Competitive catalytic hydrogenation in systems of unsaturated hydrocarbons and nitrocompounds

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Abstract

Competitive catalytic hydrogenation was studied in binary systems of aromatic and aliphatic nitrocompounds (nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 1-nitropropane) and in systems of nitrocompound–unsaturated hydrocarbon (cyclohexene, 1-methylcyclohexene and 1-*tert*-butylcyclohexene) on palladium, platinum and rhodium supported catalysts in liquid phase. Acquired kinetic parameters enabled discussion of structural effects in the course of heterogeneous catalytic hydrogenation. In the case of nitrocompounds, potential differences in values of selectivities of competitive hydrogenations were possible to unambiguously attribute to variance in adsorptivities of these substances. In the case of competitive hydrogenations in systems of unsaturated hydrocarbon–aromatic nitrocompound, depending on the amount of aromatic amine produced, selectivity increase was observed in favor of aromatic nitrocompound, which led to an entire suppression of unsaturated hydrocarbon hydrogenation. Ultimate counter-behavior was observed in the systems of unsaturated hydrocarbon–aliphatic nitrocompound. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

This work is dedicated to the determination of selectivities of competitive hydrogenations [1–11] in systems assembled by combining aromatic nitrocompounds with various location of their nitrogroup, and furthermore, to the discussion of the value of this parameter in relation to competitive hydrogenation, where one of the substrates is an aliphatic nitrocompound. Using values of initial reaction rates acquired during hydrogenation of individual model compounds, relative adsorption coefficients were derived from the selectivity of competitive hydrogenation values [1,2,11]. All these quantitative data enabled a discussion on the effect of the structure of a hydrogenated substrate in regards to the formation of an adsorbed complex and the surface reaction rate. The structural effects were further studied in systems of nitrocompound–unsaturated hydrocarbon, where substituted cyclohexenes were used as the model alkenic substrates, varying with bulkiness of their substituent (H, CH_3, $C(CH_3)_3$) bond to the reaction center — the double bond. Their behavior in competitive hydrogenation is described else-

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where [12]. In regards to the structural effect upon the course of heterogeneous catalytic reaction, competitive hydrogenation in the system of nitrocompound–alkene is paid little attention in the literature [2,13,14]. Competitive catalytic hydrogenation in the above-mentioned binary systems was studied on three different catalysts (Pd/C, Pt/C, Rh/C), which enabled a discussion on structural effects within heterogeneous catalysis, including the aspect of a different active catalyst component spread on an inert support.

2. Experimental

2.1. Chemicals

The following substrates of commercial origin were used: nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 1-nitropropane (Aldrich, USA), cyclohexene (Koch-Light, Great Britain), 1-methylcyclohexene (Aldrich), 1-*tert*-butylcyclohexene (Aroma, Czech Republic), which were distilled before use. The solvent was methanol of analytical grade (Penta, Czech Republic). Electrolytic hydrogen 4.0 (Linde Technoplyn, Czech Republic) was used.

2.2. Catalysts

The catalysts Pt/C-Secomet AN (Doducco Kat.), Pd/C-Cherox 4100ch (Chemopetrol, Litvinov), Rh/C (IOT, ICT Prague) were used. These were characterized by their particle crystallite size, total surface area and active compo-

nent surface area (Table 1). The particle crystallite size was determined using the system XRD 3000 P, Rich. Seifert & Co. (Germany). The X-ray CoK_α and a graphite monochromator were used. The particle size was computed using a one-point method, always from the most intense line of the material. Since it exhibited only a slightly elevated background on diffraction pattern, the 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 (USA). The total surface area (S_{BET}) was evaluated from the BET region. The surface areas of catalysts were subject to error, caused by the instrumentation used, which, due to their great extents, did not permit 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 [15].

2.3. Apparatus and kinetic measurements

Kinetic measurements were carried out in a semibatch-stirred reactor [16] at 25°C under hydrogen pressure of 101.3 kPa in methanol. All the measurements were carried out in the kinetic region. The course of hydrogenation of individual substrates was monitored by measuring the

Table 1
Characteristics of hydrogenation catalysts

Catalyst	Grain size (mm)	Particle size (nm)	S_{BET} (m^2/g_{cat})	S_{MET} (m^2_{metal}/g_{cat})
3% Pd/C	< 0.02	20.2	1161	n.d.
5% Pt/C	< 0.05	15.5	778	45.3
5% Rh/C	< 0.02	< 5.0	1201	75.3

n.d. — Not determined.

time dependence of hydrogen consumption and time changes of molar concentrations obtained by chromatographic analysis (GLC). In hydrogenations, 2 mmol of substrate in 15 ml of methanol were used. The catalyst amount ranged between 0.1 and 0.001 g, depending on the substrate and catalyst type used. The competitive hydrogenations in binary systems were carried out using 1 mmol of each substrate. In case that one of the substrates was 1-*tert*-butylcyclohexene, for the reason of very low concentration changes of this substance in the competitive hydrogenation course, it was necessary to use the molar ratio of a substrate:1-*tert*-butylcyclohexene equal to 1:20.

