Research Journal of Chemical Sciences ______________________________ ISSN 2231-606X
Vol. **2(6),** 50-54, June **(2012)** *Res.J.Chem.Sci.*

Preparation and activity of Pt (Pd)/WP_2O_7 catalysts for H_2 Oxidation

***Lisnyak V.V.[1], Safonova V.V.[1], Ischenko E.V.[1], Stratiichuk D.A.[2], Boldyrieva O.Yu.[1] and Yatsymyrskyi A.V.[1]**
[1]Kyiv National Taras Shevchenko University, 01601 Kyiv, UKRAINE
[2]V.N. Bakul Institute for Superhard Materials, 04074 Kyiv, UKRAINE

Available online at: www.isca.in
(Received 21st March 2012, revised 26th March 2012, accepted 27th March 2012)

Abstract

WP_2O_7 prepared by convenient technique was used as a support for platinum group metals. WP_2O_7, Pt/WP_2O_7 and Pd/WP_2O_7 were characterized by powder X-ray diffraction, Ar physisorption, SEM-EDX, and were tested in the H_2 oxidation reaction. The activity of Pt/WP_2O_7 and Pd/WP_2O_7 catalysts was compared with that of Pt/Al_2O_3 and Pd/Al_2O_3 catalysts containing the same amount of supported platinum metals. It was shown that the Pt/WP_2O_7 and Pd/WP_2O_7 catalysts exhibit enhanced activity attributed to synergistic effect realizes between Pt(Pd) metal and WP_2O_7 phase.

Key words: hydrogen oxidation, WP_2O_7, catalytic activity, supported platinum group metals, SEM-EDX

Introduction

Biodegradation[1], biofiltration[2] and chemical reactions catalyzed by solids of different nature[3-5] are among known routs used to prevent polluting the environment with different toxic chemical substances. It is known that oxidation of hydrogen (H_2), the later yields the water as only the one product, is the most prominent environmentally benign way for an energy production[6]. However, the H_2 emissions at the fuel operations can cause accumulation of high concentrations of flammable gas mixtures in the containment vessel. The same scenario can realize in reactor blocks of nuclear power plants at accidents caused the failure of the reactor pressure container[7]. The catalytic recombination (oxidation) is one of the ways can be used to prevent accumulation of H_2[8]. The catalysts for this process should characterize by a very high activity, functioned at low temperatures and at low H_2 concentrations and cannot be affected by the presence of water. Pt or cheaper Pd metals supported over various oxide carriers are known catalysts can be used for catalytic oxidation of H_2. However, phosphates resistant to different reaction media (e.g. reducing agents, solvents, acids and alkali) can be utilized instead of oxides as supports. The latter could allow achieving desired characteristics and ensuring a reasonable stability of catalytic properties. Among series of different phosphates, the tungsten (IV) diphosphate can be considered as a promising support for platinum group metal catalysts due to its proton exchange properties[9] and a certain catalytic activity in the oxidation reactions[10]. So, in the present communication we report the preparation, characterization and catalytic activity towards H_2 oxidation of Pt and Pd metals supported over WP_2O_7.

Material and Methods

Preparation of catalysts: The starting materials was a mixture of WO_3 and $(NH_4)_2HPO_4$, taken with the molar ratio of 1:4. The mixture was grounded and put into a porcelain crucible. The mixture was heated using an electric furnace at two sequential temperatures. At first temperature, about 873 K, the mixture was held for 2 h until $(NH_4)_2HPO_4$ decomposed and reacted with WO_3. The resulted product was cooled to r.t. and bi-distilled water was added. This mixture was heated up to 673 K and held with stirring for 2 h. The dark solid obtained was dissolved in hot water to recover microcrystalline powder. The microcrystals were filtered and dried in thermo-programmed desiccator at 373 K for 6 h. For preparation of Pt or Pd metal supported catalysts, the microcrystalline powder (0.5 g) was impregnated with the preset quantity of 8 mM aqueous solution of H_2PtCl_6 or $PdCl_2$ in order to reach 0.5 wt. % load of Pt or Pd. The solutions were evaporated from the samples and obtained powder was dried in thermo-programmed desiccator at 373 K for 1 h. The powders impregnated with Pt or Pd were packed within quartz wool layers inside a flow reactor and were reduced in a gas mixture H_2:Ar = 10:90 vol. % (GSV = 10^{-4} m^3/min) at 673 K for 1 h. The reduced samples, denoted further as 0.5% Pt/WP_2O_7 and 0.5% Pd/WP_2O_7, were cooled and stored under ambient conditions. To compare these samples with traditional Pt(Pd)-catalysts, 0.5 wt. % load of Pt or Pd metals were supported over α-Al_2O_3 (S_{sp} = 3.6 m^2/g) in the same way as reported above. These catalysts are denoted further as 0.5% Pt/Al_2O_3 and 0.5% Pd/Al_2O_3.

