Pt, Pd Supported on Niobium Phosphates as Catalysts for the Hydrogen Oxidation

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Abstract

Niobium phosphates NbP_2O_7 and $NbPO_5$ were synthesized by using convenient synthetic routs. The catalysts, namely, Pt or Pd metals supported on NbP_2O_7 and $NbPO_5$, were prepared by the impregnation method and characterized by means of miscellaneous techniques. Activity measurements of the H_2 oxidation reaction were performed over PGM/NbP_2O_7, $PGM/NbPO_5$, and PGM/Al_2O_3 (PGM = Pt or Pd) catalysts, the latter were used for comparison reasons, in the gas mixture with oxygen excess ($H_2:O_2:Ar = 1:20:79$ vol.%). It was found that for catalysts with the same platinum group metal (PGM) loading of 0.5 wt. %, the catalytic activity of Pt and Pd supported on the niobium phosphates was higher than that of Pt and Pd supported on alpha-Al_2O_3, correspondingly. The results showed that the conversion of H_2 is dependent on chemical nature of supports, and the activity of the catalysts decreases in the order of $PGM/NbP_2O_7 > PGM/NbPO_5 > PGM/Al_2O_3$. The enhanced activity of Pt/NbP_2O_7 and Pd/NbP_2O_7 catalysts is attributed to the presence of Nb^{4+}/Nb^{5+} states in the NbP_2O_7. These states can promote the generation of easily reduced oxygen species, which are active in the catalytic H_2 oxidation.

Keywords: Hydrogen oxidation, niobium phosphates, catalytic activity, supported platinum group metal, XPS.

Introduction

The development of alternative energetic involves finding ways of fuel switching to biofuel[1,2], biogas[3] or H_2-sourced fuel[4,5] for restructuring of energy-intensive industries. It should be mentioned that from the economic point-of-view hydrogen fuel is the most promising alternative source of energy among available ones. However, the release of hydrogen and subsequent accumulation of hydrogen-oxygen flammable gas mixtures may occur at the operation of H_2-source engine. So, for safety reasons and acting in the paradigm of clean up technology[6,7], catalytic converters, that work with hydrogen-air gas mixtures at low temperatures and low concentrations of hydrogen, can be used to for recombination of leaks of hydrogen. For functioning of these converters new highly active catalysts for the oxidation of H_2 should be developed. The use of such catalyst in these converters could improve the recombination efficiency and could reduce the severity level of H_2 leakage to an acceptable level of risk.

Platinum group metals (PGM), in particular Pt or Pd, supported on Al_2O_3 and SiO_2 oxides, i.e. on the supports which are inactive for the red-ox reactions, are traditionally used as effective solid red-ox reactions catalysts. It is known that the chemical nature of the support significantly affects the catalyst performance, so, the selection of the support is crucial for successful design of efficient catalyst. Despite the large number of known catalytic systems[8,9], a relatively small number of transition metals phosphates (TMP) have been applied for design of the reduction or the total oxidation (combustion) catalysts. It could be found

from the literature, that $Pt/B_{1-x}Y_xPO_4$[10] and $Pt/AlPO_4$[11] catalysts show high activity in the reduction of NO to N_2 by hydrocarbons for gas mixtures with oxygen excess. The $(Pt/NbPO_x)/carbon$[12] and $Pt/FePO_x$[13,14] composites are efficient catalysts of the electrochemical reduction of oxygen. $Pt/FePO_4$[15] catalysts display prominent activity in the oxidation of methanol and CO as the product of the methanol selective oxidation. Among different TMP niobium phosphates, namely, $NbP_2O_{7.5}$, $Nb_{1.91}P_{2.82}O_{12}$ as P-deficient $Nb_{2-x}(PO_4)_3$ and α-$NbPO_5$, are of considerable interest to be used as supports for preparation of oxidation catalysts, as these niobium phosphates have a certain catalytic activity in the oxidative dehydrogenation reactions[16,17]. So, in this communication we report characterization and catalytic activity for H_2 oxidation of Pt, Pd supported on NbP_2O_7 and $NbPO_5$ ($NbOPO_4$) niobium phosphates, which were prepared by convenient synthetic routs.

