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Intermediates and mechanisms of heterogeneous catalytic reactions. The simplest reactions of hydrocarbons, alcohols, and acids

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Abstract. The structures of the intermediate surface compounds in heterogeneous-catalytic reactions of hydrocarbons, alcohols, and acids, established by spectroscopic (mainly IR spectroscopic) measurements, are examined. The evidence obtained concerning the role of particular structures in catalysis is differentiated: from spectroscopic data obtained before or after catalysis; from spectroscopic data obtained in situ but without kinetic measurements; from spectroscopic data obtained in situ by comparing the kinetics of the heterogeneous-catalytic reactions with the kinetics of the changes in the concentrations of the surface compounds. The mechanisms of heterogeneous catalytic reactions obtained on the basis of the available information about the surface complexes are presented. The bibliography includes 89 references.

I. Introduction

In order to understand the mechanism of heterogeneous catalysis, it is necessary to know the sequence of the elementary stages through which the catalytic reaction proceeds. For this purpose, information on the structures and reactivities of the intermediates is first needed.

In the general case, a large set of complexes may exist on the catalyst surface. For example, in the reaction $A \rightleftharpoons B$, occurring on a catalyst K in accordance with the mechanism

$$\begin{array}{l} \quad\quad\quad\

the catalytic reaction. Therefore they cannot be regarded as proven. Furthermore, the majority of investigators confined themselves merely to stating that a particular compound is formed (it was later referred to as the intermediate) under the catalytic conditions without studying the rate of its formation and consumption.

Nevertheless, it is precisely by measuring the rates of formation and consumption of the different compounds in the reaction medium and by comparing them with the rates of the catalytic reaction proper that one can demonstrate whether a particular compound, found under the catalytic conditions, is an intermediate. In heterogeneous catalysis most of the stages of the overall processes occur on the surface. The concentration of the reactive species on the surface, calculated per unit volume, is much lower than in homogeneous reactions. Therefore sensitive spectroscopic methods must be resorted to in order to detect the intermediates on the surface.

The high resolving power of spectroscopic methods as regards time is also very important. Under stationary conditions in catalytic reactions, direct comparison of the concentration of complexes of any kind with the rate of the overall reaction cannot provide a direct answer to the question whether such complexes are intermediate or 'dead-end'. This can be done by carrying out the reaction under non-stationary conditions using methods involving the pulsed introduction of the reactants, a sharp variation of the reactant concentrations (the 'response method'), a jump in temperature, irradiation, etc. The turnover number of a catalytic reaction (i.e. the number of reaction steps occurring on a single active catalyst centre per second) is known[2] to be as a rule $10^{-2}-10^{2}$ s^{-1}†. The characteristic times of a catalytic reaction are correspondingly in the range from 10^{-2} to 10^{2} s. Evidently the resolving power of the spectroscopic methods employed in situ as regards time must not be less than this. However, in the majority of cases spectroscopic measurements are performed with interruption of the catalytic reaction, the interruption time greatly exceeding the characteristic time of the catalytic reaction.

This review presents data (mainly from communications published after 1980) concerning the intermediates in catalysis obtained by spectroscopic methods, mainly by IR spectroscopy. UV spectroscopy, spectroscopy in the visible region, X-ray photoelectron spectroscopy, low-energy electron scattering spectroscopy, NMR, and EPR have been used in individual investigations. Unfortunately, in the vast majority of studies, the above criterion, based on the correspondence between the kinetic characteristics of the concentration variation of a possible intermediate and the kinetics of the catalytic reaction itself, was not considered. Therefore the conclusions reached in them concerning the structure of the intermediates and the sequence of their reactions must be regarded as tentative and not proven.

Apart from spectroscopic methods, other procedures also exist for the investigation of the catalytic reaction mechanism: temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR), isotopic methods (exchange of isotopes under catalytic conditions, kinetic isotopic effect), kinetic transient response methods, the so called 'time analysis of the products' (TAP-reactor), and others. Without dwelling especially on the description of these methods and the results obtained with their assistance, we shall use these data as well in a number of cases.

The present review presents data concerning intermediates in the simplest heterogeneous-catalytic polymerisation and oligomerisation reactions, the metathesis of hydrocarbons, and the decomposition of alcohols and acids. The single starting material in these reactions is converted into one or several reaction products. More complex oxidation–reduction reactions will be considered in future reviews.

† These figures refer to reactions occurring under flow or static conditions at pressures not too remote from atmospheric. At ultralow and high pressures, smaller and larger turnover numbers are obtained respectively.

We shall not deal with the spectroscopic proof of the existence of a particular intermediate and so the numerical vibration frequencies will not therefore be quoted as a rule.

II. Certain problems concerning the methods for the study of processes on the surfaces of solids

IR spectroscopy in the frequency range 400–5000 cm^{-1} is usually employed to investigate the nature of the complexes arising on the surfaces of the catalysts. This is associated not only with the fact that molecular IR spectroscopy yields information directly concerning the structure of surface compounds but also with the fact that, in contrast to the majority of other physical methods, it permits a wide scale variation of the temperature and pressure in the spectrometer cell.

The amount of information derivable from IR spectroscopy may actually increase in the study of complexes on the surfaces of solids (compared with molecules in the gas phase). The point is that a fairly large number of vibrations are inactive in the IR spectrum and are manifested only in the Raman spectrum. When molecules interact with the surface, their symmetry is reduced, so that virtually all the vibrations become active in the IR spectrum. Adsorbed nitrogen, hydrogen, oxygen, etc. molecules may be successfully detected on the surfaces of solids by IR spectroscopy.

Transmission spectroscopy, reflectance spectroscopy, emission spectroscopy, and diffuse reflectance spectroscopy are used nowadays to a greater or lesser extent in the study of processes on the surface.

Massive metals are one of the commonest types of catalyst. The surface processes on such objects cannot be investigated by the traditional transmission spectroscopic methods. Emission spectroscopy is promising in this instance.

The measurement of the transmission spectra of surface compounds is frequently hindered by the intrinsic absorption of the catalyst. Difficulties of this kind can be overcome by applying the diffuse reflectance method in the IR region of the spectrum.We shall consider briefly the principal features of each of the methods listed above.

1. Infrared transmission spectroscopy

The principles of this method have been described in detail in numerous monographs (see, for example, Refs 3–5). Spectrophotometers record the transmittance T:

$$T = \frac{I}{I_0} = \exp(-kl), \tag{1}$$

where I and I_0 are the intensities of the transmitted and incident light, k is the linear absorption coefficient, and l the thickness of the absorbing layer. According to the Beer–Lambert–Bouguer law, the optical density is given by

$$D = \ln\frac{1}{T} = \ln\frac{I_0}{I} = \varepsilon c l, \tag{2}$$

where ε is the extinction coefficient and c the concentration of the absorbing layer. Eqn (2) constitutes the basis of quantitative analysis by means of spectroscopy.

The sensitivity of the method is determined both by the characteristics of the radiation detector and by the absorption coefficient of the medium. It is possible to estimate the number of absorbing molecules necessary to obtain sufficiently intense absorption bands on tranditional instruments. For example, a reliable determination requires $\sim 10^{17}$ CO molecules in the sample or 10^{12} molecules cm^{-2} for a specific surface of the specimen of 100 $m^2 g^{-1}$. Since other vibrations (C–H, C–C, etc.) are characterised by lower (by two–three orders of magnitude) absorption coefficients, the sensitivity with respect to them is significantly lower.

The appearance of the Fourier technique improved somewhat the situation in this field. Calculations have shown[5] that the use of

an interferometer instead of a dispersing element should result in an approximately 100-fold gain in sensitivity. In practice, however, the use of an interferometer with Fourier transformation yields a gain in sensitivity by a factor of only 10. The intrinsic noise of the detector precludes the attainment of the calculated gain in sensitivity.

A significant obstacle to the application of transmission spectroscopy under the conditions of a catalytic reaction is the intrinsic emission by the specimen. As a result of this, instead of the true absorption spectrum, one records a resultant spectrum due to the superposition of absorption and emission spectra. Emission can be excluded by modulating the emission in front of the specimen.

It is noteworthy that Fourier spectrometers permit measurements at high temperatures. Distortions of the spectra are possible only due to the fact that the emission by the heated specimen can alter the glow bar temperature. A very important advantage of Fourier spectroscopy is the possibility of working with low radiant energies. This means that the surface compounds can be investigated even on catalysts with a high intrinsic absorption.

Since spectroscopic measurements are performed under stationary and nonstationary conditions, the question arises of the characteristic times of the processes which can be investigated by this method. Processes with characteristic times $>1\ s^{-1}$, which constitutes the upper limit to the range of characteristic times of catalytic reactions, are accessible to study by spectroscopic methods.

The same time constant applies also to Fourier spectroscopy (the time of a single scan is ~ 1 s). In studying specimens with a high intrinsic absorption, a large number of scans is necessary in order to obtain a high quality spectrum of the surface compounds (the signal to noise ratio increases in proportion to the square root of the number of scans). In this case, the time of the measurement of one spectrum may reach 1 h. Clearly, such systems can be investigated only under stationary conditions. A Fourier spectrometer capable of performing 25 scans per second has been described recently.[6] With the aid of such instruments, it is possible to investigate reactions with characteristic times significantly less than 1 s.

It is noteworthy that the application of transmission spectroscopy has made it possible hitherto to accumulate an enormous amount of information about the structures and properties of surface compounds. However, the question of their role in the catalytic reaction remains open.

2. Infrared diffuse reflectance spectroscopy

In experiments using infrared transmission spectroscopy, it is essential to employ sufficiently thin (from the standpoint of transmission) discs of the test substance. Very often success depends precisely on the possibility of preparing such a disc (the formation of discs is necessary to suppress scattering). Furthermore, in the spectral range above 2000 cm^{-1} the transmittance is fairly low owing to the fairly considerable intrinsic absorption by the catalyst. Finally, as a result of the large optical path length in the cell, the absorption bands of the molecules in the gas phase and on the surface compounds are superimposed.

Diffuse reflectance spectroscopy is free from the above disadvantages.[7,8] Its essential feature is that the detector detects the light scattered by a powdered specimen.