Characterization of catalysts: The specific surface area (S_{sp}) was determined by means of Ar physisorption at 77 K. W and P content in the microcrystalline powder obtained was determined by X-rays fluorescence (Philips X'Unique II 1480). The powder X-ray diffraction (PXRD) patterns of grounded samples were collected using a Philips PW 3710 diffractometer (filtered $CuK\alpha_{1,2}$-radiation, λ = 1.7903 Å). The phase identification was performed by matching experimental PXRD patterns to the powder diffraction file (PDF)[11]. The morphology and elemental analysis of the catalysts were determined using a Jeol XA 88002 scanning electron microscope (SEM) equipped with a Oxford Inca 350 energy dispersive X-ray (EDX) spectrometer.

Catalytic activities: The catalytic activity in H_2 oxidation was examined in a flow U-type reactor at atmospheric pressure. 0.5 g of the sample powder (fraction 0.2–0.5 mm) was packed between layers of quartz wool and formed a uniform catalyst bed inside a glass tube of the reactor. The reactor with the sample within was immersed into a bath of a thermostat. The thermostat was programmed to heat and to cool the bath according to a defined procedure in the temperature range 273–380 K. A tube furnace was used to heat the reactor up to 800 K.

The temperature of the catalyst bed is measured by a thermopile situated in the center of the bed and connected to a digital displayer. The composition of the reaction gases mixture was monitored in the reactor inlet to a mixture H_2:O_2:Ar = 1:20:79 vol.%, GSV = 10^{-4} m^3/min. At the catalytic tests, the reaction temperature was increased from 273 K to whatever temperature was necessary to achieve complete H_2 conversion ($X(H_2)$) to H_2O. The first temperature increase refers to the pretreatment stage. This procedure was then repeated for at least two times in order to reach a steady temperature at 100% H_2 conversion ($T_{100\%}(H_2)$), which was used as a measure of the catalytic activity. The reactor outlet was sampled sequentially and gas chromatography analysis of the composition of the effluent gas mixture was achieved in a molecular sieve 5A packed column of a Shimadzu GC-2014 chromatograph (Ar carrier gas).

Results and Discussion

The X-rays fluorescence results for the microcrystalline powder obtained were as follow; found: W, 48.8%; P, 16.3%; theoretical: W, 51.4%; P, 17.3% for WP_2O_7. The PXRD patterns of the powder of WP_2O_7, 0.5% Pt/WP_2O_7 and 0.5% Pd/WP_2O_7, the latter is depicted on figure-1, are similar and typical for cubic diphosphates MP_2O_7[11, 12].

No crystalline phases of metallic Pt or Pd[11] were found from the PXRD patterns due to the metals low concentration in the catalysts, which is below the instrument detection limit. The S_{sp} values of the samples 0.5% Pt/Al_2O_3 and 0.5% Pd/Al_2O_3 are the same as for the initial α-Al_2O_3. S_{sp} reaches the value of 2.0 m^2/g for 0.5% Pt/WP_2O_7 and for 0.5% Pd/WP_2O_7. Pure WP_2O_7 with S_{sp} = 1.0 m^2/g shows no prominent activity in the H_2 oxidation at low temperature as it is shown in figure-2. The full symbols in the figure-2 correspond to $X(H_2)$ obtained from the measurements on heating, the open ones on cooling.

