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INVESTIGATION OF SURFACE PHENOMENA ON SOLID CATALYSTS BY THERMOGRAVIMETRY

I. METHYL ALCOHOL AND CUMENE ON THE SURFACE OF ZEOLITES AND SILICA GELS TREATED WITH SODIUM HYDROXIDE

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Thermogravimetry was applied to the investigation of the phenomena of adsorption, chemisorption, desorption and surface reactions on solid catalysts. The measurements were carried out with 13 NaX and NaY type zeolites and with silica gels treated with sodium hydroxide, in the presence of cumene and methanol. On the basis of the quantitative results it is possible to give an interpretation of surface phenomena and to establish the existence of various active centres on the surface of the catalysts.

Thermogravimetric measurements have been made on solid catalysts for a number of years. "Fresh" catalysts, that have not taken part in any reaction, and catalysts after reactivation or reaction exhibit quite different characteristics as regards their weight and enthalpy changes. These differences are brought about on the whole by the loss of water and by the precipitation of polymerized, carbonized or irreversibly adsorbed substances on the surface.

In this work, thermogravimetry was selected as the method of studying sorption and chemical processes on the surfaces of catalysts during catalytic reactions. It was assumed necessary to measure simultaneously the weight and enthalpy changes of the system under investigation and to use conditions which could reveal individual phases and elemental processes. This was found possible after changes were made in the measurement techniques. This article presents the first results obtained for reactions of cumene or methanol on zeolites of NaX and NaY type, and on silica gels treated with sodium hydroxide.

Experimental

Apparatus

The measurements were carried out with a Paulik–Paulik–Erdey type "Derivatograph" Model 1969 manufactured by MOM, Budapest.

Catalysts

Pure NaX zeolites produced by Inowrocławskie Zakłady Sodowe (Soda Works at Inowroclaw) and NaY produced by Linde were used. The zeolites were initially stored in air over saturated ammonium chloride solution to attain the standard degree of hydration.

The second series of measurements was performed on silica gels treated with 0.1 or 0.2 mmole of Na^+(NaOH) per g of catalyst. The method of preparing the latter has been described previously [1].

Reagents

Analytical grade cumene was first purified from peroxides by column chromatography on silica gel and then by distillation in vacuum in a nitrogen atmosphere.

Analytical grade methanol was used without additional purification.

Thermogravimetric measurements

Before starting the measurements proper, preliminary investigations were carried out for each catalyst separately in order to establish its behaviour under the same conditions as for the later measurements in the presence of organic reagents.

The measurements were carried out under standard conditions: 500 mg samples of catalysts, in ceramic crucibles, were heated to 600° for 100 minutes in an oxidizing (air or oxygen) or neutral (nitrogen or argon) atmosphere.

The same catalyst as that in the sample investigated, but calcined previously at 1100°, was used as the reference substance. This ensured the smallest possible differences in the courses of the reference curves. At the same time there were no sorption effects.

For each sample the following quantities were recorded: total change in weight (TG), first derivative of the change in weight (DTG) and differential thermoanalytical curve (DTA) as a function of temperature (T).

The investigation of surface phenomena during the contact of the catalyst with the organic reagents was carried out in three variants, depending on the properties and activity of the catalyst and on the physical properties of the substances being tested.

a) Catalyst samples were heated preliminarily in the Derivatograph to the highest temperature of the range within which the measurements were subsequently carried out. The samples thus prepared were cooled to room temperature, and liquid reagents were poured onto them from a pipette in amounts corresponding to the loss of weight during the preliminary calcinations. The heating cycle was then repeated. Several peaks were normally found on the DTA and DTG curves; these corresponded to the surface phenomena under investigation.

b) The samples of starting catalysts or those preliminarily activated were heated in the Derivatograph in an atmosphere of the vapours of the appropriate reagents. The vaporization was performed in one of the following ways: 1. by blowing the carrier gas saturated with vapours of the chosen compounds onto the sample; or 2. by placing an additional crucible containing the substance investigated into the heating zone of the apparatus, the substance being evaporated during the measurements. The latter method was particularly suitable for investigating high-boiling substances of low vapour pressure.

c) The catalyst samples were first calcinated with reagents under conditions where sorption took place, but the catalytic reaction did not. The method gave particularly good results with low-activity catalysts on which the sorption processes occurred slowly. That is why in these instances no phenomena were found when variants a) and b) were used.