The Kubelka–Munk formula,[7] which relates the fraction of the light reflected by an infinitely thick medium to the absorption and scattering coefficients, is used for the quantitative description of diffuse reflectance spectra.

$$\frac{K}{S}=\frac{(1-R_\infty)^2}{2R_\infty}, \tag{3}$$

where K is the absorption coefficient of the specimen, S its scattering coefficient, and R_∞ the fraction of the light reflected by the infinitely thick medium.

For the adsorption of molecules on an infinitely thick specimen, the Kubelka–Munk formula assumes the form

$$\frac{K+\varepsilon c}{S}=\frac{(1-R)^2}{2R}, \tag{4}$$

where ε is the extinction coefficient of the adsorbed substance, c its concentration, and R the fraction of the light reflected by the infinitely thick specimen with the adsorbed layer. The quantities R and R_∞ are determined from the spectrum.

The line intensity is found from the formula

$$I=\frac{R_\infty-R}{R_\infty}. \tag{5}$$

After obtaining the difference between Eqns (4) and (3) and taking into account Eqn (5), we obtain the relation between the intensity of the band due to the adsorbed substance and its concentration (the Kubelka–Munk function):

$$F(R)=I\left(\frac{1}{R-R_\infty}\right)=\frac{2\varepsilon c}{S}. \tag{6}$$

The optical path length for the light in the material of the catalyst can be estimated from this formula.

It has been shown[8] that the optical path length is 2–3 mm when this method is used, which is much greater than in the transmission method. The greater path traversed by light in the specimen is apparently in fact one of the causes of the high sensitivity of diffuse reflectance spectroscopy. Theoretical estimates indicate that, when effectively scattering specimens are investigated, diffuse reflectance spectroscopy is more sensitive (by more than an order of magnitude) than the traditional transmission spectroscopy.

Under real conditions, the sensitivity relation is less favourable owing to the difference between the scattering capacities of the powders (scattering spectra) and the discs (transmission spectra). Furthermore, the attachments used to measure the diffuse reflectance spectra are nonideal and are incapable of collecting all the light scattered by the specimen. However, despite this, even when only a few per cent of the scattered light reaches the detector, in the analysis of effectively scattering substances ($R_\infty \sim 1$) diffuse reflectance spectroscopy has an advantage, as regards sensitivity, over transmission spectroscopy.

It follows from the Kubelka–Munk function (3) that quantitative measurements require the determination of the scattering coefficient. However, it has been shown[8] that in the case of low-intensity bands the concentration of the absorbing substance and the intensity of the corresponding band in the spectrum are linked by a relation analogous to the Beer–Lambert–Bouguer law:

$$-\varepsilon c l_{ef}=\ln\left(\frac{R}{R_\infty}\right), \tag{7}$$

where l_{ef} is the optical path length for the light in the specimen. Eqn (7) is valid when

$$\frac{R_\infty-R}{R_\infty}\ll\frac{2(1-R_\infty)}{(R_\infty)^{1/2}}.$$

In the analysis of intense bands for the determination of concentration characteristics, it is essential to know the scattering coefficient. The procedures for the independent determination of S have been examined.[8]

The characteristic times of the processes which may be investigated with the aid of diffuse reflectance spectroscopy are the same as in measurements involving the use of transmission spectroscopy.

3. Emission spectroscopy

A large proportion of the early studies on energy emission processes were devoted to blackbody emission. The frequency distribution of the energy emitted on heating a blackbody depends on temperature but is independent of the material of the body itself, i.e. information about the substance cannot be obtained from the emission spectrum of a blackbody. However, real materials are not blackbodies. For example, the emission spectrum of a gas at a low pressure consists of a set of lines which carry information about the nature of the gas.

The expression for the distribution of the radiant energy on a non-blackbody can be obtained with the aid of the Kirchhoff–Planck laws. The emittance of a grey medium (ε_ν) at a temperature T and a frequency ν is defined as the ratio of the radiant intensities of the emission by the grey medium [$I(\nu, T)$] and blackbody [$I_B(\nu, T)$]:[9,10]

$$\varepsilon_\nu = \frac{I(\nu, T)}{I_B(\nu, T)}. \quad (8)$$

The Kirchhoff law establishes the fact that $\varepsilon_\nu = a_\nu$, where a_ν is the absorptance of the substance.

The simplest case is that of emission by a gas whose molecules are distributed uniformly in a certain volume. We shall calculate the emittance from a thin layer of molecules located at a distance d from the boundary of the emitting volume. If $I_0(\nu, T)$ is the emittance from this layer, then the emittance which has reached the boundary is $I(\nu, T) = I_0 \exp[-K(\nu, T)d]$, where $K(\nu, T)$ is the absorption coefficient of the medium. The fraction of the energy transmitted through the layer d is equal to the ratio I/I_0, so that $a = 1 - I/I_0$.

Using the Kirchhoff law and eliminating I_0, we obtain the expression

$$I(\nu, T, d) = I_B(\nu, T)\{1 - \exp[-K(\nu, T)d]\}, \quad (9)$$

which describes the emittance from a layer of gas parallel to the boundary and at a distance d from the latter. There is a possibility that I may depend on the pressure because the quantity $K(\nu, T)$ may change owing to an intermolecular interaction.

Calculation of the emittance from liquids or solids constitutes a more difficult task, because it is essential to take into account the reflection of the radiation emitted in the direction towards the boundary of the substance.

Catalytic systems partly transmit IR radiation. According to the theory of emission by semitransparent substances,[9,10] the sum of the emittance (ε_ν), reflectance (r), and transmittance (T) is approximately unity:

$$\varepsilon_\nu + r + T \approx 1. \quad (10)$$

Eqn (10), which can be derived thermodynamically, is at present the principal expression for quantitative measurements. Emission spectroscopy is much more rarely used than transmission and diffuse reflectance spectroscopy. The reason for this is the difficulty of measuring low-intensity emittances with the aid of dispersion spectrometers. The possibilities of emission spectroscopy have increased significantly only recently following the development of the Fourier technique.

If the reflectance of the specimen is low, then, according to Eqn (10), the following expression is sufficiently accurate:

$$\varepsilon_\nu(\nu) = 1 - T(\nu).$$

The absorptance of the specimen $a(\nu)$ is related to the concentration of the absorbing substance by the Beer–Lambert law:

$$a(\nu) = -\lg T(\nu) = Kcl. \quad (11)$$

In this case, the emittance from the specimen may be related to the concentration of the absorbing substance as follows:

$$c = \frac{\lg[1 - \varepsilon_\nu(\nu)]}{Kl}. \quad (12)$$

This relation holds satisfactorily for gases and semitransparent bodies.[10]

Analogous expressions exist for the calculation of emittance when the emitting substance is on the surface of a metal.[11] Certain characteristics of various IR spectroscopic methods are presented in Table 1. For a comparative assessment of the sensitivities of the dispersion and Fourier spectroscopic methods, we may recall that a reliable determination of CO requires the presence in the sample of 10^{17} and 10^{16} molecules of this substance respectively.

Table 1. Comparative characteristics of the IR methods for the study of catalytic processes.

Characteristics	Spectral range/cm^{-1}	Time resolution/s^{-1}	Equation for quantitative treatment
Transmittance	400–5000	> 1	$D = \varepsilon cl$
Diffuse reflectance	1800–5000	> 1	$F = \frac{2\varepsilon}{S}c$
Emittance	400–2500	> 1	$F = \frac{2\varepsilon}{S}c$ (for highly reflecting objects) $D = \varepsilon cl$ (for weakly reflecting objects)

4. Raman spectroscopy

The radiation scattered by the specimen is investigated in Raman spectroscopy. Suppose that the specimen is irradiated by light at a frequency ν_0. Then most of it undergoes Rayleigh scattering in which the frequency of the scattered light is also ν_0. However, the frequency of a small proportion of the scattered light changes and assumes a new value ν such that the quantity $h(\nu_0 - \nu)$ is exactly equal to the energy of the vibrational or rotational transition. The frequency shifts $\Delta\nu$ give rise to the vibrational–rotational spectra of the specimen. However, the selection rules in Raman spectroscopy differ from those in IR spectroscopy. The main requirement is that the polarisability of the molecule should change during the vibration. Vibrations active in the IR spectrum may be active or inactive in the Raman spectrum and conversely. IR and Raman spectra supplement each other, so that their joint employment makes it possible to obtain virtually complete information about the objects investigated.

The Raman spectra of many molecules adsorbed on oxide systems have now been described. The application of this method at elevated temperatures encounters a series of technical difficulties associated with the emission of light from the heated walls. This is apparently the reason why Raman spectroscopy has so far been used in catalysis to investigate the state of the catalyst itself but not of the adsorbed phase.[12] For example, the reduction of deposited molybdenum oxide catalysts has been investigated from the variation of the intensity of the Mo=O absorption band. Studies[13,14] in which it was claimed that adsorbed CH_3 and CH_2 groups are formed on oxide catalysts during high-temperature oxidative condensation of methane are an exception. This observation is apparently an artefact and is associated with the intense heating and decomposition of the organic molecules in the light beam.

An appreciable increase in the sensitivity of Raman spectroscopy has been achieved with the use of laser sources. Hence the name of the method—laser Raman spectroscopy. Its sensitivity reaches 10^{18} molecules in the specimen, which is as a rule much greater than the number of molecules in the monolayer. A further increase in sensitivity was achieved by the discovery of the SERS (surface-enhanced Raman spectroscopy) or GRS

(giant Raman spectroscopy) effect.[15] Following adsorption on Ag, Au, Cu, and certain other metals, the sensitivity (scattering cross-section) increases by a factor of 10^4-10^6.

5. X-Ray photoelectron spectroscopy, Auger spectroscopy, and electron energy loss spectroscopy

X-Ray photoelectron spectroscopy (XPES) and Auger spectroscopy make it possible, in principle, to investigate the composition of adsorbed compounds and, when the spectral resolution is satisfactory, their structures as well. Electron energy loss spectroscopy (EELS) yields information about the vibrational levels of the absorbed molecule, i.e. in principle the same information as IR spectroscopy. Its advantages are high sensitivity (0.01–0.1 of a monolayer even on smooth surfaces) and the possibility of using it in the low-frequency range of vibrations (10–800 cm^{-1}). At the same time, the EELS method is characterised by a much poorer resolution (at best 25 cm^{-1}, usually 50 cm^{-1}) than IR spectroscopy (1–2 cm^{-1}).

