GEOMETRIC FACTOR IN SKELETAL REACTIONS OF 2-METHYLPENTANE ON STEPPED SURFACES OF PLATINUM CATALYST

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The role of geometric factor in the course of skeletal reactions (isomerization, hydrogenolysis) of 2-methylpentane on stepped (119), (557) and reconstructed R(557) surfaces of single crystals of platinum was evaluated with computer designed models. These calculations were compared with reported experimental data. It was found by analysis of geometric conditions that there are accesible active ensembles on double step of the reconstructed R(557) surface. In addition, these active sites are unsaturated in their coordination sphere and thus catalytically effective. This finding is consistent with published data, confirming higher catalytic activity of this surface. The various pathways of Bond Shift isomerization mechanism of 2-methylpentane from the point of view of steric demands of surface intermediates on differently located ensembles are discussed, too.

The problem, what role plays geometric factor in heterogeneously catalyzed reactions, has existed for a long time. Especially in the field of skeletal rearrangement of hydrocarbons on metals much knowledge has been systematically accumulated[1]. Usually, these experimental data contain one-side explanation only, i.e. on the basis of intuition or speculation. For example, the investigation of the isomerization of labelled hydrocarbons on supported polycrystalline catalysts or on metal films allowed to characterize two different skeletal reactions mechanisms, the Bond Shift[2] and the Cyclic Mechanisms[3], respectively. Garin and coworkers[4] found a possible correlation between crystallographic arrangement and catalytic transformation of hydrocarbon skeleton, using well defined surfaces of platinum single crystals, with both low and high index planes.

Results obtained in our laboratory made it possible to compare the suitability of various ensembles of the active sites on surfaces and the probability of some reaction pathways in dehydration of alcohols on alumina[5] or on zeolites[6]. A method of geometric analysis of interaction of a reactant molecule with the surface was applied to skeletal transformation of 2,2-dimethylbutane (neohexane) on low index planes of Ni and Pt polycrystalline catalysts[7,8]. These calculations, based on dissociative two-site adsorption and some simplifications, showed the steric preference of $\alpha\gamma$ adsorbed over $\alpha\beta$ ones. However, results could not explain different specific activity of both metals.

The present work extends this initial study[8] by further calculations of geometric factor for both isomerization and hydrogenolysis of 2-methylpentane on well defined (119), (557) and reconstructed R(557) surfaces, respectively. The main aim of the present paper is to demonstrate how much the skeletal transformations are influenced by geometric conditions on stepped surfaces and to discuss the conclusions of Garin and coworkers[4].

METHODS

The geometric models of hydrocarbon or of catalyst surfaces were designed on computer using the same method as presented elsewhere[8]. Briefly, dissociative two-site adsorption of 2-methylpentane on platinum surfaces was considered. In accordance with literature data[9], the reaction intermediates were modeled as $\alpha\beta$ or $\alpha\gamma$ surface complexes. The first type of complexes is considered to be present in hydrogenolysis, whereas the bridged surface structures (designed as $\alpha\gamma$) appear as isomerization intermediates predominantly. In the construction, ideal goemetry was used, i.e. the standard length of chemical bonds (carbon–carbon 154 pm, carbon–hydrogen 109 pm) and tetrahedral bond angles[10]. The length of carbon–platinum bond was taken to be 216 pm. The optimal distance was also used to compare the feasibility or difficulty of 2-methylpentane adsorption on studied catalyst surfaces; this quantity is defined as the distance between two closest atom centres (the first from the catalyst surface, the second from interacting hydrocarbon molecule), from which the sum of their atomic radii is subtracted.

RESULTS AND DISCUSSION

The stepped or high index surfaces are constituted from terraces of variable width and from the steps of variable height (most frequently monoatomic). The surfaces of platinum catalyst are depicted in Fig. 1. Their description is possible both by the Miller indices or by the formulas in Lang and coworkers nomenclature[11]. Four types of pairs of active sites (ensembles) are located on these surfaces. Their notation is done in order of increasing distances between sites as A = 227 pm, B = 392 pm, C = 480 pm and D = 554 pm. These ensembles are located on free terraces, steps, edges and in hollow of the steps. Their dislocation, surface concentration and unsaturation in the coordination sphere of platinum atoms are summarized in Table I.

