

COMPETITIVE HYDROGENATION OF UNSATURATED HYDROCARBONS ON PALLADIUM CATALYSTS MODIFIED WITH LEAD AND THALLIUM

Libor ČERVENÝ^a, Ivo PASEKA^b, Karel SURMA^a, Nguyen Thi THANH^a
and Vlastimil RŮŽIČKA^a

^a *Department of Organic Technology,*

Prague Institute of Chemical Technology, 166 28 Prague 6 and

^b *Institute of Inorganic Chemistry,*

Czechoslovak Academy of Sciences, 160 00 Prague 6

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The competitive catalytic hydrogenations of pairs of 2,5-dimethyl-2,4-hexadiene with 1-heptene and 2-octyne with 1-heptene were studied on palladium black modified with lead or thallium to various degrees of coverage. The dissolved and adsorbed hydrogen was determined electrochemically and the selectivities of the competitive hydrogenations were established. The effect of the lead or thallium ad-atoms on the hydrogenation kinetics is discussed.

Palladium catalysts are highly selective with respect to hydrogenation of alkadienes and alkynes to alkenes. Various modifiers, such as metals, inorganic salts, or some organic substances, are frequently used to further increase the catalyst selectivity.

If the hydrogenation selectivity is very high, testing of its changes by hydrogenation of an alkadiene or alkyne substrate is difficult because the concentration of the paraffin product, which is the key figure in the calculation of the selectivity value, is too low to be determined accurately enough. A better approach consists in the use of competitive catalytic hydrogenation¹ of a suitably chosen alkadiene-alkene or alkyne-alkene pair. If the initial alkene used is adsorbed considerably more strongly than the alkene formed from the alkadiene or alkyne, the hydrogenation of the two starting substances is truly competitive, which extends the possibilities for examining the changes in the competitive hydrogenation selectivity¹. If an alkadiene or an alkyne alone is hydrogenated, the hydrogenation selectivity is high because the primarily formed alkene is displaced from the catalyst surface by the unreacted starting substance possessing a higher adsorptivity, and so its changes are difficult to measure. A direct relation between the selectivity of hydrogenation of a sole alkadiene or alkyne and that of the competitive hydrogenation of an alkadiene (alkyne)-alkene system must exist in cases where the slowest process is the surface reaction rather than the establishment of the adsorption equilibria.

For hydrogenation reactions on palladium catalyst whose surface is occupied by an additional metal not adsorbing hydrogen (so that the hydrogenation can be assumed not to take place on this metal), the palladium surface area available for the reaction can be expected to be reduced by this metal. Changes in the catalyst properties due to electronic interactions of the two metals in the surface layers are also conceivable. The two factors may affect the activity and selectivity of the reactions occurring on modified catalysts.

In this work, the relation is examined between the parameters of the competitive hydrogenation of 2,5-dimethyl-2,4-hexadiene or 2-octyne with 1-heptene and the degree of coverage of palladium black catalyst by either of two modifying metals, lead or thallium. The degree of coverage was determined by measuring the amounts of the absorbed (dissolved) and adsorbed hydrogen by the electrochemical potentiodynamic method, and the modified catalysts were employed for the catalytic hydrogenation with the aim to investigate the changes in the hydrogenation selectivity. The specific features of two-component catalysts are discussed with respect to the results obtained.

EXPERIMENTAL

Substances. 2,5-Dimethyl-2,4-hexadiene and 1-octyne (Schuchardt, Munich, FRG), 1-heptene (Koch-Light, England), methanol *p.a.*, ethanol denatured with methanol, hexane distilled with sodium (Lachema, Brno). All the substances were distilled prior to use and were chromatographically pure.

