

COMPETITIVE CATALYTIC HYDROGENATION IN UNSATURATED HYDROCARBON SYSTEMS WITH STERICALLY HINDERED DOUBLE BONDS

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A competitive hydrogenation of unsaturated hydrocarbons (α -methylstyrene, cyclohexene, 1-methylcyclohex-1-ene, 1-*tert*-butylcyclohex-1-ene and 3-*tert*-butylcyclohex-1-ene) in binary and ternary systems with palladium-, platinum- and rhodium-supported catalysts in a semibatch isothermal reactor at 20 °C under atmospheric pressure was studied. It was found that considerable variance in selectivity values of competitive hydrogenation in a series of substrates with increasing substituent bulkiness is caused by differences in adsorption and in reactivity of adsorbed molecules. In the case of ternary systems, a change in selectivity of competitive hydrogenation of two substrates was observed, due to the presence of a third substance, caused by a competitive adsorption of all three substrates and their interaction on a catalytic surface.

Key words: Competitive hydrogenation; Palladium; Platinum; Rhodium; Adsorptivity; Heterogeneous catalysis; Unsaturated hydrocarbons.

Research on selectivity of catalytic hydrogenations still ranks among contemporary tasks of heterogeneous catalysis¹⁻³. The obtained data gather a valuable piece of knowledge significant not only for the general theory of hydrogenation reactions but also for the industrial application. Although there exists an immense amount of literature concerning selective hydrogenations of alkene substrates, only an insignificant percentage of the studies utilize the method of competitive hydrogenation reaction³⁻⁸. This work involves determination of hydrogenation selectivities in systems formed by combination of substrates with substituents of a varied bulkiness (H, CH₃, C(CH₃)₃) close to the reaction center – double bond in a six-membered cyclic skeleton and in an alkene model. Using the initial reaction rate values acquired in the hydrogenations of individual substances, relative adsorption coefficients of individual substrates were determined from selectivity values of competitive hydrogenations. All these quantitative data allowed a discussion relating to the effect of a bulky substituent in a close vicinity to a double bond, with regard to formation of an adsorbed complex and to the surface reac-

tion rate. The obtained results also enabled discussion about structural effects in heterogeneous catalysis⁹⁻¹¹ with regard to the effects of a varied active component of a catalyst supported on an inert carrier.

EXPERIMENTAL

Chemicals

The substrates used were of commercial origin: α -methylstyrene (Slovnaft), cyclohexene (Koch-Light), 1-methylcyclohex-1-ene (Aldrich), 1-*tert*-butylcyclohex-1-ene, 3-*tert*-butylcyclohex-1-ene (Aroma) and were distilled before use. The solvent was methanol of analytical grade (Penta). Electrolytic hydrogen 4.0 (Linde Technoplyn) was used.

Catalysts

The catalysts used Pt/C-Secomet AN (Doducco Kat. GmbH), Pd/C-Cherox 4100ch (Chemopetrol Ltd.), Rh/C (DOT, ICT Prague) were characterized by the particle crystallite size, surface area and active component surface area (Table I). The particle crystallite size was determined using on XRD Seifert 3000P with CoK α and graphitic monochromator. The particle size was computed using an one-point method, always from the most intense line of the monitored material. Since it exhibited only a slightly elevated background on diffraction pattern, rhodium catalyst was X-ray-amorphous. Platinum and palladium catalysts show a definite crystallite structure. A measurement of physical adsorption of nitrogen was carried out using a Pulse Chemisorb 2700 system, Micromeritics; the total surface area (S_{BET}) was evaluated from the BET region. The surfaces of catalysts supported on activated carbon were subject to error, caused by the instrumentation used which, due to their great extents, did not enable an exact determination. The error reached approximately up to 10% of the determined value. Specific surface of the catalyst active component was determined using the method of selective hydrogen chemisorption and successive titration of its oxygen-adsorbed quantity with potentiometric indication of the equivalence point.

