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**Table Notes:***

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STUDIES ON ADSORPTION AND DECOMPOSITION
OF ISOBUTANE ON SILICA GELS
CONTAINING SODIUM IONS

By

W. GRABOWSKI*) and S. MALINOWSKI**)

(Received December 27, 1971)

Abstract

The decomposition of isobutane and the adsorption of isobutylene and isobutane on silica gels containing sodium ions were studied. Silica gels containing various amounts of sodium ions were calcinated at 550 and 750°C, and the residual amounts of “water” remaining after the calcination were determined thermogravimetrically. The results of the determinations were calculated for one hypothetical sodium ion present on the surface of the gel. They indicate that the number of “water” molecules corresponding to one sodium ion, the number of adsorbed hydrocarbon molecules and the number of hydrocarbon molecules reacting at one sodium centre decrease with increasing concentration of sodium ions on the surface of the gel. The highest number of adsorbed and reacting molecules (corresponding to one sodium ion) was observed at low concentrations of sodium accompanied by large numbers of water molecules corresponding statistically to one sodium ion. A mechanism of the surface reactions, based on a model of the surface of the catalyst and on a quantum interpretation of hydrocarbon molecules, is proposed. It differs from the generally accepted mechanism by postulating that the initial step is the formation of a carbanion.

In the authors’ opinion the decomposition of hydrocarbons is a multicentre reaction, which may involve radicals or radical-ions.

The present work is the continuation of studies on silica gels containing alkali metal ions. In previous papers1,2,3) we have reported the results of studies on adsorption of water, ammonia and carbon dioxide on silica gels containing various amounts of sodium and calcinated at various temperatures. In these investigations we have observed that the number of acidic centres on the surface does not decrease with increasing amount of alkali ions added to the gel. The acidity of the surface, determined by the amount of adsorbed ammonia, is a function of the amount of added sodium ions, which has
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maxima and minima. When sodium ions are added some of the acidic centres disappear, but new ones appear. The character and the strength of the acidic centres with respect to sodium ions are diverse. The results of investigation of CO₂ adsorption indicated that the number of basic centres increases with increasing amount of sodium and that the strength of all the basic centres in the same.

The results of our previous work¹-⁴ showed that acidic and basic centres of various strength occur side by side on the surfaces of gels containing sodium ions. We were interested in catalytic activity of such gels. In a series of papers⁵,⁶,⁷ on gas phase aldol reactions we have shown that the rates of these reactions are directly proportional to the amounts of sodium introduced to the gels. We have also found that the rate determining step in the aldol reactions is the cleavage of proton, which is facilitated by a strong polarization of the molecule due to the presence of a strongly electronegative group, such as C=O, CN or NO₂.

In the present work we have investigated reactions of isobutane in the presence of silica gels containing sodium ions. We regard this work as a model of studies on reactions of hydrocarbons in the presence of gels containing alkali metals. The investigation consists of studies on adsorption of isobutane and isobutylene and on reactions of isobutane and isobutylene in the presence of silica gels containing various amounts of sodium.

Experimental

1. The method of preparation of the catalysts was described in detail in our previous publications¹-³. Briefly, they were prepared as follows: the grains of the catalyst were formed from a thick paste obtained by mixing Aerosil (Degussa Co.) with water. After drying at 110° the grains were saturated with an aqueous NaOH solution. After drying again at 110° they were calcinated at 550 or at 750°C for 8 hours.

2. The catalytic activity was investigated in a quartz tube 15 mm diam., using catalyst grains 1.25-1.5 mm diam. The volume of the catalyst was 10 ml. Before the determinations a current of air at 450°C was passed through the catalyst layer for 1 hour. The flow rate of isobutane was 1200 ml/hr. The purity of isobutane was 99%. The reaction products were analyzed by gas chromatography.

3. The studies on adsorption were carried out by means of gas chromatography and the frontal analysis technique. In these experiments the 40-60 mesh gel fractions were used. Hydrogen was used as the carrier gas. Before the determinations the gel was activated by means of a current of
hydrogen at 400°C which was passed for 1 hour. The amounts of adsorbed hydrocarbons were calculated from the chromatographic peak areas.

