

# NANOCRYSTALLINE SUPPORTED CATALYSTS PREPARED IN SUB- AND SUPERCRITICAL WATER: CATALYTIC ACTIVITY IN OXIDATION, HYDROGENATION AND ISOMERIZATION REACTIONS

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## INTRODUCTION

Activity and selectivity of heterogeneous catalysts is determined by the synthetic and temperature treatment conditions. Therefore, the elaboration of new methods for catalysts and supports preparation is of a great importance. At the present time water in sub- and supercritical states is used widely as a reagent, acid-base catalyst and unique pollution-free solvent with tunable properties for carrying out different chemical processes. In addition the use of supercritical water could be a very promising technique both for creating new effective nanocrystalline catalytic systems and for tuning the properties of well-known catalysts.

Recently we reported how different nano-scaled oxide catalytic systems with desired characteristics can be prepared in sub- and supercritical water via the hydrolysis of metals salts [1,2]. The phase and chemical composition, morphology and surface area of nanocrystalline oxides can be varied in a wide range depending on the experimental conditions. Moreover, under unsteady-state sub- and supercritical conditions some metastable materials can be synthesized.

In the present work we report on the properties of nanocrystalline supported catalysts of the composition 1%Pd/ZrO<sub>2</sub> and 1%Pd/TiO<sub>2</sub> prepared in sub- and supercritical water. Pd-Ti-O and Pd-Zr-O systems are used widely as oxidation and hydrogenation heterogeneous catalysts. The activity and selectivity of Pd/ZrO<sub>2</sub> and Pd/TiO<sub>2</sub> samples depends strongly on the catalysts preparation conditions because the active metal in that ternary systems is located either on the surface of titania/zirconia oxides or can be incorporated into the bulk of the oxides with the formation of metastable solid solutions, intermetallic compounds and their hydrides [3]. Due to a large variety of different phases which may form in Pd-Ti-O and Pd-Zr-O systems under specific experimental conditions the investigation of supported Pd/ZrO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts prepared in sub- and supercritical water is of a great importance.

## EXPERIMENTAL

The synthesis of the oxides of the composition ZrO<sub>2</sub>, TiO<sub>2</sub> and supported catalysts 1%Pd/ZrO<sub>2</sub>, 1%Pd/TiO<sub>2</sub> was performed using a particle flow reactor [1]. To obtain the required conditions water was pumped continuously through a pre-heater and oven to reach a final temperature of 400-500°C before being mixed with a solution containing stoichiometric amounts of metal ions. A back pressure regulator (BPR) at the end of the system maintained the system pressure close to 25 MPa. At the mixing point a cold metal solution (0.2 M) was rapidly hydrolysed by a stream of sub- or supercritical water. The hot water now containing the dispersed hydrolysis products was cooled and collected after the BPR. A solid product

was recovered from the mixture by complete evaporation of water. The temperature at the mixing point was 230°C in case of titania-based systems preparation (subcritical conditions) and 380°C for zirconia and 1%Pd/ZrO<sub>2</sub> (supercritical conditions). Palladium acetate, ZrO(NO<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>COO)<sub>x</sub>Ti(OPr)<sub>4-x</sub> were selected as the precursors for the catalysts preparation.

The phases of all the materials were identified by X-ray diffraction analysis, the microstructure of the samples was investigated by transmission electron microscopy, BET surface area was measured by Nitrogen adsorption at 77 K, thermal behavior of the catalysts was investigated using differential thermal analysis (for details see [1,2]). The quantity of Palladium atoms located on the surface of 1%Pd/ZrO<sub>2</sub>(TiO<sub>2</sub>) systems was determined using a standard technique developed for supported catalysts containing Pd and Pt [2]. Before the catalytic and hydrogen chemisorption experiments the samples were pre-treated within 1 hour on air at 500°C. Some characteristics of the materials are summarized in Table 1.

Table 1.

Characteristics of the catalysts prepared in sub- or scH<sub>2</sub>O.

Catalyst	Phase composition*	Particles size, nm	BET surface area, m <sup>2</sup> /g	Initial content of Pd atoms located on the surface, %
ZrO <sub>2</sub>	M+T	3-5	172	---
TiO <sub>2</sub>	T (anatase)	7-9	201	---
1%Pd/ZrO <sub>2</sub>	M+T	3-5	158	62
1%Pd/TiO <sub>2</sub>	T (anatase)	7-9	195	54

\*M- monoclinic phase; T- tetragonal phase.