Apparatus and Kinetic Measurements

Kinetic measurements were carried out in a semibatch stirred reactor at 25 °C under hydrogen pressure of 101.3 kPa in methanol. A detailed description of the equipment is given elsewhere¹². All the measurements were carried out in the kinetic region. The reaction course was monitored by measuring

TABLE I
Characteristics of hydrogenation catalysts

Catalyst	Grain size, mm	Particle size, nm	$S_{\text{BET}}, \text{m}^2 \text{g}_{\text{met}}^{-1}$	$S_{\text{MET}}, \text{m}^2 \text{g}_{\text{met}}^{-1}$
3% Pd/C	<0.02	20.2	1 161	^a
5% Pt/C	<0.05	15.5	778	45.3
5% Rh/C	<0.02	<5.0	1 201	75.3

^a Not determined.

the time dependence of hydrogen consumption and time changes of molar concentrations obtained by chromatographic analysis (GLC). In hydrogenations, 2 mmol of substrate was used, 1 mmol of each substrate in competitive hydrogenations in 15 ml of methanol. The catalyst amount ranged between 0.1–0.01 g, depending on the substrate and catalyst type used.

In binary systems, which did not consist of 1-*tert*-butylcyclohex-1-ene substrate, competitive hydrogenations were carried out using 1 mmol of each substrate. In the case that one of the substrates was 1-*tert*-butylcyclohex-1-ene, it was necessary to use alkene/1-*tert*-butylcyclohex-1-ene molar ratio 1 : 20 because of very low concentration changes of this substance in the course of competitive hydrogenation. Similarly, the problem of low contents of *tert*-butylcyclohexane in the course of competitive hydrogenation in ternary systems was solved.

Analytical Method

Samples withdrawn at appropriately selected time intervals were analyzed using a gas chromatograph HP 5890 Series II plus (Hewlett–Packard) with flame-ionization detector (FID) and capillary column HP-20M (length 50 m, inner diameter 0.32 mm, thickness of stationary phase 0.32 μm) at temperature programs between 333–453 K and overpressure of carrier gas (N_2) 80 kPa. The substance contents in the reaction mixture were determined using the internal standard method. The internal standard was n-decane (Aldrich).

RESULTS AND DISCUSSION

For the purpose of this work, the above-mentioned alkenes can be divided into two groups, the first being made up of substances containing in their molecule a six-carbon cyclic skeleton containing a double bond and bearing substituents of a varying bulkiness (cyclohexene, 1-methylcyclohex-1-ene, 1-*tert*-butylcyclohex-1-ene). The second group consists of two comparative model substances containing a disubstituted double bond. In the case of 3-*tert*-butylcyclohex-1-ene, the equal six-carbon skeleton is involved, which contains a bulky *tert*-butyl substituent in α -position to the double bond; in the case of α -methylstyrene, the terminal double bond bears an aromatic ring conjugated with the investigated reaction center. All substances did not significantly vary in their molecular weights (82.15–138.25 g mol^{-1}), the influence of which is hence assumed insignificant, relative to their adsorption terms discussed through the relative adsorptivities.

Hydrogenation of Individual Substrates

Hydrogenations of individual alkene model substances were performed, excluding 3-*tert*-butylcyclohex-1-ene, which was available only in a mixture with 1-*tert*-butylcyclohex-1-ene. The obtained time dependencies of hydrogenated substrate concentrations were utilized to determine initial reaction rate values, which were read from the linear region of the dependence $c = f(t)$. These values were subsequently used for calculation of relative adsorption coefficients. Even at high conversions (>90%), the reactions were mostly of zeroth order with respect to substrate concentration. All

hydrogenations were accomplished with total conversion of the starting substances, having nature of a simple reaction, characterized by the scheme $A \rightarrow B$. In the case of substituted cyclohexenes on palladium and rhodium catalysts, no presence of positional isomers, resulting from the double bond migration, was detected by chromatography. A summary of the initial reaction rates for hydrogenations of individual model substances is provided in Table II.

