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Adsorption and Structural Properties of Heteropolyacid-modified Pd/Al_2O_3 Catalysts: Effects on Hydrogenation Activity

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The modification of Pd/Al_2O_3-catalysts by heteropolyacids (HPA) leads to the formation of qualitatively new surface sites, which determine the sample activity in hydrogenation reaction of C=C unsaturated bonds in organic compounds.

Heteropolyacids are familiar catalysts for the complete and partial oxidation of hydrocarbons.[1–4] Owing to their redox properties, they can be successfully employed in reduction processes, in particular, for hydrogenation. In ref. 5, for example, catalytic systems have been studied consisting of phosphomolybdenum, phosphotungsten, phosphomolybdotungsten acids and Pd^{II} ions. The proposed catalysts exhibit a high activity for the semihydrogenation of propargyl alcohol to allyl alcohol. It is suggested that aqueous solutions of HPA facilitate the transformation of Pd^{II} into a finely-dispersed Pd/C type of catalyst.

The characteristics of HPA activated hydrogenation catalysts have been studied in detail.[6–8] According to these data, modified Ni catalysts are superior in activity to pure Ni contacts in the hydrogenation of benzene, toluene and carbon distillates.

The object of this work is to study the correlation between the adsorption properties of modified $Pd + HPA/Al_2O_3$ catalysts and their activity in the hydrogenation of C≡C and C=C bonds in but-2-yne-1,4-diol and oct-1-ene.

The hydrogenation process was investigated in a glass reactor with mixing[9] under hydrogen pressure $P_{H_2} = 1$ atm and temperature $T = 298$ K in propan-2-ol (25 cm^3); the catalyst weight was 0.1 g. The hydrogenated substance (1.1×10^{-3} mol of but-2-yne-1,4-diol and 4.4×10^{-3} mol of

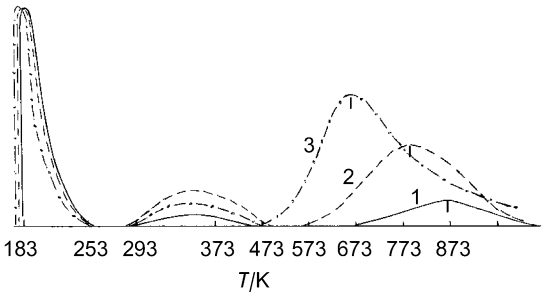


Fig. 1 Curves of hydrogen thermal desorption from the surfaces of Pd/Al_2O_3 (1), $Pd + SiMo_{12}$(2) and $Pd + PV_3Mo_9/Al_2O_3$ (3) catalysts.

Table 1 Hydrogen thermal desorption data of 1% Pd/Al_2O_3 catalysts modified by heteropolyacids.

Catalyst	Form of H_2[a]	T_{des}/K	T_{max}/K	H_{des}/cm^3 gCt^{-1}	E_{des}/kJ mol^{-1}	n[a]	Surface atom $Pd \cdot 10^{20}$	Metal surface (m^2/gCt^{-1})
Pd/Al_2O_3	α	183–298		0.5 (62%)	21	1		
	β_1	298–453	353	0.1 (13%)	67	1	0.4	3.1
	β_3	673–973	833	0.2 (25%)	145	2		
$Pd + SiMo_{12}/Al_2O_3$	α	183–298		0.5 (24%)	19	1		
	β_1	298–553	343–353	0.2 (10%)	40	1	1.0	7.4
	β_2	553–1043	768	1.4 (66%)	88	2		
$Pd + PV_3Mo_9/Al_2O_3$	α	183–298		0.5 (19%)	21	1		
	β_1	298–433	323	0.2 (7%)	58	1	1.3	9.2
	β_2	433–1043	648	2.0 (74%)	62	2		

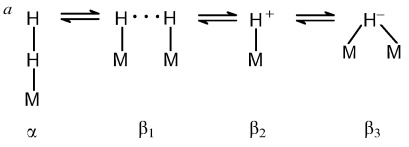
[a]  (ref. 10).

Table 2 Hydrogenation rates for but-2-yne-1,4-diol (I) and oct-1-ene (II) over 1% Pd/Al_2O_3 and 1% $Pd + HPA/Al_2O_3$ catalysts.

