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Generation, Characterization, and Transformations of Unsaturated Carbenium Ions in Zeolites[†]

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I. Introduction

Hydrocarbons (and a particular group of their derivatives) transform in acidic media via cationic mechanisms in which carbocations are the intermediates. In superacidic solutions, the lifetime of these carbenium ions at room temperature or below is long enough to allow their detection. Furthermore, most of their transformations can also be monitored, as demonstrated in the classical work of Olah and Schleyer.[1]

Acidic centers can be generated within the channel and/or cage system of zeolites. Zeolites are defined as crystalline alumino−hydro−silicates with pores of molecular dimensions. Literature data referring to the acidity of zeolites show that in general both Brønsted and Lewis acidic sites can simultaneously be present in the zeolitic pore system. Partly due to this composition, acidic zeolites contain more or less superacidic sites as well.[2]

The similarity in the acidity of superacidic solutions and solids is reflected in the similar interpretation of the mechanism of hydrocarbon reactions taking place in the two media. This idea can be followed in the works of Poutsma[3] and Jacobs,[4] and later of Wojciechowski and Corma[5] which dealt with hydrocarbon transformations over zeolite catalysts.

Acidic sites required for the generation of carbocations are accommodated in the channels and/or cages of zeolites. Consequently, these centers are accessible only for those molecules of which the kinetic diameter is equal to or less than the pore openings. Therefore, fundamental differences exist between the mechanism of the hydrocarbon reactions in superacidic solutions and in zeolites. For acidic zeolite catalysts, a molecular sieving effect and shape selectivity appear very frequently, while these phenomena are missing in superacidic solutions.

The term carbocations includes various groups of compounds of different structures with a positively charged carbon atom. According to the classification of Olah, carbonium ions contain four- or five-fold coordinate positively charged carbon atoms. The simplest example of this type is the methonium ion (CH_5^+).[6]

In carbenium ions the positive charge is sited on a three-fold coordinate carbon atom. This group in-

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[†] This work is dedicated to Professor George Olah for the 5th anniversary of receiving the Noble Prize for his pioneering contribution to the chemistry of carbocations.
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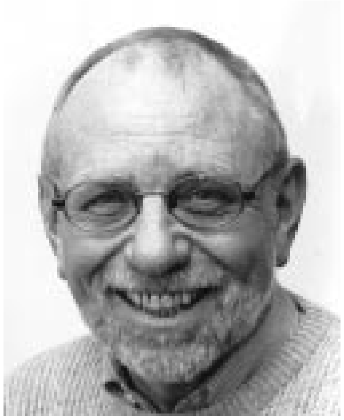
Imre Kiricsi was born in 1948 in Teglas, Hungary. He received his M.S. degree in Chemistry in 1972. The subject of his Ph.D. thesis (1975, supervisor Professor Pal Fejes) was the application of radio-gas chromatography in catalytic research. In 1986–87 he worked in the laboratory of Professor Horst Förster at the Physical Chemistry Institute of Hamburg University as an Alexander von Humboldt fellow. During the scholarship they proved the applicability of transmission UV-vis spectroscopy for the identification of surface intermediates generated from hydrocarbons and their derivatives in zeolites. In 1992, he was a visiting researcher at Eniricerche SpA, Milan, Italy. In this period he made some important contributions to the assignment of IR spectra of acidic zeolites, evidencing a new aluminum coordination generated upon heat treatment in acidic forms of zeolites. Later his interest turned toward pillared layer materials. His research group uncovered how mixed oxide pillars form and intercalate between smectite layers. In 1993, he obtained a full professorship at the Applied Chemistry Department. He is involved in environmental chemistry; in this framework he investigates the adsorption and reactions of chlorofluorocarbons on zeolites. Studies of adsorption and surface reaction induced Fermi resonance phenomenon show his theoretical chemical interest. Recently, he has been involved in research devoted to the preparation of inorganic nanotubes, including the catalytic production of carbon nanotubes. He has published over 150 scientific papers.

cludes alkyl carbenium ions formed, e.g., by interaction of alkenes with protons and alkenyl carbenium ions the generation of which can occur by interaction of protons and conjugated dienes or by hydride ion abstraction from olefins by Lewis acids.

