

Oxidation of dihydrogen molecules by composite catalysts based on highly dispersed nano-scale precious metal particles

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Objectives: Here, we report on the catalytic and adsorption properties of new metal nanocatalysts, which are highly dispersed Pd NPs supported on selected porous activated carbon (Fig. 1). The mild reduction of Pd chloride and the partial destruction of the surface amino complexes support the dispersing of nano-scale Pd.

Methods: Nitrogen adsorption-desorption isotherms were measured on an automatic gas adsorption analyzer ASAP 2405N. Electron microscopy (SEM and TEM) observations on non-coated samples were performed on Mira 3 GMU LV-FE-SEM and JEM-2000EXII instruments equipped with EDX spectrometer from Oxford Instruments. Catalytic and desorption measurements were done as earlier reported in [1, 2].

Results: The high specific surface area of the SKT support maintained a large surface-area-to-volume ratio in Pd nanocatalysts. Table 1 shows specific surface area of SKT activated carbon support treated with amines and Pd supported catalysts on their base.

Table 1. Specific surface area of sorbents vs. Pd supported catalysts

Sorbent	Specific surface area (m ² /g)		
	-	0.1 mass% Pd	0.5 mass% Pd
SKT	1200	1195	1180
SKT-C ₄ H ₁₀ N ₂	1030	1000	950
SKT-(C ₂ H ₅) ₂ NH	1180	1090	1010
SKT-H ₂ NCH ₂ CH ₂ NH ₂	1100	1120	1030
CKT-HO-CH ₂ CH ₂ -NH ₂	1120	1030	1000

Table 2. Temperature of 50% and 100% conversion of H₂ over Pd catalysts

Catalyst	Temperature of H ₂ conversion	
	T _{50%} (K)	T _{100%} (K)
0.5/0.1 mass% Pd/SKT	390/440	420/490
0.5/0.1 mass% Pd/SKT-C ₄ H ₁₀ N ₂	376/429	403/470
0.5/0.1 mass% Pd/SKT-(C ₂ H ₅) ₂ NH	350/400	380/450
0.5/0.1 mass% Pd/SKT-H ₂ NCH ₂ CH ₂ NH ₂	308/361	351/420
0.5/0.1 mass% Pd/SKT-HO-CH ₂ CH ₂ -NH ₂	273/328	323/390

Nanosized Pd metal is one of the most active catalysts that will be widely used in hydrogen recombination with oxygen (decontamination) devices. Nanopalladium is characterized by high activity in the heterogeneous-homogeneous reaction of catalytic oxidation of hydrogen. The efficiency of Pd NPs as a catalyst supported on aminated SKT as a carrier in the reaction of catalytic oxidation of hydrogen, which takes place at room and low temperatures, is shown (Table 1). The formation of HO₂^{*} and OH^{*} radicals during the oxidation reaction is proved. The using of amines and amino alcohols to create effective catalysts caused to semi-homogeneous distribution of Pd NPs (5 nm) that is shown in Fig. 2. The formation of which is largely determined by the physicochemical properties of the SKT carrier, so there is a growing interest in amination and its impact on the parameters of the specific surface area (Table 1). The activity of nanopalladium loaded on SKT, aminated with bidentate amine and amino alcohol, in the oxidation reaction of hydrogen by molecular oxygen, exceeds that of other considered Pd catalysts and is maintained by reducing the Pd content from 0.5% to 0.1% (Table 2). By analysis of the results of thermal desorption experiments with mass spectrometric detection of the desorbed species and those of photoluminescent method/fluorescent spectrometry methods, we independently proved adsorption of OH and HO₂ species on the surface of oxidation catalysts that acting in the reaction of dihydrogen recombination with oxygen. The thermal desorption spectra have confirmed the presence of weakly bound forms of water and H₃O⁺ species. Their ability to form during catalytic act correlates with the existence of temperature hysteresis in the conversion of dihydrogen (Fig. 2). The recombination is the first-order reaction, and the Eley-Rideal model can fit the experimental data. The data obtained are explained by the reactions that have occurred in its highly active non-stationary state through the heterogeneous-homogeneous mechanism. The effect of the local overheating on the surface of highly dispersed nano-scale Pd metal particles acting as adsorbent and catalysts is definitely not one reason for thermal hysteresis.