2.4. Analytical methods

Samples, withdrawn at appropriately chosen time intervals, were analyzed using a gas chromatograph HP 5890 Series II Plus (Hewlett-Packard, USA) with flame-ionization detector (FID) and capillary column VA-1 (length 60 m, internal diameter 0.25 mm, film thickness of stationary phase 0.25 μm) using temperature program ranging between 333 and 453 K and the overpressure of carrier gas (N_2) 80 kPa. The composition of the reaction mixture was determined using the method of internal standard (*n*-decane, Aldrich).

IR spectra were obtained using the FT-IR Nicolet 740 (USA). 4-Nitrotoluene was analyzed in the form of KBr tablet. The spectra of 2- and 3-nitrotoluene were recorded in the form of ''neat'' samples.

2.5. Molecular modeling

Geometry optimizations were carried out using the Cerius 2 Version 3.5 Software (MSI, USA) on SGI workstation using conjugated gradients minimization. Calculations were carried out by Dreiding force field. To find the geometry of nitrotoluenes with the minimum of their total energy, we have changed the torsional

angles between their substituents and their aromatic ring. The bonds were treated as harmonic. The torsional exocyclic to ring were scaled by 0.400. The van der Waals terms were treated as exponential −6. Switching functions to turn off van der Waals and Coulombic interations (spline-on distance, 10 Å; spline-off distance, 15 Å) were applied to the model.

3. Results and discussion

3.1. Hydrogenation of individual substrates

Hydrogenations of individual model nitrocompounds and alkenes were carried out. The measured time dependencies of concentrations of hydrogenated substrates were used to determine values of initial reaction rates, which were read from the linear region of the dependence $c = f(t)$. Consequently, these values were used for calculation of relative adsorption coefficients [1,2,11]. The reactions were of zeroth order with respect to substrate concentration up to high conversions (> 90%). All hydrogenations proceeded with total conversion of the starting substance as simple reaction according to the scheme A → B. In the case of hydrogenation of aromatic nitrocompounds, no presence of intermediates (nitrosobenzene, phenylhydroxylamine) nor the hydrogenation product of their aromatic ring (cyclohexylamine) were detected by chromatography. The same applied for the dimer-compounds (azoxybenzene, azobenzene, hydrazobenzene). In the case of substituted cyclohexene on palladium and rhodium catalyst, the presence of positional isomers, potentially produced by a double bond migration, was not detected by chromatography. The only exception was 1-nitropropane, whose hydrogenation proceeded by a system of parallel-consecutive reactions, in which 1-aminopropane was the main product. Depending on a catalyst used, other compounds (2-aminopropane, propane)

were identified in the reaction mixture in various quantities. The reaction course of 1-nitropropane hydrogenation was not possible to describe using an identical kinetic equation as in the case of other substrates: this fact was further taken into consideration during discussion on structural effects. The value of the initial reaction rate of this model substance was determined as a slope to the curve of the reactant concentration time-dependence. Table 2 shows a summary of values of initial reaction rates during hydrogenations of individual model substances. It implies that the nitrogroup hydrogenation rate decreased with all the tested catalysts along the following sequence: 2-nitrotoluene $\geq$ 4-nitrotoluene $\geq$ 3-nitrotoluene $>$ nitrobenzene $\gg$ 1-nitropropane, while the catalyst activity to nitrogroup hydrogenation decreased along the sequence: Pd/C $>$ Pt/C $>$ Rh/C. Regarding the alkenes, the sequence applied as follows: cyclohexene $>$ 1-methylcyclohexene

$>$ 1-*tert*-butylcyclohexene, Pd/C $>$ Rh/C $>$ Pt/C.

3.2. Competitive hydrogenations in binary systems

In competitive catalytic reaction of two substances, whose kinetics can be defined by reaction rate equations of the same type, it is possible to obtain a relatively simple equation for the selectivity defined by the reactivity ratio of both of these substances, which is known as the Rader–Smith equation [11]:

$$\frac{\log(c_A/c_{A0})}{\log(c_B/c_{B0})} = \frac{k_{AH} K_A}{k_{BH} K_B} = S_{AB}. \qquad (1)$$

In an ideal case, the dependence $\log(c_A/c_{A0})$ on $\log(c_B/c_{B0})$ is displayed as a straight line characterized by the slope S_{AB}. Using initial hydrogenation rates of individual substrates r_0 for replacing the values of reaction rate coefficients k_{AH} and k_{BH} in Eq. (1), and substituting acquired values of selectivities S_{AB} to this equation, it is possible to calculate the relative adsorption coefficients K_A/K_B [1,2,11].