Catalysts. Palladium black was prepared according to ref.². The modification of the black by lead was performed by using aqueous solution of lead dichloride acidified with hydrochloric acid. The concentration of lead dichloride was 1 mg/ml and different volumes of solution were taken so as to obtain a series of catalysts with various degrees of surface coverage. The adsorption and reduction ($\text{Pb}^{2+} \rightarrow \text{Pb}^0$) were performed at 50°C for 3 h with constant stirring and hydrogen feeding. Then the catalyst was filtered out under hydrogen, passivated with nitrogen, and dried in a drying oven at 60°C to constant weight. Catalysts modified with thallium were prepared similarly using a solution of thallium sulphate acidified with sulphuric acid.

The potentiodynamic determination of the absorbed and adsorbed hydrogen³ was carried out at 50–110 mV for the former and at 110–370 mV for the latter. So the charges requisite for the oxidation of the two hydrogen forms were determined and the surface area of the free palladium surface was calculated.

The liquid phase hydrogenations were performed in a standard apparatus⁴ at 20°C and atmospheric pressure. One ml of the equimolar mixture of the two substrates was taken using 10–45 mg of catalyst. The course of the hydrogenation was monitored by measuring the rate of loss of hydrogen from volumetric burettes and by chromatographic analysis of samples.

Analytical methods. The analyses were carried out on a Chrom 4 instrument fitted with a flame ionization detector. Mixtures from the hydrogenations of 2,5-dimethyl-2,4-hexadiene with 1-heptene were analyzed at 76°C on a column 4 m long, i.d. 2.5 mm, packed with 15% polyethylene glycol 1 540 on Chromosorb P (35–80 mesh), mixtures from the hydrogenations of 2-octyne

with 1-heptene were analyzed at 70°C on a column 3.5 m long, i.d. 2.5 mm, packed with 15% SE-31 on Chromaton NAW-DMCS (0.16–0.20 mm).

RESULTS AND DISCUSSION

Determination of Absorbed and Adsorbed Hydrogen

In the electrochemical method used, the absorbed or adsorbed hydrogen on palladium black powder is oxidized by means of linearly increasing voltage. The method initially suggested for platinum had to be adapted⁵ for palladium, containing larger quantities of absorbed hydrogen, so that the charge for the oxidation of absorbed hydrogen was determined in the potential region of 50–110 mV applying a potential sweep rate of 0.8 mV/s, and the charge for the adsorbed hydrogen was determined separately within the potential region of 110–370 mV using a voltage sweep rate of 8 mV/s. The free catalyst surface was calculated assuming its proportionality to $Q_{H,ad}$, using the value of $2.08 \cdot 10^{-4}$ C for the charge necessary for the oxidation of hydrogen adsorbed on a cm² of the polycrystalline palladium black. The method was tested on nonmodified samples whose surface area was also determined by the BET method; the results obtained by the two methods were identical to within 0.5%, which is less than the 5% error of an individual determination by the electrochemical method.

First the absorbed hydrogen was determined at potentials below +90 mV, because the data of refs^{5,6} indicate that at $E > 90$ mV (*vs* RHE) there is nearly no absorbed hydrogen left. However, similarly as in work⁷, the oxidation region for absorbed hydrogen shifted to higher potentials with increasing degree of coverage by the modifying metal, and so the corresponding potential region had to be extended as far as +110 mV, and the adsorbed hydrogen was determined at 110–370 mV (RHE). Still, at degrees of coverage by lead ad-atoms $\theta_{pb} > 0.55$ the determination of adsorbed hydrogen was rather inaccurate because the peak of oxidation of absorbed hydrogen broadened and encroached on the potential region corresponding to adsorbed hydrogen (Fig. 1). This was particularly marked for catalysts modified with thallium, where the discrimination between H_{ab} and H_{ad} posed a problem even at lower degrees of coverage.

The results of the potentiodynamic measurements are given in Table I (upper part). The amounts of the dissolved hydrogen (proportional to $Q_{H,ab}$) show a considerable variance, due to the partial overlap of the waves corresponding to the absorbed and adsorbed hydrogen and also to the fact that the measurements may not have been performed in the steady state, although the $Q_{H,ab}$ value did not change appreciably on extending the saturation period. Also, the accuracy of determination of the two hydrogen forms decreased with increasing degree of coverage of palladium by the modifying metal.