Conclusions. Effective oxidation catalysis is reached at room temperatures over low content of highly dispersed Pd NPs. The proposed nanocatalysts are effective to be used for remediation of dihydrogen in the mixture with the excess of oxygen. Such catalysts are required in converters that can recombine a gas mixture of air oxygen and leaked hydrogen. The latter is sourced from the emissions from tanks feeding the power engines or fuel cells. The dispersed Pd NPs are stable enough under the operating conditions and maintain a steady performance over 200 cycles of reaction.

References: [1] Yatsimirskii VK, Lesnyak VV, Gut IN, Boldyeva OYu (2005) Theor Experim Chem 41:135–138; [2] Lesnyak VV, Ishchenko EV, Gut IN, Yatsimirskii AV, Boldyeva OYu (2007) Russ J Phys Chem A 81:874–877.

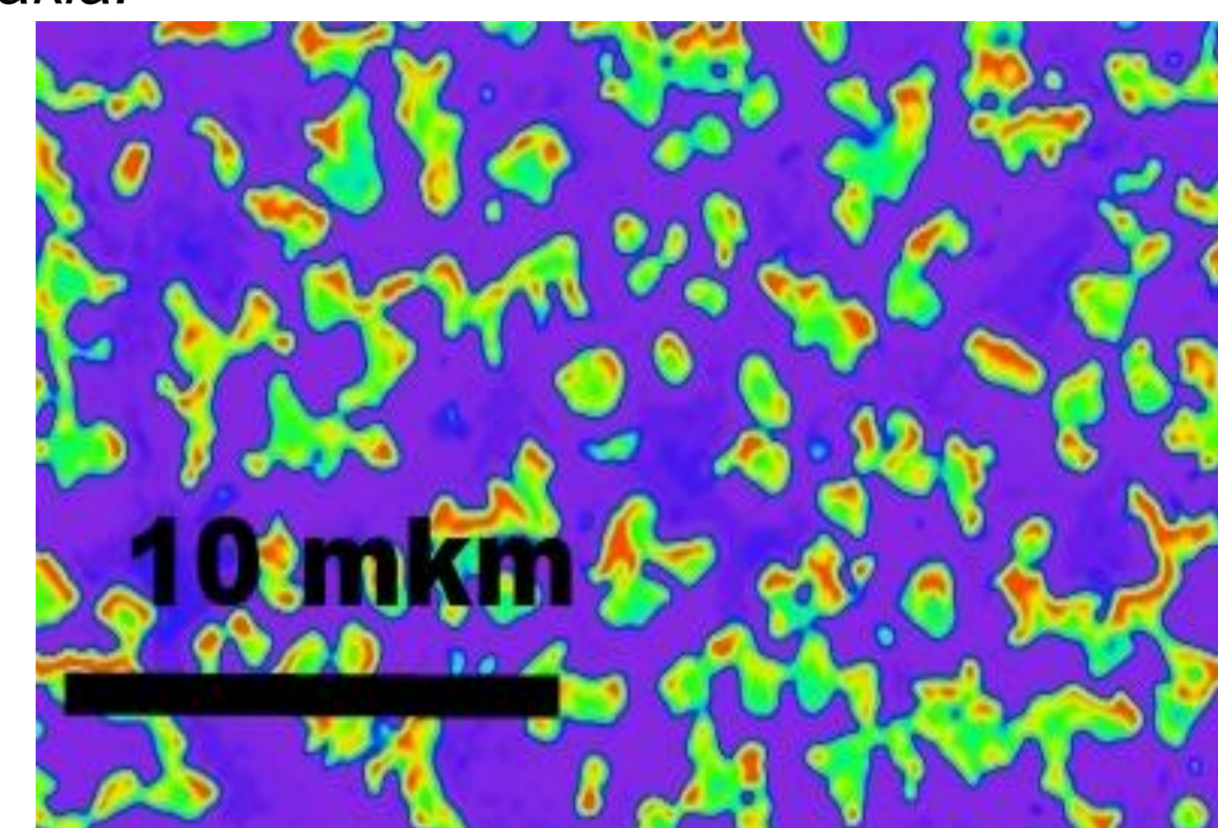


Fig. 1. SEM image of SKT with Pd

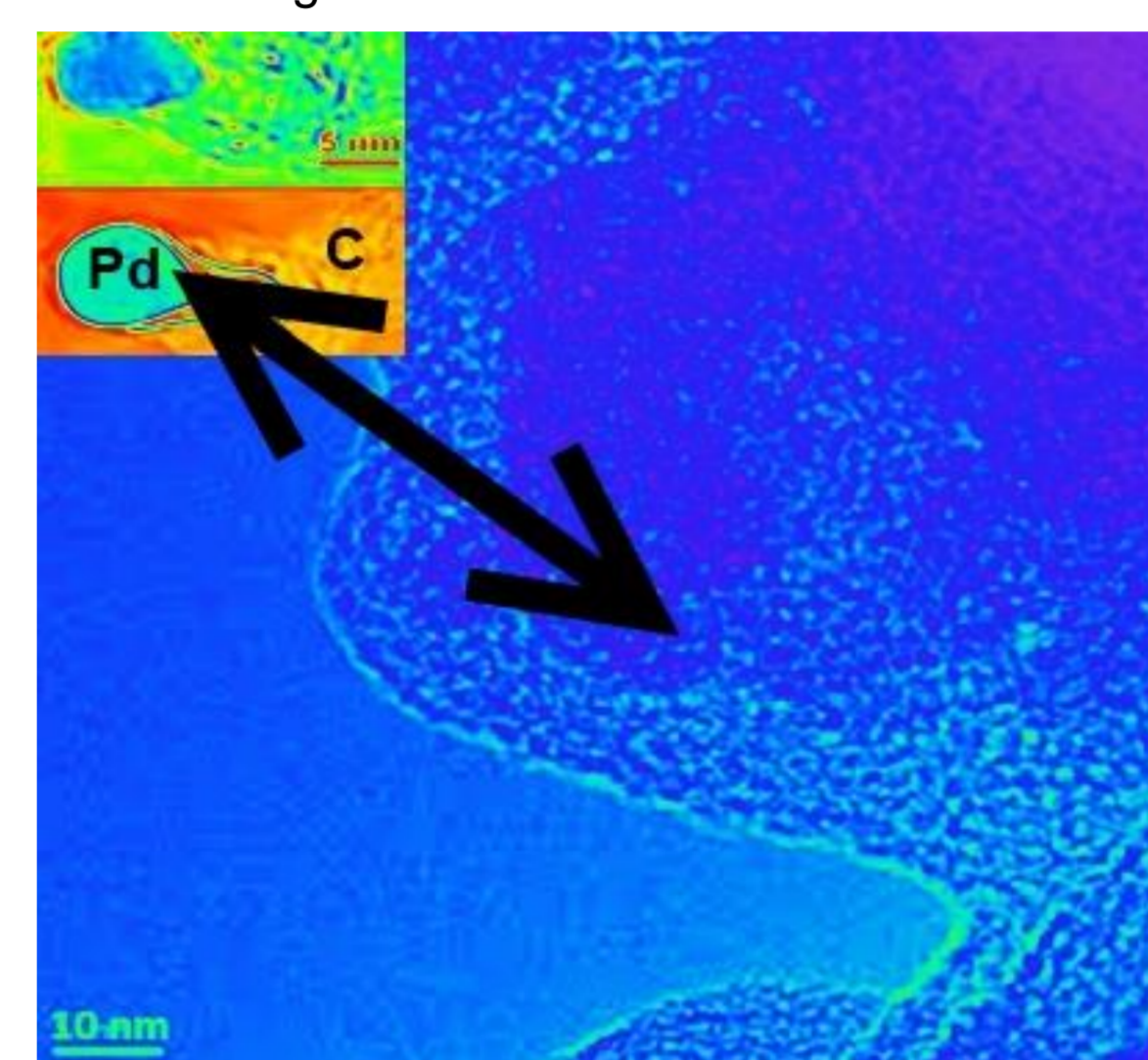


Fig. 2. TEM and EDX mapping of 0.5 mass% Pd SKT-(C₂H₅)₂NH.