The values of S_{AB}, r_{A0}/r_{B0}, K_A/K_B acquired from the competitive hydrogenations of binary systems of model substrates were a basis for a discussion on the structure effect upon reactivity and adsorptivity of the hydrogenated compounds. In a row of substrates with a similar structure, two marginal situations of the structure effect upon the course of a heterogeneous catalytic reaction may occur. In the first case, substrates exhibit the same reactivity in an adsorbed state, however, they differ significantly in their adsorptivity. The second case includes substrates with an equal adsorptivity, although differing in the reactivity of molecules in the adsorbed state. It is apparent from the presented results that a combination of both of the above-mentioned marginal cases was involved, while the particular substrate had the leading effect upon which of the two predominated.

Table 2
Initial hydrogenation rates of substrates

Catalyst	Substrate	r_0 (mmol min^{-1} g$_{cat}^{-1}$)
Pd/C	nitrobenzene	15.0 ± 1.0
	2-nitrotoluene	15.9 ± 0.2
	3-nitrotoluene	15.3 ± 0.2
	4-nitrotoluene	15.5 ± 1.0
	1-nitropropane	0.94 ± 0.10
	cyclohexene	26.0 ± 2.0
	1-methylcyclohexene	3.3 ± 0.1
	1-*tert*-butylcyclohexene	0.72 ± 0.02
Pt/C	nitrobenzene	9.4 ± 0.1
	2-nitrotoluene	10.0 ± 0.5
	3-nitrotoluene	9.5 ± 0.2
	4-nitrotoluene	9.6 ± 0.4
	1-nitropropane	0.42 ± 0.05
	cyclohexene	19.0 ± 1.0
	1-methylcyclohexene	1.5 ± 0.1
	1-*tert*-butylcyclohexene	0.13 ± 0.02
Rh/C	nitrobenzene	0.49 ± 0.01
	2-nitrotoluene	0.64 ± 0.10
	3-nitrotoluene	0.50 ± 0.05
	4-nitrotoluene	0.64 ± 0.05
	1-nitropropane	0.012 ± 0.001
	cyclohexene	24.0 ± 1.0
	1-methylcyclohexene	1.9 ± 0.1
	1-*tert*-butylcyclohexene	0.22 ± 0.01

3.3. Competitive hydrogenations in binary systems of nitrocompounds

Table 3 shows the results of competitive hydrogenations in binary systems of model nitrocompounds, which are presented as selectivity of competitive hydrogenations values, relative reactivities and relative adsorptivities. The acquired data very well agreed to the linear condition of the Rader–Smith equation. It is apparent from Table 3 that the values of selectivities of competitive hydrogenations in binary systems of nitrotoluene with a various position of its nitrogroup (substrate A)–nitrobenzene (substrate B) were always shifted in favor of nitrobenzene and increased in the row as follows: 4-nitrotoluene < 2-nitrotoluene < 3-nitrotoluene on all the tested catalysts. In all the cases, this fact was caused by adsorptivity differences. Except binary systems of 2-nitrotoluene and 4-nitrotoluene (substrate A)–nitrobenzene (substrate B) supported on rhodium catalyst, where the relative reactivities were slightly shifted in favor of nitrotoluenes, it is possible to state that the tested model sub-

stances did not differ in their surface reaction rates, but only in their adsorptivities. The provided results were confirmed by competitive hydrogenations of binary systems assembled by particular positional nitrotoluene isomers. It is apparent from Table 3 that the adsorptivity of the tested aromatic nitrosubstances decreased in the row as follows: nitrobenzene > 3-nitrotoluene > 2-nitrotoluene > 4-nitrotoluene. Therefore, it is possible to state that the presence of methyl group on the primary structural skeleton-aromatic ring substituted with nitrogroup had a negative effect upon adsorptivities of all the positional toluene isomers, while its influence upon reactivity of these substances was insignificant. The discovered fact that all the isomeric nitrotoluenes exhibit a lower adsorptivity than nitrobenzene can be related to an electron-donating character of their methyl, which by its positive induction ($+I$) and mesomeric ($+M$) effect, increases electronic density on the nitrogroup, which leads to a decrease of its adsorptivity. From the view of the determining effect upon the course of electrophilic substitution on aromatic ring, methyl causes an

Table 3
Results of competitive hydrogenations in binary systems of nitrocompounds

