ENTHALPY OF HYDROGEN ABSORPTION IN PALLADIUM DEPOSITED ON Al_2O_3 AND TiO_2 SUPPORTS

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The potentials of the Pd/TiO_2 and Pd/Al_2O_3 catalysts were measured during saturation with hydrogen and during oxidation of the absorbed hydrogen with Ce(IV) in the medium of 0.5M-H_2SO_4. From the potential values attained in the coexistence region of the α- and β-hydride phases the enthalpy of hydrogen absorption, ΔH_{ab}, in Pd deposited on various supports was evaluated. With standard supports Degussa, ΔH_{ab} approaches the value measured on Pt black; a marked decrease of the absorption enthalpy was observed on the support TiO_2 of domestic provenience.

Palladium forms a volume hydride in hydrogen atmosphere; the phase α-PdH is formed at low partial pressures of hydrogen, whereas β-PdH is formed at higher partial pressures, the former being converted to the latter. If palladium is deposited on a support, then sorption of hydrogen may be much influenced by its interaction with the support. Two phenomena are responsible for the interaction: modification of the properties of the metal by transfer of electrons from the partially reduced support, and blocking of the adsorption sites on the metal by migration of the partially reduced support[1]. If a metal-support electronic interaction takes place, it should cause a change of the chemisorption enthalpy[2].

Interaction in the systems Pt/TiO_2 and Pd/TiO_2 were studied recently by several groups of investigators. Herrman et al.[3] found by calorimetric measurements that the initial value of the enthalpy of hydrogen adsorption on Pt/TiO_2 dropped from 92.0 to 79.5 kJ mol^{-1} as a result of metal-support interactions. On the other hand, Chou et al.[4], who measured the integral adsorption enthalpy of hydrogen on Pd/TiO_2, found 60 kJ mol^{-1}, a value comparable with that measured on Pd, 64 kJ mol^{-1}, from which they concluded that the electronic properties of the metal are not appreciably influenced by the TiO_2 support. Foo et al.[2] found from measurements of the hydrogen adsorption isotherm that the absorption enthalpy dropped from 36.7 kJ mol^{-1} on Pd black to 35.5 – 32.8 kJ mol^{-1} on 2% Pd/TiO_2. They also observed that the absorption enthalpy was lower on catalysts reduced at higher temperatures; and they attributed this effect to partial reduction of the support with partial electron transfer from TiO_x to palladium.

The present work is devoted to the determination of the absorption enthalpy of hydrogen on palladium deposited on TiO_2 and Al_2O_3 supports by potentiometric methods.

EXPERIMENTAL

The electrochemical potentiometric methods used are based on the potential measurement during saturation of palladium with hydrogen (method A) and during oxidation of the absorbed hydrogen with Ce(IV) (method B)[5]. Use is made of the fact that the potential of the Pd/H electrode is nearly independent of its hydrogen content in the region of coexistence of the phases α and β.

The measurement involved Pd/TiO_2 catalysts on supports from Degussa (P-25) and Precheza, Přerov (ChZ), Pd/Al_2O_3 catalysts on support from Degussa containing 1% and 5% Pd, and palladium black. The catalysts were prepared by wetting the supports with a solution of $PdCl_2$ containg the required quantity of Pd, the suspension was thickened during stirring on a water bath, dried at 95 °C for 4 h and at 105 °C overnight, and finally calcined at 300 °C for 6 h. The dried catalyst was milled in a vibration ball mill.

For the measurement, a weighed quantity of the catalyst (0.02 – 0.075 g) was placed into a titration cell (a cylindrical cell with plane bottom) together with 20 ml of 0.5M-H_2SO_4, the cell was closed and flushed with nitrogen free of oxygen for 30 min under continuous stirring of the suspension. Afterwards the stream of nitrogen was replaced by streaming hydrogen and the potential of the suspension was recorded. To this purpose, the cell contained a Pt wire indicator electrode and was connected by a salt bridge with a saturated calomel reference electrode. The Pt wire electrode acquired the potential of the impinging particles of the catalyst suspension during intense stirring. After the saturation of the catalyst with hydrogen had been finished, usually after 45 min, the excess hydrogen was removed by flushing with nitrogen and the sorbed hydrogen was oxidized by titrating with a solution of Ce^{4+} ions, which was injected into the cell by a peristaltic pump at a constant rate. The recorded potentiometric titration curve was used to determine the mean oxidation potential of absorbed hydrogen, $E_{1/2,O}$, as well as the quantity of the titrant consumed. To minimize the non-reacted excess of the titrating solution, the flow rate of 0.005M-Ce^{4+} solution was as low as 0.06 ml/min and the titration lasted for 20 – 30 min. The content of hydrogen absorbed in Pd was calculated from the quantity of the titrant consumed. The potential of the Pt indicator electrode against SCE was measured with a Wenking potentiostat and recorded by a TZ 4100 type recorder (Laboratorní přístroje, Prague). To determine the absorption enthalpy of hydrogen, the values of $E_{1/2}$ were measured at 25, 40, 50, and 60 °C.