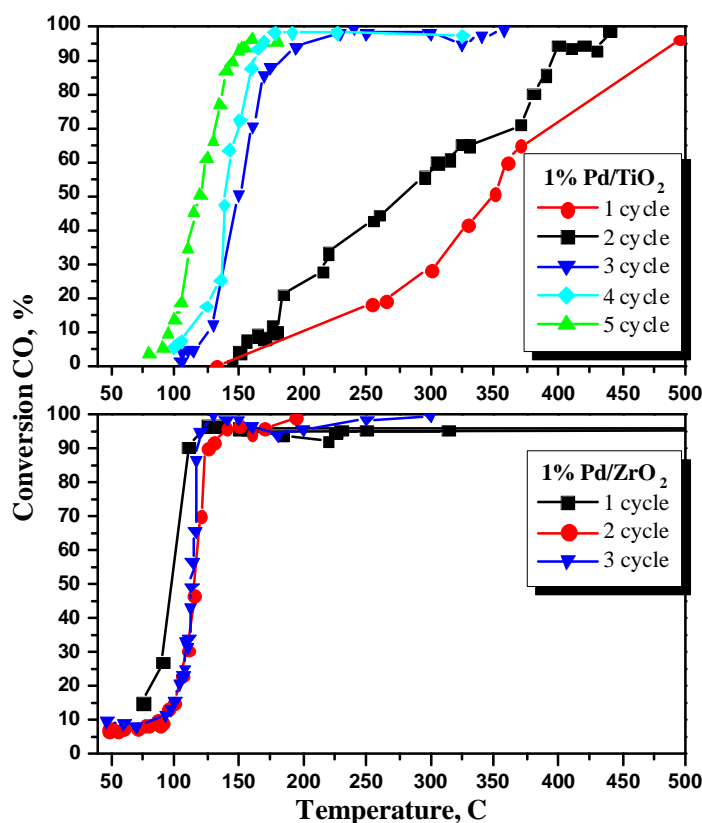
Hydrogen uptake by the samples was investigated using a static volumetric technique over the temperature range 6-200°C and pressures 22-30 Pa. Hydrogen gas was purified by passing through a Pd thimble. Water formed as a result of oxides reduction was freed out in a liquid nitrogen trap.

The catalytic activity of all the samples was studied in a flow reactor. While investigating hexene-1 hydrogenation/isomerization reactions saturated at 20°C with hexene-1 hydrogen or nitrogen flow was passed through the catalytic reactor and analyzed using HP-6890 gas chromatograph (HP-5 capillary column, l=30 m, Ø=0.53 mm) with a flame ionization detector.

CO oxidation was investigated for the reaction mixture 2.51% CO and 1.33% O<sub>2</sub> by volume in nitrogen. The composition of the gas phase was monitored continuously under polythermal conditions over the temperature range 30-500°C using MEGAKON gas analyzer.

## RESULTS AND DISCUSSION

**1. CO oxidation.** The curves of CO conversion over nanocrystalline 1% Pd/ZrO<sub>2</sub> and 1% Pd/TiO<sub>2</sub> catalysts are presented on Fig.1. As can be seen from the figure, the behavior of that systems differ severely. For the sample 1% Pd/ZrO<sub>2</sub> half CO conversion occurs at 96°C. While carrying out the second catalytic cycle a small shift of this temperature to higher values (115°C) is occurred. This shift is a result of active metal particles sintering on the surface of the catalyst. In subsequent catalytic cycles the activity of 1% Pd/ZrO<sub>2</sub> sample remains unchanged.