Catalyst	W/cm^3 min^{-1} gCat^{-1}			W/cm^3 min^{-1} m^{-2} [a]		
	I		II[b]	I		II
	C≡C	C=C	C=C	C≡C	C=C	C=C
Pd/Al_2O_3	4	9	16	1.3	2.9	5.2
$Pd + SiMo_{12}/Al_2O_3$	9	30	50	1.2	4.0	6.8
$Pd + PV_3Mo_9/Al_2O_3$	8	45	75	0.9	4.9	8.2

[a] On the metallic surface area. [b] At the moment of 50 cm^3 H_2 adsorption.

oct-1-ene) was calculated for the uptake of 100 cm^3 H_2 at NTP. The catalyst activity was inferred from the rate of hydrogen uptake.

The adsorption properties of the catalysts (the proportion of chemisorbed hydrogen forms and the bond energy between H_2 and the surface) were estimated by a hydrogen thermal desorption method (TPD). Adsorption was made from the flow of H_2 (100 cm^3 min^{-1}) during 1 h at 298 K. The catalyst was then cooled in an H_2 atmosphere to 183 K, the gas phase was replaced by Ar and desorption of chemisorbed hydrogen was then performed under a linear temperature increase (15 grad min^{-1}). In the interval 183–298 K flow heating occurs spontaneously in the air, so T_{max} for the first peak is not shown. A linear temperature increase was performed from 298 K. Thermal desorption products were recorded by a detector-catharometer as TPD-spectra.

1% Pd/Al_2O_3 and 1% $Pd + HPA/Al_2O_3$ catalysts were prepared by the impregnation method using aqueous solutions of $PdCl_2$ and HPA, then the specimens were dried (373 K) and calcined (623 K) in air. In our experiments we used silicomolybdic $H_4SiMo_{12}O_{40} \cdot xH_2O$ (abbreviated form $SiMo_{12}$–) and phosphomolybdovanadium $H_6PV_3Mo_9O_{40} \cdot xH_2O$ (PV_3Mo_9–) heteropolyacids.

Table 1 and Fig. 1 represent the thermal desorption data for Pd/Al_2O_3 and $Pd + HPA/Al_2O_3$ catalysts. Hydrogen evolves from these samples over a wide temperature range (183–1043 K) giving four desorption regions. Two desorption peaks are clearly seen, due to molecular H_2 (α- and β_1-species),[10] the peaks due to β_2-hydrogen over HPA modified catalysts and the maximum produced by β_3-hydrogen on Pd/Al_2O_3. Using the method described in ref. 10 and thermal desorption data, the hydrogen desorption orders n and activation energies of desorption E_{des} have been calculated (see Table 1). Analysis of the values obtained revealed that, comparing Pd/Al_2O_3 with $E^{III}_{des} = 145$ kJ mol^{-1} (β_3-form), the bond energy of hydrogen over modified catalysts decreases to 62–88 kJ mol^{-1} (β_2-form), but its total capacity increases. The H_{ads} species have been identified according to the classification in ref. 11.

Hydrogen with a definite metal bond energy takes part in specific reactions.[9] Considering that the C≡C bond can be hydrogenated by hydrogen of any bond energy, the lowering of the bond energy of H_2 in the HPA modified catalyst does not considerably affect its saturation rate and, on the contrary, it greatly influences the hydrogenation of the C=C double bond, producing a 3–5 fold increase in the reaction rate (Table 2).

Considering the proposed hydrogen adsorption species the metallic surface areas of Pd/Al_2O_3 samples have been calculated (see Table 1). It was apparent that the addition of HPA increases the number of adsorption sites by 2.5–3 times.

To clarify this phenomenon we carried out electron microscopic investigations (photography and extraction replics).† It was shown that the Pd particle dimensions in Pd/Al_2O_3 vary over wide limits, and thermal treatment leads to their sintering up to 130–140 A and more. Under HPA addition this phenomenon is absent. The initial dimensions of the Pd particles were 30–70 A and did not change, even after thermal treatment (973 K).

We assume that, due to the modification of Al_2O_3 by heteropolyacids, the production of a new surface, different in nature from the initial one, takes place. The HPA structure supports the formation of regular surface oxide structures which determine the distribution of Pd-contained active sites. So, on the one hand, the dispersity of Pd is supported and, on the other hand, a possible change in the actual structure of the active sites, for which the weakening of the surface energy bond of H_2 is evidence.

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