THE ROLE OF THE GEOMETRIC FACTOR IN SKELETAL REARRANGEMENTS OF NEOHEXANE ON LOW-INDEX SURFACES OF Ni AND Pt CATALYSTS

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The steric demands of two types of adsorbed complexes of neohexane (2,2-dimethylbutane) on (*100*), (*110*) and (*111*) ideal surfaces of Ni or Pt catalysts were investigated with the aid of a computer. It was shown, that $\alpha\gamma$ complexes of the adsorbed neohexane were preferred in comparison to $\alpha\beta$ ones for all studied surfaces. From the steric point of view, the feasibility of the adsorption depends on the complexity of the surface character in the following order: (*111*) < (*100*) < (*110*). Unfortunately, the experimentally observed discrepancies between the activity or selectivity in skeletal reactions on both types of catalysts could not be elucidated from our analyses.

The skeletal transformations of saturated hydrocarbons on metal catalysts have been studied for several decades[1]. Especially in recent years, much information has been collected[2 – 5] allowing the deeper insight into regularities controlling these processes. Nevertheless, the ideas on the probable mechanisms consist in the interpretation of experimental data and miss valuable evaluation from the view point of theoretical chemistry.

In literature, an increased interest is devoted to the specific role of the geometric factor in heterogeneously catalyzed reactions. Balandin[6], author of the multiple theory has drawn an attention to its significance as the first. For a long time it was evident that the geometric factor has an effect on the selectivity of this type of reactions but no suitable method allowing its investigation has been known. In the last few years, much new information about both, structural and other properties of catalytic surfaces were accumulated with the aid of modern physical methods[7] (LEED, ESCA, AES). This knowledge gave the basis for the discussion on the geometric factor importance in metal[8], redox[9] and acid-base catalysis[10], respectively. In our Laboratory, some results were obtained allowing to elucidate the suitability of various ensembles of active sites on the surface and the increased probability of some reaction pathways in comparison to others in dehydration of alcohols on alumina[10] or on zeolites[11]. The method of geometric analysis of the interaction of the reactant molecule with the surface was applied to skeletal transformations of 2,2-dimethylbutane (neohexane) on low index planes of Ni and of Pt polycrystalline catalyst. This modelling was carried out to justify the assumptions and validity of the hypotheses of Leclercq and coworkers[12] and Botman and coworkers[13]. These authors have studied the skeletal reactions (isomerization, hydrogenolysis) of neohexane on Ni/SiO_2 and Pt/SiO_2 catalysts, respectively.

METHODS

The used models, both of catalysts and of the hydrocarbon were constructed on a computer. They were realized as the system of mutually impenetrable spheres of the appropriate diameter. In the case of the hydrocarbon the valence radii were taken into account. The diameter of spheres constituting the model of the catalytic surface was considered as the distance between centres of the two neighbour metal atoms in the closed packed plane. The single crystal of these metal catalysts has the symmetry of a face centered cube with the lattice parameter 352 pm for nickel and 392 pm for platinum[14]. In our computations, the sufficiently large crystal was already prepared and then it was cut by the chosen suitable planes to obtain the surface of the required geometry (Miller indices) and size.

All models of the hydrocarbon adsorbed on the metal during skeletal transformations were constructed on the assumption of a dissociative two-site adsorption. The reaction intermediates were modelled as surface complexes $\alpha\beta$ or $\alpha\gamma$, where the Greek symbols designate the positions of reactive carbon atoms in the skeleton of substrate, in accordance with data from literature[15]. The reaction intermediate of the $\alpha\beta$ type is considered to be present during hydrogenolysis, whereas the bridged surface $\alpha\gamma$ structure appears predominantly as an isomerization intermediate. Basic conformations of the hydrocarbon-surface complexes were constructed on the assumption of the ideal geometry. The standard length of chemical bonds (carbon–carbon 154 pm, carbon–hydrogen 109 pm) and tetrahedral bond angles were used[16]. Except for the carbon–metal bonds, all the dihedral angles in the molecules corresponded to staggered conformations. The lengths of the bonds carbon–metal were taken as a sum of the appropriate radii. Here we considered the length of carbon–nickel bond equal to 201 pm and of the carbon–platinum one to 216 pm.

All metal atoms playing the role of catalytically active sites are rigidly anchored in the positions of the crystal lattice. In this respect, only specific pairs of these atoms with discrete distances exist on an actual surface. Similarly, the geometry of the hydrocarbon permits the adsorption only on surface atoms the distance of which falls into the defined interval of lengths.