Results and discussion

A series of measurements was made of surface phenomena occurring on NaX and NaY type zeolites with methanol and cumene. In order to determine the behaviour of the zeolites themselves they were heated preliminarily to 500°. The calcinated samples were then placed over a saturated solution of ammonium chloride for 48 hours. During the repeated heating to 550° it was established that the courses of the DTA, DTG and TG curves were exactly the same as for the starting zeolite. This indicated that during heating to 550° the zeolites did not undergo any irreversible transformations, and also that the dehydration process was completely reversible (Fig. 1).

The freshly activated samples of zeolite catalysts, after being cooled to room temperature, were heated to 550° once more to find out whether or not any further

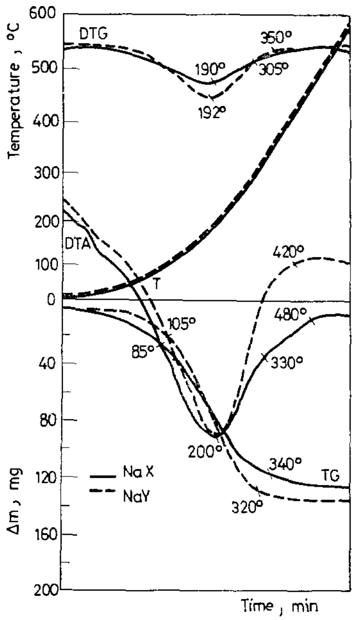

Fig. 1. Preliminary calcination of NaX and NaY zeolites

changes occurred during the repeated heating. These changes were quite negligible (Fig. 2). The resulting curves were then used as reference curves for further measurements.

The samples were heated for the third time, but no further changes were found (if hydration did not take place between the measurements). Within the range studied, the TG, DTA and DTG plots were straight lines.

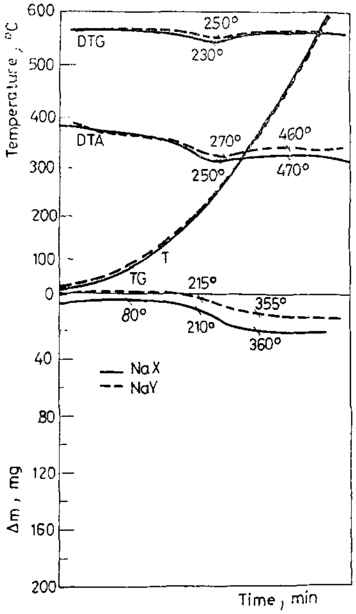

Fig. 2. The second calcination of NaX and NaY zeolites

When the organic reagents under study were poured onto samples of catalysts prepared in this way, it could be assumed that every thermal process observed on the DTA curves was connected with sorption processes and catalytic reactions, if any.

When methanol was poured onto the NaX type zeolite (according to variant a) and subsequently heated, two weight losses were observed as well as the endo- and exothermal effects connected with them (Fig. 3a).

In an oxygen atmosphere the endothermic effects were quite weak, but from about 175° there began a strong exothermal effect (with its maximum at about 250°). This effect was at first attributed to an oxidation reaction, but when an oxygen-free atmosphere was used the endothermal effects increased. At the same time the exothermic peak was shifted to about 220° (maximum about 300°). Hence, in air or oxygen there was a simultaneous oxidation reaction which hid the endothermal processes. The exothermic peaks in the case of a nitrogen atmosphere were attributed to a surface reaction. A considerable loss of weight occurred, demonstrating that the reaction products were volatile and underwent desorption.

In numerous parallel experiments [2] the presence of dimethylether and aliphatic hydrocarbons was established. An analysis of the DTA and TG curves (Fig. 3a) revealed a visible decrease in weight and enthalpy of the system at temperature below 60°. This corresponded to the evaporation of the methanol excess from the surface of the sample. The endothermic peak within the range 70 – 130° (maximum at 90°) probably corresponded to the desorption of methanol bound physically to the surface. It might be supposed that this was a process limited by diffusion, because within the range 35 – 100° the gradient of the weight loss was constant. Starting at 110° a rapid weight loss began, its maximum coinciding at 220° with the maximum of the endothermic peak. It is presumed that this was connected with the desorption of chemisorbed methanol.