4. Thermogravimetric determinations were carried out by means of derivatograph manufactured by Monikan Co. according to Paulik, Paulik and Eberley. The amounts of water present in the gels calcinated at 550 or at 750°C were calculated from the known weight of the samples at 1020°C. It was assumed that in this temperature the gel was anhydrous. Putting: 

\[ m_t = \text{mass of gel calcinated at } t^\circ \]
\[ m_0 = \text{mass of gel calcinated at 1020}^\circ \]

we obtain: 

\[ \Delta m = m_t - m_0 \]

\( \Delta m \) = amount of water removed from the catalyst on heating from \( t^\circ \) to 1029°C.

Hence:

\[ W = \frac{\Delta m}{m_t} \times 100 \]

where \( W \) = per cent water content in the gel calcinated at \( t^\circ \).

Putting \( S \) = the specific surface area of the gel we obtain:

\[ B = \frac{m_A}{m_t} \times \frac{1}{18S} \]

where \( B \) = number of moles of water per unit surface area.

5. The specific surface areas of the gels were determined by the BET method and by the method of summation of fields of individual capillaries having different radii, which were determined by the porosimetric method. The results of the porosimetric determinations showed that the average radius of the pores varied within the limits 150–220 Å.

The results of the determinations of the specific surface areas obtained by the two methods were very similar.

**Physical properties of the gels**

The preparation of the catalysts and their physical properties were described in the previous papers\(^1,2,3\). The data in Table 1 show that specific surface areas of gels calcinated at 550 and 750°C are similar, but those of gels calcinated at 750°C are in general smaller. The specific surface area of the catalysts decreases with increasing amount of added sodium, in particular in the case of gels calcinated at 750°C.

In order to facilitate the discussion of our results we introduce quantity \( \alpha \) denoting the relative concentration of sodium ions on the surface of the
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TABLE 1. Specific surface areas of gels

<table>
<thead>
<tr>
<th>Amounts of added sodium ions in mmoles/g SiO₂</th>
<th>Calcination temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 0.10 0.20 0.30 0.40 0.50 t°C</td>
<td></td>
</tr>
<tr>
<td>Specific surface area S m²/g</td>
<td></td>
</tr>
<tr>
<td>163 142 146 134 129 122 550</td>
<td></td>
</tr>
<tr>
<td>156 139 130 113 102 84 750</td>
<td></td>
</tr>
</tbody>
</table>

gel. The introduction of this quantity is based on the assumption that all the sodium ions added to the gel remain on its surface. The quantity \( a \) has no real physical meaning, but we assume that it is proportional to the concentration of sodium ions on the surface of the gel. The values of \( a \) are shown in Table 2.

TABLE 2. Relative concentration of sodium ions on the surface of gels

<table>
<thead>
<tr>
<th>Amounts of added sodium ions in mmoles/g SiO₂</th>
<th>Calcination temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 0.10 0.20 0.30 0.40 0.50 t°C</td>
<td></td>
</tr>
<tr>
<td>Relative concentration of sodium ions ( a )</td>
<td></td>
</tr>
<tr>
<td>( \mu ) moles/m²</td>
<td></td>
</tr>
<tr>
<td>0.00 0.00 0.71 1.40 2.20 3.10 4.10 550</td>
<td></td>
</tr>
<tr>
<td>0.00 0.00 0.72 1.50 2.60 3.90 6.00 750</td>
<td></td>
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</tbody>
</table>

The water contents of the gels, shown in Table 3, were determined thermogravimetrically as the weight difference between the catalysts calcinated at 1020°C and those calcinated at 550 or 750°C. \( W \) denotes the water content of the sample in per cent by weight, and \( B \) stands for the amount of water.

TABLE 3. Water contents of gels

<table>
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<tr>
<th>Amounts of added sodium ions in mmoles/g SiO₂</th>
<th>Calcination temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 0.10 0.20 0.30 0.40 0.50 t°C</td>
<td></td>
</tr>
<tr>
<td>( W )</td>
<td></td>
</tr>
<tr>
<td>1.40 0.90 1.00 0.76 0.75 0.97 550</td>
<td></td>
</tr>
<tr>
<td>( B )</td>
<td></td>
</tr>
<tr>
<td>4.80 3.52 3.90 0.15 3.23 4.42 450</td>
<td></td>
</tr>
<tr>
<td>( W )</td>
<td></td>
</tr>
<tr>
<td>0.70 0.46 0.73 0.38 0.33 0.51 750</td>
<td></td>
</tr>
<tr>
<td>( B )</td>
<td></td>
</tr>
<tr>
<td>2.70 1.84 3.12 1.87 1.80 3.37 750</td>
<td></td>
</tr>
</tbody>
</table>
per 1 m² of the surface.