In accordance with ideas on reaction mechanism by Barron and coworkers[3], four basic $\alpha\beta$ and two $\alpha\gamma$ complexes of 2-methylpentane were modeled. They are depicted together with products of both hydrogenolytic (Fig. 2) and isomerization reactions (Fig. 3). Platinum is considered to be typical isomerization catalyst. For this reason, the main attention was paid to the investigation of geometric conditions in the key moments of the isomerization, i.e. during interaction of 2-methylpentane with the surface of platinum.

The two-site dissociative adsorption of 2-methylpentane on the stepped (119), (557) and reconstructed R(557) surfaces of platinum, respectively, is evaluated on the basis of three quantities: the optimal distance, the surface concentration of ensembles and the coordination unsaturation of platinum atoms in the ensembles. The results of calculations are summarized in Table II.

It follows from the values of the optimal distance between the reactant and the surface of various structure, that successful adsorption is achieved on ensembles whose atoms lie in the shortest mutual distance (*A*, 277 pm). The higher distance between these sites, the more atoms of the hydrocarbon come in contact with the surface atoms and the steric hindrance for the adsorption is then higher. Nevertheless, both modes of adsorption (1, 3 and 1, 6) on the ensembles *A* (277 pm) are always realized, whereas no adsorption proceeds on the ensembles of type *D* (554 pm).

On all surfaces studied, the effect of the location of ensembles of the same size was investigated. For example, the ensembles of type *A3* (277 pm), located on free terraces give very good conditions (from geometric point of view) for adsorption of both $\alpha\gamma$ complexes of 2-methylpentane. On the contrary, there are ensembles in the hollows of the steps (*A5*), where a very narrow space for adsorption of the hydrocarbon

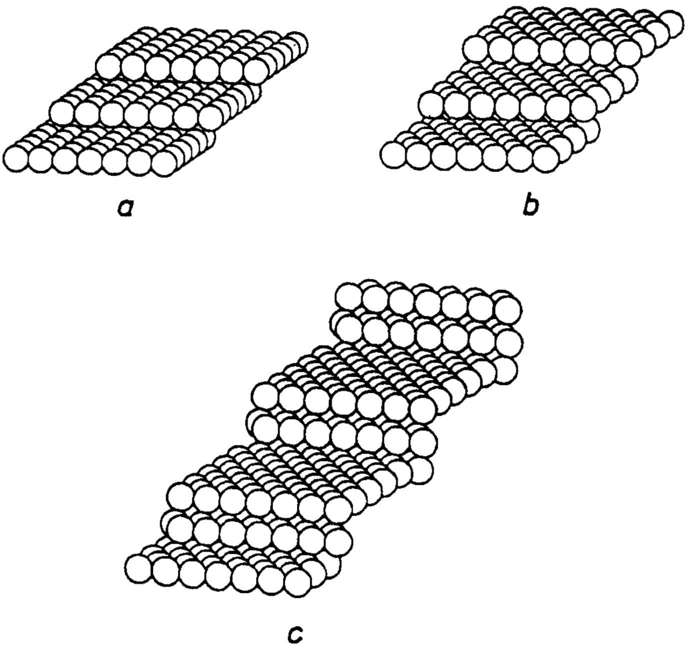

FIG. 1
The studied surfaces of the platinum catalyst: *a* (119) or Pt(S)[5(100) × (111)]; *b* (557) or Pt(S)[6(111) × (100)]; *c* R(557) or Pt(S)[10(111) × (311)]