The $X(H_2)$ of 5 and 25% reach over WP_2O_7 at 520 K and 725 K, correspondingly. Figure-3 show that the temperature of a certain H_2 conversion ($T_{X(H_2)}$) over 0.5% Pd/WP_2O_7 is about on 40 K lower than that over 0.5% Pt/Al_2O_3. The temperature hysteresis of $X(H_2)$, can be seen on the figure-3, is typical for Pt or Pd metals supported on oxides[13].

Figure-4 shows that $T_{X(H_2)}$ over 0.5% Pd/WP_2O_7 is 40–50 K lower than over 0.5% Pd/Al_2O_3.

It is clearly seen from these figures that 0.5% Pt/WP_2O_7 and 0.5% Pd/WP_2O_7 catalysts show excellent H_2 conversion with $T_{100\%}$ = 335–338 K, their activity in H_2 oxidation is close. The temperature hysteresis loop becomes wider if compare its width for the platinum metals supported on WP_2O_7 and on Al_2O_3. The platinum group metals supported over WP_2O_7 are more active in H_2 oxidation than supported over inert carrier Al_2O_3. So, it could be conclude that enhanced activity is attributed to synergistic effect between Pt (Pd) metal and WP_2O_7.

The impregnation method[14] used for the platinum metals (Pt, Pd) supporting on WP_2O_7 and α-Al_2O_3 gives a wide spectrum of supported metals particles from nanosized to micrometric. Pt metal particles of different dimensions were registered by EDX Pt Lα1 mapping, typical mapping of a part of catalyst surface can be seen on figure-5.

Non-uniform distribution of Pt or Pd confirms by EDX data registered from selected surface area. For example EDX spectra from areas 1 to 6, depicted on the figure-5, show from 0.15 to 0.65 at. % Pt. The same observation is clear also for Pt or Pd supported on α-Al_2O_3. So, the effect of the platinum metals dimension on the catalytic activity could not be clearly estimated from the data.

Conclusion

WP_2O_7 was prepared by convenient technique was used as support for platinum group metals. The supported catalysts were characterized by PXRD, SEM-EDX, Ar physisorption, and tested in the H_2 oxidation. The Pt/WP_2O_7 and Pd/WP_2O_7 catalysts show higher activity than traditional Pt and Pd catalysts supported over inert carrier α-Al_2O_3. Enhanced activity of the Pt/WP_2O_7 and Pd/WP_2O_7 catalysts is attributed to the synergistic effect between platinum metal (Pt or Pd) and WP_2O_7.

References

1. Rahul, Mathur A.K. and Balomajumder Ch., Biodegradation of Waste Gas containing Mixture of BTEX by B. Sphaericus, *Res. J. Chem. Sci.*, **1(5),** 52-60 **(2011)**
2. Thakur P.K., Rahul, Mathur A.K. and Balomajumder Ch., Biofiltration of Volatile Organic Compounds (VOCs) – An Overview, *Res. J. Chem. Sci.*, **1(8),** 83-92 **(2011)**
3. Sonawane V.Y., Mechanistic study of chromium (VI) catalyzed oxidation of benzyl alcohol by polymer supported chromic acid, *Res. J. Chem. Sci.*, **1(1),** 25-30 **(2011)**

4. Pandey B. and Fulekar M.H., Nanotechnology: Remediation Technologies to clean up the Environmental pollutants, *Res. J. Chem. Sci.*, **2(2),** 90-96 **(2012)**

5. Pandey Bh. and Fulekar M.H., Environmental Management - strategies for chemical disaster, *Res. J. Chem. Sci.*, **1(1),** 111-117 **(2011)**

6. Kotz J.C., Treichel P. and Townsend J.R., Chemistry and chemical reactivity, Interchapter: The chemistry of Fuels and Energy Recourses, Brooks/Cole, Belmont **(2011)**

7. Hewitt G.F. and Collier J.G., Introduction to nuclear power, Taylor Francis, London **(2000)**

8. Chakraborty A.K., Klatt K.-H., Konrad R., Rohde J. and Wenzl H., Catalyst for the removal of hydrogen from an atmosphere containing hydrogen, oxygen and steam, US Patent 5198405, March, **(1993)**