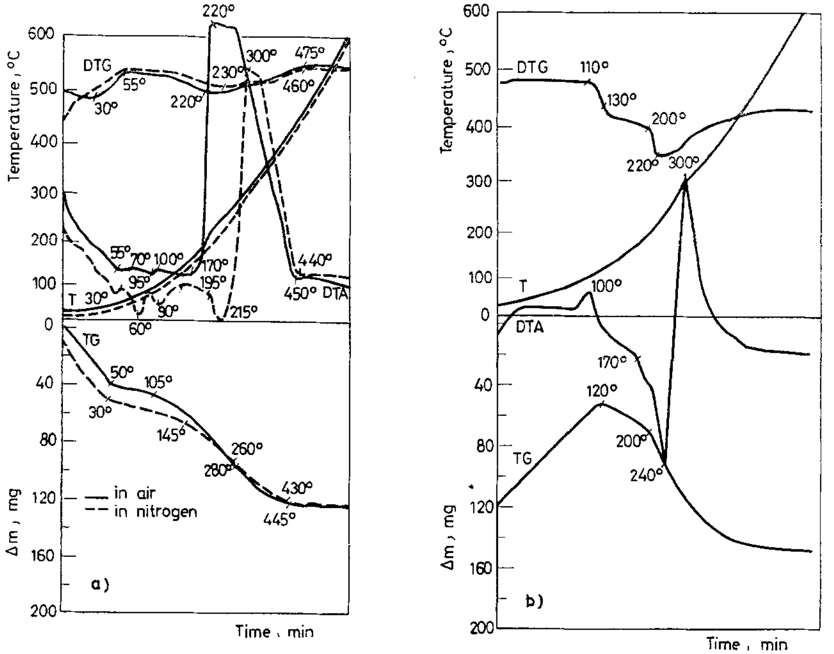

Fig. 3. Sorption of methanol on the surface of NaX zeolite. a) Zeolite over which liquid methanol has been poured (variant a); b) zeolite in methanol vapour (variant b)

When variant b) was applied the picture was quite different (Fig. 3b).

At first, while heating up to 100° a constant increase of weight could be observed, due to adsorption. In the DTA curve there was an initial exothermic effect up to 40°, then plateau up to 85°, and again an exothermic effect up to 100°. This suggests that two kinds of sorption occurred – a physical one and chemisorption. In addition, there was a certain intermediate state. Above 120° and up to about 200° the weight decreased, at first slowly, but later more rapidly and at the same time the endothermic effect was observed.

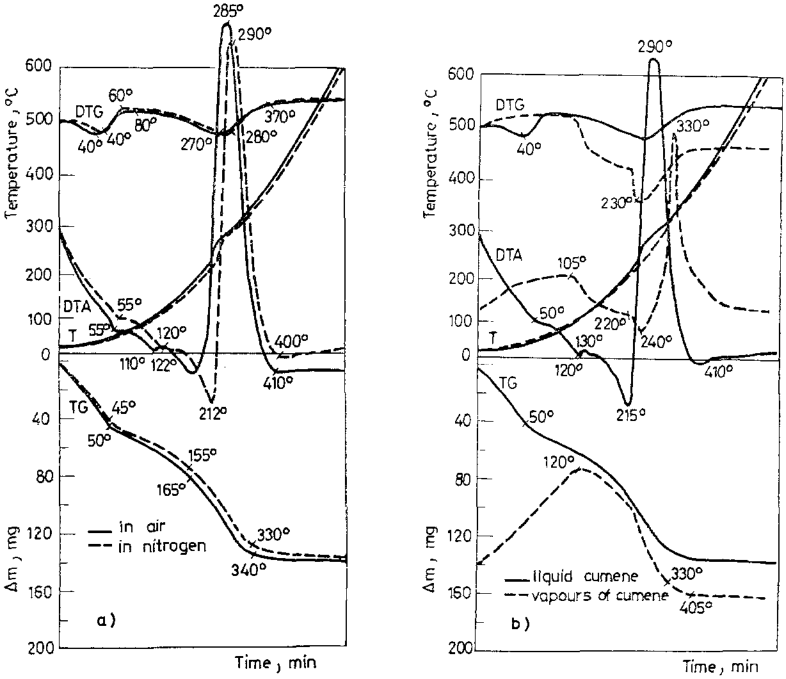

Fig. 4. Sorption of methanol on the surface of NaY zeolite. a) Zeolite with variant a; b) zeolite with variant b