TABLE I
The characteristics of ensembles on surfaces studied

Type	Location	Surface concentration[a]			Coordination unsaturation[b] of atoms in ensembles		
		(119)	(557)	R(557)	(119)	(557)	R(557)
A1	terrace	4.75	8.70	4.35	4 – 5	3 – 5	3 – 5
A2	edge	4.75	4.35	2.18	5 – 5	5 – 5	5 – 5
A3	terrace	23.76	43.50	47.85	4 – 4	3 – 3	3 – 3
A4	step	9.50	4.35	2.18	2 – 5	2 – 5	2 – 5
A5	hollow	4.75	4.35	2.18	2 – 2	2 – 2	2 – 2
A6	terrace	4.75	8.70	4.35	2 – 4	2 – 3	2 – 3
A7	step	–	–	2.18	–	–	2 – 5
A8	hollow	–	–	2.18	–	–	2 – 2
A9	narrow[c] terrace	–	–	4.35	–	–	2 – 5
A10	edge	–	–	2.18	–	–	5 – 5
B1	terrace	9.50	–	–	4 – 5	–	–
B2	terrace	19.00	–	–	4 – 4	–	–
B3	step	–	8.70	8.70	–	2 – 5	2 – 5
B4	terrace	9.50	–	–	2 – 4	–	–
C1	terrace	–	47.85	50.03	–	3 – 5	3 – 5
C2	step	9.50	–	–	2 – 5	–	–
C3	terrace	–	4.35	2.18	–	2 – 3	2 – 3
C4	terrace	–	8.70	4.35	–	2 – 3	2 – 3
C5	bridged[d]	9.50	8.70	4.35	4 – 5	3 – 5	3 – 5
C6	narrow terrace	–	–	4.35	–		2 – 5
C7	bridged	–	–	4.35	–		5 – 5
D1	terrace	4.75	43.50	47.85	4 – 5	3 – 5	3 – 5
D2	edge	4.75	4.35	2.18	5 – 5	5 – 5	5 – 5
D3	hollow	4.75	4.35	2.18	2 – 2	2 – 2	2 – 2
D4	terrace	4.75	8.70	4.35	2 – 4	2 – 3	2 – 3
D5	hollow	–	–	2.18	–	–	2 – 2
D6	edge	–	–	2.18	–	–	5 – 5

[a] In μmol m^{-2}. [b] The number of neighbouring atoms, missing in coordination sphere of surface atoms (bulk atom coordination number is 12 for platinum). [c] Considered only for R(557), where two differently long terraces are (Fig. 1c). [d] First active site is located on edge, the second on lower terrace.

exists (28 pm only). The best adsorption conditions offer the ensembles of *A2* type on edges, taking into consideration also the coordinative unsaturation of edge atoms. The optimal distance of the later is of the same value as for the ensembles of type *A3* on free terraces (89 pm). This value is limited by the distance between the β-carbon and a surface atom.

The analysis of geometric conditions for adsorption of 2-methylpentane on the stepped surfaces of platinum gave a quantitative evaluation of steric demands of the reactant in various regions of the catalytic surface. It cannot be proved from the results in Table II firmly which of the studied surfaces are suitable for the isomerization reactions. The steric demands of both 2-methylpentane complexes studied (1,3 and 1,6) are almost the same. The regions, where the surfaces exhibit different structural and electronic properties, are situated on edges, steps and or in hollows. Therefore in this situation, when the geometric factor effect on studied surfaces is comparable, the conclusion can be done that the adsorption and catalytic activity depends rather on the local density of states and other electronic properties of surface atoms.

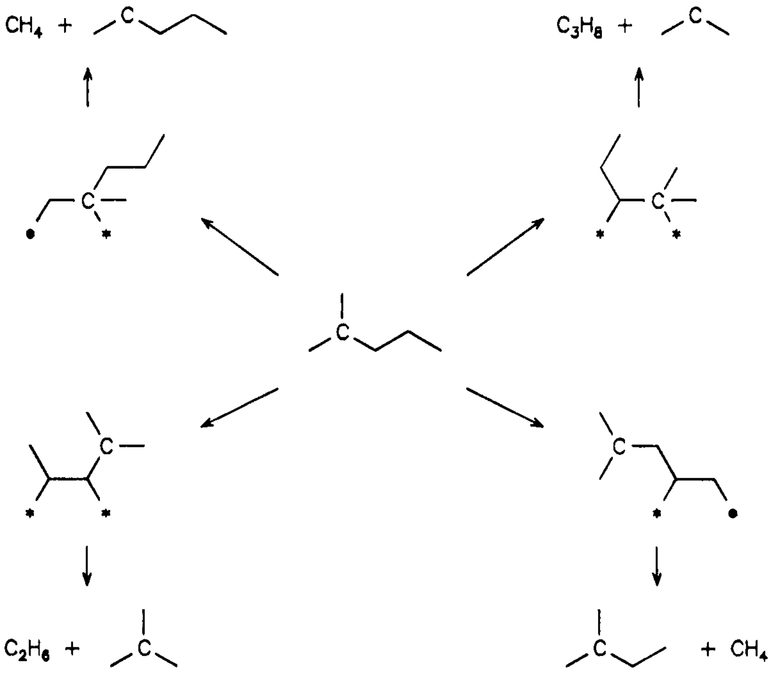

Fig. 2

The scheme of the reaction pathways of hydrogenolysis of 2-methylpentane (C in structural formulas is labelled carbon; • marks the position of metal atom on the catalyst surface)