The theoretical degree of coverage of the palladium surface by the modifier was calculated from the amount of the metal salt used and from the size of the metal atoms assuming a complete deposition of the metal on the catalyst surface. Similarly as previously⁷, for low amounts of salt in solution the actual degrees of coverage were higher than the theoretical values whereas for high amounts of salt in solution

TABLE I
Results of potentiodynamic measurements

Catalyst	Charge for the oxidation of hydrogen, C/g		Specific surface area B_H m^2/g	Degree of surface coverage by modifying metal θ_{Me}
	$Q_{H,ab}$	$Q_{H,ad}$		
Pd black	515.90	73.0	35.10	0.00
Pd-Pb	284.08	50.38	24.22	0.31
Pd-Pb	421.01	39.42	18.95	0.46
Pd-Pb	680.34	31.39	15.09	0.57
Pd-Tl	586.00	47.5	23.80	0.35
Pd-Tl	593.10	42.7	20.50	0.42
Pd-Tl	758.00	40.9	19.65	0.44
Pd-Pb	553.50	65.70	31.59	0.10
Pd-Pb	551.50	61.32	29.48	0.16
Pd-Pb	565.10	56.95	27.38	0.22
Pd-Pb	503.70	36.86	17.73	0.50
Pd-Pb	131.21	27.74	13.34	0.62
Pd-Pb	99.63	22.63	10.88	0.69

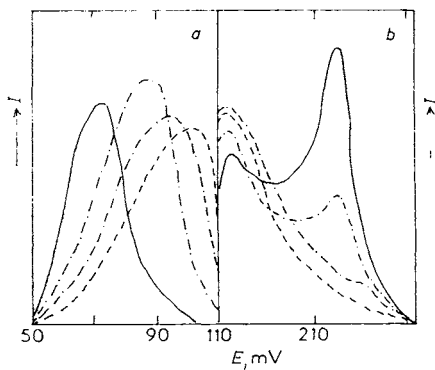


FIG. 1

Potentiodynamic curves for the oxidation of absorbed (a) and adsorbed (b) hydrogen on palladium black modified by lead ad-atoms. Degree of surface coverage: — 0, - - - - 0.22, - · - · - 0.49, - - - - 0.69

the reverse was true. The latter fact can be explained so that the adsorption of the salt and reduction of lead or thallium on the palladium surface were not quantitative at higher degrees of coverage.

Seeking for the cause of the higher experimental degrees of coverage than as corresponds to the theoretical values (for low degrees of coverage) we carried out blank experiments with distilled water from a conventional copper distillation apparatus as used for the modification and with water redistilled in an all-glass apparatus, using the same conditions as in the actual experiments. In the former case the palladium black surface area, determined *via* adsorbed hydrogen, decreased by as much as 37%, whereas in the latter case only a 3% decrease was observed. This documents the great importance of purity of the distilled water used, with respect to the active palladium surface. A possible explanation of this effect lies in the different copper content of the two kinds of water (0.05 mg/l from the metal apparatus against 0.005 mg/l from the glass apparatus) although the decrease in the active surface of palladium is higher than as corresponds to a quantitative reduction of the copper.

With regard to this effect, a new series of Pd-Pb catalysts was prepared using water from the glass apparatus. The potentiometric measurement data for them are given in the lower part of Table I.

At low θ_{Pb} values the amount of absorbed hydrogen increased with increasing θ_{Pb} ; as θ_{Pb} surpassed the value of 0.5, however, this amount dropped rapidly. The amounts of the modifying metal determined *via* the experimental $Q_{\text{H,ad}}$ data again did not agree precisely with the theoretical values based on the used amounts of salt; a good agreement was only obtained at low θ_{Pb} values (not exceeding 0.22), whereas at higher θ_{Pb} values the experimental amounts of metal were lower than the theoretical, corresponding to an incomplete reduction of Pb^{2+} .