An evident disadvantage of all the varieties of electronic spectroscopy is the impossibility of using them at a high pressure, which usually occurs in catalytic processes. The maximum possible pressure is 10^{-3} Pa (10^{-5} torr). However, even at a pressure below 10^{-3} Pa, the mechanism of the catalytic reaction must be studied on surfaces cleaned in an ultrahigh vacuum. Here one has to bear in mind that the catalytic reaction under the usual conditions, i.e. at higher pressures, can proceed via a different mechanism. The problem of the pressure gap is widely discussed in the literature on catalysis. There are cases where the kinetic data obtained at a low pressure can be referred to high pressures, but the converse cases also occur.

6. Spectroscopy in the visible and ultraviolet regions

The spectroscopy in the visible and ultraviolet regions (UV-VIS) is distinguished by a fairly high sensitivity. In particular, the intensity of the absorption for allowed one-electron $d-d$ transitions is characterised by a molar absorption coefficient of the order of $\sim 10^4$. For this absorption coefficient, it is possible to detect $\sim 10^{16}$ molecules of the test substance in a 1 cm^3 sample. The absorption coefficient for $d-d$ transitions in complexes with a high symmetry is significantly lower and hence the sensitivity is appreciably worse.

The advantage of UV-VIS spectroscopy over IR spectroscopy is the simplicity of the design of the cell-reactors: there is no need to use 'windows' made from special materials and quartz cells can be employed. This method is widely used to determine the electronic state and the coordination of transition metal ions forming part of the composition of the catalysts. It is fairly rarely used to investigate the catalytic reaction intermediates and surface compounds. Organic compounds with C=C, C≡C, C=O, etc. multiple bonds, specially with conjugated bonds, and aromatic compounds are mainly investigated. The electronic transitions in compounds with C–C, C–H, and C–O single bonds occur in the far UV region and are therefore difficult to observe under the conditions of the catalytic reaction. The studies are usually carried out at room temperature, since technical difficulties, associated with light emission from the heated walls, arise at an elevated temperature.

7. Electron paramagnetic resonance

Electron paramagnetic resonance has by a high sensitivity; the presence in the specimen of 10^{11} spins is sufficient for the measurement.

The EPR method is used widely to investigate transition metal ions and other radical centres in catalysts. Its application to the investigation of adsorbed compounds in situ is limited, firstly, by the fact that the lifetime of the free radicals on the surface is as a rule short under catalytic conditions (high temperatures and pressures) and because of this the sensitivity of the method proves to be insufficient. Secondly, the EPR signal from the surface paramagnetic complexes is frequently broadened under catalytic conditions (up to complete disappearance) involving physical adsorption of O_2, H_2O, etc. molecules on the surface due to the dipole–dipole interaction.

The EPR method is frequently employed to observe the radical states of oxygen, NO, and certain other molecules on the surface. For this purpose, the cell-reactor is usually cooled rapidly to low temperatures. Accordingly the time required for the observation of the test molecules increases to ~ 10 s.

8. Nuclear magnetic resonance

The NMR method has been finding increasing application in catalysis during recent times.[16] The NMR method with a magic angle of rotation is used in the study of solids, especially catalysts.

When applied to catalysis in situ, the NMR method has been used successfully to investigate reactions such as catalytic polarisation under the conditions of an isolated static reactor. However, the technical difficulties associated with the necessity for the continuous introduction of the reactants into a rotating tube-reactor have so far precluded the wide scale employment of NMR.

* * *

Among all the spectroscopic methods listed above, IR spectroscopy has remained the most widely used procedure since it has been most thoroughly developed. Therefore it is in fact recommended that IR spectroscopy be used to determine the intermediates and to investigate the dynamics of catalytic reactions.[17]

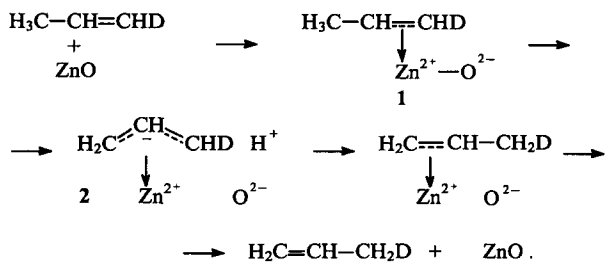
A large proportion of the studies published nowadays concern the measurement of the spectra of adsorbed molecules at room temperature (these investigations were initiated by Terenin and coworkers[18]) and the spectra of surface compounds after 'freezing' the reaction. Evidently, conclusions concerning the role of surface complexes in the reaction, based on such measurements, are to a large extent tentative. The application of IR spectroscopy in the study of the dynamics of heterogeneous catalysis was pioneered by Tamaru,[19,20] who drew attention to the need for the simultaneous measurement of the rate of the catalytic reaction and the rate of reaction of the surface compounds. Together with his coworkers, he investigated the intermediates formed during the decomposition of HCOOH on Al_2O_3, SiO_2, and ZnO and also during the oxidation of methanol on ZnO.

The extents to which the involvement of particular surface compounds as intermediates in catalysis has been demonstrated are differentiated in the present review. In most studies, the conclusion concerning the participation of surface compounds in catalysis is based on spectroscopic measurements before and after the reaction. The reliability of such conclusions will be designated by the letter L (lowest). Measurements of IR spectra in situ are resorted to much more rarely in order to establish the role of the surface compound in the reaction. The reliability of the conclusions reached on the basis of such measurements will be designated by the letter M (moderate). Publications in which the role of the surface complex in the reaction is estimated by comparing the rate of its reaction with the rate of formation of the reaction product are altogether rare. It is quite evident that agreement between these quantities serves as an adequate basis for the claim that the surface compound detected is an intermediate in the reaction. The reliability of such conclusions will be designated by the letter H (highest).

III. Isomerisation of alkenes

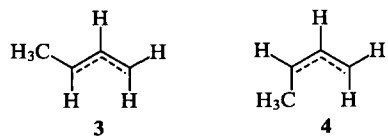
The simplest type of catalytic reaction is A → B, where A and B are substances of similar chemical nature. The isomerisation of alkenes belongs to reactions of this type.

The isomerisation of deuteriopropenes on zinc oxide results in the formation of an equilibrium mixture of $CH_2D-CH=CH_2$, $CH_3-CH=CHD$, and $CH_3-CD=CH_2$.[21] A band corresponding to the vibration of the OH group and five bands corresponding to the formation of the symmetrical π-allyl are observed in the IR spectrum. This indicates that the isomerisation proceeds via dissociative cleavage of a C–H bond. The intermediate (π-allyl) probably exists in the anionic form $C_3H_5^-$:



The first stage of the reaction is evidently the formation of the π-complex **1**. Bands corresponding to the formation of π-complexes following the adsorption of alkenes on a series of oxides have indeed been observed in the IR spectra.[22] In chemical terms, one can also imagine the formation of π-complexes of the alkene with the acid OH groups and the subsequent formation of the carbonium ion $C_3H_7^+$. However, the formation of such ions has not been detected in any of the investigations.

In the isomerisation of but-1-ene to but-2-ene on ZnO, bands corresponding to the π-complexes of but-1-ene and *cis*- and *trans*-butenes as well as π-allyl complexes were observed in the IR spectra.[23] Of the two possible methyl-π-allyls

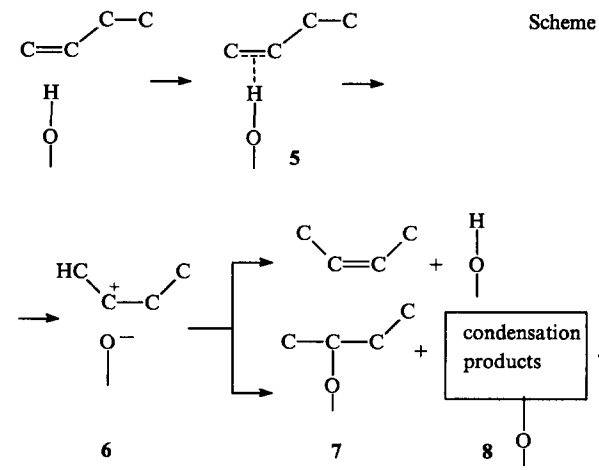


the allyl **3** may be a precursor of *trans*-butene, while the allyl **4** may be a precursor of *cis*-butene. However, only complex **4** was detected on the surface. The most intense absorption bands in the spectra of the π-complexes are those of the *cis*-butene π-complex, although a greater amount of *trans*-butene is formed in the equilibrium gas mixture. Consequently, the form **3** exists only as a short-lived precursor in the reaction **4** ⇌ **3** ⇄ *trans*-butene. Under catalytic conditions, the intensity of the signal due to π-C_4H_8-1 diminishes slowly, while that of the signals of π-*cis*- and π-*trans*-C_4H_7 increases slowly. At the same time, complex **4** is formed initially at a rate close to the overall rate of isomerisation, which then remains constant. Hence one may conclude that π-allyl is a true intermediate.

The formation of a π-complex with acid OH groups was observed in a study of the isomerisation of but-1-ene to *cis*-butene on HY zeolites and other acid silicates at 0–200 °C.[24] The attempts to detect the $C_4H_9^+$ carbonium ions failed in this case too, although a correlation was observed between the rate of reaction and the number of acid OH groups. It is suggested that the reaction proceeds in acordance with scheme 1. According to Paukshtis et al.,[24] the conversion of complex **5** into complex **6** is the rate-limiting stage. In a kinetic study, it was observed that the continuous increase in the intensity of the absorption bands of the saturated complexes **7** and **8** is accompanied by a decrease in the rate of isomerisation. Evidently complexes **7** and **8** are 'dead-end' compounds which deactivate the catalyst.

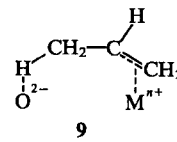
A band at 1510 cm^{-1}, characteristic of a C=C bond with an OH group, was observed in the IR spectra in the isomerisation of hex-1-ene to hex-2-ene and the subsequent *cis–trans* isomerisation on the HZSM-5 zeolite at 200 °C. At the same

Scheme 1



time, the spectrum of the OH groups changed also. On this basis, the authors[25] concluded that the reaction proceeds via the intermediate formation of a carbonium ion (a reaction of the **5** → **6** type)‡.