The origin of the removed water is unknown. It can be the adsorbed water, but it could also be formed from the surface hydroxylic groups. The data in Table 3 show that there are no linear relationships between the values of \( W \) and \( B \) and the sodium content of the gel.

**Studies on the catalytic activity**

We have found that in the presence of silica gels containing sodium dehydrogenation and decomposition of isobutane take place. The products of these reactions are methane and propylene:

a) \( i-C_4H_{10} \rightarrow CH_4 + C_3H_6 \)

b) \( i-C_4H_{10} \rightarrow i-C_4H_8 + H_2 \)

![Fig. 1. The relation between the molar degree of isobutane change and \( a \) for the gels calcinated at 550°C.](image-url)
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Figure 1 shows the relation between the molar degree of isobutane change (for reactions a and b) per unit specific surface area and the relative concentration of sodium ions \( a \) for the gels calcinated at 550°C. It is seen from the graph that the addition of small amounts of sodium ions to the sodium-free gel (0.70 \( \mu \)mole Na\(^+\)/m\(^2\)) causes a sharp increase of the catalytic activity and of the rate of degradation of isobutane. Further increases of the amount of sodium cause a decrease of the activity down to the minimum value, after which the activity starts to increase.

The affect of the addition of sodium ions on the dehydrogenation reaction is much smaller than that on the decomposition. The plot of the activity against the amount of sodium shows the presence of a small minimum.

![Graph of Figure 1](image-url)

**Fig. 2.** The relation between the molar degree of isobutane change and \( a \) for the gels calcinated at 750°C.
The same relationships for the gels calcinated at 750°C are shown in Fig. 2.

The curves representing the degradation and dehydrogenation reactions in the presence of gels calcinated at 750°C are quite different from those obtained for the gels calcinated at 550°C. In general the catalytic activity of gels calcinated at 550°C is higher. In the case of gels calcinated at 750°C the curves representing the decomposition and dehydrogenation have the general tendency to rise and to pass through the extrema with increasing relative concentration of sodium ions \( a \).

Studies on adsorption

Adsorption of isobutane and isobutylene was studied on samples of the gels used for the determination of the catalytic activity of the degradation
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and dehydrogenation of isobutylene.

The relation between the amounts of adsorbed hydrocarbons and the amounts of sodium present in the gels calcinated at 550°C is shown in Fig. 3. It shows that the relation between the amount of sodium and that of adsorbed isobutane is not linear. The character of the course of adsorption of isobutylene is different. Fig. 3 shows that the amount of adsorbed isobutylene has the tendency to increase with increasing amount of sodium in the gel.

The same relationships for the gels calcinated at 750°C are shown in Fig. 4.

Also in this case the curve of isobutane adsorption passes through several extrema, and the adsorption of isobutylene has the tendency to increase with increasing sodium ions content in the catalyst.

Fig. 4. The relation between the amounts of adsorbed hydrocarbons and $a$ for the gels calcinated at 750°C.
Indexes

In order to facilitate the analysis of the obtained results we have represented them in a slightly different form. All the determined quantities, such as amounts of water, number of adsorbed molecules and the degree of decomposition of the hydrocarbons were calculated first with respect to unit surface area, (see the Tables and Figs. 1–4) and then with respect to a hypothetical sodium ion present on the surface.

The re-calculation of the results was carried out by means of the formula:

\[ I = \frac{i}{a} \]

where \( i \) is the experimentally determined value referred to \( 1 \text{ m}^2 \);

\( a \) is the relative concentration of sodium ions in \( \mu \text{mole/m}^2 \).

We will first discuss the water index \( \beta \), which represents the number of molecules of water per one surface sodium ion (bearing in mind the

Fig. 5. The relation between \( \beta \) and \( a \) for the gels calcinated at 550 and 750°C.
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above discussed assumptions). Fig. 5 shows these indexes for both groups of gels as functions of the relative concentration of sodium ions.