9. Jin Y.C., Yang L., Nishid M., Kanematsu W. and Hibino T., Partially proton-exchanged WP_2O_7 with high conductivity at intermediate temperatures, *Electrochem. Solid-State Lett.*, **13(11),** B123-B126 **(2010)**

10. Lesnyak V.V., Slobodyanik N.S., Yatsimirsky V.K. and Boldyreva N.A., Catalytic activity of tungsten phosphate (IV), (V), (VI) at carbon monoxide oxidation, *Stud. Surf. Sci. Catal.*, **130,** 3807-3812 **(2000)**

11. PDF-2 Data Base JCPDS-ICDD 2007. JCPDS International Centre for Diffraction Data: Newtown Square, PA, USA **(2007)**

12. Lisnyak V.V., Stoos N.V., Slobodyanik N.S., Belyavina N.M. and Markiv V.Ya., Crystal structure of a novel cubic pyrophosphate WP_2O_7, *J. Alloys Compd.*, **309(1),** 83-87 **(2000)**

13. Yatsimirskii V.K., Lesnyak V.V., Gut I.N. and Boldyreva O.Yu., Effect of Pt, Pd, and Cs^+ Additives on the Surface State and Catalytic Activity of WO_3 in Oxidation of Hydrogen, *Theor. Exper. Chem.*, **41(2),** 135-138 **(2005)**

14. Strizhak P.E., Trypolskyi A.I., Kosmambetova G.R., Didenko O.Z. and Gurnyk T.N., Geometric and electronic approaches to size effects in heterogeneous catalysis, *Kin. Catal.*, **52(1),** 128-138 **(2011)**