The formation of stable carbonium ions of the type $(CH_3)_2C^+CH_2CH_3$ has been postulated in the adsorption of isoalkenes on zeolites.[22] The possibility of the isomerisation of the double bonds via cyclic complexes of the type



in accordance with an associative, 'concerted' mechanism was considered in the same investigation.

Table 2 presents a compilation of data concerning the intermediates formed in the adsorption of alkenes on heterogeneous catalysts; the reliability of the evidence for the role of a particular complex in the isomerisation reaction, in conformity with the criteria described above, is indicated.

A dissociative isomerisation mechanism, involving the cleavage of a C–H bond with formation of π-allyl anions or carbonium ions, has been postulated in all the studies considered. We may note, however, that virtually no direct spectrokinetic confirmations of such a mechanism exist (apart from the detection of the π-allyl complex itself). The observed changes in the IR spectra of the adsorbed molecules are associated in most cases with dead-end compounds not involved in the main reaction.

The data presented in table 2 refer to the isomerisation of alkenes involving the double bond. As regards their skeletal isomerisation, there have been virtually no investigations in which intermediates were identified with the aid of IR spectroscopy. The mechanisms of the skeletal isomerisation quoted in individual communications (see, for example, Cuong Pham-Hun et al.[26]) are based on indirect data.

‡The migration of carbon along the chain of carbon atoms in octane at 20–70 °C on the HZSM-5 zeolite has been recently demonstrated by ^1H and ^{13}C NMR methods [A G Stepanov, M V Luzgin, V N Romannikov, K I Zamaraev *Catal. Lett.* **24** 271 (1994)]. The authors believe that this proves the formation of a carbenium ion. The direct spectroscopic detection of this ion is impossible because it is in equilibrium with an alkyl silyl ether.

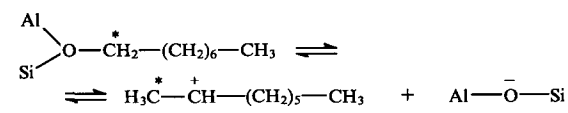
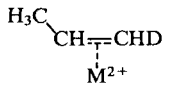
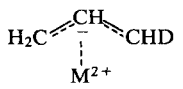
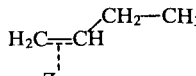
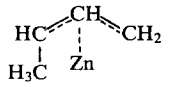
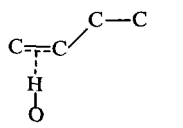
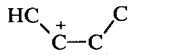
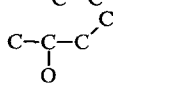
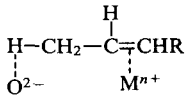


Table 2. Intermediates formed in the isomerisation of alkenes.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Isomerisation of deuteriopropenes on oxides		M	21, 22
		M	21, 22
Isomerisation of butenes on ZnO		H	23
		H	23
Isomerisation of butenes and higher alkenes on zeolites and other acid silicates		M	24, 25
		L	22, 25
		L	22, 25
		L	22
Isomerisation of oct-1-ene on HZSM-5 zeolite		M	

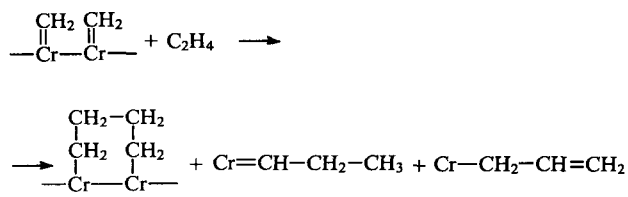
IV. Oligomerisation of alkenes and certain other reactions

1. Oligomerisation, alkylation, and aromatisation of alkenes

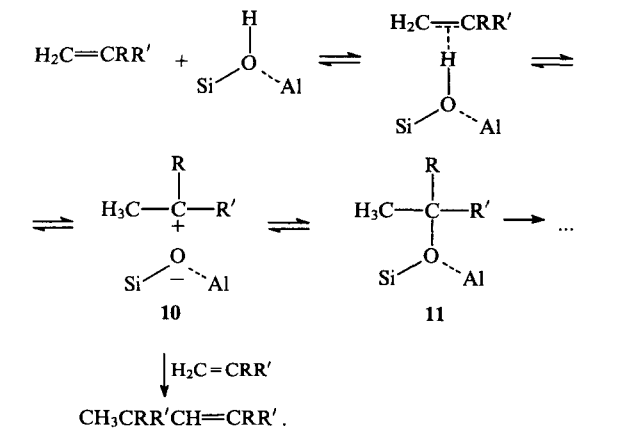
The oligomerisation of alkenes $n\mathrm{A} \rightarrow \mathrm{B}$ formally belongs to the class of reactions of a more complex type than isomerisation. However, the fact that the reaction product—an oligomer or a polymer—is not desorbed into the gas phase facilitates the spectrokinetic investigation and this renders the results more unambiguous. UV-VIS and NMR spectroscopy have been used together with IR spectroscopy to identify the intermediates.

Mainly the stable starting materials and oligomers as well as stable long-lived alkoxy-derivatives have been dectected in situ by IR [25,27–29] and NMR [30–32] spectroscopy in the oligomerisation of C_2H_4, C_3H_6, and C_4H_8 on zeolites at 0–200 °C.

The initial stage of the interaction—the formation of a π-complex with an OH group—was discovered in a study of the NMR spectra of isobutene on the HY and HZSM zeolites at a low temperature (−150 °C). [31] The oligomerisation of propene to 4-methylpentene and hex-1-ene on NiO/SiO_2 involves the formation of a π-complex between C_3H_6 and Ni^{2+}. [33] The nature of the IR spectra, obtained in situ in a study of the polymerisation of C_2H_4 on Cr/SiO_2, [27] indicates the existence of dissociative forms of ethylene adsorption. This provided grounds for the hypothesis that carbenes participate in the reaction, although these intermediates were not detected directly.

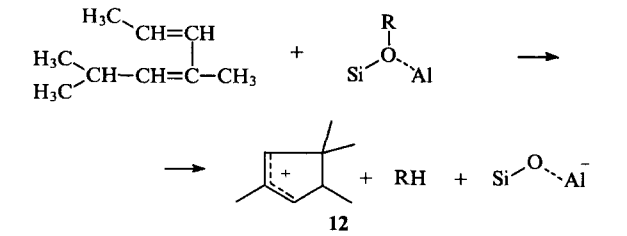


The π-complex of the alkene with an OH group can be converted into a carbonium ion. It can be formed as a transition state, but carbonium ions have not been detected in the study of the reactions of alkenes by IR and NMR spectroscopic methods even at low temperatures. [31–32] Apparently they are immediately converted into long-lived alkoxide groups $\equiv Si-OR$ on alumino-silicates. A study of the kinetics of the oligomerisation of C_2H_4 and C_3H_6 on the TsVK zeolite and silicalite [29] from the change in the IR band at 2935 cm^{-1} (due to CH_2 groups in the reaction products) showed that the rate of reaction initially diminishes and then increases. This is due to the fact that the CH_3O groups are relatively unreactive, although the $O(CH_2)CH_3$ groups are reactive in relation to the alkene. The band due to the CH_3O group (2977 cm^{-1}) gradually disappears from the spectrum. The initial stages of the oligomerisation reaction may be represented by the following scheme: [31–33]



This is followed by the formation of the alkoxide $\equiv Si-O-CH_2-CRR'-CH_2-CHRR'$ and a further increase in the chain length of the oligomer. The rate-limiting stage may be the conversion of the intermediate carbonium ion **10** into a dimer, after which both linear and branched polyalkenes are produced.

Stable cyclic carbonium ions **12**, formed via the scheme

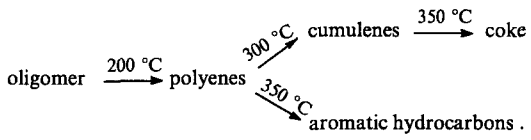


after the consumption of the entire monomer, have been detected in a study of the oligomerisation of C_3H_6 by the NMR method. [32] However, they are not intermediates in the oligomerisation reaction.

The oligomer chain is apparently terminated via β-limination. Peaks corresponding to the products of the interaction of the terminal $-CH=CH_2$ group of the growing oligomer with an OH group of the catalyst have been observed in the IR spectra obtained in the polymerisation of C_2H_4 on 0.5% Cr/SiO_2. [34]

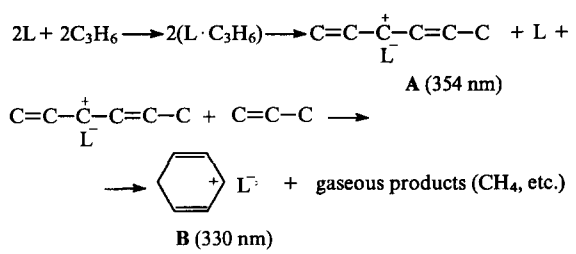
The subsequent stages of the reaction of oligomers at a higher temperature (260–400 °C) were investigated by UV-VIS spectroscopy. [29,35–37] Polyenyl and other condensed structures

were then detected. Starting from 250–300 °C, aromatisation takes place, while at a still higher temperature (350 °C) coke is formed. The overall scheme of the reactions of oligomers on zeolites assumes the following form:[29]



Polyenes are stabilised under catalytic conditions on the same OH groups as oligomers. It has been confirmed by the IR [28] and NMR [38] spectroscopic methods that coke and aromatic hydrocarbons are formed via independent pathways.