It is seen from the graph that index $\beta$ rapidly decreases with increasing number of sodium ions, but when a certain value of $a$ is reached this decrease becomes very slight. The curves corresponding to both groups of gels are in general similar. As a rule small amounts of sodium ions correspond to large numbers of water molecules statistically calculated per one sodium ion. It should be remembered that the total amounts of water per $1\,\text{m}^2$ of the surface area are similar for all the gels, although the relationship between the amounts of water and the amounts of sodium ions is neither linear nor uniform (see Table 3).

We are also considering the quantity $7$, which we called the activity index, and which is proportional to the number of isobutane molecules that decompose on one hypothetical sodium centre. We will show this index for the cracking reaction only. The shape of the curve for the dehydrogenation reaction is the same. The relation between the index $7$ and the

\[ i-C_4H_{10} \rightarrow CH_4 + C_3H_6 \]

1. $\text{SiO}_2/550^\circ$  
2. $\text{SiO}_2/750^\circ$

![Graph](image)

**Fig. 6.** The relation between $7$ and $a$ for the gels calcinated at 550 and 750°C.
relative concentration of sodium ions for both groups of gels is shown in Fig. 6. As in the case of index $\beta$, the value of index $\gamma$ decreases with increasing concentration of sodium ions. This decrease is particularly rapid for gels calcinated at 550°C. The character of the curves is similar to that of curves shown in Fig. 5, and for this reason in Fig. 7 we show the relationship $\gamma = f(\beta)$.

It is clearly seen from Fig. 7 that at low concentrations of sodium ions large values of $\beta$ correspond to large values of $\gamma$.

Adsorption of isobutane and isobutylene can be represented analogously. We have introduced index $\alpha$, which shows the statistical number of adsorbed hydrocarbon molecules per one hypothetical surface sodium ion. The relation

\[ i-C_4H_{10} \rightarrow CH_4 + C_3H_6 \]

\[ \frac{i}{1500 \left[ \mu\text{mol Na}^+ \right]} \]

\[ \mu\text{mol H}_2O/\mu\text{mol Na}^+ \]

Fig. 7. The relation between $\gamma$ and $\beta$ for the gels calcinated at 550 and 750°C.
Fig. 8. The relation between $\alpha$ and $\beta$ for the gels calcinated at 550 and 750°C.

between index $\alpha$ and the relative concentration of sodium ions in the case of isobutane adsorption is shown in Fig. 8, which demonstrates the pronounced tendency of the value of index $\alpha$ to decrease with increasing concentration of sodium ions. This is observed in both groups of gels.

The relation between index $\alpha$ and index $\beta$ in the case of isobutane adsorption is shown in Fig. 9.

This graph shows that within the range of index $\beta$ values 1.5–2.62 the number of adsorbed isobutane molecules per one sodium centre is higher in the case of gels calcinated at 750°C (at constant value of index $\beta$). However, a definite value of index $\beta$ corresponds to various values of the concentration of sodium ions.

The same relationships for the case of isobutylene adsorption are shown in Figs. 10 and 11.

In the case $\alpha=f(\alpha)$ the curves of the curves is analogous to that obtained in the case of isobutane adsorption, and very similar values of index $\alpha$ correspond to the same values of sodium ions concentration.
Fig. 9. The relation between $\alpha$ and $\beta$ in the case of isobutane adsorption.

Fig. 10. The relation between $\alpha$ and $\alpha$ in the case of isobutylene adsorption.
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Fig. 11. The relation between \( \alpha \) and \( \beta \) in the case of isobutylene adsorption.

Fig. 11 shows the similarity of adsorption of isobutylene to that of isobutane, but at high values of \( \beta \) the values of \( \alpha \) are considerably higher for gels calcinated at 750°C.

Discussion

The above outlined representation of the results of the investigation facilitated their systematic interpretation by referring them to one hypothetical sodium ion. The Figures clearly show that all the quantities connected with water, degradation of hydrocarbons and their adsorption, referred to one hypothetical sodium ion, change in a very similar way with changing sodium ions concentration. The common feature is the decrease of each of these indexes with increasing sodium ions concentration. As a results indexes \( \alpha \) and \( \gamma \) increase with increasing values of index \( \beta \).