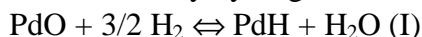
**Fig.1. The temperature dependences of CO conversion over 1%Pd/ZrO<sub>2</sub>(TiO<sub>2</sub>) catalysts.**

The initial activity of 1% Pd/TiO<sub>2</sub> catalyst is not very high and half CO conversion is achieved at 350°C only. However, with every subsequent catalytic cycle the activity is increased and after the fifth experiment half CO conversion for 1% Pd/TiO<sub>2</sub> occurs at 120°C. As can be seen from the Table 1, after the synthesis in subcritical water only 54% of Palladium located on the surface of titania. The remainder of Pd is incorporated into the bulk of TiO<sub>2</sub> particles possibly with the formation of Pd<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> solid solution or intermetallic-like phase. After the catalysis already 79% of Pd particles was determined to be supported on the titania surface. Therefore, the observed increase in catalytic activity for 1% Pd/TiO<sub>2</sub> sample with every subsequent catalytic cycle is a result of metastable Pd<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> phase segregation with the formation of Pd or PdO and titania. The absence of such effect in case of 1% Pd/ZrO<sub>2</sub> system probably can be explained by higher thermodynamic stability of hypothetical Pd<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> solid solution or intermetallic-like phase which are not decomposed under the experimental conditions selected for CO oxidation study.

It should be noted, that under the same experimental conditions nanocrystalline 1%Pd/ZrO<sub>2</sub>(TiO<sub>2</sub>) catalysts being prepared in sub- and supercritical water provide complete CO conversion at temperatures 150-200°C lower compared to the industrial Pd-containing catalysts [2].

**2. Hydrogen uptake.** To reveal the possibility of Pd<sub>x</sub>M<sub>1-x</sub>O<sub>2</sub> (M=Zr, Ti) solid solutions or intermetallic-like phases formation while preparing the catalysts under unsteady-state conditions we have investigated the kinetics of H<sub>2</sub> uptake by nanocrystalline Pd-Zr-O system. Generally when this system is exposed to hydrogen the following processes may occur.

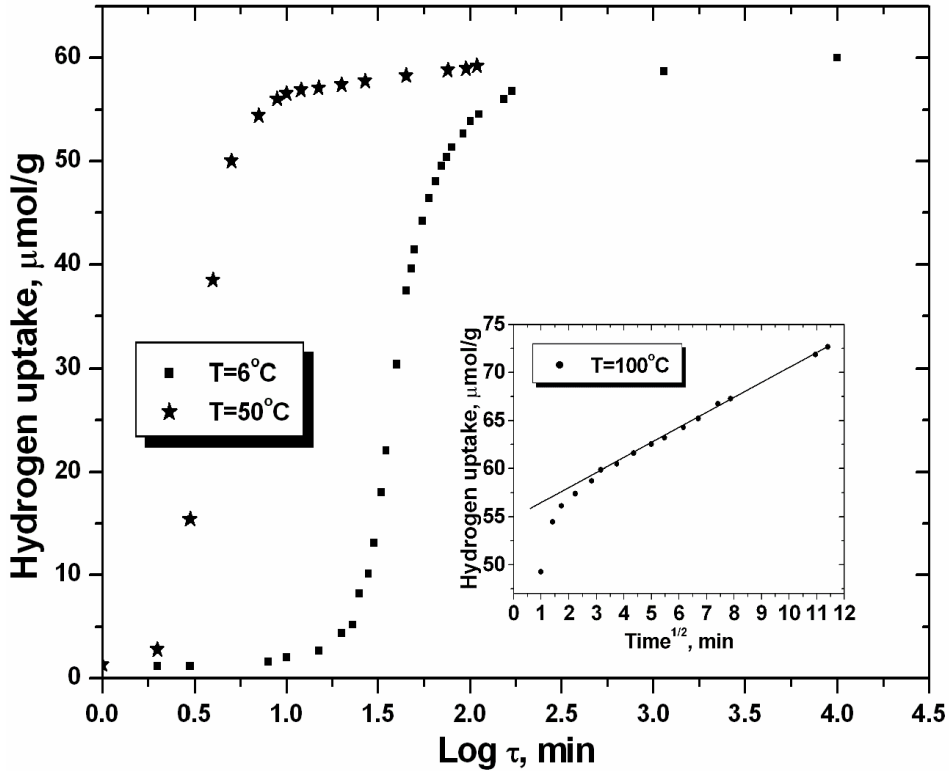
- a. Palladium oxide reduction followed by hydrogen chemisorption:



Hydrogen diffusion into the bulk of reduced Palladium with the formation of hydrides can also be observed. It should be noted, that under our experimental conditions (P,T) hydrogen diffusion into Pd crystallites is eliminated [4].