The formation of stable unsaturated cations has also been observed by UV-VIS spectroscopy. It has been shown [35] that C_3H_6 is aromatised on the Lewis acid centres of γ-Al_2O_3 at 180–300 °C via the mechanism



where L is a Lewis acid centre. The rate of formation of compound **B**, characterised by the 330 nm vibration frequency, is proportional to the concentration of compound **A** (354 nm vibration frequency) and the pressure of C_3H_6 in the gas phase. After the reaction has occurred, various condensed compounds are detected on the surface.[23,35,36]

It has also been shown by the EPR method that, when HM, HY, etc. zeolites with adsorbed alkenes are heated, free-radical products are formed. For example, C_3H_6 affords the radicals [39]

$$CH_2{=}\dot{C}H{=}CH_2 \text{ and } CH_2{=}\dot{C}H{=}CH{-}CH(CH_3)_2.$$

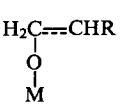
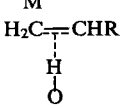
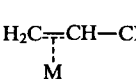
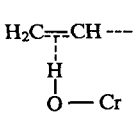
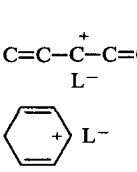
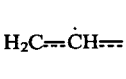
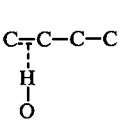
The EPR spectra were recorded after extensive cooling and not under catalytic conditions.

Alkylation on zeolites proceeds via a mechanism analogous to the oligomerisation mechanism. The π-complexes of C_4H_8 and alkoxide compounds were detected in situ in a study of the alkylation of isobutane by butenes on the HNaCaX zeolite by IR spectroscopy. According to the authors,[40] butane can also give rise to the intermediate carbonium ion $(CH_3)_3C^+$, which participates in hydride (H^-) transfer to $C_4H_9^+$ with formation of the alkoxy-group $(CH_3)_3C{-}O{-}$ or a C–C bond in oligomers via an associative mechanism. Isobutane is capable of being adsorbed mainly on the basic (nucleophilic) centres of the zeolite, whereas butenes are adsorbed on the acid centres.

We may note that the oligomerisation examined above probably proceeds via an associative mechanism (for example, by the reaction of the carbonium ion **10** with the alkoxide **11**). Its occurrence apparently requires two active centres: one with the alkoxide chain and the other with the carbonium ion. The lack of a direct relation between the concentration of the alkoxide structure and the rate of oligomerisation indicates the possible existence of equilibria of the type **10** ⇌ **11**. The main bulk of the surface may serve as a reservoir supplying the reaction when its conditions are varied. It may be that cyclic carbonium ions **12** play the same role.

A compilation of data on the intermediate compounds formed in the oligomerisation of alkenes, aromatisation, and alkylation is presented in Table 3.

Table 3. Intermediates formed in the oligomerisation and certain other reactions of alkenes.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Oligomerisation of alkenes on zeolites		L	25, 27–33
		M	31
Oligomerisation of propene on NiO/SiO_2		L	33
Polymerisation of ethylene on Cr^{3+}/SiO_2		L	27, 33
Aromatisation of propene on Al_2O_3		H	35
Aromatisation of propene on zeolites		L	39
Alkylation of isobutane by butenes on zeolites		L	40

The polymerisation of alkenes, for example on Ziegler–Natta catalysts, apparently proceeds via a coordination mechanism. The alkene molecule forms a π-complex with the transition metal ion, which simultaneously retains the polymer chain. CH_2 groups, interacting with the catalyst to some extent, have been detected in a high concentration in an IR spectroscopic study of this process.

2. The cracking of hydrocarbons

The cracking of hydrocarbons can be regarded as a reaction which is to some extent the reverse of oligomerisation. It too proceeds on aluminosilicates. However, cracking occurs at much higher temperatures and therefore the intermediates may be different. A generally accepted view is that carbonium ions are formed as intermediate species. The application of spectroscopic methods in situ to investigate the cracking is difficult owing to the high process temperatures. The same intermediates as in oligomerisation have been detected by the NMR method among the cracking products of propene oligomers on HY at 220 °C.[38] Dissociative mechanisms are more probable at higher temperatures.

In the cracking of the methylcyclohexane and 3-methylpentane on H-mordenite above 100 °C, adsorbed free radicals were detected by the EPR method.[41] They are stable up to 100 °C, while at a higher temperature they are converted into the final products, possibly via the formation of intermediate carbonium ions. The EPR signal is not observed at room temperature. The authors suggest that a strong Lewis acid centre abstracts an electron from a tertiary C–H bond in the first stage of the reaction with formation of a radical-cation. The latter loses a H atom and gives rise to a free radical. This is followed by the two-stage elimination of the hydride ion.

The cracking on metals proceeds via a different mechanism. On decomposition of C_2H_6 on Pt/SiO_2, absorption due to ethylidyne structures $CH_3C{\equiv}Pt$ and possibly $PtCH_2-CH_2Pt$ were observed in the IR spectra. At 200–300 °C, these compounds decompose with formation of CH_4 and a carbon residue.[42]

V. Metathesis of alkenes

The metathesis of alkenes

$$2A \rightarrow B + C$$

is formally a reaction of a more complex type than those examined above. However, in reality its mechanism is simple, since all the reactants (A, B, and C) belong to the same class of alkenes (for example A may be propene, B ethylene, and C butene). Therefore the intermediates should also be of the same type. Intermediate carbene complexes have been detected in this reaction.

The present authors investigated the UV-VIS diffuse reflectance spectra of molybdenum, tungsten, and rhenium oxides deposited on Al_2O_3 and SiO_2.[43,44] The mechanisms of the metathesis of propene in the presence of such a catalyst are different at low (50–250 °C) and high (300 °C) temperatures judging from the content of the butene isomers. It was postulated that the metathesis can proceed via quasi-cyclobutane and carbene mechanisms at low and high temperatures respectively.

$$H_3C-CH=CH_2 + 2M \longrightarrow H_3C-CH{:}M + H_2C{:}M$$

$$H_2C{:}M + H_3C-CH=CH_2 \longrightarrow \underset{\textbf{13}}{H_3C-\overset{\overset{CH_2}{\vdots}}{\underset{\diagdown\,\diagup}{CH}}-CH_2} \longrightarrow$$

$$\longrightarrow H_3C-\underset{\diagdown\,\diagup}{CH}-CH_2 + CH_3CH=CHCH_3 + C_2H_5CH=CH_2$$
$$\qquad\qquad CH_2$$

$$H_2C{:}M + H_3C-CH=CH_2 \longrightarrow H_3C-CH{:}M + C_2H_4$$

$$H_3C-CH{:}M \longrightarrow M + C_2H_4$$

M = metal

However, conclusions concerning the mechanism were reached on the basis of indirect data, namely by analysing changes in the coordination in the Mo, W, and Re complexes, which are reflected in the nature of the UV-VIS spectra.

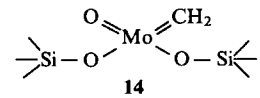
UV-VIS spectroscopy has been applied[45,46] directly under the conditions of the propene metathesis reaction. The rate of reaction was determined simultaneously with the measurement of the spectra. Comparison of these data made it possible to establish that the activation of the $Mo(CO)_6/\gamma\text{-}Al_2O_3$ catalyst is associated with the formation and rearrangement of subcarbonyl structures on the surface. The formation of the $Mo_2(CO)_6$ active centre may be represented schematically as follows:

$$Mo(CO)_6 \rightleftharpoons Mo(CO)_4 \underset{-CO}{\overset{L}{\rightleftharpoons}} Mo(CO)_3L \underset{-L}{\rightleftharpoons} Mo_2(CO)_6,$$

where L is the ligand (possibly a surface OH group).

The kinetic parameters of the formation of the active centre in the metathesis reaction have been established as a function of the state of the hydroxyl coating of the surface. The decrease in the activation energy for the formation of $Mo_2(CO)_6$ active centre is associated with the decrease in the energy expenditure on overcoming the hydroxy-group barrier when it arises. The nature of the temperature dependence of the activity of the catalyst is determined by the ratio of the rates of evolution of CO and of the rearrangement of the subcarbonyl surface structures.

The formation of the carbene complex



14

stable in vacuo up to 400–450 °C, has been observed by IR and UV-VIS spectroscopy in the adsorption of cyclopropane on MoO_3/SiO_2, in which Mo^{6+} had been reduced photochemically to Mo^{4+}.[47] Isotope exchange between complex **14** and C_2D_4 is observed at room temperature.

$$Mo{=}CH_2 + C_2D_4 \rightleftharpoons Mo{=}CD_2 + D_2C{=}CH_2.$$

At 0–350 °C, complex **14** interacts with alkenes via the mechanism

$$Mo{=}CH_2 + H_2C{=}CH-CH_3 \rightleftharpoons$$

$$\rightleftharpoons Mo{=}CH-CH_3 + C_2H_4\uparrow \rightleftharpoons \underset{\vdots}{\overset{H_2C{=}CH_2}{Mo}}.$$

There is also a possibility of the formation of the cyclobutane complex **15**, which has been confirmed by the appearance of new bands in the spectrum.

$$Mo{=}CH_2 + H_2C{=}CH-CH_3 \rightleftharpoons \underset{\textbf{15}}{\overset{CH_3}{Mo\diagup\diagdown}} \rightleftharpoons$$

$$\rightleftharpoons Mo{=}CH-CH_3 + C_2H_4$$

The same bands appear also in the interaction of cyclopropane with the Mo=O bond. The energy of the $Mo{=}CH_2$ bond in complex **14** is 435 kJ mol^{-1}.[48]

It is noteworthy that the catalyst in the study of Vikulov et al.[47] was subjected to photochemical reduction. However, in the usual thermal metathesis of alkenes there is also a possibility of the appearance of carbenes. In the metathesis of propene on Nb/SiO_2, the intermediate carbene complex $Nb{=}CH_2$ was formed.[49] Its structure was investigated by IR spectroscopic and EXAFS methods. It was found that the Nb–C distance in the complex is 0.195 nm, which corresponds to the length of the Nb=C double bond (whereas the length of the normal Nb–C bond is 0.210 nm). The IR bands correspond to vibrations of the CH_2 group.

Data concerning the intermediates formed in the metathesis of alkenes are compiled in Table 4.

The kinetics of the formation and decomposition of the carbene were not compared in the above studies[43,44,47–49] with the kinetics of the overall metathesis reaction.