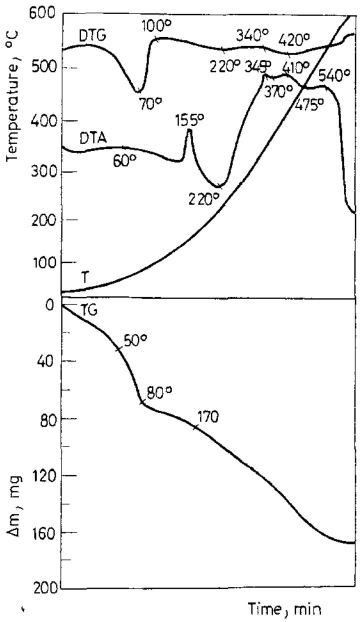

Fig. 5. Sorption of liquid cumene on the surface of NaX zeolite (variant a)

Within the range 240–300° there was a sudden shift from the endothermic to the exothermic effect. It is presumed that this was connected with the initial desorption and the endothermic dehydration reaction of methanol. In the latter stage it was connected with the exothermic reaction of the decomposed systems. When the temperature was further increased, the products were desorbed.

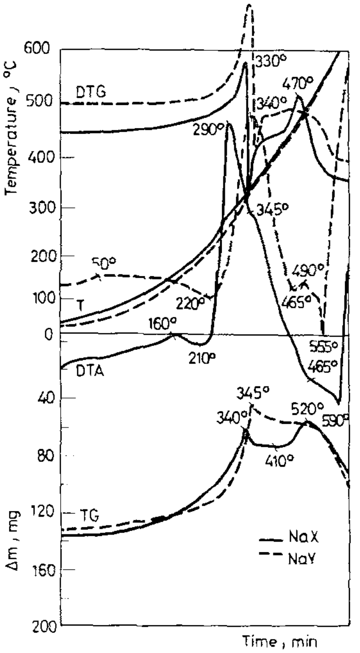

Fig. 6. Sorption of cumene vapour on the surface of NaX and NaY zeolites (variant b)

In case of the NaY zeolite with methanol poured onto it, the effects were analogous. The effect of air was much weaker here, and the exothermic peaks were almost identical in the case of air and nitrogen; in nitrogen, however, the endothermic effect was more marked at 210°, probably due to oxidation in air. The range of desorption at about 100° was less marked (Fig. 4a).

The results of measurements by variant b) on NaY with methanol are shown in Fig. 4b, and can be seen to agree well with the variant a) results (except for the initial period of physical sorption or desorption). On the other hand, marked differences from the NaY measurements are seen. In the latter a much larger endothermic effect is observed within the range 180–260°.

Parallel measurements on cumene were also carried out. They showed that a number of endo- and exothermic processes took place. The results, presented in Fig. 5, were obtained by spreading cumene onto dehydrated zeolite catalyst of the NaY type (variant a).

The plots are almost identical for a neutral gas atmosphere and for air. When the temperature is raised a rapid decrease in weight is observed.

Within the range 140–200° (maximum at 160°) there developed an inhibition of the weight decrease, but there was a small exothermic peak, which can be attributed to the adsorption of cumene on the zeolite surface. Within the range 240–535° a number of partly overlapping effects occurred, with a rapid decrease of weight. These must be surface effects and desorption of cumene and its reaction products. It has been established in catalytic investigations that from 350° upwards catalytic cracking occurs on the same catalysts. Among the products are benzene, propylene, ethylbenzene, and styrene.