- b. Hydrogen can be consumed also due to zirconia reduction. It was established, that nanocrystalline  $ZrO_2$  can not be reduced during our experiments.
- c. Additional  $H_2$  uptake may take place as a result of hydrogen spillover from Pd onto zirconia. Usually spilled hydrogen desorbs while sample evacuation at the same temperatures under which it was absorbed. In our case taken up by the sample hydrogen practically not evolved at temperatures below  $200^\circ$ . Therefore, spillover phenomenon can be excluded in our experiments.
- d. Intermetallic  $Zr_xPd_y$  phases or oxide  $Pd_xZr_{1-x}O_2$  systems can also absorb hydrogen with the formation of corresponding hydrides [3].

The typical kinetic curves of  $H_2$  uptake by 1%Pd/ $ZrO_2$  prepared in supercritical water are shown on Fig.2. The form of that curves is determined by a superposition of three processes. In the initial stage a breakdown time is observed which is typical for topochemical reactions [5]. The duration of this period is decreased with a rise of temperature of the experiments.



**Fig.2. Hydrogen uptake kinetics for the nanocrystalline 1%Pd/ $ZrO_2$  catalyst.**

An ascending part of the kinetic curve corresponds to simultaneous passing of two processes according to the equation (I). After each experiment we determined the quantity of water formed due to palladium oxide reduction. It was found, that quantity of water is independent of the temperature and comprise  $40 \pm 4 \mu\text{Mol/g}$ . Therefore, the amount of Pd atoms which is contained in the sample in the form of PdO is about 50% against total Palladium loading. At pressures below 30 Pa and temperatures in the range of  $6-100^\circ$  the stoichiometry of hydrogen chemisorption on metallic Palladium comprises  $H/Pd \leq 1$  [6]. Hence, in our case, no more than  $20 \pm 2 \mu\text{Mol/g}$  of hydrogen is required for chemisorption with

the formation of PdH. Consequently, total hydrogen uptake for the reaction (I) should amount to  $60 \pm 6 \mu\text{Mol/g}$ . The limiting values of hydrogen consumption for the temperatures  $6-50^\circ\text{C}$  are just equal to  $60 \mu\text{Mol/g}$ . This fact confirms our assumption about the nature of  $\text{H}_2$  uptake for the second part of the kinetic curves.

Additional hydrogen consumption is observed at higher temperatures ( $100^\circ\text{C}$ ). A linear dependence of  $\text{H}_2$  uptake versus one-half power of time (see Fig.2) for values more than  $60 \mu\text{Mol/g}$  suggests that the third processes has a diffusion character [7]. This uptake can be explained only by the presence in the sample of intermetallic phases or oxide solid solutions able to absorb hydrogen.

**3. Hexene-1 hydrogenation and isomerisation.** Hexene-1 isomerization and hydrogenation was studied both for freshly prepared and annealed Pd/ZrO<sub>2</sub>(TiO<sub>2</sub>) samples. Freshly prepared samples are characterized with high concentration of acetic or nitric acids adsorbed on the surface. These acids are formed during catalysts preparation as a result of precursors hydrolysis in sub- or supercritical water. The annealing of the samples on air at  $500^\circ\text{C}$  within 1 hour leads to complete removal of nitrogen- or carbon-containing species from the surface [1].

All the catalysts exhibit high activity in hexene-1 isomerization and hydrogenation even at room temperatures for volumetric flow rates  $6000\text{h}^{-1}$ . For Pd-containing samples in hydrogen atmosphere the complete hexene-1 conversion is observed at  $20^\circ\text{C}$  and hexane is the only product observed under this conditions.

Hexene-1 isomerization with the formation of *trans*-hexene-2 and *cis*-hexene-2 is observed for the oxides ZrO<sub>2</sub>, TiO<sub>2</sub> both in hydrogen and nitrogen medium and for supported 1%Pd/ZrO<sub>2</sub> and 1%Pd/TiO<sub>2</sub> catalysts in nitrogen environment only. In most cases the selectivity of hexene-1 isomerization does not depend on temperature and catalyst treatment and comprise 60% for *trans*-hexene-2 and 40% for *cis*-hexene-2.