Table 4. Intermediates formed in the metathesis of alkenes.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Metathesis of propene on MoO_x/SiO_2	$\equiv Mo{=}CH_2$	M	43,44, 47,48
	$\equiv Mo{=}CH-CH_3$	M	
	$\equiv Mo\diagup\diagdown CH_3$	L	48
Metathesis of propene on Nb_2O_5/SiO_2	$\equiv Nb{=}CH_2$	L	49

VI. Decomposition of alcohols

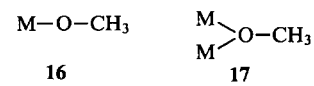
Alcohols decompose via two principal pathways: with dehydration and the formation of an alkene and water or with dehydrogenation and the formation of hydrogen and an aldehyde (or ketone). Both pathways involve reactions of the type

$$A \rightarrow B + C.$$

On dehydration of the first member of the series of aliphatic alcohols (methanol), formaldehyde CH_2O or dimethyl ether $(CH_3)_2O$ may be formed. The dehydration of methanol to CO and H_2 will not be considered here. The conversion of methanol into hydrocarbons will be examined below in Section VIII.

1. Dehydration of alcohols

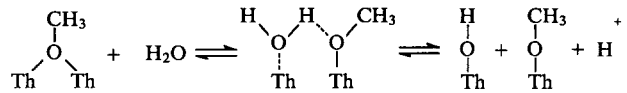
Surface methoxy-groups were detected in situ by IR spectroscopy in all the studies on the decomposition of methanol on oxides. They are present on α-Fe_2O_3,[50] CeO_2 and ThO_2,[51] Cr_2O_3,[52] ZnO,[53] and ThO_2.[54] Linear (compound **16**) and bridging (compound **17**) methoxy-groups were distinguished on CeO_2 and ThO_2.



16 **17**

The decomposition of complex **16** results in the reformation of methanol, while the decomposition of complex **17**, or more precisely the decomposition of two such complex species next to one another, affords the $CH_3OH + (CH_3)_2O + CO$ mixture.[52]

There is also a possibility of the interconversion of complexes **16** and **17**.[54]



17 **18** **16**

The interconversion of the methoxide complexes **16** and **17** proceeds in essence via the associative catalytic dehydration mechanism.

Methanol bound to the oxide by the CH_3OH ... OM hydrogen bond was also detected at a low temperature (150 °C). It may be a precursor of the methoxide.[50] Heating to high temperatures (> 200 °C) leads to the conversion of the alkoxides into formates and carbonates.[50,53]

Periodic modulation of the free stream of CH_3OH with a 1 s resolution made it possible[55] to distinguish two mechanisms of the dehydration of methanol on γ-Al_2O_3—the dissociative mechanism

$$CH_3OH_{ads} + CH_3O_{ads} \longrightarrow CH_3OCH_3(g) + OH_{ads}$$

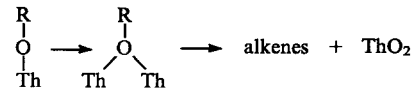
$$2\,OH_{ads} \longrightarrow H_2O(g) + O_{ads},$$

and the associative mechanism

$$CH_3OH_{ads} + O_{ads} \longrightarrow CH_3O_{ads} + OH_{ads} \longrightarrow$$

$$\longrightarrow CH_3OCH_3(g) + H_2 + H_2O.$$

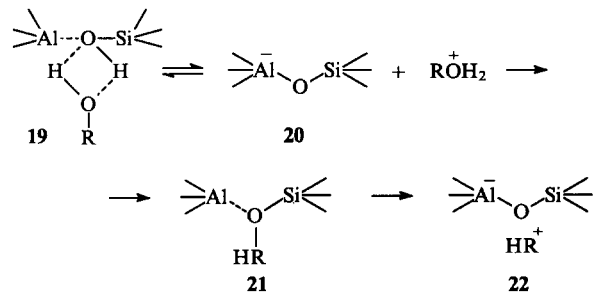
Alkoxy-groups are also formed in the dehydration of higher alcohols: isopropyl alcohol on ThO_2,[54] isobutyl alcohol on Al_2O_3,[56] and various alcohols on the HZSM-5 zeolites.[57] An attempt has been made[54] to correlate the kinetics of the dehydration of *tert*-butyl alcohol and isopropyl alcohol, based on the measurement of the rate of evolution of gaseous products, with the kinetics of the decomposition of linear and bridged alkoxides. The authors proposed the following scheme:



However, bearing in mind that the curves obtained[54] are insufficiently distinct, the reaction may also proceed via a bimolecular mechanism.

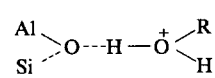
The change in the diffuse IR spectra in situ and the kinetics of dehydration of a series of alcohols (C_2H_5OH, iso-C_3H_7OH, *tert*-C_4H_9OH) on Al_2O_3 have been investigated by the response method at 140–280 °C.[56] The removal of alcohol from the gas phase at 260 °C leads immediately to the disappearance of the bands due to the hydrogen-bonded or coordinated alcohol; the bands of the alkoxide vanish somewhat more slowly, while those of the carboxylates remain unchanged. The dehydration rate constants, found from the analysis of the IR spectra and from the yield of the gaseous products, are the same. Hence the authors concluded[56] that the alkoxide is an intermediate.

In the adsorption of various alcohols, ranging from C_1 to C_4, on the HZSM-5 zeolite,[57,58] each alcohol molecule is adsorbed near an Al atom, which is indicated by the disappearance from the IR spectrum of the band due to the acid OH group. The results of exchange studies in isopropyl alcohol and *tert*-butyl alcohol, on the one hand, and D_2O, on the other, indicate that the alcohol molecules are dehydrated with formation of a carbonium ion before desorption. However, 1-butanol does not exchange with D_2O, which can be explained, according to the authors,[57] by a bimolecular mechanism in which two alcohol molecules are involved. A hydrogen bond is formed in the first stage of the interaction (complex **19**), after which the oxonium ion **20** and then the carbonium ion **22** appear.



19 **20** **21** **22**

The covalent structure **21** predominates in zeolites with nucleophilic centres, whilst the ionic structure **22** predominates in zeolites with more acid centres. The ionic structures **20** and **22** are not manifested in the IR spectra (at any rate it is difficult to distinguish them from the covalent structures), but the authors[57] assume that they may arise as a result of stabilisation due to interaction with the zeolite lattice, for example with formation of the bridged ions



as in homogeneous catalysis.[58] Such stabilisation helps to overcome the energy barrier in the endothermic stages of the reaction.

We may note that the formation of association complexes in the dehydration of isopropyl alcohol on Al_2O_3 was demonstrated previously by kinetic and calorimetric methods.[59] A four-stage scheme was proposed:

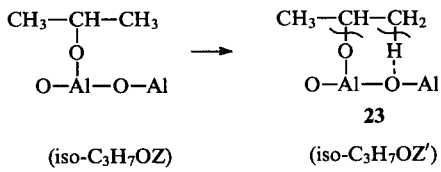
$$\text{iso-}C_3H_7OH + ZOH \rightleftharpoons [\text{iso-}C_3H_7OH \cdot ZOH],$$

$$[\text{iso-}C_3H_7OH \cdot ZOH] \rightleftharpoons \text{iso-}C_3H_7OZ + H_2O,$$

$$\text{iso-}C_3H_7OZ \xrightarrow{Z'} \text{iso-}C_3H_7OZ + Z,$$

$$\text{iso-}C_3H_7OZ' \longrightarrow C_3H_6 + Z'OH.$$

A complex of type **19** is formed in the first stage, whilst the third stage (possibly rate-limiting) represents surface diffusion of the isopropoxide groups to another active centre Z′ incorporating a surface oxygen atom.

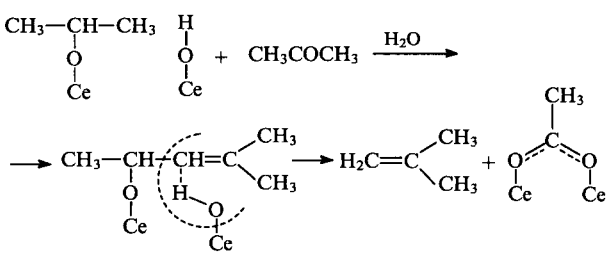


(iso-C_3H_7OZ) (iso-C_3H_7OZ')

The activation energy for this stage is 106 kJ mol^{-1}. The measured enthalpy of the first stage (26 kJ mol^{-1}) corresponds approximately to the energy of two hydrogen bonds in the type **19** complex or to a lifetime of the complex of $\sim 10^{-10}$ s.

Consequently the mechanisms proposed [57,60] agree with one another as regards the formation of hydrogen-bonded association complexes and alkoxy-groups, which do in fact largely cover the surface under stationary conditions. On the other hand, the formation of propene (the concluding stage of the reaction) proceeds, according to Aronson et al., [57] with participation of a carbonium ion, while Sadovnikov and Gefter [60] believe that it proceeds with participation of basic centres. The question whether all the alkoxy-groups (Z centres) or only some of them (Z′ centres) participate in the formation of the final product while the remaining ones serve as a reservoir for the latter remains unresolved.

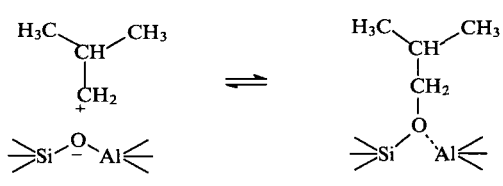
According to the view of Zaki and Sheppard, [61] based on the analysis of the IR spectra recorded after heating CeO_2 in isopropyl alcohol at 150–400 °C, the dehydration also proceeds via an associative mechanism. Apart from the direct dehydration, aldol condensation with the acetone formed on dehydrogenation of the alcohol takes place.



24

At a low temperature, close to room temperature, the aldol condensation proper, with formation of the unsaturated ketone $CH_3COCH=C(CH_3)_2$ from complex **24**, takes place. A similar process involving CH_3CHO on Na/SiO_2 has been investigated by Raman spectroscopy at room temperature. [61] Enolate complexes and complexes retained on the surface by two C–O–M bonds were detected. Physically adsorbed 2,4-dimethyl-1,3-dioxane was also found. On heating to 130 °C, it decomposes, affording crotonaldehyde $CH_3CH=CH-CHO$, acetaldehyde (or the adsorbed enolate $CH_3=CHOH$), and water.