From Table II it is apparent that the values of initial reaction rates of selected alkene substrates exhibit considerably dissimilar figures, whose trend, in regard to a substrate type, is in all the selected catalysts identical and decreases in the series: α -methylstyrene > cyclohexene > 1-methylcyclohex-1-ene > 1-*tert*-butylcyclohex-1-ene. From the values of initial reaction rates of individual alkenes, it is also possible to set up the following sequence of the selected catalysts in the order of decreasing activity in the double bond hydrogenation: Pd/C > Rh/C > Pt/C.

From the provided results of hydrogenation of individual substrates it follows that the assumption of an equal mechanism of the catalytic reaction with all model substances was fulfilled. Furthermore, all the three catalysts selected for quantitative assessment of the bulky-substituent effect upon the course of a heterogeneous catalytic reaction conducted a constant-like factor manner and changes in reactivity and adsorptivity incurred only due to the structure of hydrogenated substances.

TABLE II
Initial hydrogenation rates of substrates

Catalyst	Substrate	r_0 , mmol min ⁻¹ g _{cat} ⁻¹
Pd/C	α -methylstyrene	14.4 ± 0.2
	cyclohexene	26.0 ± 2.0
	1-methylcyclohex-1-ene	3.3 ± 0.1
	1- <i>tert</i> -butylcyclohex-1-ene	0.72 ± 0.02
Pt/C	α -methylstyrene	2.1 ± 0.1
	cyclohexene	19.0 ± 1.0
	1-methylcyclohex-1-ene	1.5 ± 0.1
	1- <i>tert</i> -butylcyclohex-1-ene	0.13 ± 0.02
Rh/C	α -methylstyrene	7.2 ± 0.2
	cyclohexene	24.0 ± 1.0
	1-methylcyclohex-1-ene	1.9 ± 0.1
	1- <i>tert</i> -butylcyclohex-1-ene	0.22 ± 0.01

Competitive Hydrogenations in Binary Systems

A relatively simple relation for selectivity, defined using the reactivity ratio of both substances, can be established if the kinetics of these substances involved in a competitive reaction can be expressed with an equation of the same form. If the rate-determining step is a surface reaction and the reaction is carried out far from equilibrium, in the simplest case with an assumption of ideal behaviour, it is possible to write for the hydrogenation of A and B substrates:

$$r_A = \frac{k_{AH}K_A c_A}{1 + K_A c_A + K_B c_B + K_H c_H + \sum K_i c_i} = - \frac{dc_A}{dt} \frac{V}{w} \quad (1)$$

$$r_B = \frac{k_{BH}K_B c_B}{1 + K_B c_B + K_A c_A + K_H c_H + \sum K_i c_i} = - \frac{dc_B}{dt} \frac{V}{w} \quad (2)$$

The hydrogen concentration and its adsorption constant are included in the kinetic constant k_{AH} . From Eqs (1) and (2), it is possible to derive a relation for the selectivity of competitive hydrogenation commonly known under the name Rader–Smith equation [18]:

$$\frac{\log(c_A/c_{A0})}{\log(c_B/c_{B0})} = \frac{k_{AH}K_A}{k_{BH}K_B} = S_{AB} \quad (3)$$

In ideal case, the dependence $\log(c_A/c_{A0})$ on $\log(c_B/c_{B0})$ is a straight line characterized by the slope S_{AB} . The measured data very well fulfilled the linear characteristic of this equation, which is apparent from the values of correlation coefficients (f) which ranged in an interval (0.91–1.00). Table III shows the S_{AB} selectivity values obtained using this procedure. Relative adsorption coefficients K_A/K_B , shown also in Table III, were computed using the acquired S_{AB} values and initial reaction rates r_0 of hydrogenation of individual substrate, which were in the above Eq. (3) substituted for reaction rate constants k_{AH} and k_{BH} .