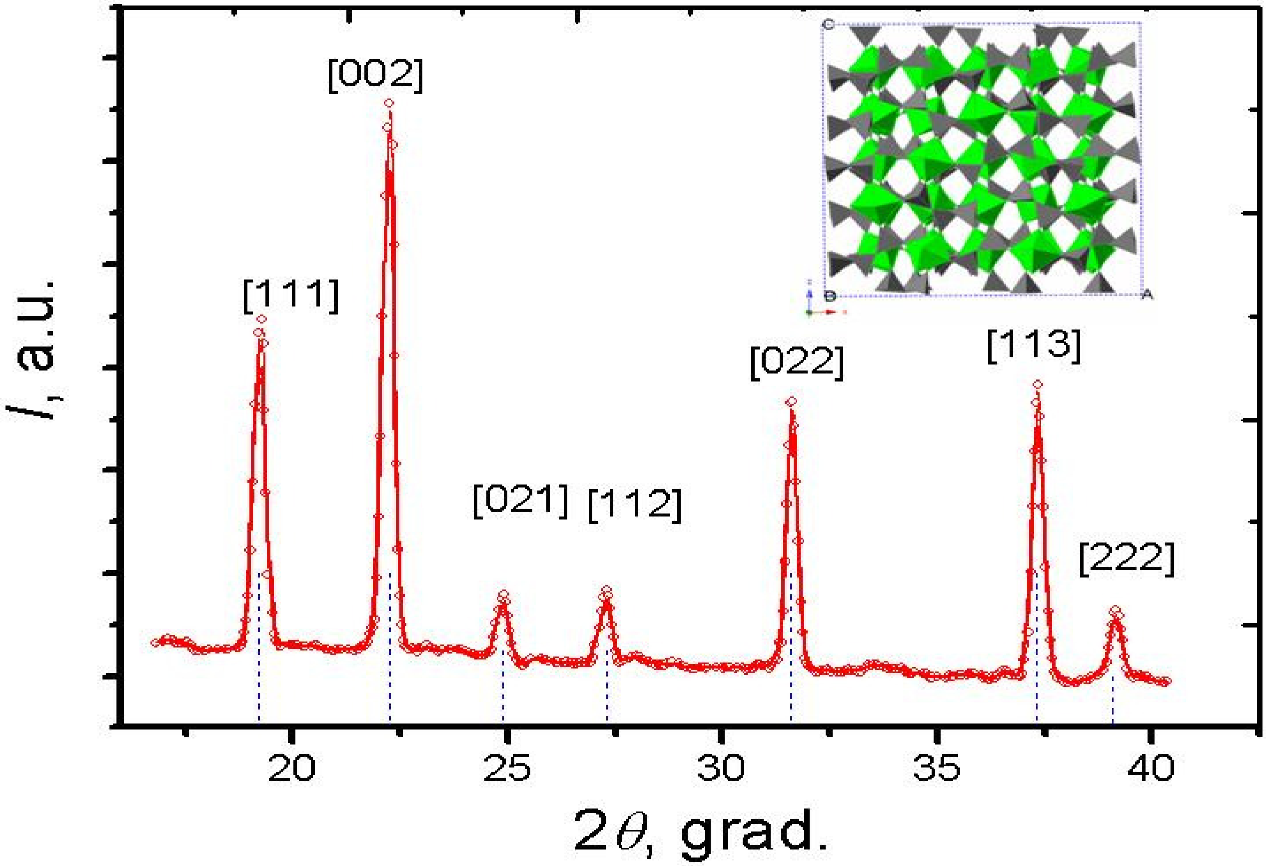

Figure-1

PXRD patterns of the 0.5% Pd/WP_2O_7 catalyst, the insert shows the perspective view of WP_2O_7 unit cell directed on [010]

