

SELECTIVITIES OF SOME HYDROGENATIONS ON METAL-MODIFIED PLATINUM CATALYSTS

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The rates and selectivities of hydrogenation on platinum catalysts modified with monolayers of copper, thallium, lead, or bismuth were studied at 20°C and atmospheric pressure for the competitive hydrogenation of 1-hexene and 1-undecene in cyclohexane and for the consecutive hydrogenation of 1,5-cyclooctadiene in cyclohexane or ethanol. For the former system, the selectivity was unaffected by the modifying metal and the degree of the surface coverage with the metal, and the relative specific hydrogenation rate decreased only slightly with the degree of surface coverage. For the latter system, the selectivity of hydrogenation to cyclooctene increased with the content of the modifying metal, while the relative specific hydrogenation rate decreased markedly.

Hydrogenation catalysts modified with inactive metals exhibit some interesting properties, which result not only from the partial blocking of the active surface, but also from changes induced by the metal in the electronic structure of its environment, hence, of the metal which acts as the carrier of the catalyst activity. Several papers have recently been published¹⁻⁹ dealing with the properties of metal-modified platinum catalyst. In the present work, the degree of coverage of the platinum surface with the modifying metal was related to the selectivity and rate of hydrogenation of olefinic and dienic bonds.

EXPERIMENTAL

Substances and catalysts. 1-Hexene, 1-undecene, 1,5-cyclooctadiene (Koch-Light, England), cyclohexane *p.a.* (Lachema, Brno). All the substances were distilled prior to use and were chromatographically pure. Platinum black was prepared in the conventional manner¹⁰. The catalysts modified with thallium, bismuth, and lead were made up by feeding hydrogen into stirred suspensions of platinum black in aqueous solutions of thallium sulfate, lead dichloride, and bismuth trichloride, respectively, acidified with the corresponding acid and heated at 50°C. After 2.5 h of hydrogen feeding, the catalysts were filtered out under hydrogen, washed with water, passivated with nitrogen, and dried at 60°C. The catalysts modified with copper were prepared⁴ by decomposition of copper formate with platinum black in aqueous solution. The degree of cover-

age of the platinum surface with the modifying metal was determined electrochemically by the potentiodynamic method¹¹.

Apparatus and procedure. All measurements were carried out in a standard equipment¹² at 20°C and atmospheric pressure; the arrangement was such as to eliminate any effect of mass transport on the reaction course¹³. 10 ml of solvent and 1 ml of substrate were taken; the amount of catalyst was 5–200 mg. The reaction course was monitored chromatographically.

For studying the competitive hydrogenation of 1-hexene and 1-undecene, an equimolar mixture of the substrates was used in cyclohexane solution. The hydrogenation rates were measured on catalysts modified with the various metals to different extents so as to leave different fractions of free platinum surface (Θ_{Pt}). The selectivities of the competitive hydrogenations were calculated as the ratios of the reactivities of 1-hexene to 1-undecene. The reaction rates were determined as the slopes of the time dependences of the hydrogen uptake in time $t = 0$. These values were related to the free platinum surface to give the specific hydrogenation rates, which in turn were converted to the relative specific hydrogenation rates (r_{r_s}) by relating them to the hydrogenation rate on pure platinum black.

For examining the dependence of the selectivity in the 1-hexene–1-undecene system on the degree of coverage of the catalyst surface, catalysts with the following free platinum surface area fractions were employed (modifying metal, Θ_{Pt}): Cu: 1.00, 0.82, 0.52, 0.20, 0.11; Pb: 1.00, 0.17, 0.10; Bi: 1.00, 0.62, 0.34; Tl: 1.00, 0.52, 0.16.

Analytical methods. The analyses were performed on a Chrom 4 apparatus with flame ionization detection, using a glass column 3.5 m long, i.d. 2.5 mm, packed with 15% Carbowax 20M on Chromaton NAW-DMCS, grain size 0.16–0.20 mm; temperature 74°C.

RESULTS AND DISCUSSION

Competitive Hydrogenation of 1-Hexene and 1-Undecene

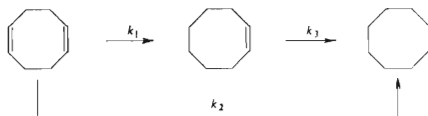
The dependence of the relative specific hydrogenation rates on the free platinum fraction of the surface area is shown in Fig. 1. The rates decrease with increasing occupation of the surface by the modifying metal only slightly; a marked drop is observed only in the series of catalysts modified with thallium.

The selectivity of the competitive hydrogenation was expected to increase with the increasing occupation of the surface, as sites sterically accessible to 1-hexene only might increasingly appear. However, on all the catalysts used the selectivity was identical, *viz.* $S = 1.82$; hence, within the applied regions of coverage of the platinum surface by the metals, no such presumed active centres accessible to the lower olefin solely occur. Possibly, the effect under consideration could manifest itself at still higher degrees of modification (at which, however, the catalysts are little active) or if the substrates involved were sterically more different.