Carbonium ions play a dominant role in high-temperature paraffin cracking, since they are the initiators for starting the cracking chain proceeding via complex ionic mechanisms. Alkyl carbenium ions are involved in the chain propagation of cracking, skeletal and double bond isomerization, and alkylation and oligomerization reactions. As this review is discussing the generation and transformation of alkenyl carbenium ions, for further information on the nature of carbonium and alkyl carbenium ions, the reader is referred to the work of Olah and Schleyer.[1,6]

Formation and transformations of alkenyl carbenium ions have been investigated in detail in superacidic solutions.[7] Alkenyl carbenium ions are generally the end products of most carbenium ion transformations in superacid systems.

After a brief summary of the role of alkenyl carbenium ions in the transformation of hydrocarbons in superacidic solutions, we shall discuss the participation of these ions in hydrocarbon conversions over zeolite or zeolite-like catalysts.

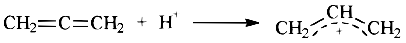


Horst Förster was born in 1932 in Döbeln, Germany. He studied chemistry at the University of Leipzig and graduated in 1957. His Diplom work concerned the thermal diffusion of high molecular weight polymers. From 1957 to 1961 he carried out research in the fields of solid-state chemistry and photochemistry under the guidance of Professor H. Staude at the Institute of Physical Chemistry. In 1961, he joined the University of Hamburg where he worked under the direction of Professor A. Knappwost on the kinetics of precipitation of superparamagnetic particles from alloys and received his Dr. rer. nat. degree in 1966. After his appointment as assistant, he turned to the field of heterogeneous catalysis where he built up a research group starting with studies on transition metal catalysts. Since 1974, investigations of elementary processes in zeolitic systems, e.g., fundamental studies on the interaction of simple probes like homonuclear diatomics, isomerization and cracking, formation of carbocations and -anions, and solid-state ion exchange, have become predominant. His main research interest was the application of surface vibrational and electronic spectroscopies assisted by supplementary techniques and theoretical work. In 1977, he became Professor at the University of Hamburg. From 1981 to 1987 and 1991 to 1995 he was the representative of the direction or elected director of the Institute of Physical Chemistry, respectively. Since 1988, he has been member of the DECHEMA committee “Zeolites”. In 1996 he was given an honorary doctorate by the József Attila University of Szeged. He is author or coauthor of about 170 scientific papers.

II. Formation and Reactions of Carbenium Ions in Superacidic Solutions

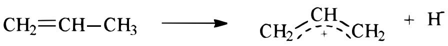
In this chapter we will outline the regularities observed in superacids and those which we regard as the important features of the formation and transformation of hydrocarbons over zeolites.

Generation of alkenyl carbenium ions can occur via protonation of di- and/or polyenes or hydride ion abstraction from olefins. The simplest examples are as follows:



$$CH_2{=}C{=}CH_2 + H^+ \longrightarrow CH_2{\overset{CH}{\overset{+}{\cdots}}}CH_2 \qquad (1)$$

and



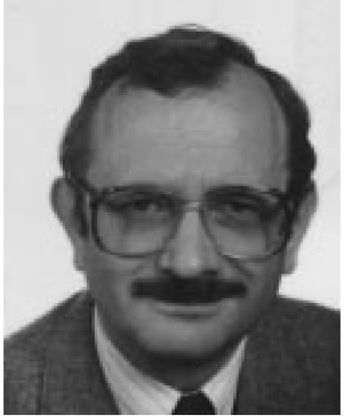
$$CH_2{=}CH{-}CH_3 \longrightarrow CH_2{\overset{CH}{\overset{+}{\cdots}}}CH_2 + H^- \qquad (2)$$

Reaction 1 takes place in Brønsted acidic media, while reaction 2 occurs in Lewis acidic media.

In general, solid acids contain both Brønsted and Lewis acid sites; therefore, reactions 1 and 2 can hardly be separately considered. In most hydrocarbon transformations, various carbenium ions form, cover the primary acid sites more or less completely, and themselves act as hydride ion abstraction centers.

Regardless of the origin of the carbenium ions, they may undergo any of the following processes: (i)

Gyula Tasi was born in Dorog, Hungary. He studied chemistry, as well as three semesters of biology, and received his diploma in chemistry in 1985 from József Attila University, Szeged, under the supervision of Professor I. Kiricsi and Professor K. Varga. Since 1985, he has studied the adsorption and transformations of small hydrocarbon molecules and their derivatives over zeolites using catalytic, spectroscopic, and theoretical methods. He finished his Ph.D. thesis at József Attila University of 1993 (under the supervision of Professor Fejes). At present, he is an Associate Professor at József Attila University. In 1990 and 1992 he spent several months as Visiting Researcher with Professor Förster at the University of Hamburg. From October 1995 to October 1996, he worked as an AIST research fellow with Professor Fujio Mizukami at the National Institute of Materials and Chemical Research (NIMC) in Tsukuba. Since April 1998, he has been working as a NEDO research fellow with Professor Mizukami (NIMC, Tsukuba). One of his main research interests concerns the theoretical study of the geometric, electronic, and thermodynamic properties of alkenyl carbenium ions.