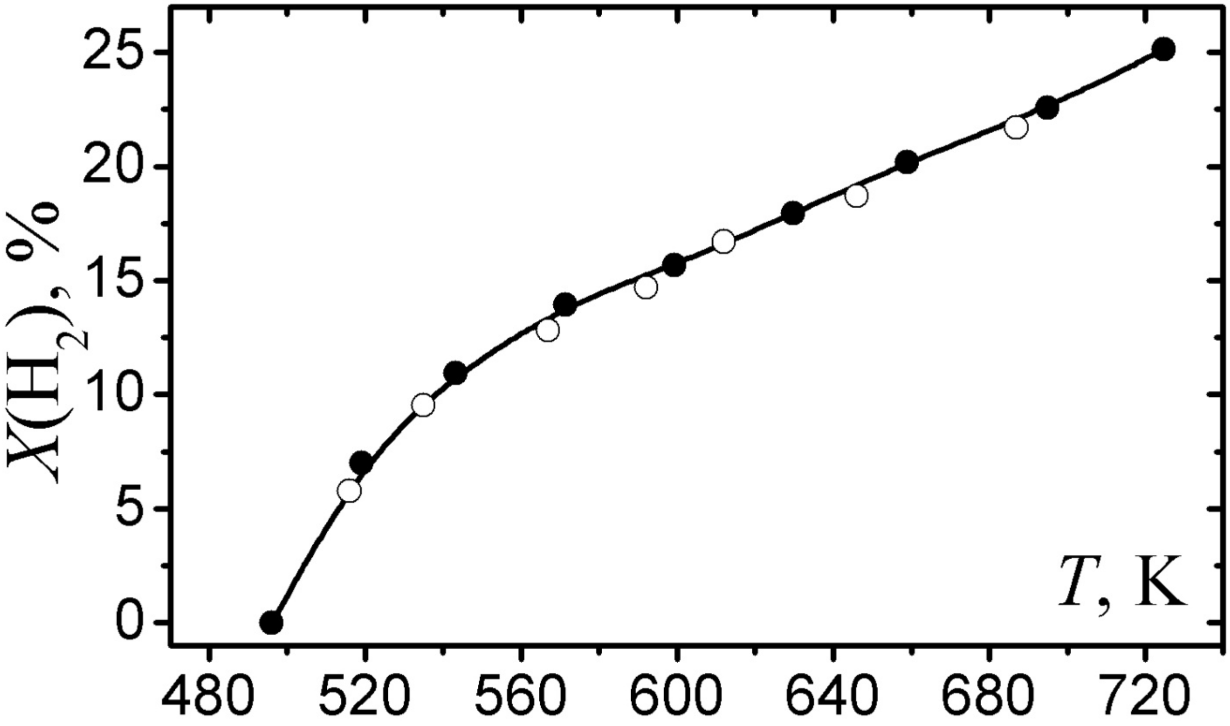

Figure-2
H_2 conversion over WP_2O_7 against the temperature

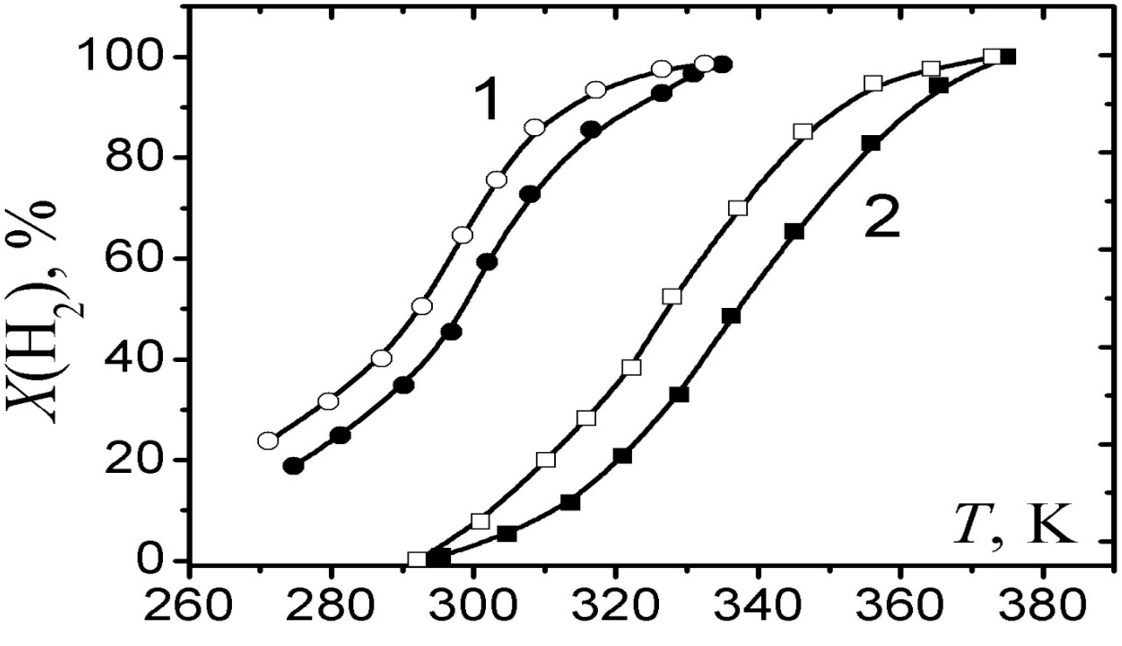

Figure-3
H_2 conversion against the temperature over catalysts: 1) 0.5% Pt/WP_2O_7, 2) 0.5% Pt/Al_2O_3