Let us demonstrate this situation on hydrocarbon-metal complexes designated in this work as $\alpha\beta$ complexes (Fig. 1*a*). The position one of the presumed center on the metal surface (symbolized as asterisk (*) is fixed here, whereas the second one can rotate around the single bond between α-carbon (C_α) and β-carbon (C_β). Thus, the mutual distance between these centers depends on the rotation angle φ and increases from minimum (r_{min}) for $\varphi = 0°$ to maximum (r_{max}) for $\varphi = 180°$. The distances between these two presumed centers (active sites on the metal surface) fall for the $\alpha\beta$ complexes into the interval 288 – 476 pm for Ni and 297 – 502 pm for Pt, respectively.

In the case of intermediates of the $\alpha\gamma$ type the situation is more complex. The mutual distance between the two presumed positions of the active sites depends on two rotational angles φ_1 and φ_2 because the configuration of this intermediate allows mutually independent rotations around the both C_α–C_β and C_α–C_γ bonds, respectively as shown in Fig. 1*b*. In our calculations, such conformations of these complexes were chosen where the rotation angles were equal but their senses were in the same (conrotation) or in the opposite direction (disrotation). The interval of these distances falls in the region of lengths of 142 – 580 pm for Ni and 135 – 601 pm for Pt, respectively.

Geometric models of the reactant-catalyst complexes were designed in the following way:

a) Provided that the interaction is realized via two single bonds between the reactive carbon atom and the surface metal one, such conformations have been found (by single rotation around the C_α–C_β bond in the $\alpha\beta$ intermediates and by conrotation or disrotation around the both appropriate carbon–carbon bonds in $\alpha\gamma$ complexes, respectively) in which both the presumed sites of metal atoms have the same distance from each other as the chosen pair of the real sites one the surface of the catalyst model.

b) The hydrocarbon, in the required conformation obtained in the mentioned manner was subjected as such to translation and rotation so that the presumed positions of the metal atoms were identical with those of the metal atoms of the chosen pair of a catalyst.

c) By rotation of the hydrocarbon adsorbed in such a way around the joint of the two surface metal sites, such a mutual position of the adsorbed hydrocarbon against to surface of the catalyst was looked for in which the distance between the molecule and

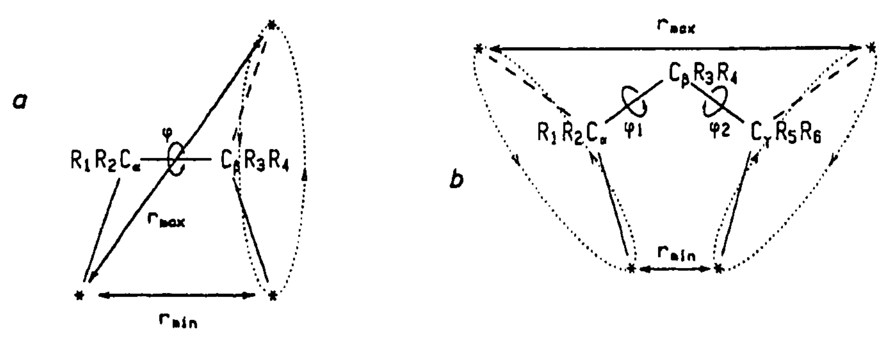

FIG. 1
The modelling of adsorption complexes of neohexane of types $\alpha\beta$ (*a*) and $\alpha\gamma$ (*b*)

the surface atoms is maximum. The reactant–catalyst distance, or optimum distance is defined here as the distance between centres of the two closest atoms, the first one being the reactant, and the second one from the catalyst surface from which the sum of their radii is subtracted. These operations and appropriate relations are described in detail elsewhere[10,11].

RESULTS AND DISCUSSION

Low-index surfaces of both studied metals have the same symmetry. The discrepancies arise from their lattice parameters only. All investigated surfaces are depicted in Fig. 2.