Hydrogenation of 1,5-Cyclooctadiene

1,5-Cyclooctadiene was chosen as a substance in which the mutual position of the two double bonds is fixed to a high degree owing to the ring nature of the molecule.

A plot of the time dependence of the concentrations of the various components in the reaction mixture during the hydrogenation of 1,5-cyclooctadiene on platinum black in cyclohexane is shown in Fig. 2. It is clear that the hydrogenation can formally be written as



The data fail, of course, to provide information on the mechanism of step k_2 , in which cyclooctane can form either by a simultaneous addition of hydrogen to both double bonds activated by the adsorption, or consecutively, by hydrogenation of the primarily formed cyclooctene that had not desorbed into the bulk phase. However, from the point of view of interpretation of our results this ambiguousness is irrelevant because both variants involve the reasonable assumption of the necessary activation of both double bonds of the starting substance.

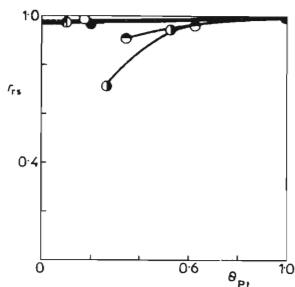


FIG. 1

Dependence of the relative specific rate of hydrogenation of an equimolar mixture of 1-hexene and 1-undecene on the free platinum fraction of catalyst surface area. Modifying metal: ○ Pb, ● Cu, ◐ Bi, ◑ Tl

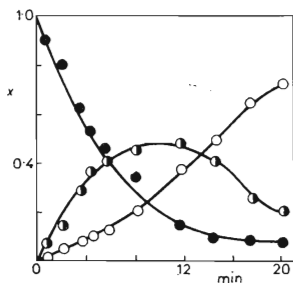


FIG. 2

Time dependence of the concentrations of the reaction components in the hydrogenation of 1,5-cyclooctadiene on platinum black in cyclohexane. Amount of catalyst 80 mg. Components: ● 1,5-cyclooctadiene, ◐ cyclooctene, ○ cyclooctane. x is the dimensionless concentration (instantaneous concentration of component divided by initial concentration of 1,5-cyclooctadiene), t is time (min)

The hydrogenation of 1,5-cyclooctadiene on the modified catalysts was qualitatively similar to that on platinum black, only the ratios of the rates of formation of cyclooctane and cyclooctene at the beginning of the reaction were different and consequently, so were the maximum concentrations of cyclooctene as the intermediate product in the consecutive reaction. Since on the highly modified catalysts the hydrogenation proceeded very slowly, the maximum was not determined in all experiments, and the differences between the various catalysts were characterized in terms of the selectivity, here defined either as the ratio of the rate of formation of cyclooctene to the rate of loss of cyclooctadiene at the beginning of the reaction, $S_1 = k_1/(k_1 + k_2)$, or as the ratio of the rates of hydrogenation of cyclooctadiene to cyclooctane and to cyclooctene (S_2). In the region of high selectivities, changes in S_2 values are more marked than in S_1 .

The selectivities established are given in Table 1. Clearly, on all the catalysts the selectivity of hydrogenation of 1,5-cyclooctadiene to cyclooctene increases with increasing content of the modifying metal, especially for thallium. The selectivity was invariably higher in ethanol than in cyclohexane as solvent. This effect is probably due to the different polarity of the two solvents and seems to be of general nature¹⁴

TABLE I
Selectivities of hydrogenation of 1,5-cyclooctadiene to cyclooctene on modified platinum catalysts

Modifying metal	θ_{Pi}	Selectivity in			
		cyclohexane		ethanol	
		S_1	S_2	S_1	S_2
—	1.00	0.81	4.3	0.84	5.4
Cu	0.68	—	—	0.88	7.7
Cu	0.11	0.92	11.6	—	—
Pb	0.83	—	—	0.96	27.0
Pb	0.75	—	—	0.97	33.3
Pb	0.60	—	—	0.99	81.1
Pb	0.17	0.96	25.6	—	—
Tl	0.65	0.84	5.3	0.97	29.4
Tl	0.52	0.89	7.8	—	—
Tl	0.42	0.96	23.9	0.98	62.5
Tl	0.26	—	—	0.99	84.0
Bi	0.85	—	—	0.93	13.5
Bi	0.62	0.82	4.3	0.97	31.3
Bi	0.39	0.92	11.6	—	—

For monitoring the changes in the selectivity in dependence on the degree of coverage of the platinum surface using ethanol as solvent, catalysts with low contents of the modifying metals had to be employed, the selectivity being too high at higher degrees of surface coverage.

Figs 3 and 4 shows the dependences of the relative specific rates of hydrogenation of 1,5-cyclooctadiene to cyclooctene 1 and to cyclooctane 2, again defined as the initial rates related to the free platinum fraction of the surface area and to the rate observed on pure platinum black. In comparison with the values for the 1-hexene-1-undecene system (Fig. 1) the relative specific hydrogenation rate of 1,5-cyclooctadiene decreases more markedly with increasing degree of coverage of the catalyst surface. In cyclohexane this decrease is again most pronounced for thallium as the metal applied, in ethanol the effect of the various modifying metals is comparable. The formation of cyclooctane is suppressed by the increasing modification more than that of cyclooctene.