Substrate A	Substrate B	Catalyst	S_{AB}	f	r_{A0}/r_{B0}	K_A/K_B
2-Nitrotoluene	nitrobenzene	Pd/C	0.31 ± 0.02	0.9894	1.06 ± 0.09	0.30 ± 0.05
3-Nitrotoluene	nitrobenzene	Pd/C	0.35 ± 0.01	0.9986	1.03 ± 0.09	0.35 ± 0.03
4-Nitrotoluene	nitrobenzene	Pd/C	0.19 ± 0.01	0.9956	1.0 ± 0.1	0.2 ± 0.1
1-Nitropropane	nitrobenzene	Pd/C	0.008 ± 0.001	0.9525	0.06 ± 0.01	0.14 ± 0.04
2-Nitrotoluene	3-nitrotoluene	Pd/C	0.90 ± 0.05	0.9928	1.04 ± 0.03	0.87 ± 0.03
2-Nitrotoluene	4-nitrotoluene	Pd/C	1.43 ± 0.03	0.9989	1.03 ± 0.08	1.48 ± 0.06
3-Nitrotoluene	4-nitrotoluene	Pd/C	1.70 ± 0.05	0.9954	1.00 ± 0.08	1.70 ± 0.08
2-Nitrotoluene	nitrobenzene	Pt/C	0.50 ± 0.01	0.9971	1.07 ± 0.07	0.47 ± 0.04
3-Nitrotoluene	nitrobenzene	Pt/C	0.90 ± 0.06	0.9898	1.01 ± 0.03	0.90 ± 0.09
4-Nitrotoluene	nitrobenzene	Pt/C	0.29 ± 0.01	0.9968	1.03 ± 0.06	0.29 ± 0.03
1-Nitropropane	nitrobenzene	Pt/C	0.011 ± 0.001	0.9748	0.045 ± 0.006	0.25 ± 0.06
2-Nitrotoluene	3-nitrotoluene	Pt/C	0.50 ± 0.03	0.9948	0.94 ± 0.06	0.53 ± 0.02
2-Nitrotoluene	4-nitrotoluene	Pt/C	1.73 ± 0.03	0.9981	1.1 ± 0.1	1.6 ± 0.2
3-Nitrotoluene	4-nitrotoluene	Pt/C	3.27 ± 0.05	0.9967	0.99 ± 0.05	3.4 ± 0.2
2-Nitrotoluene	nitrobenzene	Rh/C	0.54 ± 0.01	0.9990	1.30 ± 0.05	0.42 ± 0.03
3-Nitrotoluene	nitrobenzene	Rh/C	0.96 ± 0.04	0.9985	1.0 ± 0.1	1.0 ± 0.1
4-Nitrotoluene	nitrobenzene	Rh/C	0.35 ± 0.01	0.9979	1.3 ± 0.1	0.3 ± 0.1
1-Nitropropane	nitrobenzene	Rh/C	0.012 ± 0.001	0.9789	0.025 ± 0.003	0.49 ± 0.09
2-Nitrotoluene	3-nitrotoluene	Rh/C	0.58 ± 0.03	0.9952	1.3 ± 0.1	0.5 ± 0.1
2-Nitrotoluene	4-nitrotoluene	Rh/C	1.59 ± 0.05	0.9957	1.0 ± 0.1	1.6 ± 0.2
3-Nitrotoluene	4-nitrotoluene	Rh/C	3.01 ± 0.07	0.9948	0.8 ± 0.1	3.8 ± 0.6

Table 4
IR spectroscopy results

Substrate	ν_{as} (cm^{-1})	ν_s (cm^{-1})
2-Nitrotoluene	1523	1348
3-Nitrotoluene	1527	1350
4-Nitrotoluene	1510	1343

increase of electronic density mainly in the positions *ortho* and *para*. The presence of nitrogroup in these alternating positions leads to a significant increase of its polarization in comparison to 3-nitrotoluene, which can be considered as the reason for which this isomer is the best sorbing from nitrotoluenes. To evaluate the donor effect of methyl in the case of 2- and 4-nitrotoluene, it could be assumed that due to its electron-donating effect, methyl in *ortho*-position would tend to polarize more to the nitrogroup than in the case of the *para*-position, furthermore, its proximate vicinity to the reaction center should have by its steric effect a significantly negative effect upon the 2-nitrotoluene sorption. Consequently, both of the effects would be expected to operate in the same direction and deteriorate the adsorptivity of 2-nitrotoluene, which is in direct discord with the acquired data. The condition for applying the mesomeric effect is a planarity of such system. In this case, free rotation of nitrogroup around the C−N bond would be hindered. The methyl presence in the proximate steric vicinity to the nitrogroup would lead to a deformation of the torsion angle on the tie-line of the O−N−C(2)−C(1) nuclei, which would violate the system co-planarity and disturb the conjugation as well as the shift of electronic density. Consequently, this fact would lead to a lower

polarization of the nitrogroup in 2-nitrotoluene with the join-effect of an increased adsorptivity of this isomer in comparison to 4-nitrotoluene. To evaluate the electronic density delocalization on the aromatic ring, IR spectroscopy was used. The results acquired on the basis of evaluation of measured spectra are summarized in Table 4. Based on these results, it can be enunciated that most of the significant divergences can be identified in asymmetric vibration of the nitrogroup, while the most conspicuous change occurred in the case of 4-nitrotoluene. This shift is possible to relate to a polarity increase on this bond. Thus, the overall sequence fully correspond to the sequence of adsorptivities of individual isomeric nitrotoluenes obtained during competitive hydrogenations of pertinent binary systems of these substances on the catalysts used in this study. To explain such significant divergence in the shifts of 2-nitrotoluene on one side and 4-nitrotoluene on the other, it is possible to assume the break of the nitrogroup planarity in relation to the aromatic ring, with all the above-mentioned effects upon the behavior of both of the isomers during interaction with the catalytic surface. To verify this hypothesis, molecular modeling was carried out with all the isomeric nitrotoluenes using the software Cerius 2. Inspection of various potential rotamers was performed and the structures with the lowest energy content were evaluated. Table 5 shows the results. It is apparent from them that in the case of 2-nitrotoluene, in consequence of the steric effect of methyl, deflection of nitrogroup from the co-planaric arrangement with the aromatic ring occurs, while the two remained isomers are ideally planar molecules. Based on the