The types of pairs af active sites and their properties are summarized in Table I. The results of investigation of steric demands for the adsorption of neohexane αγ complexes on both metal catalysts are in Table II. The geometric conditions for the adsorption of neohexane in the form of αβ complexes are very unfavourable on all the surfaces studied. The satisfactory interaction of neohexane realized between metal atoms and the reactive carbons center number 3 and 4 was achieved on B1 ensembles of both (*110*) metal surfaces (Fig. 3 – optimum distance is 79 pm for Ni and 89 pm for Pt). This fact is consistent with the character of (*110*) surface which is created of "valleys" and "ridges". On all others flat surfaces collision takes place between the fundamental

TABLE I
Characteristics of ensembles found on studied surfaces of Ni and Pt catalysts

Surface	Symbol for ensemble	Distance of atoms[a,c]	Concentration [b,c]
	A1	249 (277)	53.6 (43.3)
(*100*)	B1	352 (392)	53.6 (43.3)
	D1	497 (554)	53.6 (43.3)
	A1	249 (277)	18.9 (15.3)
	A2	249 (277)	75.8 (61.2)
	A3	249 (277)	18.9 (15.3)
(*110*)	B1	352 (392)	18.9 (15.3)
	C1	431 (480)	37.9 (30.6)
	D1	497 (554)	18.9 (15.3)
	D2	497 (554)	18.9 (15.3)
	A1	249 (277)	92.8 (75.0)
(*111*)	C1	431 (480)	92.8 (75.0)
	D1	497 (554)	92.8 (75.0)

[a] In pm; [b] in μmol m^{-2}; [c] values in parentheses are valid for the platinum catalyst.

TABLE II
The modelling of neohexane adsorption on low-index surfaces of Ni or Pt catalysts

Surface	Symbol for ensemble	Type of complex[a]	Optimum distance[b]
(100)	A1	1,3	56 (61)[c]
		1,5	56 (61)[c]
	B1	1,3	no[d]
		1,5	no[d]
(110)	A1	1,3	87 (89)[c]
		1,5	90 (89)[c]
	A2	1,3	no[d]
		1,5	no[d]
	A3	1,3	no[d]
		1,5	no[d]
	B1	1,3	43 (36)[c]
		1,5	43 (43)[c]
	C1	1,3	no[d]
		1,5	no[d]
(111)	A1	1,3	45 (37)[c]
		1,5	45 (37)[c]
	C1	1,3	no[d]
		1,5	no[d]

[a] The $\alpha\gamma$ complexes are considered only (the numbers designate reactive carbons in the skeleton). [b] For the definition see Methods, in pm. [c] Values in parentheses are valid for the Pt catalyst. [d] No satisfactory adsorption can be achieved.

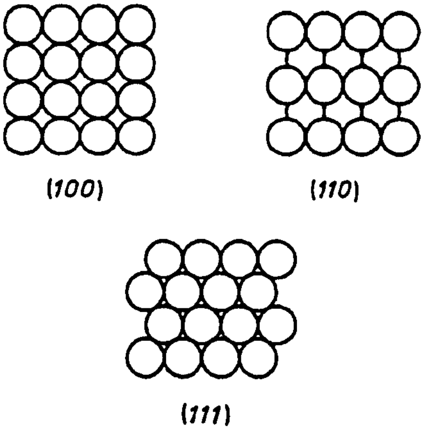

FIG. 2
The studied surfaces of metal catalyst

skeleton of the hydrocarbon and surface atoms of the catalyst. Nevertheless, successful adsorption of neohexane as αβ intermediates was found when fundamental tetrahedral angles of skeletal bonds of neohexane were deformed (approximately 2.5°).

From the geometric point of view, no adsorption on the ensembles of type D proceeds on all the surfaces. Namely, it was found that the hydrocarbon molecule is "pulled" into the surface with the increasing distance between metal atoms in the ensemble. A comparison of the adsorption feasibility of neohexane could be made too. The order of surface was determined as follows: (*111*) > (*100*) > (*110*). This trend reflects the increasing grade of saturation of the surface metal atoms and the decreasing values of the surface ensemble concentration in both cases, i.e. for Ni or for Pt. The increasing steric demands of neohexane in the form of αγ complexes are connected with close packing of the surface studied. It may be shown, that an alkyl substitution influences the feasibility of the adsorption. For example, the differences in steric demands of 1,3 and 1,5 adsorbed neohexane on the ensemble of the B1 type of (*110*) surfaces between both the metals are evident because the methyl substituent is more voluminous than the hydrogen one.