Janos B. Nagy is a Professor at Facultes Universitaries Notre-Dame de la Paix, Namur, Belgium. His basic training was in physical organic chemistry. He made contributions to various fields of chemistry. Charge transfer complexes in solution were his first interest. He studied their spectroscopic behavior and their role in catalytic reactions including specific solvent effects. This led to the elaboration to the so-called Competitive Preferential Solvation Theory. His contribution to the study of chemical reactions in situ in the adsorbed state using ^{13}C NMR is important. The synthesis and characterization of various zeolites form a large part of his research field, especially the application of high-resolution solid-state multi-NMR techniques. He made an important contribution to the preparation and stabilization of monodispersed nanoparticles using microemulsions: metal, metal salts, and organic particles. Quite recently, he also started research in the promising field of fullerenes and fullerenic nanotubes. Coiled nanotubes were prepared for the first time in his laboratory.

charge or hydride transfer, (ii) skeletal isomerization, (iii) chain growth and/or shortening, and (iv) cyclization.

In the works dealing with carbenium ions, it is concluded that these ions can easily be formed from dienes (and/or polyenes) while from alcohols and other hydrocarbons they can be formed via alkyl carbenium ions. It was established that their formation takes place with difficulty from paraffins. Provided there is any observation of their formation, it is explained via generation of alkyl-type carbenium ions. Rosenbaum and Symons found that the ability of the generation of carbenium ions in sulfuric acid solution follows the order dienes > olefins > alcohols > paraffins.[8,9]

The influence of the composition of acidic solutions on the formation of carbenium ions from hydrocarbons and hydrocarbon derivatives was cleared up in the 1950s. It was established that the stability of carbenium ions increases with the acid strength.[10] Generally, 96% H_2SO_4 is sufficiently acidic for the direct observation of the tetraalkylated allyl cations.

From the results of IR spectroscopic investigations on the formation and rearrangement of alkenyl carbenium ions, Deno assumed that the band which appeared near 1530 cm^{-1} has to be assigned to the vibration of the $[\_\mathrm{C}\_-\_\ \mathrm{C}\_-\_\mathrm{C}\_]^+$ unit of the structure. It was concluded that the extinction coefficient of the vibration of this structural unit was quite large. Experimentally it was found that the intensity of the band at 1530 cm^{-1} attributed to alkenyl carbenium ions is approximately 10 times that of the C=O stretching vibration.[11]

Already at the beginning of the 1960s NMR spectroscopy was applied to investigate the generation, structure, and transformations of alkenyl carbenium ions.[12] Multinuclear NMR spectroscopy proved to be one of the most frequently used techniques for the study of the intermediates in hydrocarbon transformations irrespective of their generation either in acidic solutions or in solids.

Alkenyl carbenium ions can be detected due to the delocalized electrons in their structure by UV−vis spectroscopy.[13] The position of the band, characteristic for the alkenyl part of the carbenium ions, strongly depends on the degree of unsaturation, i.e., on the number of delocalized electron pairs. Sorensen found the following empirical correlation between the number of delocalized electron pairs and the position of the UV−vis band for the alkyl-substituted alkenyl carbenium ions:[14a]

$$(\mathrm{CH_3})_2\underline{-\mathrm{C}-\mathrm{CH}^+-[\mathrm{CH}-\mathrm{CH}]_n-\mathrm{C}-}(\mathrm{CH_3})_2$$

$$\lambda_{\mathrm{max}} = (330.5 + 65.6n)\ [\mathrm{nm}]$$

where $n = 0-4$ refers to the number of delocalized electron pairs.

Hafner established a similar correlation for phenyl-substituted alkenyl carbenium ions:[14b]

$$\mathrm{Ar}\underline{-[\mathrm{CH}-\mathrm{CH}]_n-\mathrm{CH}^+}-\mathrm{Ar}$$

$$\lambda_{\mathrm{max}} = (420 + 67n)\ [\mathrm{nm}]$$

where $n = 0-4$ refers to the number of delocalized electron pairs in the alkenyl part of the structure.