Garin and coworkers[4] showed that the surface R(557) is formed from original surface (557) by the action of the reaction mixture. It was assumed that the increased amount of isomerization products and higher participation of the Bond Shift isomerization mechanism on the reconstructed R(557) in comparison with the surface (119) are caused by this reconstruction.

On reconstructed surface R(557) the ensembles of the *C7* type (480 pm) were found which are highly unsaturated and easily accesible for adsorption. No similar active sites exist on the original surface (557) or (119). This fact could probably explain the higher isomerization activity of the R(557) than of the (119) or of the original (557) surfaces, respectively.

Garin and coworkers[4] discussed the considerable increase of the isomerization Bond Shift mechanism (BS) to the Cyclic Mechanisms (CM) on the reconstructed R(557) and (119) surfaces, expressed as the CM/BS ratio. Some of their geometric ideas are based on speculations. The BS mechanisms includes these reaction pathways; *1* and *2* (the

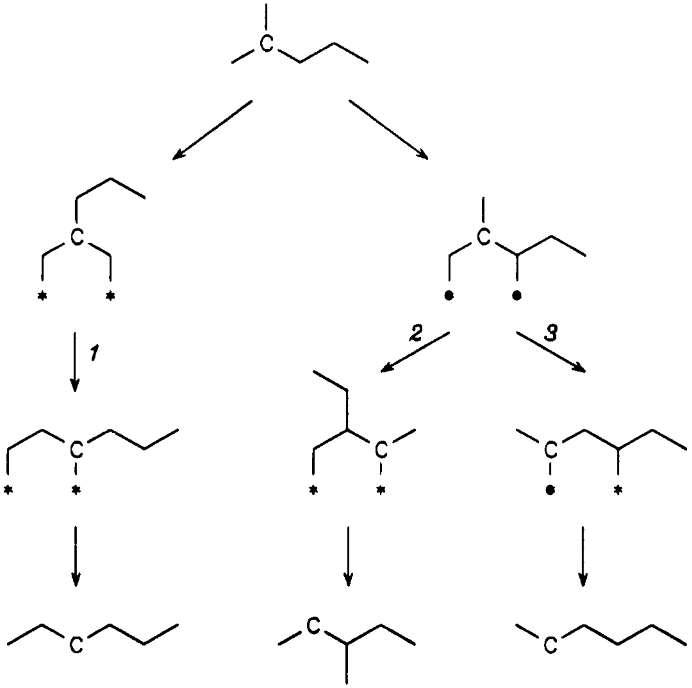

FIG. 3
The scheme of the reaction pathways of isomerization of 2-methylpentane via Bond Shift mechanism of type *1* or *2* (methylshift) and of type *3* (chain lengthening)[2,3] (C in structural formulas is labelled carbon; * marks the position of metal atom on the catalyst surface)

TABLE II
Geometric conditions in adsorption of 2-methylpentane in positions 1,3 or 1,6 on (119), (557) and R(557) surface of Pt catalyst

Type	Location	1,3-Complex			1,6-Complex		
		(119)	(557)	R(557)	(119)	(557)	R(557)
A1	terrace	89[a]	89	89	89	89	89
A2	edge	89	89	89	89	89	89
A3	terrace	89	89	89	89	89	89
A4	step	26	30	30	26	no[b]	no
A5	hollow	28	28	28	28	28	28
A6	terrace	30	28	28	no	26	no
A7	step	–	–	30	–	–	no
A8	hollow	–	–	28	–	–	28
A9	narrow[c] terrace	–	–	26	–	–	26
A10	edge	–	–	89	–	–	89
B1	terrace	37	–	–	37	–	–
B2	terrace	37	–	–	37	–	–
B3	step	–	37	37	–	37	37
B4	terrace	37	–	–	32	–	–
C1	terrace	–	no	no	–	no	no
C2	step	no	–	–	no	–	–
C3	terrace	–	no	no	–	no	no
C4	terrace	–	no	no	–	no	no
C5	bridged[d]	63	63	63	63	no	53
C6	narrow terrace	–	–	no	–	–	no
C7	bridged	–	–	63	–	–	63

