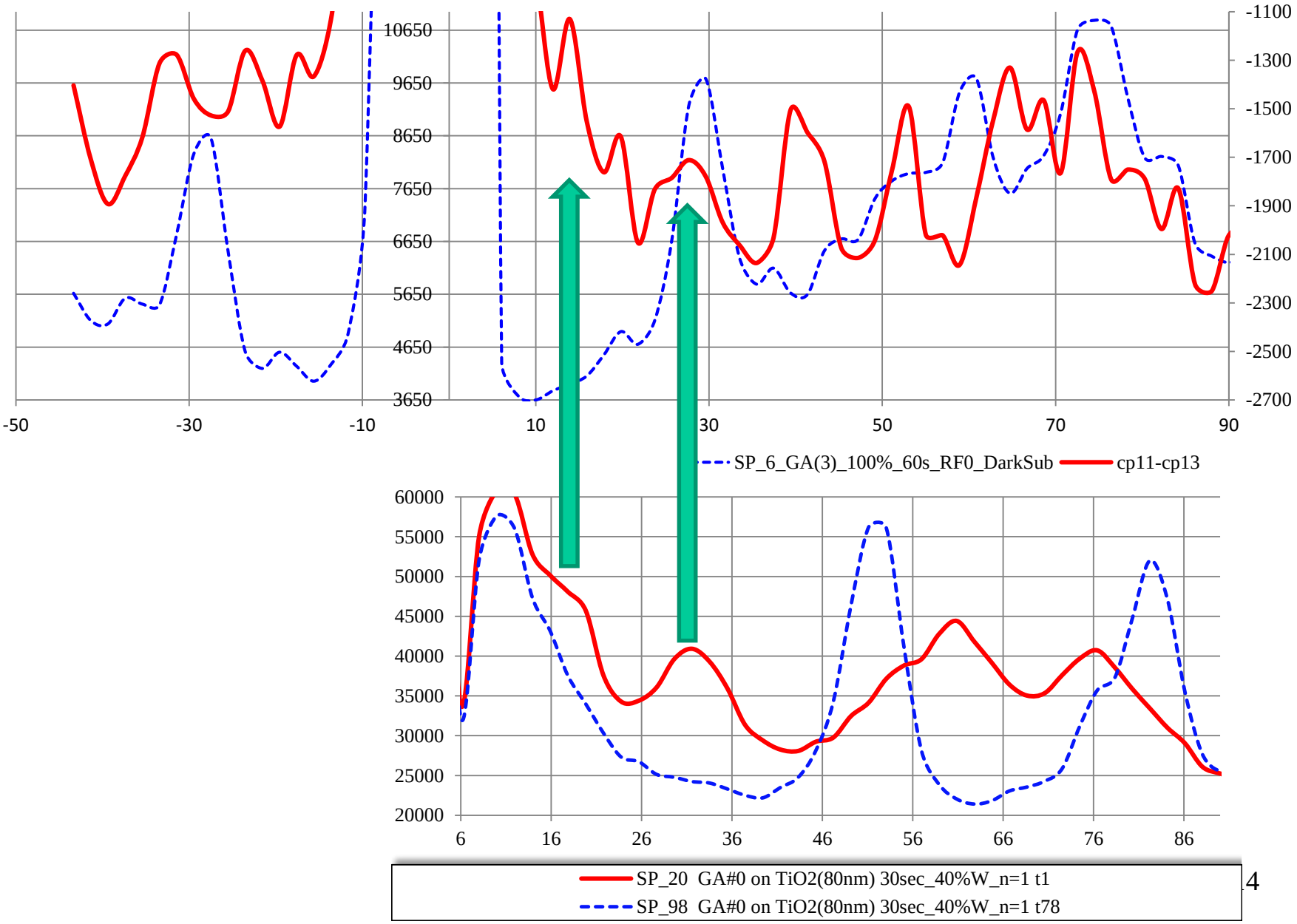
$Ca_{10}(PO_4)_6(OH)_2$

1 Khamova T.V., Frank-Kamenetskaya O.V., Shilova O.A., Chelibanov V.P., Marugin A.M., Yasenko E.A., Kuz'mina M.A., Baranchikov A.E., Ivanov V.K. // Crystallogr Rep. 2018. V. 63(2). P. 254–260.
2 Dorozhkin S. V. // Biology and Medicine J. Materials. 2009. T. 2.