RESULTS AND DISCUSSION

The time course of the potential during hydrogenation and the way of determination of the potential $E_{1/2,H}$ is illustrated in Fig. 1. In Fig. 2 is shown the time course of the potential during oxidation of absorbed hydrogen on Pd black, Pd/TiO_2 (Degussa) and Pd/Al_2O_3, curve *1* (the curves overlap), and on Pd/TiO_2 (ChZ Přerov), curve *2*. A typical feature of curve *1* is that in the coexistence region of phases α and β the potential of the suspension changes only little with the time (which is proportional to the quantity of the injected titrant) and so it is possible easily to determine the value of $E_{1/2,O}$. During titration, the molecular hydrogen dissolved in the catalyst pores (region [*a*–*b*] is oxidized first. Oxidation of absorbed hydrogen proceeds in the region [*b*–*c*], whereas in the region [*c*–*d*] oxidation of adsorbed hydrogen takes place. The course of the oxidation of hydrogen absorbed in the Pd/TiO$_2$ catalyst (ChZ Přerov) is markedly different (curve *2*). The oxidation of hydrogen proceeds at much higher potentials and the horizontal portion on the E–t curve is missing. The values of $E_{1/2,\mathrm{O}}$ were set equal to the potentials at one half of the less steep curve *2*. The standard enthalpy of the phase change of absorbed hydrogen, ΔH_{ab}, is given by the Gibbs–Helmholtz equation in the form

$$\partial(E_{1/2}/T)\,/\,\partial(1/T) = -\Delta H_{\mathrm{ab}}\,/\,nF\,,$$

where $E_{1/2}$ denotes potential (V) of the delay, T absolute temperature, F Faraday constant, and $n = 2$. The values of ΔH_{ab} were calculated by linear regression from the measured $E_{1/2}$ values at various temperatures. The results are presented in Table I.

The value of ΔH_{ab} obtained from the values of $E_{1/2,\mathrm{H}}$ measured during hydrogenation of Pd black is identical with the value given by Ratchford[6], 38.8 kJ mol^{-1}, corresponding to absorption of hydrogen in compact palladium. The value of ΔH_{ab} obtained during oxidation of hydrogen is but slightly lower. The two values lie within the interval given by various authors[6].

The values of ΔH_{ab} corresponding to the supports from Degussa are close to those measured on Pd black, but systematically higher. It follows from the values of ΔH_{ab} for Pd/TiO$_2$ (Degussa) that they are somewhat influenced by the mode of measurement of $E_{1/2}$. The values calculated from $E_{1/2,\mathrm{H}}$ measured during the first hydrogenation are nearly identical with those measured on Pd black, whereas ΔH_{ab} calculated from the $E_{1/2}$ values obtained during subsequent oxidation and during another hydrogenation are significantly higher. Further increase of ΔH_{ab} is observed during another oxidation. The

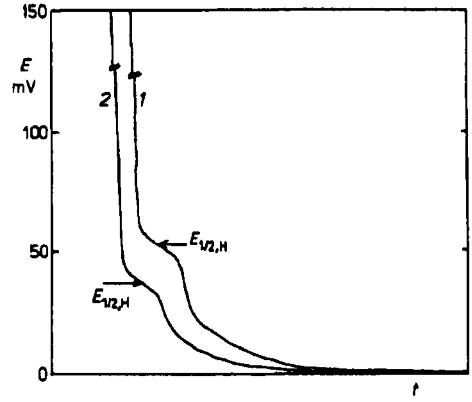

FIG. 1

Time course of the potential during hydrogenation of 5% Pd/TiO$_2$ (Degussa) at 25 °C (*1*) and 50 °C (*2*)