Table 5
Results of molecular modeling

Substrate	Total energy (kJ/mol)	Torsionals (°)	
		O−N−C(2)−C(1)	H−C(7)−C−C
2-Nitrotoluene	117.3	36.3	53.5
3-Nitrotoluene	85.4	0	0
4-Nitrotoluene	87.1	0	0

above-provided results and their comparisons with the literature data [17–19], it can be stated that the designed model reflects the actual situation. Thus, in the case of 2-nitrotoluene, it is the repulsion between methyl and nitrogroup which results in an expected nitrogroup polarity decrease and a higher adsorptivity of this isomer in comparison to 4-nitrotoluene.

The Hammett equation [20] represents the basis for evaluation of electronic effects of substituents upon the physical and chemical properties of substituted aromatic compounds. The Hammett equation was developed and its constant determined for homogeneous reactions. The applicability to heterogeneous catalytic reactions has been proven by several authors [21]. The validity of the Hammett equation is limited to the cases, in which entropy change in a series of studied substances is constant, alternatively to the case where a linear relation exists between changes of entropy and enthalpy. The studied system of aromatic nitrocompounds has fulfilled these conditions. The following values of the polar constants for methyl substituent were found in the literature [22]: $\sigma_m = -0.07$ and $\sigma_p = -0.17$. These values are in an agreement with the sequence of relative adsorptivities of 3-nitrotoluene and 4-nitrotoluene. Polar constants for evaluation of the *ortho*-substituent effect were found as well. The Hammett equation does not apply for this kind of substitution. The errors to Hammett equation have several causes, which relate to their common source-*ortho*-effect, under which electrostatic effect of a substituent and of the reaction center, steric effect and the formation of hydrogen bonds are included. Several values of polar constants for *ortho*-substitution were found in the literature [20]: $\sigma_o = -0.10$, $\sigma_o = -0.12$, $\sigma_o = -0.13$. Although these values are markedly different, they are between values for *meta* and *para* substitution, which is in concord with the values of the relative adsorption coefficients.

Furthermore, possibility of an indirect determination of competitive hydrogenation selectivities was confirmed [1,2,11] with the above-mentioned binary systems from the values obtained for other substrate couples, based on an assumed validity of the following equation:

$$S_{AB} S_{BC} S_{CA} = 1 \qquad (2)$$

while, followed from the definition, it must apply:

$$S_{AB} = 1/S_{BA}. \qquad (3)$$

Table 6 shows values of multiplication products located on the left side of Eq. (2), which imply a very reliable accord of the experimentally acquired results with the above equation. Based on these results, a possibility to estimate selectivity values of competitive hydrogenations from values measured independently for other aromatic nitrocompounds of a similar structural type can be enunciated.

Table 3 shows values of kinetic parameters obtained by the competitive hydrogenations in binary system of 1-nitropropane (substrate A)–nitrobenzene (substrate B) on all the tested catalysts. It was apparent from hydrogenations of both of the individual substrates that the reaction course cannot be described using the identical kinetic equation. Nevertheless, the data obtained from competitive hydrogenations very well fulfilled the linear characteristic of the Rader–Smith equation. The results presented in Table 3 show that the selectivity values of competitive hydrogenations were significantly shifted in favor of aromatic nitrocompound on all the catalysts. Presented in the form of relative reactivities, this shift has apparently been caused by great differences in surface reaction rates of both of the substrates. The relative reactivities increased in a sequence: Rh/C > Pt/C > Pd/C and predominated over the effect of relative adsorptivities, which decreased along the sequence: Pd/C > Pt/C > Rh/C.

3.4. Competitive hydrogenation in the binary systems of alkene–nitrocompound

Binary systems were assembled from aromatic nitrocompounds (nitrobenzene, 4-nitro-

Table 6
Confirmation of feasibility of an indirect determination of competitive hydrogenation selectivities