Although nickel and platinum have a similar structure of electron shells, their effect in skeletal transformations is different. In literature the platinum is considered to be a typical isomerization catalyst[5]. On the nickel catalyst, hydrogenolytic reactions proceed predominantly, especially the cleavage of the terminal carbon–carbon bond of the hydrocarbon to form methane. Nevertheless, many analogies were found between both metals. The differences in values of the optimum distance signalize various conditions for adsorption from the geometric point of view. It was mentioned, that the lattice parameter is about 40 pm shorted for Ni. Mutual distances between surface nickel atoms are thus lower and this surface is less accessible for the interaction with reactive centers in the hydrocarbon. The length of adsorption bonds considered between active (Ni) and reactive (C) centers is reduced too. The molecule of neohexane is then placed

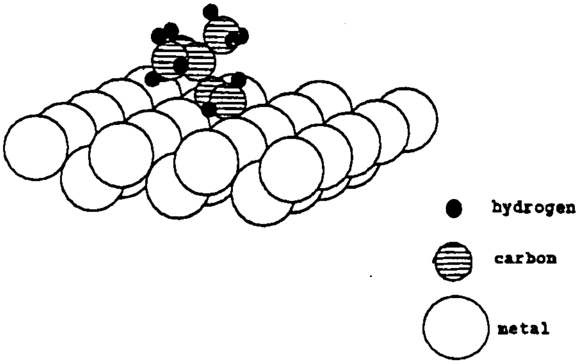

FIG. 3
Interaction of neohexane realized between metal atoms and the reactive carbon center number 3 and 4 on B1 ansambles of (*110*) metal surfaces

near to surface nickel atoms by some parts of its skeleton. Thus, the steric hindrances are greater in the comparison with the platinum catalyst. The changes in the distance between nickel atoms in active ensembles is the last geometric reason for the difference in neohexane adsorption. These shorter distances cause greater stretching of the hydrocarbon skeleton in the space above the nickel surface. This fact, in turn, improves the conditions for better contact with the nickel surface. All these investigated effects are added to each other and mutually combined. Therefore, the result of these influences depends on the actual complex molecule–catalyst. Thus the adsorption of neohexane in the forms of $\alpha\gamma$ intermediates on *(111)* nickel surface proceeds more easily than on the same platinum surface. In opposite to this fact investigated by us, the *(111)* nickel surface is found to be more compact than the same platinum surface and therefore less accessible for the high neohexane molecule.

The distribution of reaction products of the neohexane transformation on Ni/SiO_2 or Pt/SiO_2 led to the presumption of the possible chemisorbed complexes. It was assumed, that the reorganization of the neohexane skeleton occurs due to Bond Shift mechanism action. Burton[17] stated, that *(100)* or *(111)* surfaces have their representation on the polycrystalline metal catalysts predominantly. We have confirmed from our calculations the preferred role of $\alpha\gamma$ adsorbed species as potentially existing intermediates in the course of neohexane isomerization. Very low concentrations of neopentane formed by the cleavage of the terminal carbon–carbon bond of the considered $\alpha\beta$ neohexane intermediates together the low occurence of the *(110)* surface on the Pt catalyst point to a low probability of this reaction pathway. In opposite to this surprising agreement of the experimental and computed results, is the reality, that there is no reason for the confirmation of the preference for 1,3 adsorbed neohexane structures. From the geometrical insight, the both $\alpha\gamma$ neohexane complexes (i.e. 1,3 or 1,5) have the same steric demands on all the studied surfaces. These investigated facts enable a partial interpretation of the data obtained on the Pt/SiO_2 catalyst only. For the case of the nickel catalyst similar knowledge was identified. Two possible explanations exist for the very limited feasibility of the existence of $\alpha\beta$ neohexane species on all nickel surfaces: *1*) the considered types of adsorbed neohexane complexes do not reflect the actual situation and or *2*) in the course of the interaction of the hydrocarbon with the catalyst surface deformations of the skeleton bonds occur. The latter presumption was verified by computing the optimum distance in structures with deformed tetrahedral angles (approximately 5.8°). The neohexane adsorbed on nickel surfaces in the form of $\alpha\gamma$ complexes has the same steric conditions as in the case of platinum. From this fact it follows that it is necessary to find the reasons for the different selectivity of both catalysts in some phenomena included under the common name “electronic factor”.

CONCLUSIONS

Modelling of the geometric factor in some skeletal transformations of neohexane on ideal surfaces of Ni or Pt catalysts brought much interesting information which enlight the experimental knowledge in this field. Our results demonstrated that geometric conditions for the neohexane interaction on catalyst surfaces of the studied metals influence often considerably the course of the heterogeneous catalyzed reaction. It is not possible to explain some of the observed phenomena in this way so far. Nevertheless, the method mentioned here serves as a simple tool of approach to the understanding of regularities controlling heterogeneous reactions.

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