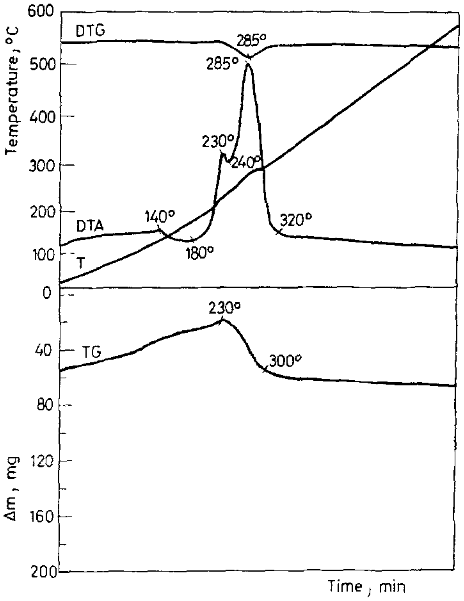

Fig. 7. Sorption of cumene vapour on the surface of NaY zeolite. Period of heating 600 minutes

It has not yet proved possible to separate the individual phases of the complicated process by means of the thermogravimetric method. Since the overall process is exothermal, it is clear that it is not pure cracking, but other strongly exothermal reactions taking place simultaneously (the details will be published elsewhere).

The possibility had to be considered that by dropping cumene onto the catalyst there may be an excess of the reagent which could partly mask the surface phenomena. Consequently, a series of measurements was carried out on the same catalysts, but by means of vaporizing the hydrocarbon during the heating process (method b).

In this case the picture obtained is simpler and complementary at the same time (Fig. 6). Whereas in the dropping method there is a rapid decrease in weight within the range from room temperature to 120°, the decrease corresponding to the endothermic effect, in the vaporizing method a weak exothermic effect and a weight increase can be observed. The latter indicates sorption of a physical or transition type. The exothermal peak at about 150° together with the weight increase indicates the maximum of the sorption of this type. At about 260° there are a sudden weight increase and an exothermal peak. Both these phenomena are presumed to be connected with chemisorption. At higher temperatures the surface reaction of the chemisorbed substrate can be observed, with a simultaneous, rapid weight decrease. The shapes of the curves depend largely on the conditions of the analysis.

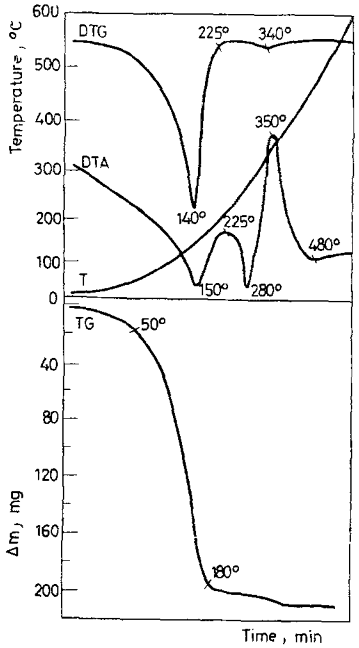

Fig. 8. Desorption of cumene from the surface of silica gel containing 0.2 millimole of Na^+ per g (variant c)

Figure 7 represents the same course as in Fig. 6, but using a far smaller heating rate, 1 degree per minute, compared with the previous 6 degrees per minute.

The plots are analogous, but a more distinct separation of the individual phenomena is observed, as well as a lowering of the temperatures at which they occur. The values obtained seem to be more realistic and more precise.

An analysis of NaX dehydration under the same conditions showed that the decrease in weight (water) was constant up to 400° and no thermal effects were observed. This proves that heat was probably dispersed and that the sensitivity of the apparatus is lower under these conditions of measurements.

This is only one of the parameters which influence the results. The problems concerning the position of the thermocouples, the kind of crucibles, etc. have been presented in detail, for example, in reference [3].

In the case of low-activity catalysts on whose surface sorption phenomena occurred relatively slowly, both methods presented above failed and did not give any idea of what took place on the surface. In these cases the method of heating the catalyst samples with the reagents was used (variant c).

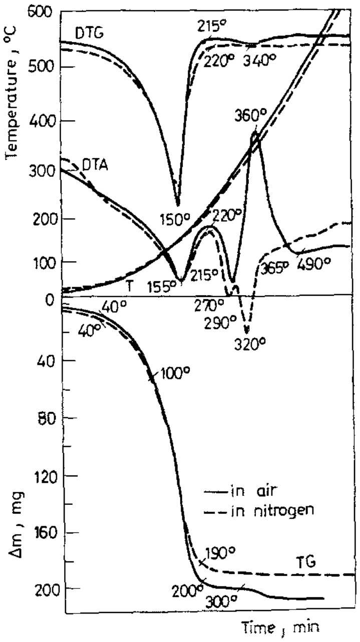

Fig. 9. Desorption of cumene from the surface of silica gel containing 0.2 millimole of Na^+ per g in oxidizing and oxygen-free atmospheres

Results have been reported for the reaction of cumene on silicate with sodium hydroxide [1].