Substrates A, B, C	S_{AB}	S_{BC}	S_{CA}	$S_{AB} S_{BC} S_{CA}$
				Palladium catalyst
Nitrobenzene	3.22	0.90	1/2.84	1.02
2-Nitrotoluene				
3-Nitrotoluene				
Nitrobenzene	3.22	1.43	1/5.00	0.92
2-Nitrotoluene				
4-Nitrotoluene				
Nitrobenzene	2.84	1.70	1/5.00	0.97
3-Nitrotoluene				
4-Nitrotoluene				
2-Nitrotoluene	0.90	1.70	1/1.43	1.07
3-Nitrotoluene				
4-Nitrotoluene				
				Platinum catalyst
Nitrobenzene	2.02	0.50	1/1.12	0.90
2-Nitrotoluene				
3-Nitrotoluene				
Nitrobenzene	2.02	1.73	1/3.40	1.03
2-Nitrotoluene				
4-Nitrotoluene				
Nitrobenzene	1.12	3.27	1/3.40	1.08
3-Nitrotoluene				
4-Nitrotoluene				
2-Nitrotoluene	0.50	3.27	1/1.73	0.95
3-Nitrotoluene				
4-Nitrotoluene				
				Rhodium catalyst
Nitrobenzene	1.83	0.58	1/1.06	1.00
2-Nitrotoluene				
3-Nitrotoluene				
Nitrobenzene	1.83	1.59	1/2.86	1.02
2-Nitrotoluene				
4-Nitrotoluene				
Nitrobenzene	1.06	3.01	1/2.86	1.12
3-Nitrotoluene				
4-Nitrotoluene				
2-Nitrotoluene	0.58	3.01	1/1.59	1.10
3-Nitrotoluene				
4-Nitrotoluene				

toluene), or aliphatic nitrocompounds (1-nitro-propane) on one side and individual model alkenic substances on the other. It was found for the binary systems of alkene (substrate A)–nitrobenzene (substrate B) that the measured data cannot be described by use of the Rader–Smith equation due to their marked divergence from linearity of this relation. Typical course of the competitive hydrogenation of the above-mentioned binary systems is depicted in Fig. 1,

where the time changes of the product concentrations are plotted and compared to hydrogenation courses in the individual arrangements. Although the hydrogenations of individual substrates could be described using an identical kinetic equation, which is a necessary presumption for deriving the Rader–Smith equation [11], significant changes in behavior of hydrogenated substrates, containing in their molecules various hydrogenated function groups, occurred in a
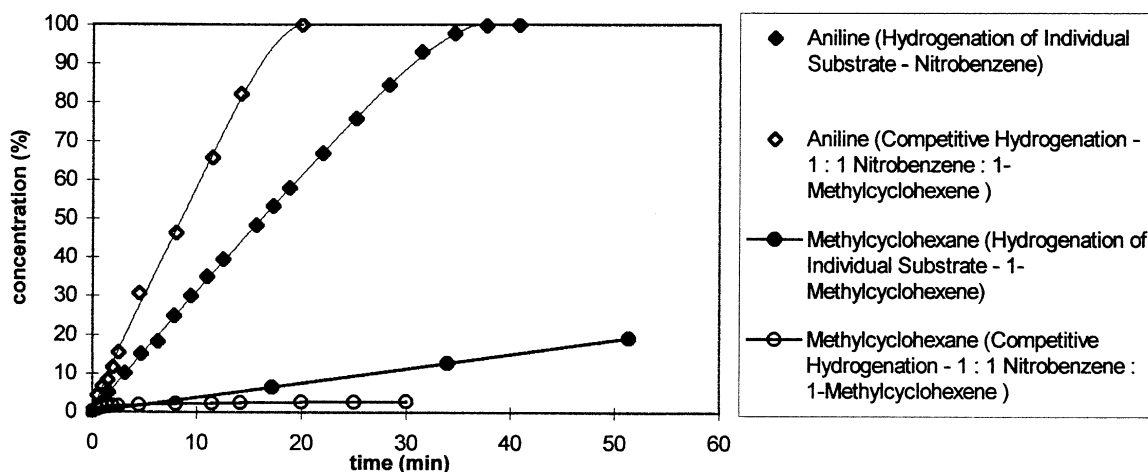
Fig. 1. Courses of hydrogenation in individual and competitive arrangement for system 1-methylcyclohexene:nitrobenzene.

competitive arrangement. It is apparent from the case of the competitive hydrogenation depicted in Fig. 1 that the hydrogenation of aromatic nitrocompound was significantly preferred during its course. Nitrobenzene hydrogenation as well as hydrogenation of alkenic substance occurred in the initial stages of this competitive hydrogenation. When a certain conversion of nitrocompound was reached, i.e. approximately 10% as presented in Fig. 1, a change of hydrogenation rates of both of the substrates occurred, which became apparent from changes of the slopes of their $c = f(t)$ dependencies. While an increase of hydrogenation rate of aromatic nitrocompound occurred on one side, significant decrease of hydrogenation rate of alkenic sub-

strate occurred, which was related to occupation changes on active centers, i.e. to changes in relative adsorptivity. In the next course of this competitive reaction, the extent of hydrogenation of alkenic substrate was insignificant, although still detectable and the hydrogenation rate of nitrobenzene increased almost twice in comparison to the individual substrate hydrogenation. This was in consent with the fact that the ratio of nitrocompound:catalyst was twice as high as in the case with nitrobenzene hydrogenation, and the alkenic substrate has occupied the catalytic surface only insignificantly. It is apparent from Fig. 1 that even after a diminishing of aromatic substance, no increase of alkene formation rate occurred and the hydrogenation
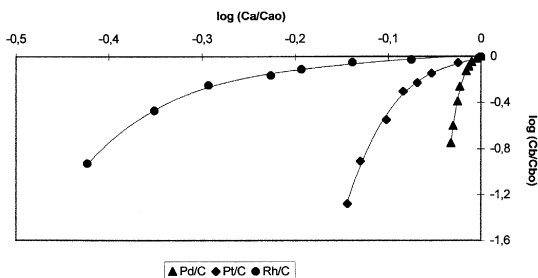