Material and Methods

Preparation of catalysts: Niobic acid ($Nb_2O_5 \cdot nH_2O$) was obtained by hydrolysis rout[18]. Niobium acid was mixed with 85 wt. % H_3PO_4 to form slurry. This slurry was calcined at 1073 K for 3 h to prepare $NbPO_5$. NbP_2O_7 was synthesized from $Nb_6Cl_{14} \cdot 8H_2O$ and phosphoric acid[19]. 0.5 wt. % load of Pt or Pd metal was supported over $NbPO_5$ and NbP_2O_7. The same load of Pt or Pd was supported over α-Al_2O_3 ($S_{sp} = 3.6$ m^2/g), to be used for comparison. The supporting of platinum and palladium metals was performed as follows. The $NbPO_5$, NbP_2O_7 and α-Al_2O_3 powders were impregnated with the preset quantity of 8 mM aqueous H_2PtCl_6 or $PdCl_2$ solution. These solutions were

evaporated from the samples at 353 K and wet powders obtained were dried at 373 K for 1 h[20]. Dried powders of $NbPO_5$, NbP_2O_7 and α-Al_2O_3, which contain adsorbed Pt^{4+} or Pd^{2+}, were packed within quartz wool layers inside a continuous-flow U-type reactor and form a uniform catalyst bed. The packed in the reactor powders were reduced in a stream of hydrogen-argon gas mixture (10:90 vol. % H_2:Ar) at 673 K for 1 h. The reduced samples, denoted further as 0.5 wt. % $PGM/NbPO_5$, 0.5 wt. % PGM/NbP_2O_7 and 0.5 wt. % PGM/Al_2O_3, where PGM = Pt or Pd, were cooled and stored in a desiccator with P_2O_5 under ambient conditions.

Characterization of catalysts: The samples specific surface area (S_{sp}) was determined by means of Ar physisorption at 77 K. Nb and P element analyses were carried out on fused glass beads by X-ray fluorescence spectrometry (XRF) on a Phillips X'Unique PW1480 XRF spectrometer. The content of PGM in the samples was determined by inductively coupled plasma-mass spectrometry (ICP-MS) on an Agilent 7500 quadrupole ICP-MS instrument. The crystalline phases in the samples were identified by matching experimental powder X-ray diffraction (PXRD) patterns, which were collected using a Philips PW 3710 diffractometer (Cu Kα-radiation), to the powder diffraction file (PDF)[21]. XPS spectra of the catalysts were recorded using a Kratos AXIS spectrometer with a monochromated radiation source (Al Kα, hv = 1486.7 eV). It was considered that the Nb core level XP spectra are the sum of Nb^{5+} and Nb^{4+} valence levels. So, the Nb^{4+}/Nb^{5+} ratio originated from different amounts of Nb^{5+} and Nb^{4+} valence states in the Nb-containing catalysts was determined by deconvolution of the Nb core level XP spectra.

Catalytic activity: The catalytic tests were performed in the same continuous-flow reactors which were used for the PGM reduction in the H_2-Ar gas mixture. The fraction size of the catalysts powders was 0.2–0.5 mm; the mass of all catalysts was 0.5 g. The catalytic tests were done at an atmospheric pressure.

Analytical grade H_2, O_2 and Ar gases were used as inlet gases, which flow was controlled by calibrated mass-flow controllers. The total gas inlet was 0.1 L/min, containing 1 vol. % H_2, 20 vol. % O_2 (oxygen excess), rest Ar. The hydrogen and oxygen contents in inlet and outlet gas mixtures were determined on a gas chromatograph LHM 8MD (Yagot, Moscow, Russia). This chromatograph was equipped with thermal conductivity detector and with a steel column (Ø = 3 mm, 3 m) packed with SKT-active carbon. The temperature of the column, injector port, and conductivity detector was 100°C. Argon was used as a gas-carrier with a flow rate of 40 mL/min. The volume of the gas sample was 2 mL.

The catalytic activity in the H_2 oxidation was examined in the temperature range 273–380 K for the supported PGM catalysts and at 273–380 K for the supports. The temperature control at the catalytic tests was performed by means of a thermometer connected to a digital thermal sensor. The thermometer sensor was situated in the center of the packed catalyst bed to determine the temperature inside the catalyst layer. The reactor was gradually heated from 273 K to a temperature at which complete H_2 conversion ($X(H_2)$) was observed and then cooled down. This procedure was then repeated for at least three times in order to reach a steady temperature at a certain H_2 conversion ($T_{X\%}(H_2)$), which was used as a measure of the catalytic activity.

