SELECTIVITY OF HYDROGENATION IN AN ALKYNE–ALKENE SYSTEM ON PALLADIUM CATALYSTS MODIFIED WITH INORGANIC SALTS

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The competitive catalytic hydrogenation of 2-octyne and 1-heptene in methanol has been studied on catalysts 3% Pd on activated carbon and Pd black, modified with ammonium chloride, potassium chloride, potassium carbonate, or calcium carbonate. The rates of hydrogenation of the two substrates and the rate of isomerization of 1-heptene have been determined. The effect of inorganic salts on the activity and selectivity of the catalysts is discussed.

Competitive catalytic hydrogenation reactions in alkyne–alkene mixtures can serve as a means for determining the selectivity of hydrogenation of the triple bond to the corresponding double bond[1]; a model substrate pair can be chosen such that the alkene in this pair is substantially more reactive than the alkene emerging from the partial hydrogenation of the alkyne. With highly selective catalysts, the latter alkene remains intact as long as the parent alkyne is present, due to the tremendous difference between the adsorptivities of the triple and the double bonds. On the other hand, in systems where the structures of the two substrates are chosen conveniently so that the double bond can be hydrogenated in competition with the triple bond (whose adsorptivity is lowered owing to the alkyne structure), the changes in the selectivity of hydrogenation of the triple bond in the presence of alkene can be observed well. A suitable substrate pair is formed, for instance, by 2-octyne, involving a 1,2-disubstituted triple bond, and 1-heptene, in which the double bond is monosubstituted.

The selectivity of hydrogenation of triple bonds on palladium catalysts, which by itself is rather high, can be additionally increased, in unchanged reaction conditions, by intervening suitably into the reaction system, particularly by modifying the catalyst itself[1]. Catalysts can be modified ("partly poisoned") with metals (lead[2] and cadmium[3] in particular), organic bases such as pyridine[4] or quinoline[5], carbon monoxide[6], ammonia[7], or alkali salts or hydroxides[8]. The effect of the modifier can be explained[9] in terms of a mechanical blocking of some active centres or interventions into the electronic structure of the surface atoms of the active metal.

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The aim of the present work was to study how the competitive hydrogenation in a model mixture of 2-octyne with 1-heptene is affected by the modification of the catalyst, 3% Pd on activated carbon or Pd black, with some inorganic salts.

EXPERIMENTAL

Catalysts. The catalyst of 3% Pd on activated carbon was a commercial product, Cherox 41-00, of Chemical Works in Litvínov; the sample was ground prior to use and a fraction of grain size below 0·063 mm was selected by screening. Pd black was prepared conventionally.

Substrates. 2-Octyne (Schuchardt) and 1-heptene (Koch-Light) were distilled prior to use to attain the chromatographic purity grade. Methanol and cyclohexane of reagent grade purity (Lachema) served as solvent for the hydrogenation.

Modification procedure. A suitable amount of the salt of choice of reagent grade purity (Lachema) was dissolved in 100 ml of water, the palladium catalyst was added, the mixture was stirred for 2 h, and water was removed by evaporation in a vacuum rotary evaporator. The catalyst was dried at 80°C to constant weight.

Apparatus and methods of measurement. The hydrogenations were performed in a conventional apparatus[10] at 20°C and atmospheric pressure. The reaction rates were determined by measuring the time dependence of hydrogen uptake and the time dependences of the concentrations of the reacting substances. A Chrom-4 chromatographic instrument with flame ionization detection was used, equipped with a glass column 3·5 m × 2·5 mm i.d., packed with 15% SE-31 on Chromaton NAW-DMCS with a grain size of 0·16—0·20 mm; temperature 70°C. The competitive hydrogenations were examined on 0·48 ml of 1-heptene and 0·5 ml of 2-octyne in 10 ml of methanol, the amount of catalyst lay within the region of 0·01—0·03 g.

RESULTS AND DISCUSSION

The measurements were conducted in conditions in which the reaction was unaffected by mass transport[11]. The effect of external diffusion was eliminated by vigorous stirring, the effect of internal diffusion, if any, was suppressed by using catalysts with small grain size.

The time course of concentrations of the reactants in the competitive hydrogenation afforded the initial rates of hydrogenation of 2-octyne and 1-heptene and the initial rate of isomerization of 1-heptene to 2-heptene (*cis* + *trans*). The sum of these values represents the activity of the catalyst under examination. The initial rates were evaluated to give the selectivities of the competitive reaction of 2-octyne and 1-heptene (S_1) and the selectivities of the hydrogenation of the double bond with respect to the isomerization (S_2). The data for the modified 3% Pd on activated carbon are given in Table I. The modification leads to a decrease in the catalyst activity, the decrease being the higher, the greater the amount of the salt used. The highest drop in activity was observed with ammonium chloride. This effect is not surprising, and obviously arises from a mechanical blocking of the palladium surface by the salt, most of the salt being presumably adsorbed on the support.

Of more interest is the effect of the inorganic salts on the selectivity of the competitive hydrogenation. While the modification with potassium chloride left the selectivity virtually unchanged, modification with ammonium chloride brought about a decrease in the selectivity (*i.e.*, a relative decrease in the reactivity of the alkyne with respect to the alkene), practically independent of the salt content in catalyst. On the other hand, the selectivity increased on the modification with carbonates, the increase being the more pronounced the higher content of the salt. This effect is more marked with calcium carbonate.