For both groups of gels we observe the characteristic rapid decrease of the values of \( \alpha \), \( \beta \) and \( \gamma \) at low sodium ions concentrations. When a certain value of this concentration is exceeded the decrease becomes very slow. The range of sodium concentration in which the decrease is very
rapid is 0.7–2.3 μmoles Na⁺/m². The corresponding values of index β are 5.00–1.40 and 2.62–0.70 for the gels calcinated at 550 and at 750°C respectively. Remembering that these are statistical values and that we do not know the origin of water molecules, we can represent graphically the limiting situations on the surface of a gel calcinated e.g. at 550°C (Fig. 12). Only a limited range of sodium ions concentration was investigated in the present work. It is to predict the behavior of the considered relationships for sodium ions lower than 0.7 μmole/m² and higher than 5 μmoles/m².

The structure of silica containing sodium ions

Our next problem was the determination of charges on atoms in three different fragments occurring in the gel. These fragments consist of three atoms and belong to the gel:

1. Si  Si

2. Si  H

3. Si  Na
We attempted the solution of this problem by means of quantum mechanical treatment of these simple systems. The calculations were carried out according to Hoffmann\textsuperscript{12,13}. The net charges on the atoms in the three systems are shown below.

\begin{align*}
1) & \text{Si} \quad \text{O} \quad \text{Si (H, Na)} \\
& +0.723 \quad -1.445 \\
2) & \text{Si} \quad \text{O} \quad \text{H} \\
& +0.732 \quad -1.230 \quad +0.489 \\
3) & \text{Si} \quad \text{O} \quad \text{Na} \\
& +0.693 \quad -1.726 \quad +1.033
\end{align*}

Although the calculations obtained by this method have been limited to three atoms, the results obtained by this method are in agreement with our interpretation of consequences resulting from the differences in electronegativity.

The large positive charge on the sodium atom can cause the coordination of water molecules in which this ion in the centre, \textit{i.e.} the sodium ion is the Lewis acid centre. It can activate the neighbouring water molecules according to the scheme:

\[
\text{Na}^+ + \text{OH}_2 \rightarrow \text{Na}^+\text{O}^-\text{H}_2 \quad \text{(scheme)}
\]

As a result fairly strong Brønsted acid centres can be formed. This interpretation has been expressed by other investigators\textsuperscript{8,9}.

The introduction of sodium ion causes an increase of the negative charge on the oxygen atom present in the framework, \textit{i.e.} an increase of the basic character of this atom. This is in agreement with the fact that in the aldol reaction the catalytic activity increases with increasing amount of sodium ions in the gel. We have observed this fact in the previous investigations carried out in our laboratory\textsuperscript{5-7}. The results of our studies are not in agreement with the postulate that addition of sodium ions to silica gel causes a decrease of the acidity of its surface. It appears that the addition of sodium ions causes an increase of the acidity accompanied by an increase of the basicity. As a result we obtain a surface containing a larger number of various active centres. An entirely different effect on the surface is observed in the case of poisoning of acidic catalysts with pyridine bases, and it appears that there is no similarity between the pyridine poisoning and the effect of sodium ions.
Proposed mechanism of the reaction

Before discussing the mechanism of the reaction taking place on the surface of the gel let us consider the structure of the second reagent, i.e. the hydrocarbon molecule. In the present work we were using the models of hydrocarbons proposed by HOFFMANN on the basis of quantum mechanical calculations carried out according to the Extended Huckel Theory. In Fig. 13 we show the net charges on the individual atoms (according to the Mullican population analysis) and the populations of overlap integrals. The ionization potentials calculated by this method are in a good agreement with the results of our investigation.

In general it appears that the C-H bond is polarized in the direction of the carbon atom, and as a result this atom is the bearer of the negative
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charge. This result of the calculations is in a qualitative agreement with the results obtained by other authors\textsuperscript{15,16}.

In the case of carbocation \textsuperscript{Hoffmann} differentiated two forms: a flat trigonal form called \textit{tri}, and a form in which the tetrahedral structure is preserved (called \textit{tetr}). The results of calculations indicate that the flat structure of carbocation is more stable.