Results and Discussion

Nb and P content obtained by XRF confirms formation of $NbPO_5$ (Nb, 45.2%; P, 15.0%) and NbP_2O_7 (Nb, 34.2%; P, 23.0%), ICP-MS data proves 0.5 wt. % of Pt or Pd metals load in the catalysts prepared. The PXRD patterns of PGM supported catalysts are similar to that of respective supports, namely, pseudo-cubic NbP_2O_7[14] and α-$NbPO_5$ phases[15]. For example indexed PXRD patterns of the 0.5 wt. % $Pt/NbPO_5$ (1) and 0.5 wt. % Pt/NbP_2O_7 (2) catalysts were depicted on figure-1.
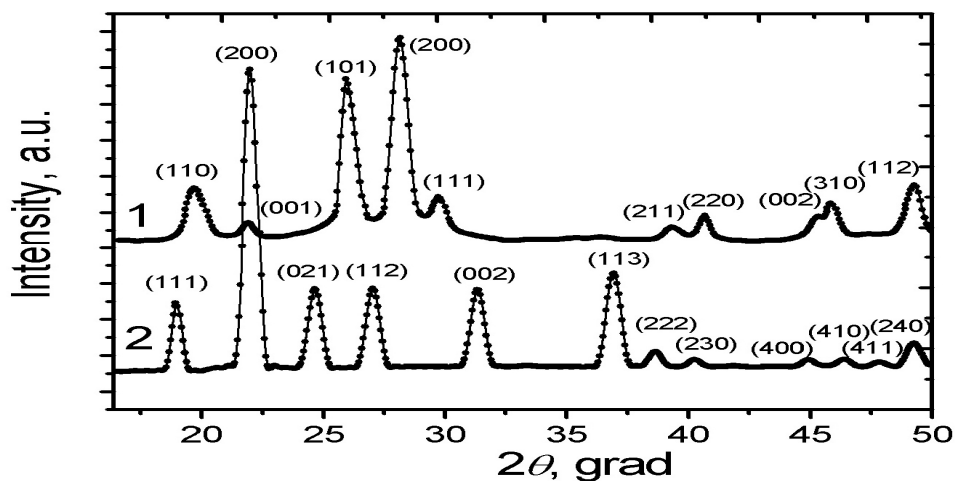

Figure-1
Indexed PXRD patterns of catalysts: 1) 0.5 wt. % $Pt/NbPO_5$ and 2) 0.5 wt. % Pt/NbP_2O_7

XPS data indicate that Pt and Pd in the catalysts studied are present in the metallic state. The catalysts characteristics S_{sp}, $T_{X\%}(H_2)$ and Nb^{4+}/Nb^{5+} ratio taken from XPS data are listed in table-1.

The catalysts are characterized by S_{sp} values lesser than 4 m^2/g. Pure $NbPO_5$ and NbP_2O_7 phosphates exhibit no low-temperature activity in the H_2 oxidation. $T_{20\%}(H_2)$ of $NbPO_5$ and NbP_2O_7 reaches a value of 680 K and 630 K, correspondingly. No prominent H_2 conversion was observed over pure α-Al_2O_3 at these temperatures. The temperature dependence of H_2 conversion over Pt and Pd supported metal catalysts characterized by the temperature hysteresis, as it can be seen on figure-2 for the Pt catalysts.