The values S_{AB} , r_{A0}/r_{B0} , K_A/K_B acquired from competitive hydrogenations of binary systems of model substrates fostered a discussion about the structural effect upon reactivity and adsorptivity of substituted alkenes. In a series of structurally similar substrates, two extreme cases of substituent effect upon the course of a heterogeneous catalytic reaction may arise. In the first case, substrates exhibit the same reactivity in the adsorbed state; however, they differ significantly in their adsorptivity. The second case includes substrates with an equal adsorptivity, differing, however, in the reactivity of molecules in the adsorbed state. It is apparent from Table III that a combination of

TABLE III
Results of competitive hydrogenations

Substrate A	Substrate B	Catalyst	S _{AB}	f	r _{A0} /r _{B0}	K _A /K _B
α-Methylstyrene	cyclohexene	Pd/C	1.68 ± 0.03	0.9966	0.56 ± 0.04	3.11 ± 0.06
α-Methylstyrene	1-methylcyclohex-1-ene		29.0 ± 0.4	0.9981	4.4 ± 0.1	6.6 ± 0.1
Cyclohexene	1-methylcyclohex-1-ene		16.8 ± 0.3	0.9932	7.9 ± 0.4	2.1 ± 0.1
α-Methylstyrene	1- <i>tert</i> -butylcyclohex-1-ene		508 ± 24	0.9655	20.0 ± 0.3	25 ± 1
Cyclohexene	1- <i>tert</i> -butylcyclohex-1-ene		394 ± 32	0.9932	36.1 ± 1.8	10.9 ± 0.3
3- <i>tert</i> -Butylcyclohex-1-ene	1- <i>tert</i> -butylcyclohex-1-ene		22.5 ± 1.8	0.9365	—	—
1-Methylcyclohex-1-ene	1- <i>tert</i> -butylcyclohex-1-ene		22.2 ± 1.3	0.9571	4.6 ± 0.1	4.8 ± 0.2
α-Methylstyrene	cyclohexene	Pt/C	1.98 ± 0.02	0.9994	0.11 ± 0.01	16.5 ± 0.2
α-Methylstyrene	1-methylcyclohex-1-ene		15.2 ± 0.3	0.9956	1.40 ± 0.3	10.8 ± 0.1
Cyclohexene	1-methylcyclohex-1-ene		10.7 ± 0.1	0.9932	12.7 ± 0.2	0.9 ± 0.1
α-Methylstyrene	1- <i>tert</i> -butylcyclohex-1-ene		431 ± 24	0.9525	16.2 ± 0.5	27 ± 1
Cyclohexene	1- <i>tert</i> -butylcyclohex-1-ene		267 ± 12	0.9721	36.1 ± 1.8	7.4 ± 0.1
3- <i>tert</i> -Butylcyclohex-1-ene	1- <i>tert</i> -butylcyclohex-1-ene		36.7 ± 0.2	0.9997	—	—
1-Methylcyclohex-1-ene	1- <i>tert</i> -butylcyclohex-1-ene		27.9 ± 2.5	0.9146	11.6 ± 0.2	2.4 ± 0.2
α-Methylstyrene	cyclohexene	Rh/C	1.04 ± 0.02	0.9957	0.30 ± 0.01	3.47 ± 0.05
α-Methylstyrene	1-methylcyclohex-1-ene		26.5 ± 0.8	0.9901	3.8 ± 0.1	7.0 ± 0.1
Cyclohexene	1-methylcyclohex-1-ene		25.3 ± 1.0	0.9856	12.7 ± 0.2	2.0 ± 0.1
α-Methylstyrene	1- <i>tert</i> -butylcyclohex-1-ene		257 ± 17	0.9648	32.8 ± 0.6	8 ± 1
Cyclohexene	1- <i>tert</i> -butylcyclohex-1-ene		244 ± 24	0.9307	109 ± 1	2.2 ± 0.3
3- <i>tert</i> -Butylcyclohex-1-ene	1- <i>tert</i> -butylcyclohex-1-ene		23.4 ± 1.4	0.9619	—	—
1-Methylcyclohex-1-ene	1- <i>tert</i> -butylcyclohex-1-ene		25.1 ± 0.6	0.9924	8.6 ± 0.1	2.9 ± 0.1

both above-mentioned extreme cases is involved with the selected catalysts, where it depended upon what particular substrate effect of the two predominated.