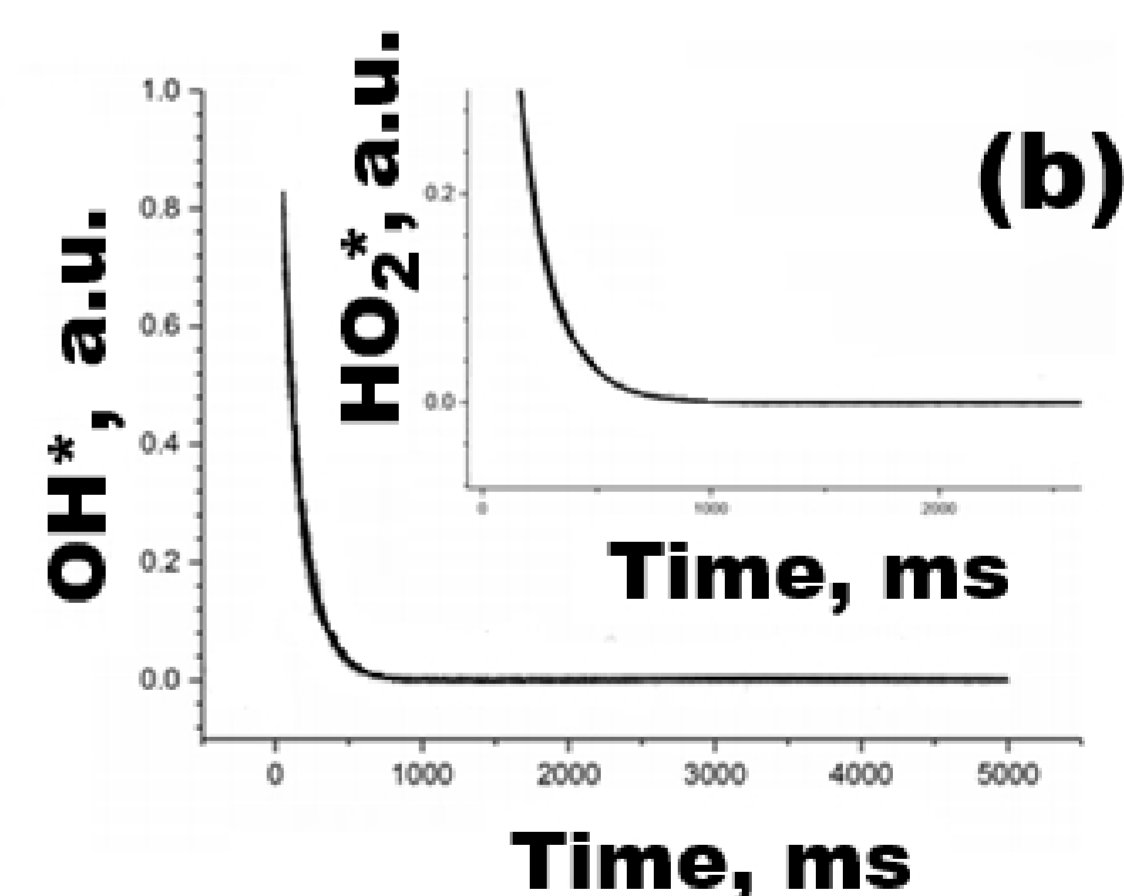
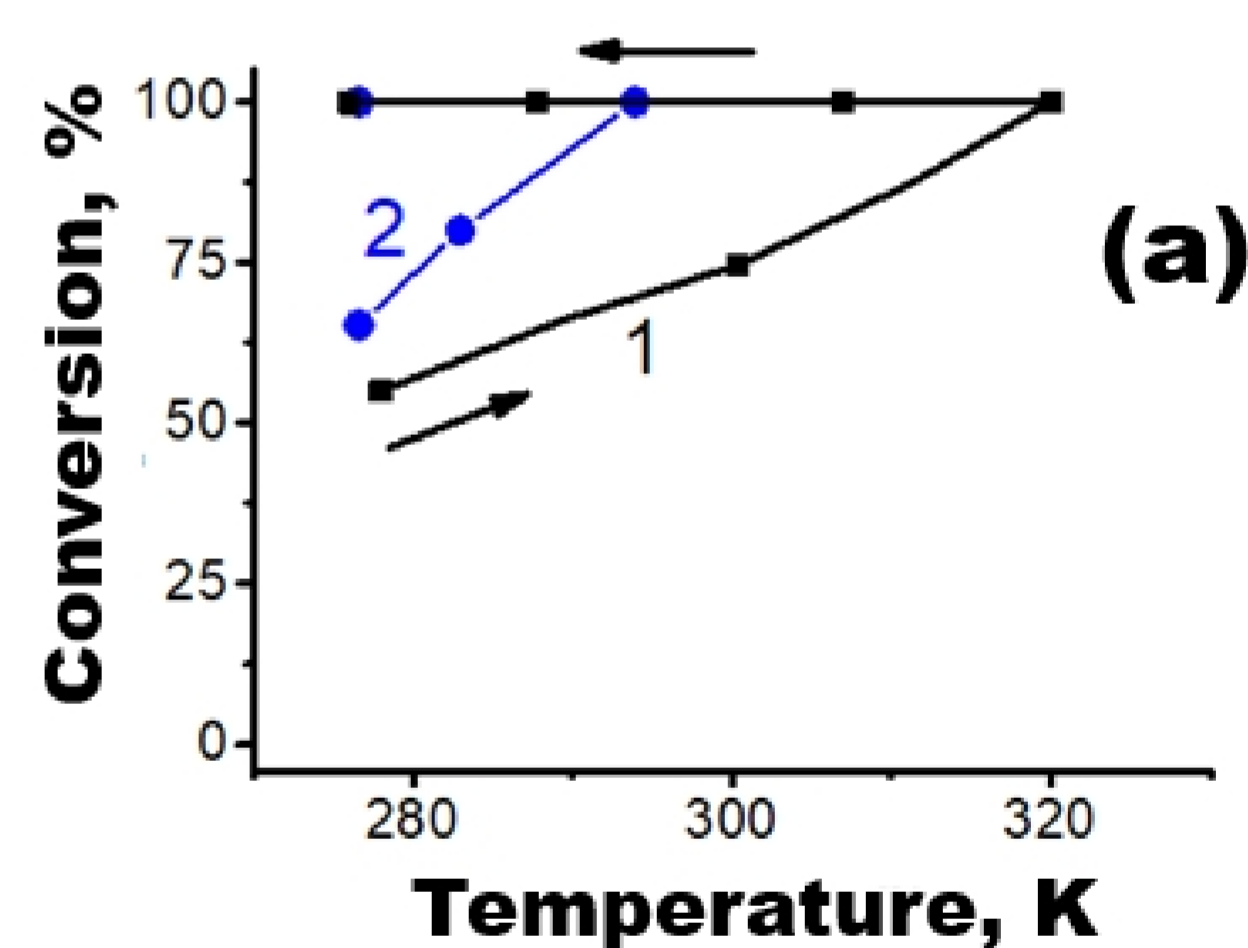


Fig. 3. (a) Temperature dependent H₂ + O₂ reaction catalyzed by 0.5 mass% Pd/SKT-HO-CH₂CH₂-NH₂. 1st and 2nd heating and cooling cycle. (b) Time dependence of the content of radicals in the presence of 0.5 mass% Pd/SKT-HO-CH₂CH₂-NH₂ catalyst at T_{100%}. HO₂ and OH radicals were detected at 248 and 308 nm.