[a] Optimal distance (in pm). [b] Adsorbed complex cannot exist because of steric hindrance. [c] Considered only for R(557), where two differently long terraces are (Fig. 1c). [d] First active site is located on edge, the second on lower terrace.

shift of methyl group) or *3* (the shift of the other alkyl groups) that are summarized in Fig. 3. In addition, the assumptions have been accepted, that more than one single metal atom must operate in agreement with both mechanisms of Anderson and coworkers[2] and Barron and coworkers[3]. The transformation of a skeleton of 2-methylpentane begins by two-site dissociative adsorption in $\alpha\gamma$ position. The interaction between further surface atom and β-carbon of a skeleton envolves new electronic perturbations of the carbon–carbon bonds in the skeleton. Consequently, a reorganized complex of the same type is formed, where original β-carbon takes the role of the γ-carbon of skeleton.

For example, the catalytic effectivity in the pathway *1* is assigned[4] to the ensembles *A3* on the surface (119) and to the ensemble *A10* on the edges of the reconstructed R(557), respectively. This hypothesis[4] can be confirmed by geometric analysis. These ensembles really exhibit favourable conditions for the adsorption. However, similar dispositions can be found on the ensembles *A1* and *A2* on the (119) surface or on the ensembles *A1* – *A3* of reconstructed surface R(557). However, the adsorption of 2-methylpentane on ensembles *A3* of the surface (119) cannot be successful in the light of proposed mechanism. This mechanism requires cooperation of a further surface metal atom with β-carbon and the 1,6-complex would have to go through energetically demanding deformation. The steric demands of this type of activated hydrocarbon complex are better satisfied on an edge (ensemble *A2*) with opportunity of the further interaction of β-carbon with metal atoms of a hollow. Further possibility for applying the pathway *1* occurs on ensemble *B1* (392 pm) on the terrace of (119) surface. In this way, the molecule of 2-methylpentane is in closer contact with the surface there, but the unsaturated coordination sphere of metal atoms at the edge are easily accesible for interaction with the β-carbon. Similar considerations can be applied for other reaction pathways *2* and *3*, respectively. Some of present results confirm the hypothesis of Garin and coworkers[4], others indicate restriction for the proposed Bond Shift mechanism on some ensembles of surfaces studied.

The adsorption of 2-methylpentane as an $\alpha\beta$ complex could not be realized for the conditions of ideal geometry. These structures were placed so close to the surface, that the carbons of skeleton get into a collision with the surface atoms during an optimization of hydrocarbon position on the surface. Nevertheless, Garin and coworkers[4] detected the products of hydrogenolytic reactions mixture. In literature, $\alpha\beta$ complexes are considered as probable intermediates in a hydrocarbon cleavage on metal. On the other hand, present results based on the ideal geometry analysis exclude an existence of hydrocarbon complexes of this type. A possible explanation can be suggested as the existence of the intermediates of other type (for example cyclic). The further possibility considered in this regard, is the deformation of both tetrahedral angles in $\alpha\beta$ complexes. A satisfactory adsorption can be achieved, when both of the Pt–C_α–C_β and C_α–C_β–Pt angles increase about 2.5°.

CONCLUSIONS

The results of modeling of the two-site dissociative adsorption of 2-methylpentane on stepped surfaces of platinum catalyst demonstrate, that the both surface complexes (1,3 and 1,6) of hydrocarbon have favourable conditions from the geometric point of view. The opposite situation, i.e. no successful adsorption, resulted for intermediates of hydrogenolysis (αβ complexes). The role of geometric factor for hydrocarbon isomerization on stepped platinum surfaces is significant, because some differences were found in the adsorption of 2-methylpentane on various located ensembles of surfaces studied. However, the geometric analysis could not satisfactorily answer all questions, for example the question of different isomerization activity of the (119) and reconstructed R(557) surfaces.

The present calculations proved that geometric conditions of hydrocarbon interaction with metal surface really have an effect in the course of heterogeneously catalyzed reaction. On the other hand, geometric factor cannot explain some observed phenomena and it is necessary to look for their causes elsewhere (for example in electronic factor).

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