The way in which the application of the modifying metal to the catalyst surface affects the selectivity and relative specific rate of hydrogenation can be discussed based on a comparison of the results obtained for the two systems studied. In the 1-hexene-1-undecene system the selectivity of the competitive hydrogenation does not vary with the degree of surface coverage, and the relative specific rate decreases

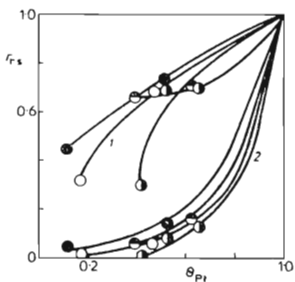


FIG. 3

Dependence of the relative specific rate of hydrogenation of 1,5-cyclooctadiene to cyclooctene 1 and to cyclooctane 2 in cyclohexane on the free platinum fraction of catalyst surface area. Modifying metal: ○ Pb, ● Cu, ◐ Bi, ● Tl

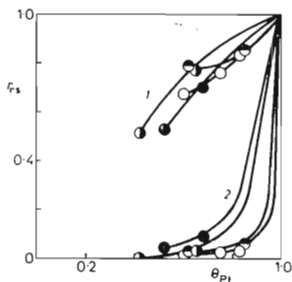


FIG. 4

Dependence of the relative specific rate of hydrogenation of 1,5-cyclooctadiene to cyclooctene 1 and to cyclooctane 2 in ethanol on the platinum fraction of catalyst surface area. Modifying metal: ○ Pb, ● Cu, ◐ Bi, ● Tl

only slightly with increasing content of the modifying metal. This does not surprise if the fact is taken into account that the two substrates differ only in the length of the chain following the double bond; it is only the double bond carbons and not the remaining chain that are involved in the chemisorption, and so the modification of the platinum surface with ad-atoms of other metals should not affect the hydrogenation of the two substrates in a different manner, whatever the nature of the changes induced in the platinum catalyst properties.

In the hydrogenation of 1,5-cyclooctadiene, on the other hand, the selectivity of hydrogenation to cyclooctene increases with increasing degree of modification and the relative specific rate of hydrogenation decreases appreciably. Of the two conceivable ways in which the ad-atoms of the metals can affect the catalyst properties, *viz.* either by altering, in some so far unspecified manner, the electronic properties of the surface platinum atoms, or by hindering mechanically the adsorption of the reactants (hydrogen and substrate), the latter is rather supported by these results. The enhanced selectivity can be explained so that with increasing degree of modification the probability decreases of the cocurrence of free platinum atoms in an arrangement such as would allow a simultaneous adsorption of both double bonds in the molecule of 1,5-cyclooctadiene, the mutual motion of which is restricted by the ring nature of the molecule. And naturally, the limited possibility of adsorption of substrate, in particular in a vicinity to adsorbed hydrogen, results also in a lowered relative specific hydrogenation rate. The fact that of the two reactions, the formation of cyclooctane by a direct hydrogenation becomes more suppressed as the degree of surface coverage is increased (Figs 3 and 4, curves 1, 2) is consistent with the concept that the adsorption *via* both double bonds is relatively more hindered. The less marked decrease in the hydrogenation rate for 1-hexene and 1-undecene then is probably associated with the changes in the adsorption heats of hydrogen and substrate on the modified catalysts and with the ability of olefinic substrates to adsorb also on modified surfaces.

REFERENCES

1. Furuya N., Motov S.: *J. Electroanal. Chem. Interfacial Electrochem.* **98**, 189 (1979).
2. Furuya N., Motov S.: *J. Electroanal. Chem. Interfacial Electrochem.* **100**, 771 (1979).
3. Schultze J. W., Habib M. A.: *A. Appl. Electrochem.* **9**, 255 (1979).
4. Červený L., Paseka I., Stuchlý V., Růžička V.: *This Journal* **46**, 1958 (1981).
5. Červený L., Paseka I., Stuchlý V., Růžička V.: *This Journal* **47**, 853 (1982).
6. Červený L., Růžička V.: *React. Kinet. Catal. Lett.* **17**, 161 (1981).
7. Paseka I., Červený L., Šmigolová D., Růžička V.: *This Journal* **47**, 1222 (1982).
8. Červený L., Kuncová M., Mojžišová J., Růžička V.: *J. Chem. Tech. Biotechnol.* **32**, 571 (1982).
9. Paseka I., Červený L., Mach J., Růžička V.: *This Journal* **45**, 3541 (1980).
10. Marko M., Krasnec L.: *Základy preparativnej organickej chémie*, p. 157. Published by SVTL, Bratislava 1962.

11. Kinoshita K., Stonehart P.: *Modern Aspects of Electrochemistry* 12, 225 (1977).
12. Červený L., Heral V., Růžička V.: *Chem. Listy* 68, 1285 (1974).
13. Červený L., Červená J., Růžička V.: *This Journal* 37, 2946 (1972).
14. Červený L., Vopatová J., Růžička V.: *React. Kinet. Catal. Lett.* 19, 223 (1982).

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