Fig. 2. Competitive hydrogenation in binary system cyclohexene (A)–nitrobenzene (B).
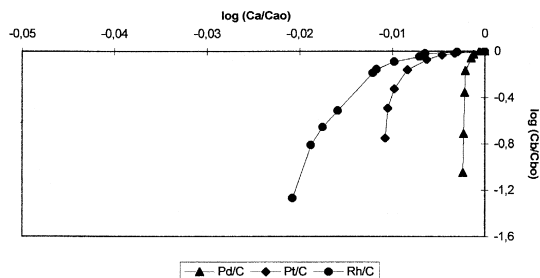

Fig. 3. Competitive hydrogenation in binary system 1-methyl-cyclohexene (A)–nitrobenzene (B).
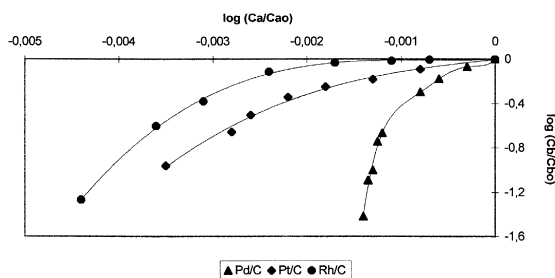
Fig. 4. Competitive hydrogenation in binary system 1-*tert*-butyl-cyclohexene (A)–nitrobenzene (B).

of the alkenic substrate had not practically occurred.

This typical course of the competitive hydrogenation was observed in all the binary systems of alkene (substrate A)–nitrobenzene (substrate B), whose reaction courses are depicted using Rader–Smith coordinates in Figs. 2–4. It is apparent from these figures that all the binary systems varying in the cyclohexene substituent used exhibited significant divergences from the linear characteristic of the Rader–Smith equation on all the catalysts. It is apparent from the graphs that each selectivity value of competitive hydrogenation had increased during the reaction course in the sense of an increased reactivity of a substrate, which contained nitrogroup in its molecule. Following a deliberate research, it was found that catalyst surface process had been effected within very low conversions of sub-

strates reacting competitively, which in the macroscopic extent resulted in a diversion from the linear dependence of $\log(c_A/c_{A0})$ upon $\log(c_B/c_{B0})$ and in a competitive hydrogenation selectivity change. Experiments of competitive hydrogenation with an alkenic substrate performed with various input ratios of nitrobenzene:aniline proved that this phenomenon was caused by the aniline presence in the reaction mixture. Transferring the curve plotted in the Rader–Smith coordinates for binary system alkene (substrate A):mixture of nitrobenzene–aniline (substrate B) into the point, on the curve for competitive hydrogenation without aniline input, corresponding to the composition of the starting mixture of nitrobenzene–aniline, resulted in overlapping of both curves. This can be considered as the proof that the phenomenon is not the result of interaction between reactive intermediates during transformation of nitrobenzene to aniline on the catalyst surface. Effect of the produced water as a side product of the nitrogroup hydrogenation upon the course of competitive hydrogenation was verified by separate experiments as well. Low sensitivity of hydrogenation reactions of both of the substrates in the methanolic environment to the water presence was found. Related to even five times higher amount of the solvent than the theoretically possible in 100% of nitrobenzene conversion added at the reaction beginning, it

Table 7
Results of competitive hydrogenations in alkene–nitrocompound binary systems