The mechanism of the alcohol dehydration has also been investigated by the NMR method in situ. [63–69] The dehydration of *tert*-butyl alcohol and isobutyl alcohol at 100 °C, proceeds with formation of isobutene, water, and a C_8 oligomer according to the NMR data. The short-lived carbonium ion **25** may be an



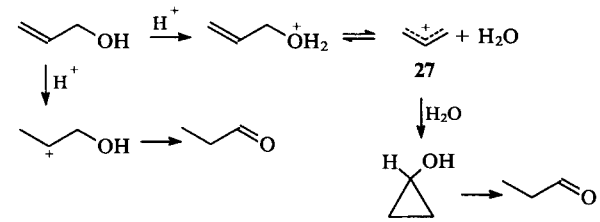
25 **26**

intermediate. [64,65] The alcohol molecule is localised at an intersection of the zeolite channels. Under these conditions, the alkoxide **26** (C_4H_9OSi) is an intermediate in the dehydration of isobutyl alcohol but not *tert*-butyl alcohol.§

The stable triphenylmethyl carbonium ion was detected in the dehydration of triphenylcarbinol on acid catalysts. [67]

The formation of the isobutyl carbonium ion, also in the dehydration of *tert*-butyl alcohol on HZSM-5, could not be detected by the NMR method, [62] although the same authors [57] had previously postulated the appearance of complex **22** in this process on the basis of IR spectroscopic data. Only type **21** alkoxide was detected. The same complex was found by these investigators also in the adsorption of methylpropane. The carbonium ion formed as a result of the adsorption of C_3H_8 on the zeolite [68] likewise belongs, according to Stepanov et al., [64] to the class of ethers Si–O–R. The formation of a carbonium ion on the HY zeolite is more probable than on HZSM-5 owing to its higher relative permittivity and nucleophilicity.

NMR study of the dehydration of allyl alcohol on the HZSM-5 zeolite made it possible to detect the intermediate oxonium and carbonium compounds and to establish the sequence of the reactions. [69]



27

The interaction of the allyl cation **27** with allyl alcohol afforded diallyl ether $(CH_2=CH-CH_2)_2O$.

The formation of the isopropoxide was likewise observed in a study of the decomposition of isopropyl alcohol on metallic molybdenum by the EELS method. [70] C_3H_6, C_3H_8, H_2, and H_2O were also found among the reaction products.

A compilation of data concerning the intermediates formed in the dehydration of alcohols is given in Table 5.

Summarsing the data presented above on the dehydration of alcohols, we may note that the formation of linear and bridged alkoxides is acknowledged in all the investigations and in some of them also the formation of carbonium ions. Spectrokinetic measurements have scarcely been made with the exception of some not very clear-cut data. [54,56] However, on the basis of the combination of a large number of results, one may assume that the above complexes are very probably reaction intermediates.

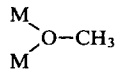
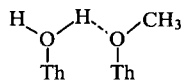
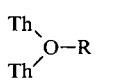
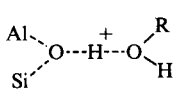
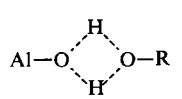
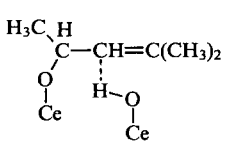
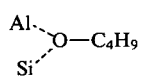
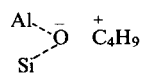
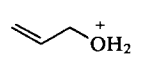
2. Dehydrogenation of alcohols

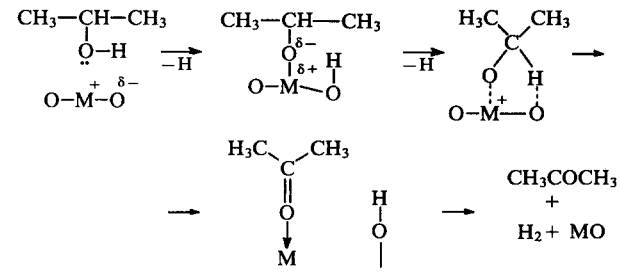
When alcohols are dehydrogenated on an oxide surface, bands corresponding to alkoxide structures are also observed in the IR spectra, [60,71] but the presence of a strong basic (nucleophilic) centre next to an acid centre is essential for the occurrence of this reaction pathway.

According to Efremov and Davydov, [71] the conversion of isopropyl alcohol occurs only in the absence of the weakly bound alcohol, blocking the neighbouring centres (possibly O^{2-}), i. e. the occurrence of the reaction via an associative mechanism is impossible in this case.

§It has been possible to demonstrate by the NMR method that the decomposition of isobutyl alcohol on the HZSM-5 zeolite involves the transfer of the $^{13}CH_2$ label from isobutyl alcohol to isobutyl silyl ether **26** and a further redistribution of ^{13}C among the C atoms in butane [J Kokes, A L Dent *Adv. Catal.* **22** 1 (1972)]. According to the authors, this demonstrates the occurrence of the transition **26** → **25** and the participation of the carbonium ion **25** in the dehydration of C_4H_9OH.

Table 5. Intermediates formed in the dehydration of alcohols.

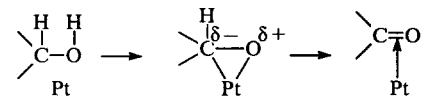
Reaction, catalyst	Intermediate complex	Reliability	Ref.
Dehydration of methanol on oxides	$M-O-CH_3$	M	50–55
		M	50–55
Dehydration of methanol on ThO_2		M	54
	$Th\cdots H-O-CH_3$	L	50
Dehydration of isopropyl and isobutyl alcohols on ThO_2	$Th-O-R$	H	54
		H	54
Dehydration of alcohols on Al_2O_3	$Al-O\cdots H-O-R$	H	56
	$Al-O-R$	H	56
Dehydration of C_1-C_4 alcohols on zeolites		L	57
Dehydration of isopropyl alcohol on Al_2O_3		M	59
Ditto on CeO_2		L	60
Dehydration of isobutyl alcohol on HZSM-5		L	64, 65
		L	64, 65
Dehydration of allyl alcohol on HZSM-5		L	69
		L	69
Dehydration of triphenyl-carbinol on acid catalysts	$(C_6H_5)_3C^+$	L	67



The IR bands at 2910 and 2960 cm^{-1}, observed when isopropyl alcohol was dehydrogenated on Fe_2O_3 at 150 °C,[72] were attributed to the enolate, which is evidently an intermediate between the alkoxide complex and the final product.

The formation of the $C_2H_5O^-$ and the $C_4H_8O^-$ alkoxides as well as acetates and carbonates, which are apparently side products, was noted in a ^{13}C NMR study of the decomposition of C_2H_5OH on MgO.[73]

On dehydrogenation of cyclohexanol to cyclohexanone on Pt/SiO_2, a shift of the C=O vibration bands was observed in the IR spectra and was attributed to the occurrence of the process

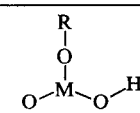
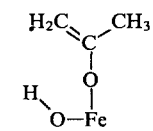
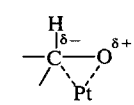


The broad bands at 1400 and 1610 cm^{-1} were assigned to the enol group.

Aldehydes and ketones may also be formed in the oxidation of alcohols with participation of the oxygen of the oxide lattice.

Data on the dehydrogenation of alcohols are compiled in Table 6.

Table 6. Intermediates formed in the dehydrogenation of alcohols.

Reaction, catalyst	Intermediate complex	Reliability	Refs
Dehydrogenation of alcohols on oxides		L	60, 71
Dehydrogenation of isopropyl alcohol on Fe_2O_3		L	72
Dehydrogenation of cyclohexanol on Pt/SiO_2		L	74

Thus the number of reliable data on intermediate compounds participating in the dehydrogenation of alcohols is much smaller than for their dehydration. The formation of enolates or enolate anions is more probable.

VII. Decomposition of acids

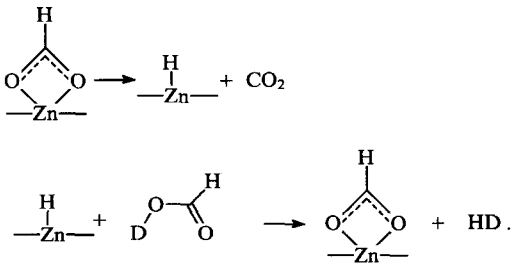
Like alcohols, formic acid may decompose via two pathways: dehydration and dehydrogenation. The principal substances formed on the catalyst surface are formates.[19, 20, 50, 75–77]

In the studies by Tamaru and coworkers already mentioned,[19, 20, 77] a catalyst disc was heated in the cell to the reaction temperature and then DCOOD was introduced until the attainment of a steady rate of decomposition. After this,

the DCOOD in the gas phase was rapidly replaced by HCOOH and the reaction was continued, observing simultaneously both the behaviour of the chemisorbed species and the rate of the overall reaction. The experiments on the dehydration of formic acid at 150–190 °C on Al_2O_3 showed that most of the adsorbed $DCOO^-$ ions vanish during the reaction, but the corresponding number of molecules appear in the gas phase as HCOOH, i.e. a rapid exchange takes place. A correlation was observed between the rate of dehydration of HCOOH and the number of proton centres on the surface. It was concluded that the $HCOO^-$ groups are not intermediate complexes and that the dehydration of formic acid proceeds when HCOOH molecules interact with the H^+ centres. The adsorption of molecular HCOOH on SiO_2 was observed, but formates were not detected under these conditions. According to the authors,[20] in this case too HCOOH molecules in the gas phase react with OH groups.

The dehydration of HCOOH on TiO_2 and zeolites has been investigated by ^{13}C NMR.[73] A monodentate formate, bound to an OH group, was detected on TiO_2, while on the zeolite a bidentate formate was found. The rate-limiting stage may be the removal of H_2O from the surface on condensation of the surface OH groups.

On the other hand, study of the dehydrogenation of HCOOH on ZnO at 145–220 °C confirmed the hypothesis that the reaction proceeds via intermediate formates.[19,20] When HCOOH was removed from the gas phase, evolution of H_2 ceased, but the rate of evolution of CO_2 did not change. On reintroduction of HCOOH into the gas phase, the rate of evolution of H_2 was restored. Almost the entire surface of ZnO was coated by the formate during the reaction. On the basis of these data, the following mechanism of the dehydrogenation of HCOOH on ZnO was proposed:



When HCOOH was dehydrogenated on α-Fe_2O_3, vibration bands of the bidentate formates, OH groups, and HCOOH molecules bound to the surface via the O–H and C=O groups were found in the IR spectra.[50] When the reaction was carried out in a closed vessel, a decrease in the intensity of the formate bands was observed.