Raman spectra of HA and (HA + Pt)



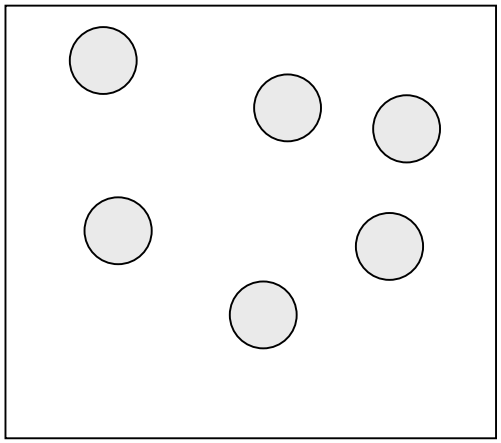
Formation of a Gallic Acid complex on the Hydroxyapatite surface



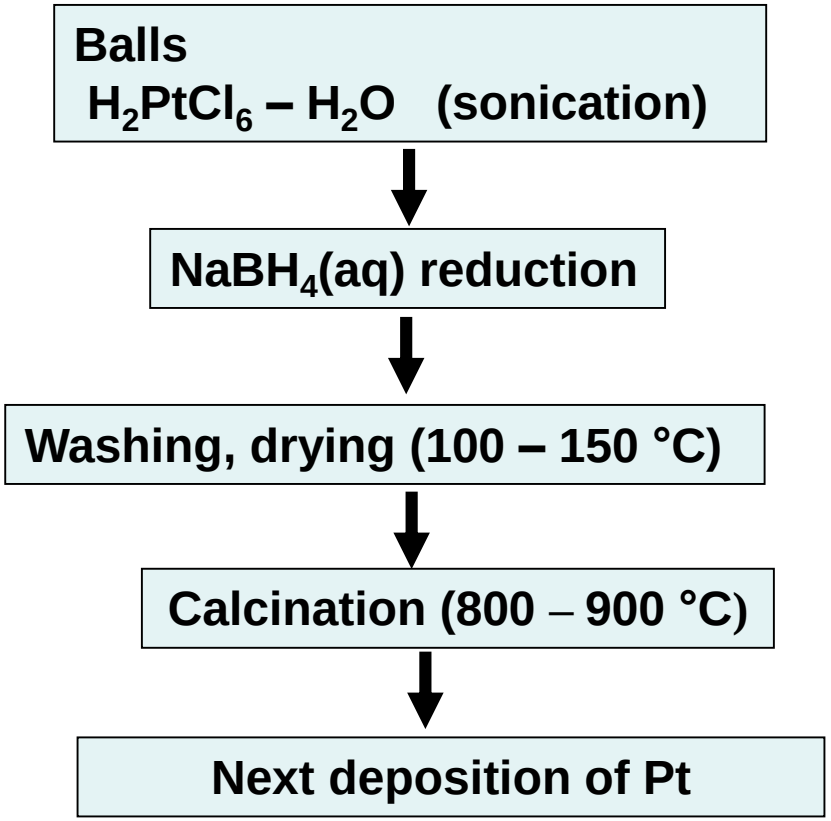
Deposition of Pt on porcelain balls

The reaction apparatus of gas analyzers usually uses backfills made of bulk materials of sufficiently large size for the free passage of gases through the apparatus.

Porcelain balls



Diameter — 3 mm.



The resulting catalyst is characterized by a uniform coating of the surface of the PT.

Deposition of Pt on porcelain balls

- The catalytic activity was tested using an atmospheric air analyzer GAMMA-ET chromatograph.
- Hydrocarbons have low chemical activity, especially methane.
- The catalyst was tested in air, which was additionally injected with a certain amount of methane.

The stainless steel reactor was filled with the catalyst, heated to 500 °C, and air containing methane (C = 150 ppm) was passed through the reactor).

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Tests have shown good catalytic activity (≈98 %) of the resulting catalyst.

Conclusions

Methods for obtaining new composite materials by deposition of platinum nanoparticles on various support are presented.

The obtained materials have a field of rational use.