The reaction rates and selectivity for hexene-1 isomerization at  $100^\circ\text{C}$  are listed in Table 2. The reaction rates increase with temperature but starting from  $200^\circ\text{C}$  the catalysts deactivation is observed due to the coke formation. In general the activity of the catalysts is higher significantly in hydrogen atmosphere. Moreover, as can be seen from the Table, freshly prepared samples are more active in hexene-1 isomerization compared to the annealed catalysts. This fact can be explained from the viewpoint that carbonic cations formation is favoured in the presence of acetic or nitric acids on the surface of the catalysts.

Table 2.

Reaction rates and selectivity for hexene-1 isomerization over nanocrystalline catalysts at  $100^\circ\text{C}$ .

Sample	Reaction medium	Reaction rate, molecule·s <sup>-1</sup> ·g <sup>-1</sup>	Selectivity, %		
			<i>trans</i> -hexene-2	<i>cis</i> -hexene-2	Hexane
ZrO <sub>2</sub> , fresh	H <sub>2</sub>	$1.60 \cdot 10^{17}$	61	39	---
TiO <sub>2</sub> , fresh	H <sub>2</sub>	$1.05 \cdot 10^{18}$	75	25	---
ZrO <sub>2</sub> , annealed	H <sub>2</sub>	$2.64 \cdot 10^{16}$	65	35	---
TiO <sub>2</sub> , annealed	H <sub>2</sub>	$8.91 \cdot 10^{17}$	48	26	26
1%Pd/ZrO <sub>2</sub> , fresh	N <sub>2</sub>	$5.37 \cdot 10^{16}$	59	41	---
1%Pd/TiO <sub>2</sub> , fresh	N <sub>2</sub>	$4.62 \cdot 10^{18}$	67	33	---
1%Pd/TiO <sub>2</sub> , annealed	N <sub>2</sub>	$8.08 \cdot 10^{16}$	62	38	---

For annealed titania samples parallel with two isomers hexane formation was also detected in hydrogen medium (see Table 2). Hydrogenation is observed probably due to the presence of metallic Titanium active centers formed while annealing the sample. Under this conditions acetic acid is decomposed partially with the formation of CO which can reduce titania.

It should be noted that if saturated with hydrogen 1%Pd/ZrO<sub>2</sub> catalyst is annealed on air at 300° all surface Palladium atoms will be oxidized [8]. While performing hexene-1 isomerization over that sample in nitrogen atmosphere at the initial stage of the reaction the formation of significant amounts of hexane is observed. This fact confirm again the presence of intermetallic-like phases in Pd-Zr-O system prepared in supercritical water. The absorbed by these phases hydrogen is released in subsequent catalytic process which leads to hexane-1 hydrogenation even in nitrogen atmosphere.

In conclusion we would like to note that synthesis of the supported catalysts in sub- or supercritical water simplify essentially the preparation procedure. In this case there is no need to prepare at first the support and then to impregnate it with the solution of the active metal. In sub- or supercritical water nanocrystalline supported systems can be obtained via one-stage hydrolysis process. Moreover, nanocrystalline catalysts prepared under unsteady-state conditions possess new interesting properties and exhibit high catalytic activity in oxidation, hydrogenation and isomerization reactions compared to the same systems synthesized via traditional routes.

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#### REFERENCES

- [1] GALKIN, A.A., KOSTYUK, B.G., KUZNETSOVA, N.N., TURAKULOVA, A.O., LUNIN, V.V., *Kinetics and Catalysis*, Vol.42, **2001**, p.172.
- [2] GALKIN, A.A., TURAKULOVA, A.O., KUZNETSOVA, N.N., LUNIN, V.V. *Vestnik MSU (Russian), Chemistry*, Vol.42, **2001**, p.405.
- [3] CANTRELL, J.S., BOWMAN, R.C., MAELAND, A.J., *J. Alloys Comp.*, Vol.330-332, **2002**, p.191.
- [4] BENSON, J.E., HWANG, H.S., BOUDART, M., *J. Catal.*, Vol.30, **1973**, p.146.
- [5] ROZOVSKY, A.Ya. *Heterogeneous chemical reactions (Russian)*, Moscow, Nauka, **1980**, p324.
- [6] BOUDART, M., HWANG, H.S., *J. Catal.*, Vol.39, **1975**, p.44.
- [7] TRAPNELL, B.M.W. *Chemisorption*, Butterworths Scientific Publication, London, **1955**, p.15.
- [8] LAM, Y.L., BOUDART, M., *J. Catal.*, Vol.47, **1977**, p.393.