Using these equations, the absorption maxima can be estimated for mono-, di-, tri-, and tetraenyl carbenium ions generated in superacidic solutions.

In strong acidic solutions, the absorption maxima in the UV–vis spectra of alkenyl carbenium ions shift to higher wavelengths with increasing alkyl substitution. This feature is in accordance with the stability of these type of ions, i.e., it increases with the number and the chain length of the alkyl groups.[15]

The typical transformation of alkenyl carbenium ions with an open carbon chain is cyclization. The ability of alkenyl carbenium ions to take part in these reactions increases with increasing unsaturation, i.e., with increasing number of delocalized electron pairs.

In the next sections of this review, we will show that the behavior of alkenyl carbenium ions on solid acid surfaces, particularly on zeolites, is similar or, in some cases, identical to those observed in superacidic solutions.

III. Zeolites

A. Fundamentals of the Zeolite Structure

Zeolites are a well-defined class of crystalline alumino–hydro–silicates, with a framework structure composed of joined $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra. By definition, these tetrahedra are arranged such that the oxygen at each tetrahedral corner is shared with that of an identical tetrahedron containing either Si or Al in its center. The tetrahedra form cages and channels of molecular dimensions. This corner sharing forms an infinite lattice comprising identical building blocks, the unit cells, in a manner common to all crystalline materials.

These recurring units are the secondary building units and the simplest description of all known zeolite frameworks is an arrangement of eight linking secondary building units. However, they represent only the aluminosilicate skeleton and exclude the consideration of water molecules and cation siting within the cavities and channels of the framework.

The number of cations present in the pore system of zeolites is determined by the number of $[AlO_4]^{5-}$ units. This arises from the isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedra, causing a residual negative charge on the oxygen framework. These negative charges are compensated by the cations present during the synthesis and kept in the interstices of the structure upon crystallization. These cations can easily be exchanged for other cations.

In their hydrated forms, the cavities and cages of zeolites are filled with water. The extent and location of water molecules depends on the overall architecture of the zeolite, such as the size and shape of the cavities, channels, and the number and nature of cations present in the structure. This water can easily be removed by simple heating of the zeolite above several hundred degrees Celsius.

The ion-exchange property of zeolites, which allows the replacement of cations held in their cages or channels by ions present in the external solutions or melts, has been intensively studied and is now utilized on a large scale in detergent manufacturing. In principle, every cationic form of the elements in the periodic table can be introduced into a zeolitic framework.

The other important characteristic of zeolites is their molecular sieving property. The apertures of the pores are of a size being able to selectively take up some molecules into their pore structure while rejecting others on the basis of their large effective molecular dimensions. Pore diameters and number of tetrahedra forming the pore openings of some selected zeolites are listed in Table 1.

Due to their distinguished catalytic activity, zeolites are of particular interest for the chemical industry. Several monographs[17–22] and review articles have been published[23–25] about zeolite chemistry and catalysis. They are recommended for more insights into these topics. In the *Special Issue of Microporous and Mesoporous Materials* standard, verified synthesis methods of numerous zeolites have been described.[26]

B. Acid–Base Properties of Zeolites

A solid acid is capable of converting an adsorbed basic molecule into its conjugate acid form. Therefore, the acid site is able to either transfer a proton from the solid to the adsorbed molecule (this type of acid center is called a Brønsted site) or transfer an electron pair from the adsorbed molecule to the solid surface (this type of acidity is known as Lewis acidity). Generally, both types of acid sites are simultaneously present in zeolites.

For the generation of Brønsted acid sites in zeolites, such OH groups should be formed on the surface which are able to transfer protons to the adsorbed molecules. This requires OH groups with loosely bound protons. Every procedure is suitable to generate Brønsted acidity which leads to the formation of surface OH groups of the previously mentioned nature.

Surface hydroxyl groups can be generated in zeolites by different methods: (i) Direct ion exchange of zeolites with acids such as diluted HCl, HNO_3, acetic acid etc. Using this method only zeolites with a high Si/Al ratio may be transformed into their protonic forms. (ii) Furthermore, Brønsted acidity is introduced by exchanging the nonframework cations (M^+) with ammonium or alkylammonium ions followed by calcination,[4,19] (iii) dissociation of water molecules under the influence of the strong electrostatic field of multivalent cations, and (iv) reduction of transition and noble metal ion containing zeolites with hydrogen, resulting in Brønsted acid sites and metal particles in the zeolite hollows.