Hydrogenation of Unsaturated Hydrocarbons

The hydrogenations were conducted in conditions preventing influence of substrate transport on the hydrogenation course. The results of kinetic measurements for the catalytic hydrogenation of an equimolar mixture of 2,5-dimethyl-2,4-hexadiene and 1-heptene on the catalysts listed in the upper part of Table I are given in Table II, demonstrating that both the initial rate and the relative rate r_{rel} decreased with increasing degree of palladium surface coverage by the metal. The specific rate r_{sp} was virtually constant.

The hydrogenation of 2,5-dimethyl-2,4-hexadiene to 2,5-dimethyl-2-hexene was highly selective; 2,5-dimethylhexane formed at high degrees of conversion only. In addition to the hydrogenation to heptane, 1-heptene also isomerized to *trans*- and *cis*-2-heptenes. Since the isomerization also concerned part of the active surface catalyst, the isomers were added to the reacted 1-heptene in the selectivity calculations, hence, the reactivity of 1-heptene was regarded globally as the sum of rates

of hydrogenation and isomerization. The selectivity of the competitive hydrogenation of 2,5-dimethyl-2,4-hexadiene (A) and 1-heptene (B) on palladium black in ethanol was $S_1 = 0.12$. The values for catalysts modified with thallium were roughly the same. Since the specific hydrogenation rates established based on the hydrogen takeup at the beginning of the hydrogenation did not vary appreciably either, it can be concluded that in the series of Pd-Tl catalysts, part of the palladium active centres was only mechanically blocked by the thallium. The value measured in this system in hexane as solvent was very low, $S_1 = 0.04$, and moreover, the logarithmic dependence of the actual concentrations of the two substances was curved (compare Fig. 2).

The selectivity of the competitive hydrogenation increased with increasing degree of occupation of the palladium surface by lead, from $S_1 = 0.12$ for Pd black to $S_1 = 0.36$ on a catalyst with $\theta_{Pb} = 0.57$. With hexane as solvent this effect was less marked, and moreover, the selectivity varied during the competitive hydrogenation (Fig. 2) so that the rate of hydrogenation of the alkadiene became relatively preferred over that of the alkene as the degree of conversion increased. This may be partly due to the isomerization of 1-heptene to 2-heptenes which hydrogenate more slowly. For 1-heptene alone, the initial ratio of the rates of isomerization to hydrogenation was 6.5 in ethanol and 10.5 in hexane. The plot of the hydrogen takeup *vs* time

TABLE II

Results of kinetic measurements for hydrogenation of 2,5-dimethyl-2,4-hexadiene (A) and 1-heptene (B)

Catalyst	Degree of coverage θ_{Me}	Solvent	Initial rate of hydrogenation of an equimolar mixture		
			r	r_{rel}	r_{sp}
Pd black	0.00	ethanol	504.2	1.00	1.00
Pd-Tl	0.35	ethanol	318.3	0.63	0.97
Pd-Tl	0.42	ethanol	293.0	0.58	1.01
Pd-Tl	0.44	ethanol	266.6	0.53	0.95
Pd-Pb	0.31	ethanol	309.2	0.67	0.97
Pd-Pb	7.46	ethanol	237.5	0.51	0.95
Pd-Pb	0.57	ethanol	180.9	0.39	0.91
Pd black	0.00	hexane	934.0	1.00	1.00
Pd-Pb	0.31	hexane	660.0	0.71	1.02
Pd-Pb	0.46	hexane	494.3	0.53	0.98
Pd-Pb	0.57	hexane	382.0	0.41	0.95

for 1-heptene alone starts to bend at degrees of conversion of $x = 0.8$ and 0.6 in the two solvents, respectively. These observations are consistent with the fact that the bending of the logarithmic dependences of concentrations of the two starting substances during their hydrogenation is particularly marked in hexane. However, the isomerization of 1-heptene does not seem to be the sole cause of the effect discussed, because this effect has been observed also for the competitive catalytic hydrogenation of 2-octyne and 1-heptene on supported palladium catalysts^{1,8}, where the curves began to bend at considerably lower degree of conversion and the bending, in favour of the hydrogenation of 2-octyne, was again much more pronounced in the non-polar solvent. A concept has been adopted^{1,8} of the hydrogenation of the two substances involving two forms of hydrogen which are not in equilibrium during the reaction.