As on can see form the table-1 and the figure-2, that $T_{X\%}(H_2)$ over 0.5 wt. % PGM/NbP_2O_7 is about on 20–30 K lower than that over 0.5 wt. % PGM/Al_2O_3. The Pd catalysts are less active than Pt ones. The temperature hysteresis loop width for PGM/NbP_2O_7 and $PGM/NbPO_5$ is narrowed in comparison with PGM supported on Al_2O_3 catalysts. The activity of catalysts decreases in a sequence of PGM/NbP_2O_7 > $PGM/NbPO_5$ > PGM/Al_2O_3 (PGM = Pt or Pd). The platinum group metals supported over NbP_2O_7 are more active in H_2 oxidation than supported over inert carrier Al_2O_3. It should be suggested that a minor amounts of reduced Nb^{4+} in $NbPO_5$, which are found from XPS data, can not play determining role for H_2 oxidation. The enhanced activity of Pt/NbP_2O_7 and Pd/NbP_2O_7 catalysts is attributed to interplay between Nb^{4+}/Nb^{5+} states in the NbP_2O_7 affects on the surface red-ox reactions.
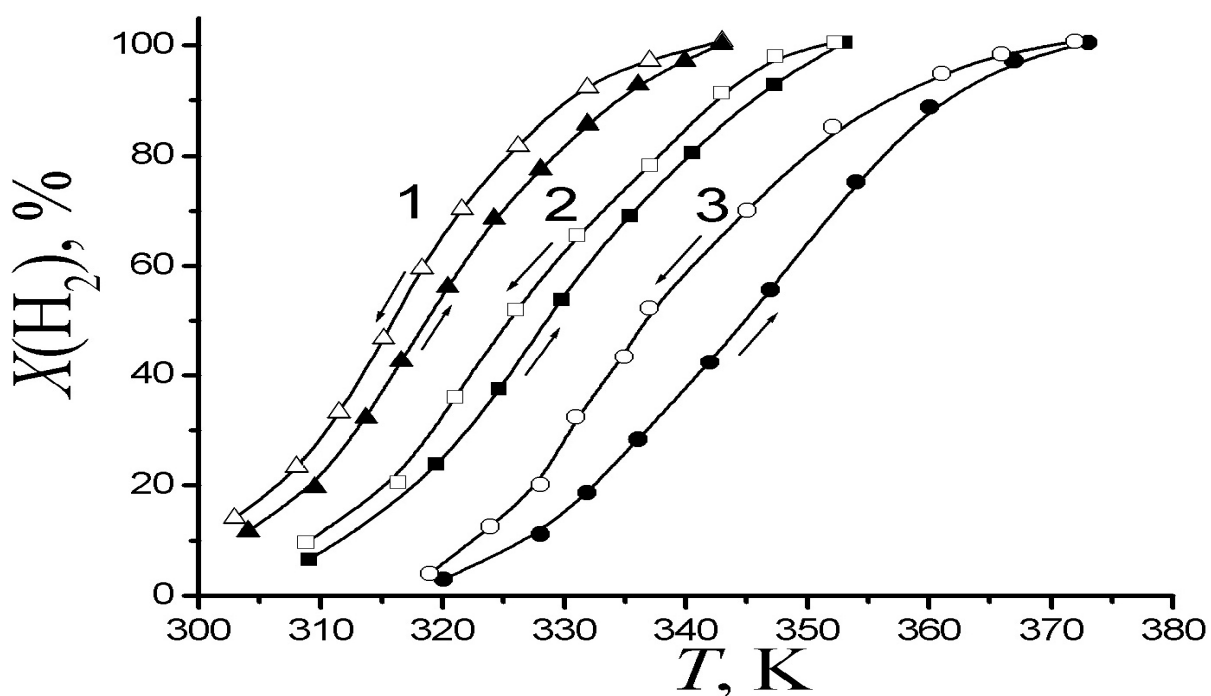

Figure-2
H$_2$ conversion against the temperature over catalysts: 1) 0.5 wt. % Pt/NbP$_2$O$_7$, 2) 0.5 wt. % Pt/NbPO$_5$,
3) 0.5 wt. % Pt/Al$_2$O$_3$

Table-1
The catalyst composition, specific surface area (S_{sp}), the temperature at a certain H$_2$ conversion ($T_{X\%}(H_2)$) and the ratio of Nb^{4+}/Nb^{5+}

Catalyst composition	S_{sp}, m^2/g	$T_{X\%}(H_2)$, K		Ratio of Nb^{4+}/Nb^{5+}
		$T_{30\%}$, K	$T_{100\%}$, K	
NbPO$_5$	1.8	744	-	0/100
NbP$_2$O$_7$	2.1	704	-	36/64
0.5 wt. % Pt/Al$_2$O$_3$	3.6	337	373	-
0.5 wt. % Pd/Al$_2$O$_3$	3.6	358	394	-
0.5 wt. % Pt/NbPO$_5$	3.3	323	353	8/92
0.5 wt. % Pd/NbPO$_5$	3.0	332	362	5/95
0.5 wt. % Pt/NbP$_2$O$_7$	3.8	313	342	42/58
0.5 wt. % Pd/NbP$_2$O$_7$	3.5	314	353	38/62

Conclusion

Oxidation of hydrogen over PGM/NbP_2O_7, $PGM/NbPO_5$ and PGM/Al_2O_3 (PGM = Pt or Pd) catalysts was studied. The activity of PGM/NbP_2O_7 for the H_2 oxidation is higher than that of $PGM/NbPO_5$ and PGM/Al_2O_3 catalysts. It was suggested that the enhanced activity of PGM/NbP_2O_7 catalysts is attributed to interplay between Nb^{4+}/Nb^{5+} states in the NbP_2O_7 affects on the oxygen activation on the catalysts surface.

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