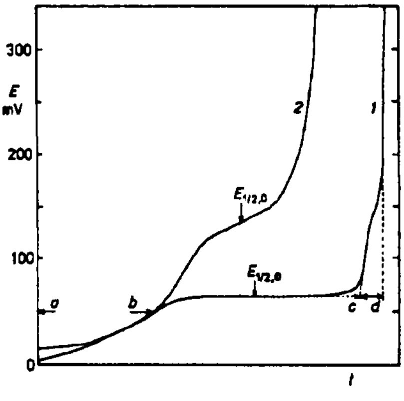

FIG. 2

Time course of the potential during oxidation of absorbed hydrogen with Ce^{4+} ions at 25 °C. *1* 5% Pd/TiO$_2$ (Degussa); *2* 5% Pd/TiO$_2$ (ChZ) content of Pd, i.e. 1 or 5%, does not influence the values of ΔH_{ab} within the limits of reproducibility of the measurement.

The catalyst prepared from the support TiO_2(ChZ) shows quite a different behaviour (Fig. 2). In contrast to the supports from Degussa, no discernible potential delay occurs during hydrogenation, hence it is not possible to use the method A for the evaluation of ΔH_{ab}. Owing to the course of oxidation of the absorbed hydrogen, the determination of $E_{1/2,O}$ is very inaccurate and so is the determination of ΔH_{ab}. However, it follows from the results that the value of $E_{1/2,O}$ is independent of the temperature in the interval from 25 to 60 °C, and therefore ΔH_{ab} is very low.

Our results show that the properties of the support may profoundly influence the enthalpy of hydrogen absorption in the deposited metal. The supports from Degussa influence this enthalpy relatively little, especially during first hydrogenation. During subsequent oxidation and repeated hydrogenation, ΔH_{ab} changes more markedly, but in the opposite sense as compared with the finding of Foo and coworkers[2]. These authors observed a small decrease of ΔH_{ab} on Pd/TiO_2 against Pd black, which became more marked with increasing reduction temperature of the catalyst (in the range 373 – 673 K). However, it should be noted that Foo and coworkers measured in the system catalyst/hydrogen, whereas our data refer to the system containing, in addition, also sulfuric

TABLE I
Values of ΔH_{ab} for particular catalysts

Catalyst	$-\Delta H_{ab}{}^{1}$ kJ mol^{-1}	$-\Delta H_{ab}{}^{2}$ kJ mol^{-1}
Pd black	38.74 ± 0.31	37.88 ± 0.29
1% Pd/Al_2O_3 (Degussa)		47.95 ± 7.7^{c}
5% Pd/Al_2O_3 (Degussa)		47.56 ± 5.7^{c}
1% Pd/TiO_2 (Degussa)	40.93 ± 3.8^{a}	47.2 ± 1.5^{a}
	46.28 ± 0.8^{b}	57.07 ± 5.0^{b}
	43.63 ± 4.1^{c}	52.14 ± 6.1^{c}
5% Pd/TiO_2 (Degussa)	39.24 ± 2.7^{a}	42.44 ± 3.6^{a}
	47.91 ± 0.9^{b}	52.44 ± 0.7^{b}
	43.57 ± 4.3^{c}	47.44 ± 4.9^{c}
1% Pd/TiO_2 (ChZ)		15.82 ± 17^{a}
		17.94 ± 16^{b}
5% Pd/TiO_2 (ChZ)		12.82 ± 11^{a}
		9.58 ± 12^{b}

[1] Found from $E_{1/2,H}$ values; [2] found from $E_{1/2,O}$ values; [a] first determination on a virgin sample; [b] repeated determination; [c] ΔH_{ab} calculated from all determinations.

acid solution. The results suggest that during repeated hydrogenation–oxidation cycles, when ΔH_{ab} increases, not only the metal and support are reduced, but (in contrast to the non-aqueous system) also hydration of the partly reduced surface oxides of the support takes place. The latter effect is probably responsible for the increase of ΔH_{ab} on the catalysts Pd/TiO_2 or Al_2O_3 from Degussa.

In the case of the support TiO_2 (ChZ), in contrast to that from Degussa, a very strong interaction between Pd and the support takes place, which is manifested by a profound decrease of hydrogen absorption enthalpy. In addition, also the solubility of hydrogen in palladium is appreciably lowered. In contrast to Pd black and catalysts Pd/Al_2O_3 or TiO_2 (Degussa), where the molar ratio of H : Pd was in the range 0.5 – 0.6, with Pd/TiO_2 (ChZ) it was equal only to 0.35 – 0.4.

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