The results for the competitive hydrogenation of 2-octyne and 1-heptene in methanol on the catalysts modified with lead are given in Table III. The specific reaction rate decreases and the selectivity of the competitive hydrogenation (S_1) increases with growing degree of occupation. In this case the selectivities were evaluated based on the initial reaction rates; in the $\log c_A$ vs $\log c_B$ coordinates the curves were bent in favour of the hydrogenation of 2-octyne. The selectivity of hydrogenation with respect to isomerization (S_2) was higher on the modified catalysts than on Pd black. Probably, part of the adsorbed alkene molecule is present above the surface blocked by the ad-atoms of the modifying metal, whereby the possibility of interaction of this part with the palladium surface is substantially reduced; and this interaction seems to be prerequisite for the isomer formation, be it *via* the so-called dissociative adsorption or *via* a semihydrogenated state formation following by de-

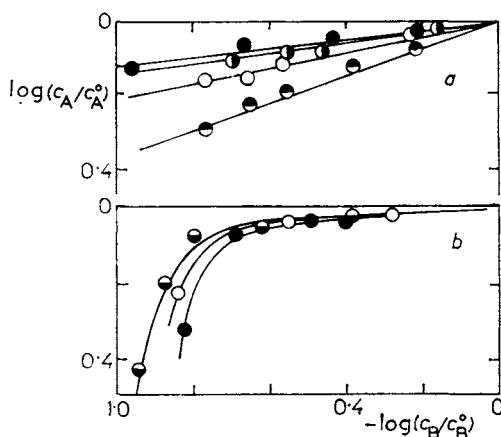


FIG. 2

Dependence of the concentrations of 2,5-dimethyl-2,4-hexadiene (A) and 1-heptene (B) during the competitive hydrogenation on Pd-Pb catalysts in ethanol (a) and in hexane (b). Degree of coverage: ● 0.00, ◐ 0.31, ○ 0.47, ● 0.57

tachment of a hydrogen particle from a carbon different from that making up the initial double bond. This concept is consistent with the results obtained for Pt-Cu catalysts⁹, where the degree of occupation of the free platinum surface by the adsorbed alkene decreased with increasing θ_{Cu} . This agrees with the idea of part of the adsorbed molecule being above the surface blocked by atoms of the modifying metal¹⁰.

With regard to the facts mentioned above, a new series of Pd-Pb catalysts was prepared using water distilled in a glass apparatus (lower part of Table I). First, 1-heptene in ethanol was hydrogenated. The relative specific rate of hydrogenation at the beginning of the reaction was approximately unity until the degree of coverage surpassed the value of 0.2, at higher degrees of coverage the relative specific rate

TABLE III

Results of competitive hydrogenation of 2-octyne (A) and 1-heptene (B) in methanol on palladium-lead catalysts

Degree of coverage θ_{Pb}	Initial hydrogenation rate of an equimolar mixture			Selectivity	
	r	r_{rel}	r_{sp}	S_1	S_2
0.00	76.4	1.00	1.00	4.5	0.69
0.31	35.8	0.47	0.68	5.3	0.80
0.46	25.2	0.33	0.61	5.8	0.84
0.57	19.9	0.26	0.60	6.4	0.84