The data on the decomposition of formic acid are compiled in Table 7.

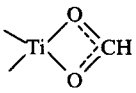
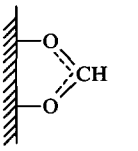
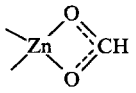
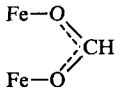
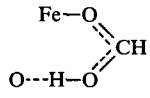
Thus the formates frequently detected under conditions for the decomposition of formic acid are most probably intermediates in the dehydrogenation of HCOOH, which proceeds via an associative mechanism. On dehydration of HCOOH, the protons are such intermediate forms.

VIII. Conversion of methanol into hydrocarbons

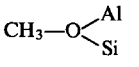
On zeolite catalysts, methanol is dehydrated to dimethyl ether, which is subsequently converted into hdyrocarbons. These reactions are referred to as the Mobil or the MTG (methanol to gasoline) process. The first stage, the formation of the ether $(CH_3)_2O$ on simple oxides, has already been considered in Section VI.

The mechanism of the conversion of methanol into hydrocarbons on the HZSM-5, HY, and SAPO-34 zeolites was investigated by the IR,[78,79] EPR,[80] and NMR[81–84] spectroscopic methods.

Table 7. Intermediates formed in the decomposition of HCOOH.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Dehydration on Al_2O_3	HCOOH	M	19, 20, 77
Dehydration on TiO_2		L	75
Dehydration on zeolites		L	75
Dehydrogenation on ZnO		M	19, 20
Dehydrogenation on Fe_2O_3		L	50
		L	50

When methanol interacted with the HZSM-5 zeolite in the absence of CH_3OH in the gas phase, the vibration bands due to different methoxy-groups were detected in the IR spectrum, viz.: the zeolite group CH_3O_{Zeol}, the oxygen atom of which is linked to the Al and Si atoms, i.e.



the CH_3O–Al and CH_3O–Si groups, and also weakly coordinated CH_3OH.[78] When CH_3O_{Zeol} is heated, methane and formaldehyde are formed. According to Novakova et al.,[78] this reaction proceeds via the mechanism

$$CH_3O_{Zeol} + (CH_3O\text{–}Al)^{n+} \longrightarrow CH_2O + CH_4 + Al^{(n+1)+} + O^-_{Zeol}$$

$$2\,CH_2O_{ads} + O^-_{Zeol} \longrightarrow CH_3OH + COO^-_{ads.\,Zeol}.$$

In the presence of methanol in the gas phase, C_2–C_5 hydrocarbons, mainly C_2H_4 and C_3H_6, were detected in the reaction products. Their formation was attributed to the associative interaction of CH_3OH with CH_3OZ, the details of which were not discussed.

The stage involving formation of the C–C bond is the most problematical. According to a hypothesis,[85] it is achieved via the intermediate formation of carbenes.

$$CH_3OH \longrightarrow CH_3OZ \longrightarrow :CH_2 \longrightarrow C_2H_4$$

$$\downarrow CH_3OR$$

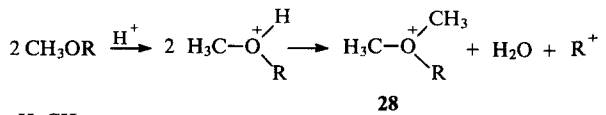
$$CH_3CH_2OR \longrightarrow C_2H_4 + HOR$$

Under the conditions of the interaction of CH_3OH with C_3H_6 on the HTsVK and HY zeolites at 200–240 °C, absorption bands of various substances, attributed to oligomeric alkyl, allyl, and polyenyl cations, were observed in the IR and UV spectra.[79]

The study of the conversion of CH_3OH into hydrocarbons on zeolites by the ^{13}C and ^1H NMR methods in situ with rapid freezing of the reactor at the temperature of liquid nitrogen made it possible to follow the formation of the reaction products.[81–83]

The compositions of the products in the gas phase and within the zeolite cavities were different. When HZSM-5 was used, mainly aromatic hydrocarbons were obtained. Mostly toluene, *m*- and *p*-xylenes, and 1,2,4-trimethylbenzene were found in the reaction products, while the adsorbed phase contained *o*-xylene and 1,2,4,5-tetramethylbenzene. Hence it follows that the molecules within the cavities are formed in equilibrium proportions and their emergence into the gas phase depends on the size of the windows in the zeolite.[82] On the SAPO-34 zeolite, which has even narrower channels, C_1-C_3 hydrocarbons emerge into the gas phase, while branched C_4-C_8 hydrocarbons remain in the intercrystalline space. In contrast to HZSM-5, aromatic products are not formed here.[81]

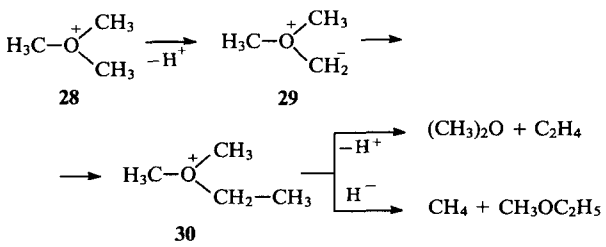
The hypothesis of the intermediate formation of oxonium ions in the synthesis of hydrocarbons from methanol was first put forward on the basis of isotopic and chemical data and not spectroscopic measurements.[86,87] According to Mole and Whiteside,[86] the oxonium ion **28** is formed in the interaction of methanol or dimethyl ether with the CH_3O^+RH surface group.



28

R = H, CH_3

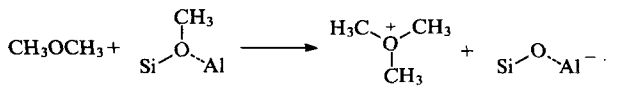
This process was investigated using the WO_3/Al_2O_3 bifunctional catalyst with the aid of the ^{13}C carbon label. According to the authors' hypothesis,[87] in the presence of basic centres on the surface the trimethyloxonium ion **28** is converted into methylene-methyloxonium ylide **29** and the latter undergoes intramolecular methylation in the excess of dimethyl ether with formation of dimethylethyloxonium **30**.



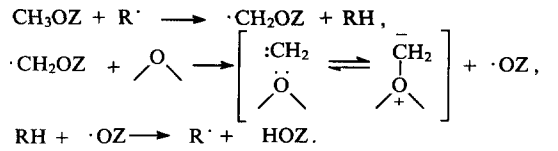
28 **29** **30**

This results in the formation of a C–C bond.

The kinetics of the conversion of CH_3OH into hydrocarbons on zeolites at 250 °C were investigated by the NMR method in situ.[84] An induction period was observed initially, after which the rate of reaction attained a steady level. The authors suggest[84] that the induction period is associated with the formation from $(CH_3)_2O$ of trimethyloxonium ion, first discovered by Hunter and Hutchings.[88] However, when ether and CH_3OH were adsorbed jointly, the trimethyloxonium ions were not detected and their kinetic role is therefore not clear. Manson et al.[84] postulated that the trimethyloxonium ion **28** is formed as a result of the activated interaction of $(CH_3)_2O$ with an alkoxide group:



Another, radical mechanism of the formation of the C–C bond has been put forward.[89] Free radicals had been previously detected by the EPR method in the decomposition of $(CH_3)_2O$ on HZSM-5.[80] It had also been shown[89] that the addition of NO inhibits the synthesis of hydrocarbons via a free-radical mechanism. Paramagnetic centres had been found in heat-treated HZSM-5. The following reaction mechanism was proposed:



The radical R· can be an alkyl, alkoxyl, alkoxyalkyl, etc. The reactive carbene species participates in the formation of the C–C bond, possibly via an oxonium ion.

Consequently the formation of the alkoxides ROZ as intermediates in the synthesis of hydrocarbons from CH_3OH may be regarded as more or less demonstrated (degree of reliability M), while the formation of oxonium ions is rather tentative (degree of reliability L). Their real kinetic role has not been elucidated. An associative mechanism, i. e. the participation of two molecules or fragments in the rate-limiting stage, is most likely.

IX. Conclusion

The results of studies of the intermediates in the simplest heterogeneous catalytic reactions of hydrocarbons, alcohols, and acids, obtained by spectroscopic methods during the last 15 years, were described above. We may note that in the vast majority of the studies quoted the reliability is low. The level of sophistication of even recent studies does not exceed that in the fundamental studies by Tamaru,[19,20,76,77] in which a parallel relationship between the rate of a catalytic reaction and the changes in the IR spectra of the adsorbed species under the reaction conditions was first noted.

The most reliable evidence concerning the real role of an intermediate is provided by the agreement between the rate of reaction of the surface complex and the rate of formation of the product.

There have been very few studies in which this approach has been employed. This is associated with the considerable experimental difficulties, among which the following may be noted: (1) the need to construct reactor-cells for the simultaneous study of the spectroscopic and catalytic properties of the system; (2) the need to develop methods for the determination of absorption coefficients; (3) inadequate time resolution in both kinetic and spectroscopic measurements; (4) the presence on the surface of a large number of different surface compounds, some of which are intermediates, whilst others are dead-end complexes.

The majority of the possible intermediate complexes listed above are chemical compounds with a saturated valence; these are alkoxides, formates, acetates, etc. The π-alkene and π-allyl complexes detected in the reactions with participation of alkenes are also fairly stable.

Free radicals were detected by the EPR method only on zeolites at low temperatures, while carbonium ions, which should be more reactive than the saturated intermediates, were found by the NMR method. By resorting to shorter measurement times, at least millisecond times (the lower limit of the characteristic times of catalytic reactions), it is possible to detect short-lived (and hence more reactive) intermediates.

It is also noteworthy that the low reliability of results obtained in the study of the catalytic reactions of hydrocarbons is associated with low intensity (low extinction coefficients) of the C–H and C–C vibrations. The adsorbed substances can be detected in these reactions only when their concentration is fairly high. This explains the small number of data referring to very familiar catalytic reactions such as oligomerisation, isomerisation, and the metathesis of hydrocarbons.

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