Substrate A	Substrate B	Catalyst	S'_{AB25}	S'_{AB50}	S'_{AB75}
Cyclohexene	nitrobenzene	Pd/C	0.13 ± 0.01	0.078 ± 0.003	0.050 ± 0.001
Cyclohexene	nitrobenzene	Pt/C	0.39 ± 0.05	0.27 ± 0.02	0.18 ± 0.01
Cyclohexene	nitrobenzene	Rh/C	1.7 ± 0.1	1.03 ± 0.04	0.63 ± 0.02
1-Methylcyclohexene	nitrobenzene	Pd/C	0.016 ± 0.001	0.0072 ± 0.0002	0.0038 ± 0.0001
1-Methylcyclohexene	nitrobenzene	Pt/C	0.063 ± 0.006	0.032 ± 0.002	0.018 ± 0.001
1-Methylcyclohexene	nitrobenzene	Rh/C	0.09 ± 0.01	0.046 ± 0.004	0.028 ± 0.001
1-*tert*-Butylcyclohexene	nitrobenzene	Pd/C	0.0038 ± 0.0003	0.0027 ± 0.0001	0.0020 ± 0.0001
1-*tert*-Butylcyclohexene	nitrobenzene	Pt/C	0.0088 ± 0.0012	0.0065 ± 0.0005	0.0047 ± 0.0003
1-*tert*-Butylcyclohexene	nitrobenzene	Rh/C	0.020 ± 0.004	0.010 ± 0.001	0.0060 ± 0.0004
1-Methylcyclohexene	4-nitrotoluene	Pd/C	0.081 ± 0.02	0.032 ± 0.001	0.019 ± 0.001
1-Methylcyclohexene	4-nitrotoluene	Pt/C	0.22 ± 0.02	0.11 ± 0.01	0.060 ± 0.001
1-Methylcyclohexene	4-nitrotoluene	Rh/C	0.24 ± 0.02	0.13 ± 0.01	0.081 ± 0.003

still had no effect upon both of the hydrogenation rates (in the individual as well as competitive arrangements).

Selectivity values of competitive hydrogenation at 25%, 50% and 75% of nitrobenzene conversion were read using the graphs in Figs. 2–4. These quantities are not the real selectivities of competitive hydrogenation, but at least express the actual status of this quantity in the point corresponding to the given nitrobenzene concentration. The values of these quantities are shown in Table 7, from which it is apparent that the selectivity values (S'_{AB25}, S'_{AB50}, S'_{AB75}) exhibited an identical trend on all the tested catalysts and decreased with an increasing conversion of nitrobenzene. Very interesting course was detected in the binary system of cyclohexene:nitrobenzene on rhodium catalyst, where the selectivity of competitive hydrogenation value was shifted in favor of alkenic substrate at 25% conversion of nitrobenzene. At 50% conversion, it was approximately unitary, consecutively it grew in favor of nitrocompound. This fact was probably caused by a marked difference in the surface reaction rates of both of the substrates, i.e. by the high value of relative reactivity ($r_{A0}/r_{B0} = 51 + 5$). It is apparent from Table 7 that the selectivity of competitive hydrogenation values (S'_{ABX}) decreased with an increasing bulkiness of a substituent (H, CH_3, $C(CH_3)_3$) on the double bond of the cyclohexene skeleton always by one order, which was in a very good agreement with the results obtained from the competitive hydrogenations of these alkenic substrates [12]. It is also possible to compile a sequence of the tested catalysts according to their increasing selectivity values of competitive hydrogenations (S'_{ABX}), which is as follows: Rh/C > Pt/C > > Pd/C. Table 7 shows also the selectivity of competitive hydrogenation values in binary systems of 1-methylcyclohexene:4-nitrotoluene, which confirmed the results formulated for the binary systems of substituted cyclohexene:nitrobenzene.

Additionally, competitive hydrogenations in binary system of 1-methylcyclohexene:1-nitropropane were carried out. It was found that having used the method of competitive hydrogenation of equimolar mixture of both of substrates or using 20-mol-excess of 1-nitropropane against alkene, it was not possible to determine the competitive hydrogenation selectivity, since no 1-aminopropane was detected during the course of alkenic substrate hydrogenation in both of the cases, providing that 1-nitropropane hydrogenation started in a detectable rate no earlier than after alkenic substance practically disappeared from the reaction mixture.

4. Conclusion

The results obtained using the method of competitive hydrogenation in binary systems of aliphatic and aromatic nitrocompounds and binary systems of nitrocompound–alkene enabled discussion on structural effects involved during heterogeneous catalytic hydrogenation. In the binary systems of aromatic nitrocompounds (nitrobenzene, 2-, 3-, 4-nitrotoluene), a negative effect of methyl group upon adsorptivity of these substances and almost zero differences in surface reaction rates of all these substrates were found and expressed quantitatively. The adsorptivity sequence of the individual positional isomers was induced by the prevailing electronic effect over the steric effect. In binary systems of aromatic nitrocompounds on one side and aliphatic nitrocompound on the other, it was stated that a significant effect of the hydrocarbonic skeleton upon the hydrogenation reaction course is involved due to differences in reactivities and adsorptivities of these molecules. In binary systems of aromatic nitrocompound–alkene, impossibility to describe the acquired data using the Rader–Smith equation was enunciated as a reason of significant divergences from the linearity of this relation. During the course of this competitive hydrogenation, selectivity of competitive hydrogenation increased in favor of aromatic nitrocompound. This fact was caused by the specific interactions on the cata-

lyst surface or by effecting the adsorbed molecules by a change of composition of bulky phase in consequence of aniline production and substituted aniline as the product of hydrogenation of aromatic nitrocompounds, respectively. Entirely opposite behavior, expressed with the selectivity of competitive hydrogenation, was found in systems of unsaturated hydrocarbon–aliphatic nitrocompound.

Acknowledgements

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