With the methods of dropping-in, dropping-on and vaporization, no effects could be observed.

On the other hand, after heating with cumene for 24 hours at about 350° and distilling away the excess of cumene in vacuum in the hot, the results presented in Figs 8 and 9 were obtained. On heating to about 200°, a rapid weight decrease and an endothermal peak were observed (maximum at about 150°). These are attributed to the desorption of physically adsorbed cumene.

At about 200° the process was stopped and one or two endothermic peaks occurred caused by very slight changes. These phenomena are ascribed to the desorption of cumene adsorbed chemically on various centres of the surface.

At about 500° there was a slight break in the curve indicating that the most strongly bound cumene underwent cracking, this having been determined by a chemical method [2].

On the other hand, there was an interesting finding that in samples prepared by method c), slight, reproducible quantities of adsorbed cumene were obtained. In the case of gels containing 0.2 mmole of Na^+ per g of gel, the quantity amounted to 3 mg of cumene per g of catalyst. In contrast, in measurements performed according to variants a) or b), the quantities were variable, depending on a number of factors, primarily on the amount of cumene.

In this case it was also observed that the conditions of analysis had an observable effect on the results. The more rapid the heating, the more dispersed and inaccurate were the results.

Conclusions

The investigations presented qualitatively show the possibility of studying sorption and surface phenomena on catalysts under conditions similar to those of a chemical reaction. The notable advantage is that changes in thermal effects and changes in weight are observed simultaneously. The method permits forecasts of whether a given catalyst has any chance of being active, without making time-consuming measurements of catalytic activity. It is also possible to establish whether or not various kinds of active centres occur on its surface, this being done on the basis of various conditions of desorption. The higher the desorption temperature of the chemisorbed compound, the stronger is the bonding between the surface and the compound studied.

The results of measurements may be a valuable supplement of information obtained by means of such methods as Temperature Programmed Desorption or Frontal Gas Chromatography.

A great deal of information could be obtained from the quantitative determination of the heats of adsorption and reaction from the areas of the endo- and exothermal peaks in the DTA curves. However, this involves numerous difficulties and the necessity of making parallel measurements by various methods.

Attempts at this are now being made and will be the subject of the next publication.

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References

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RÉSUMÉ — On a appliqué la méthode thermogravimétrique à l'étude des phénomènes d'adsorption, de chemisorption et de désorption ainsi qu'aux réactions de surface sur des catalyseurs solides. Les mesures ont été effectuées sur zéolites de type 13 NaX et NaY et sur des silicagels traités par la soude en présence de cumène et de méthanol. Des résultats quantitatifs permettent de donner une interprétation des phénomènes de surface et d'établir l'existence de divers centres actifs à la surface des catalyseurs.

ZUSAMMENFASSUNG — Adsorptions-, Chemisorptions- und Desorptionserscheinungen, sowie Oberflächenreaktionen an festen Katalysatoren wurden thermogravimetrisch untersucht. Die Messungen wurden an Zeoliten der Typen 13 NaX und NaY und an mit Natriumhydroxid behandelten Silikagelen in Gegenwart von Cumol und Methanol durchgeführt. Aufgrund der quantitativen Ergebnisse war es möglich, die Oberflächenerscheinungen zu deuten und das Vorhandensein von verschiedenen aktiven Zentren an der Katalysatoroberfläche nachzuweisen.

Резюме — Описано использование термогравиметрического метода для исследования адсорбции, хемосорбции, десорбции и реакций, происходящих на поверхности твердых катализаторов. Этот метод, хотя и имеет некоторые недостатки, но обладает тем преимуществом, что дает возможность определять одновременно изменения массы и тепловых эффектов, происходящие в исследованной системе. Измерения проведены с цеолитами типа 13 NaX и NaY и силикагелем, обработанным гидроокисью натрия в присутствии кумена и метанола. На основании полученных количественных результатов возможна интерпретация поверхностных явлений и установление наличия различных активных центров на поверхности катализатора.