Symbols $\textit{QH}_{(p)}$, $\textit{QH}_{(t)}$, $\textit{QH}_{(olef.)}$ and $\textit{QH}_{(par)}$ correspond to the charges on hydrogen atoms at primary, tertiary, olefinic and parafinic carbon atoms respectively.

According to the generally accepted theory the ionic decomposition of a hydrocarbon is initiated by the formation of a carbocation:

$$\text{A}^+ \rightarrow \text{R-CH}_3\text{R} \rightarrow \text{R-CH-R + AH}$$

The results of calculations show that in the case of isobutane the energy of the reaction:

$$i-\text{C}_4\text{H}_{10} \rightarrow i-\text{C}_4\text{H}_5^+ + \text{H}^-$$

is 15.475 eV, \textit{i.e.} it is a very high energetic barrier.

Taking into account the structure of the hydrocarbon and the fact that the surface of the gel contains as many basic centres as acidic ones we propose a mechanism of the reaction in which the initiating step is the formation of a carbanion:

$$i-\text{C}_2\text{H}_{10} \rightarrow i-\text{C}_2\text{H}_5 + \text{H}^+$$

According to our mechanism the reaction chain can be represented as follows:
The part of the acidic centra $A^{+4}$ can be played by sodium ion or by the Brønsted acid centre, and the part of basic centers by oxygen atoms present in the framework of the gel, in water molecules or in the hydroxylic groups.

In the step 1 the negatively charged peripheral carbon atom reacts with the acidic centre and gives the surface complex. As a result of the reaction in this complex the electronic cloud in the hydrocarbon can be distorted causing an increase of the positive charge on the hydrogen atom. This facilitates the reaction in step 2, in which the proton cleavage from the polarized fragment of the hydrocarbon can take place fairly readily. As a result of further reaction of the acidic centre—carbanion complexes with the new acidic centre (3) the C–C bond can be ruptured (step 4) and the surface carbocation can be formed. The reaction chain is terminated according to step 5.

The formation of the carbocation takes place very readily in the case of surface reaction between the acidic centre and an olefin: 

$$i-C_4H_8 + H^+ \rightarrow i-C_4H_9^+$$

This reaction should be exothermic ($\Delta E = -3.078$ eV). This corroborates the hypotheses proposed by other authors\textsuperscript{17,18}, according to which admixtures of olefins increase the rates of cracking of paraffins by facilitating the formation of carbocations. In our opinion the process may be more complex. The carbocation is the most stable in the flat form. It carries a considerable positive charge on the second $sp^3$ carbon atom (see Fig. 13). At the same time the peripheral carbon atoms retain their negative charges. In this situation the carbocation can be attached to the surface by various fairly strong interactions with the acidic and basic centres of the surface. This is shown in Fig. 14.

It is possible that such carbocation can play the part of a new catalytically active centre. It can react with saturated hydrocarbons, carbanions and olefins.
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Fig. 14. The situation of carbocation on the surface of a gel.

The mechanism proposed in this part of our work does not exclude other possible mechanisms. The fact that dehydrogenation takes place on the surfaces of the gels indicates the formation of free radicals or radical-ions.

The results of studies on the adsorption of isobutane and isobutylene indicated that the adsorbed amounts of these hydrocarbons are similar. Hence it appears that the energies of formation of the surface complexes involving these hydrocarbons are also similar. The results of calculations showed that the difference between the energy of formation of the carbocation from the olefin and that from the saturated hydrocarbon is very large (over 18 eV). Therefore it is improbable that the adsorption of isobutane could take place according to the cationic mechanism. On the other hand it was found that gasous decomposition products were absent in the isobutylene degradation products; in this case oils and tar were found on the surface of the gel. This fact is in agreement with the hypothesis postulating the catalytic effect of the centre formed from the carbocation and the surface.

Summing up our investigation we suggest that the characteristic features of the decomposition of hydrocarbons are:

1) polycentric character,
2) initiation of the reaction by the formation of the carbanion,
3) possibility of the formation of the carbocation from the olefin, followed by the formation of a new catalytically active centre,
4) the possibility of the occurrence of reactions involving free radicals and
radical-ions.
Our conclusions are based on the structures of hydrocarbons, the structures of fragments of the surface of the catalyst and the results of our experiments.

References