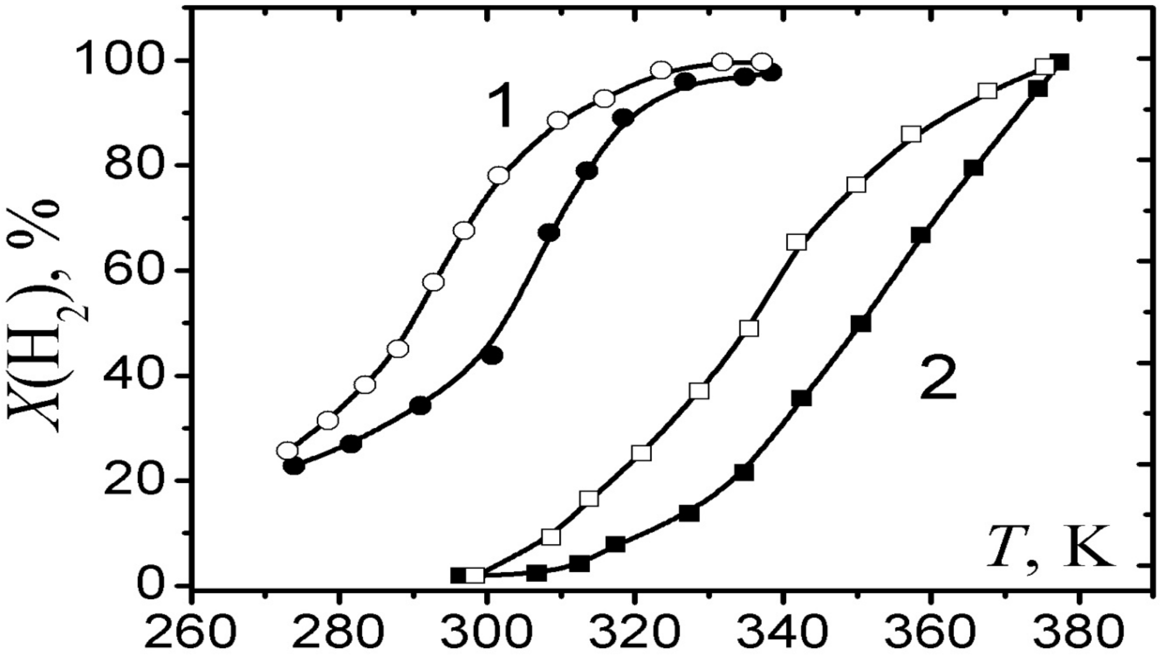

Figure-4
H_2 conversion against the temperature over catalysts: 1) 0.5% Pd/WP_2O_7, 2) 0.5% Pd/Al_2O_3

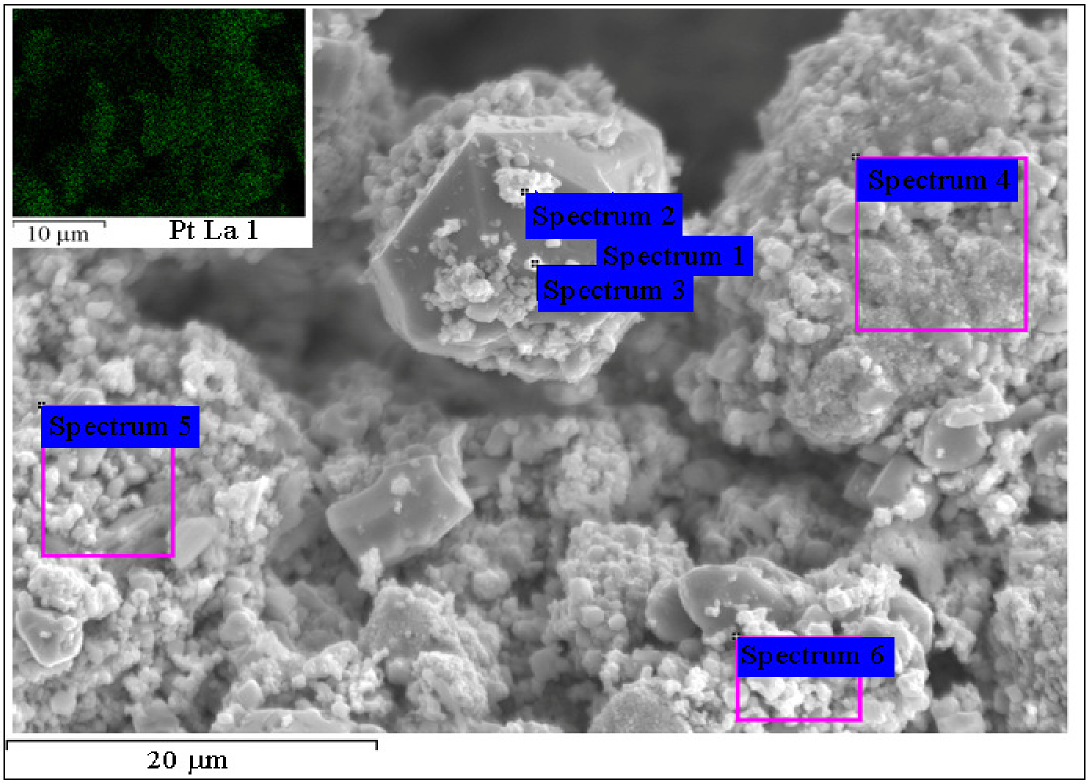

Figure-5
SEM-EDX microphotos of catalyst 0.5% Pt/WP_2O_7, the insert shows EDX Pt Lα1 mapping of surface