It is also apparent from Table III that selectivity values of competitive hydrogenations in binary systems α -methylstyrene (substrate A)–cyclohexene with a varying bulky substituent bonded on the double bond (substrate B) are always shifted in favor of a substrate with di-substituted terminal double bonds, which is in conformity with the generally known principles^{9,10}. The only exception was the system α -methylstyrene–cyclohexene on rhodium catalyst, where the selectivity was shifted in the assumed direction only very inexpressively, which was primarily due to a different reactivity of these substances. Selectivity of competitive hydrogenation in these binary systems increases with growing bulkiness of the substituent hindering the double bond in the series $H < CH_3 < C(CH_3)_3$ always by one order of magnitude. This phenomenon is caused on the platinum catalyst by a higher adsorptivity of α -methylstyrene due to the terminal double bond; on palladium, there is a less significant difference between reactivity and adsorptivity effects. It is impossible to conclude similarly for the rhodium catalyst though, since the adsorptivity effect again prevailed in the case of cyclohexene and 1-methylcyclohex-1-ene, whereas in the case of 1-*tert*-butylcyclohex-1-ene the case was just opposite.

The obtained values of discussed quantities in systems of substrates containing the same skeleton, cyclohexene ring, were interesting. In this case, even the potential influence of the rest of α -methylstyrene molecule was no longer present, location of the double bond, and the substituent on the reaction center remaining the sole variables. In competitive hydrogenation in cyclohexene–1-methylcyclohex-1-ene and cyclohexene–1-*tert*-butylcyclohex-1-ene, there was again an order-of-magnitude in selectivity values depending on the substituent bulkiness. In all these binary systems on all the selected catalysts, a highly increasing negative influence upon the surface reaction rate with increasing substituent bulkiness was evident, whereas the adsorbed complex formation had only a trifling effect, which is evident from a minimum sensitivity of relative adsorption coefficients to the substituent size. From the acquired data, it follows that adsorptivity is affected mainly by the cyclohexene skeleton and the bulky substituents do not play a significant role, which is very markedly displayed in the case of rhodium catalyst. All these conclusions were confirmed by competitive hydrogenations of the 1-methylcyclohex-1-ene–1-*tert*-butylcyclohex-1-ene binary systems. Again, the reactivity effect here predominated over the effect of adsorptivity. The palladium catalyst was an exception: the influence of both of the mentioned factors was approximately the same; however, the value of relative adsorptivity was relatively low. The difference in selectivities of competitive hydrogenations of the 1-methylcyclohex-1-ene–1-*tert*-butylcyclohex-1-ene binary system, related to the individual catalysts, was insignificant in comparison with all the above discussed binary systems.

Selectivity values in the 1-*tert*-butylcyclohex-1-ene–3-*tert*-butylcyclohex-1-ene system were determined as well. Since the cyclohexene molecular skeleton was again involved, the position of the bulky substituent was the sole variable factor. Selectivities of competitive hydrogenations on all the selected catalysts show values one order of magnitude different from the cyclohexene–1-*tert*-butylcyclohex-1-ene system and equal, in the case of palladium and rhodium catalyst, or similar, in the case of platinum catalyst to those for the 1-methylcyclohex-1-ene–1-*tert*-butylcyclohex-1-ene system. Since the 3-*tert*-butylcyclohex-1-ene substrate was not available in required purity, it was not possible to determine the values of relative reactivity and relative adsorptivity. Nevertheless, it is possible to claim that the effect of *tert*-butyl group in the α -position to the double bond of cyclohexene has approximately the same influence as the methyl group bonded directly to the reaction center.

The feasibility of an indirect determination of competitive hydrogenation selectivity¹³ was confirmed in the above mentioned binary systems from values obtained for other substrate pairs, based on the assumed validity of the following relation:

$$S_{AB} S_{BC} S_{CA} = 1 . \quad (4)$$

As follows from the definition, Eq. (5) must hold:

$$S_{AB} = 1/S_{BA} . \quad (5)$$

The product values appearing on the left-hand side of Eq. (4) are provided in Table IV. A relatively great variance is partially caused by the product of the values subject to an error of instrumentation, which was not here considered. It is necessary to realize that the determination of selectivity values in binary systems formed by substrates α -methylstyrene, 1-methylcyclohex-1-ene, 1-*tert*-butylcyclohex-1-ene on rhodium catalyst is impossible. This is perhaps caused by specific interactions among the mentioned substrates on the catalytic surface, alternatively also to interactions among substrates and molecules of the solvent from the bulk phase. Nevertheless, the relation (4) can be applied, at least when used for rough selectivity assessments of values measured independently for other alkene substrates of a similar structure type. Selectivity values calculated in this way for binary mixture of 1-methylcyclohex-1-ene–3-*tert*-butylcyclohex-1-ene, which could not be measured for the above given reasons, are after a calculation based on the relation (4), 1.14 for palladium catalyst, 0.93 for rhodium catalyst and 1.32 for platinum catalyst. These values confirm the above conclusion, according to which the effect of *tert*-butyl group in the α -position to the double bond of cyclo-

TABLE IV
Confirmation of feasibility of an indirect determination of competitive hydrogenation selectivities

Substrate	A	S_{AB}	S_{BC}	S_{CA}	$S_{AB} S_{BC} S_{CA}$
	B				
	C				
Pd catalyst					
α -Methylstyrene		1.68	16.8	1/29.0	0.97
Cyclohexene					
1-Methylcyclohex-1-ene					
α -Methylstyrene		1.68	394	1/508	1.30
Cyclohexene					
1- <i>tert</i> -Butylcyclohex-1-ene					
α -Methylstyrene		29.0	22.2	1/508	1.27
1-Methylcyclohex-1-ene					
1- <i>tert</i> -Butylcyclohex-1-ene					
Cyclohexene		16.8	22.2	1/394	0.95
1-Methylcyclohex-1-ene					
1- <i>tert</i> -Butylcyclohex-1-ene					
Pt catalyst					
α -Methylstyrene		1.98	10.7	1/15.2	1.39
Cyclohexene					
1-Methylcyclohex-1-ene					
α -Methylstyrene		1.98	267	1/431	1.23
Cyclohexene					
1- <i>tert</i> -Butylcyclohex-1-ene					
α -Methylstyrene		15.2	27.9	1/431	0.98
1-Methylcyclohex-1-ene					
1- <i>tert</i> -Butylcyclohex-1-ene					
Cyclohexene		10.7	27.9	1/267	1.12
1-Methylcyclohex-1-ene					
1- <i>tert</i> -Butylcyclohex-1-ene					
Rh catalyst					
α -Methylstyrene		1.04	25.3	1/26.5	0.99
Cyclohexene					
1-Methylcyclohex-1-ene					
α -Methylstyrene		1.04	244	1/257	0.99
Cyclohexene					
1- <i>tert</i> -Butylcyclohex-1-ene					

TABLE IV
(Continued)

Substrate	A	S_{AB}	S_{BC}	S_{CA}	S_{AB}	S_{BC}	S_{CA}
	B						
	Rh catalyst						
α -Methylstyrene		26.5	25.1	1/257			2.59
1-Methylcyclohex-1-ene							
1- <i>tert</i> -Butylcyclohex-1-ene							
Cyclohexene		10.7	25.1	1/244			1.10
1-Methylcyclohex-1-ene							
1- <i>tert</i> -Butylcyclohex-1-ene							

hexene skeleton is approximately concurrent with the effect of methyl group bonded directly on the reaction center.

Competitive Hydrogenation in Ternary Systems

Ternary systems were formed by a substrate pair consisting of a bulky substituent on the cyclohexene skeleton, 1-*tert*-butylcyclohex-1-ene or 3-*tert*-butylcyclohex-1-ene, and a model alkene substrate, α -methylstyrene or cyclohexene, respectively. The results of performed experiments are presented in Table V. The selectivities were determined using straight line slopes, which were produced interpolating the experimental data plotted in the Rader–Smith coordinates. A typical course is depicted in Fig. 1. Addition of a third substance, capable of competitive adsorption on the catalytic sur-