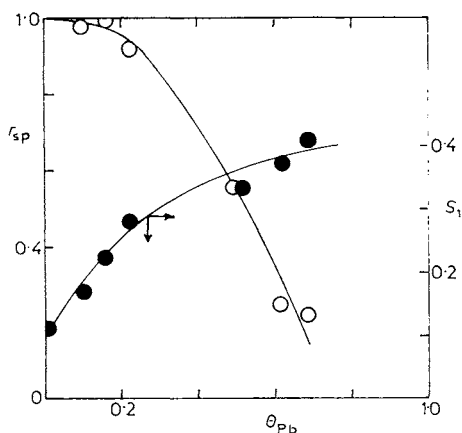


FIG. 3

Dependence of the specific rate of hydrogenation of 1-heptene in ethanol at the beginning of the reaction (O) and of the selectivity of the competitive hydrogenation of 2,5-dimethyl-2,4-hexadiene and 1-heptene S_1 on the degree of coverage of the palladium surface by lead (θ_{Pb})

was always lower (Fig. 3). Hence, at low degrees of occupation the modifying metal either only blocks the surface mechanically or acts as inhibitor to the reaction step in which the particle adsorbed on one site takes part. At higher degrees of occupation the effect of modification is considerably more pronounced so that the area formally blocked by an ad-atom is at least twice as large as that actually occupied by it.

The plot of the selectivity of the competitive hydrogenation of 2,5-dimethyl-2,4-hexadiene and 1-heptene in dependence on the degree of occupation of the palladium surface by lead (Fig. 3) shows that the reactivity of the alkadiene is relatively preferred over the alkene as θ_{Pb} is increased. This relative increase in the hydrogenation rate for 2,5-dimethyl-2,4-hexadiene is even more marked in the range of low θ_{Pb} values than at $\theta_{\text{Pb}} \geq 0.2$. The results of the competitive hydrogenation on the two series of Pd-Pb catalysts are qualitatively similar. The changes in the selectivity of the competitive hydrogenation, where the hydrogenation of the bulky alkadiene or alkyne molecules becomes relatively less inhibited as the degree of surface modification by the lead ad-atoms is increased, suggest that the mechanical blocking of the palladium surface is not the dominant factor determining the relative hydrogenation rates. In fact, if only the mechanical blocking were involved, the selectivity would have to decrease because the number of sites on which the sterically more demanding 2,5-dimethyl-2,4-hexadiene or 2-octyne can hydrogenate would diminish more rapidly with the increasing degree of coverage than the number of sites on which the smaller molecule of 1-heptene can be hydrogenated.

The results rather suggest that decisive for the adsorptivity and, consequently, for the hydrogenation rate is the molecule-metal bond strength which determines the ability to form surface π -complexes involving delocalized π -electrons¹¹. Really, modification of the palladium surface by the metals in question brings about lowering in the d -nature of palladium, whereupon the ability to form π -bonds with the adsorbing molecules also lowers, and this affects the weaker interactions of alkenes, with fewer π -electrons, to a relatively greater extent than the interactions of alkadienes or alkynes.

LIST OF SYMBOLS

B_{H}	specific surface area (m^2/g)
c_{A}	concentration of substance A (mol/l)
c_{A}^0	initial concentration of substance A (mol/l)
E	voltage (mV)
I	current response (mA)
$Q_{\text{H,ab}}$	charge for the oxidation of absorbed hydrogen (C/g)
$Q_{\text{H,ad}}$	charge for the oxidation of adsorbed hydrogen (C/g)
r	initial hydrogenation rate ($\text{ml}_{\text{H}_2}/\text{min g}$)
r_{rel}	relative hydrogenation rate, ratio of rates of hydrogenation on the modified catalyst and on Pd black

r_{sp}	specific initial hydrogenation rate, ratio of the reaction rate with respect to free palladium surface to the rate on Pd black
S_1	selectivity of competitive hydrogenation, ratio of selectivities of substances A and B at the beginning of reaction
S_2	selectivity of hydrogenation of 1-heptene with respect to isomerization, initial hydrogenation rate with respect to the sum of hydrogenation and isomerization rates at the beginning of the reaction
θ_{Mc}	degree of occupation of the Pd catalyst by the modifying metal
θ_{Pd}	free fraction of the palladium surface

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