The selectivity of hydrogenation of the double bond of 1-heptene with respect to the isomerization (S_2) was identical on all of the catalysts within the limits of experimental error.

TABLE I

Kinetic parameters of the competitive hydrogenation of 2-octyne and 1-heptene in methanol on a catalyst of 3% Pd on activated carbon modified with inorganic salts

Modifier		Initial reaction rate, mmol/min g Pd			Catalyst activity[a]	Selectivity[b]	
Salt	amount in catalyst %	hydrogenation of 2-octyne	hydrogenation of 1-heptene	isomerization of 1-heptene		S_1	S_2
—	—	315·0	119·0	14·1	448·1	2·36	0·89
NH_4Cl	5	211·2	117·7	12·1	341·0	1·63	0·91
NH_4Cl	15	193·9	112·4	11·2	317·5	1·57	0·91
NH_4Cl	20	184·5	108·4	10·5	303·4	1·55	0·91
KCl	10	302·5	113·5	13·8	429·8	2·37	0·89
KCl	20	286·6	110·8	10·5	407·9	2·36	0·91
KCl	30	276·4	108·0	10·3	384·7	2·33	0·91
K_2CO_3	5	309·3	113·1	12·9	435·3	2·45	0·90
K_2CO_3	20	304·6	95·8	11·5	411·9	2·83	0·89
K_2CO_3	30	296·9	85·3	10·4	392·6	3·10	0·89
$CaCO_3$	5	301·7	100·3	13·7	415·7	2·64	0·88
$CaCO_3$	20	195·6	84·1	12·4	392·1	3·06	0·87
$CaCO_3$	30	286·6	73·0	10·9	370·5	3·40	0·87

[a] Sum of the initial rates of hydrogenation of 2-octyne and 1-heptene and of isomerization of 1-heptene; [b] S_1 is the selectivity of the competitive hydrogenation, *i.e.* the ratio of the rate of hydrogenation of octyne to the rate of hydrogenation and isomerization of 1-heptene, S_2 is the selectivity of hydrogenation of the double bond with respect to the isomerization, *i.e.* the ratio of the rate of hydrogenation of heptene to the rate of hydrogenation and isomerization of heptene.

In order to eliminate effects from salts adsorbed on the support in a close vicinity to the active component, a series of modified samples of palladium black was prepared. The amount of salts in them with respect to palladium approached that in the supported catalysts containing 30% salt. In view of the high content of salt in the support-free catalyst and of the preparation procedure, the solid phase can be supposed to be a mechanical mixture of the pure salt and Pd black with the adsorbed

TABLE II

Kinetic parameters of the competitive hydrogenation of 2-octyne and 1-heptene in methanol on Pd black modified with inorganic salts

Modifier		Initial reaction rate mmol/min g Pd			Catalyst activity	Selectivity	
Salt	amount in catalyst %	hydrogenation of 2-octyne	hydrogenation of 1-heptene	isomerization of 1-heptene		S_1	S_2
—	—	62·6	9·5	4·3	76·4	4·5	0·69
NaCl	95	34·4	7·7	1·7	43·8	3·6	0·80
KCl	95	60·2	9·5	3·4	73·1	4·7	0·73
K_2CO_3	95	41·3	6·0	1·7	49·0	5·3	0·78
$CaCO_3$	93·6	44·7	6·9	1·6	53·2	5·2	0·80

TABLE III

Kinetic parameters of the competitive hydrogenation of 2-octyne and 1-heptene in cyclohexane on Pd catalysts modified with potassium carbonate

Catalyst	Amount of K_2CO_3 %	Initial reaction rate, mmol/min g Pd			Catalyst activity	Selectivity	
		hydrogenation of 2-octyne	hydrogenation of 1-heptene	isomerization of 1-heptene		S_1	S_2
3% Pd/act. C	—	32·8	12·3	3·3	48·4	2·1	0·79
3% Pd/act. C	30	6·9	2·1	0·4	9·4	2·7	0·85
Pd black	—	37·8	8·6	3·4	49·8	3·1	0·71
Pd black	95	6·9	1·4	0·3	8·6	4·0	0·82

salt. The results (Table II) are on the whole consistent with those obtained with the supported catalysts.

The effects observed may be due to interactions of the adsorbed salt with the palladium surface, and also to interactions of the salts partly dissolved in methanol. In order to eliminate the latter possibility, a series of measurements on catalysts modified with potassium carbonate was carried out using cyclohexane as a solvent in which the solubility of inorganic salts is very low. The results are summarized in Table III. The hydrogenation rate is here lower than in methanol; on 3% Pd/C catalyst the drop amounted to an order of magnitude, on Pd black it was nearly 40%. The lowering of the reaction rate by the modification of the catalysts with potassium carbonate was considerably more pronounced than in methanol.

The selectivity of the competitive hydrogenation in cyclohexane was invariably lower than in methanol and increased on the modification of the catalysts with potassium carbonate.

The results obtained thus point to an interesting effect of inorganic salts on the activity and selectivity of palladium catalysts in competitive hydrogenations of substances containing double and triple bonds. This effect is apparently due to interaction of the salts with palladium, influencing the interaction of the latter with unsaturated substances and possibly also with hydrogen.

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