FIG. 1

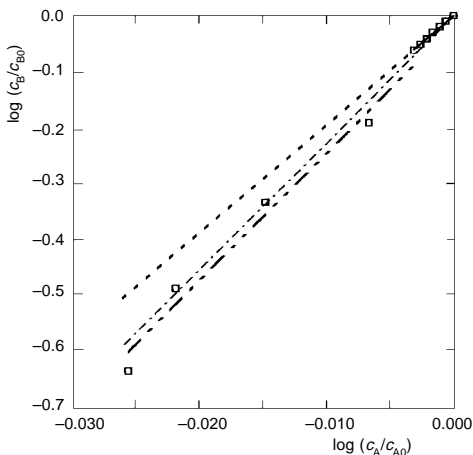
Competitive hydrogenation in ternary system 3-*tert*-butylcyclohex-1-ene–1-*tert*-butylcyclohex-1-ene–cyclohexene on Pd/C catalyst.

— Ternary system 1-*tert*-butylcyclohex-1-ene–3-*tert*-butylcyclohex-1-ene–cyclohexene.

- · - · - Binary system 1-*tert*-butylcyclohex-1-ene–3-*tert*-butylcyclohex-1-ene after cyclohexene vanishing from the reaction mixture.

---- Hypothetical reaction course in ternary system.

- · - · - Binary system 1-*tert*-butylcyclohex-1-ene–3-*tert*-butylcyclohex-1-ene



face and not causing just a blocking of the surface, significantly affected not only hydrogenation rates of all the substrates, but notably altered selectivity values of the competitive hydrogenations as well. As it is apparent from Table V, in all the ternary systems on all the selected catalysts, a decrease in selectivity occurred in the 3-*tert*-butylcyclohex-1-ene-1-*tert*-butylcyclohex-1-ene system ($S_{(AB)C}$). After the fastest reacting substrate, α -methylstyrene or cyclohexene vanished, a selectivity (S'_{AB}) increase occurred which, within the frame of a variety of experimental data, returned to its original value.

TABLE V

Changes in selectivity in transition from binary (3-*tert*-butylcyclohex-1-ene-1-*tert*-butylcyclohex-1-ene) to ternary system (3-*tert*-butylcyclohex-1-ene-1-*tert*-butylcyclohex-1-ene-C)

S_{AB}	Substrate C	Catalyst	$S_{(AB)C}$	S'_{AB}
22.5 ± 1.8	cyclohexene	Pd/C	19.3 ± 1.3	23.3 ± 1.6
22.5 ± 1.8	α -methylstyrene	Pd/C	17.6 ± 1.2	23.4 ± 1.2
36.7 ± 1.2	cyclohexene	Pt/C	32.6 ± 1.1	35.9 ± 1.8
36.7 ± 1.2	α -methylstyrene	Pt/C	26.1 ± 1.7	37.1 ± 1.1
23.4 ± 1.4	cyclohexene	Rh/C	19.3 ± 1.4	23.3 ± 1.4
22.5 ± 1.8	α -methylstyrene	Rh/C	18.8 ± 1.6	23.3 ± 1.6

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SYMBOLS

A	substrate (substance to be hydrogenated)
B	substrate (substance to be hydrogenated)
c_A	concentration of substance A, mol dm ⁻³
c_{A0}	initial concentration of substrate A, mol dm ⁻³
f	correlation coefficient
k_A	rate constant of hydrogenation of substrate A
K_A	adsorption coefficient of substrate A
K_A/K_B	relative adsorption coefficient
r_A	rate of hydrogenation of substrate A, mol min ⁻¹ g _{cat} ⁻¹
S_{AB}	selectivity of competitive hydrogenation of substrates A and B
$S_{(AB)C}$	selectivity of competitive hydrogenation of substrates A and B in presence of substance C
S'_{AB}	selectivity of competitive hydrogenation of substrates A and B after vanishing substance C from the reaction mixture
S_{BET}	total surface area, m ² g _{cat} ⁻¹

S_{MET}	metal surface area, $m_{metal}^2 g_{cat}^{-1}$
t	time, min
V	volume of reaction mixture, dm^3
w	weighed amount of catalyst, g

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