The simplest way for the generation of Lewis acid sites is to prepare the metal ion forms of zeolites since each metal ion acts as a Lewis site due to its electron pair abstraction ability. Consequently, applying the method described under iii at high temperature (above 800 K) and presuming a high thermal stability of the zeolite considered, at complete dehydration the bare multivalent cations compensate for the negative charge of the framework. In practice, this situation can very rarely occur since either the thermal stability of the zeolite is appropriate (for high Si/Al zeolites) and then the distance between the negative charges is too far to allow such arrangement or there are

Table 1. Classification of Some Zeolite-Type Materials by Their Structural Characteristics[a]

Typical material (code)	Symmetry	Channel dimensions	Typical unit cell content	Remarks
MCM-41	hexagonal			meso-
MCM-48	cubic			porous
Cloverite (CLO)	cubic	<100> **20** 1.32 x 0.4 | <100> **8** 0.38	$Ga_{96}P_{96}O_{372}(OH)_{24}$	ultra
VPI-5 (VFI)	hexagonal	[001] **18** 1.21	$Al_{18}P_{18}O_{72}$	large
$AlPO_4$-8 (AET)	ortho-rombic	[001] **14** 0.79 x 0.87	$Al_{36}P_{36}O_{144}$	pores
Beta (BEA)	tetragonal	[001] **12** 0.55 x 0.55 ↔ <100> **12** 0.76 x 0.64	$Na_nAl_nSi_{64-n}O_{128}$ n<7	
Faujasite (FAU)	cubic	<100> **12** 0.74	$Na_{58}Al_{58}Si_{134}O_{384}$	large
Mazzite (MAZ)	hexagonal	[001] **12** 0.74 | [100] **8** 0.34 x 0.56	$Na_{10}Al_{10}Si_{26}O_{72}$	
$AlPO_4$-5 (AFI)	hexagonal	[001] **12** 0.73	$Al_{12}P_{12}O_{48}$	
ZSM-12 (MTW)	monoclinic	[010] **12** 0.55 x 0.59	$Na_nAl_nSi_{28-n}O_{56}$ n<2.5	
Mordenite (MOR)	ortho-rombic	[001] **12** 0.65 x 0.7↔ [010] **8** 0.26 x 0.57	$Na_8Al_8Si_{40}O_{96}$	pore
ZSM-18 (MEI)	hexagonal	[001] **12** 0.69↔⊥ [001] **7** 0.32 x 0.35	$Na_nAl_nSi_{34-n}O_{68}$ n=2.1-5.7	
Ferrierite (FER)	ortho-rombic	[001] **10** 0.42 x 0.54↔ [010] **8** 0.35 x 0.48	$Na_6Al_6Si_{30}O_{72}$	medium
ZSM-5 (MFI)	ortho-rombic	[010] **10** 0.53 x 0.56↔ [100] **10** 0.51 x 0.55	$Na_nAl_nSi_{96-n}O_{192}$ n<27	
ZSM-11 (MEL)	tetragonal	<100> **10** 0.53 x 0.54	$Na_nAl_nSi_{96-n}O_{192}$ n<16	pores
Chabazite (CHA)	trigonal	[001] **8** 0.38 x 0.38	$Na_{12}Al_{12}Si_{24}O_{72}$	small
Sodium A (LTA)	cubic	<100> **8** 0.41	$Na_{12}Al_{12}Si_{12}O_{48}$	pores

[a] Under the common name of the zeolite their structural codes are given in brackets. Interconnected channels are separated by a double arrow (↔), while the vertical bar (|) means the lack of access from one channel to the other. The figures in bold denotes the number of oxygens in the pore apertures. ⟨100⟩ means channels parallel to all crystallographically equivalent axes of the cubic structures. [001] means the channel parallel to [001]. For the sake of simplicity, the compositions are given for sodium forms, water and organic contents are neglected.

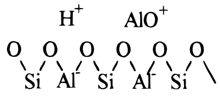
negative charges on every second atom of the framework (e.g., for A type zeolites where the Si/Al = 1) but the thermal stability of the zeolite is low.

Generally, heat treatment influences the state and localization of aluminum in zeolites. Upon heat treatment, the Brønsted acid centers are converted by dehydroxylation into Lewis acid sites with release of water. When the temperature of treatment is lower or equal to 573 K, essentially Brønsted acid sites are generated by calcination of the ammonium forms of zeolites. At higher temperatures, however, e.g., at 773 K, dehydroxylation takes place resulting in the formation of one Lewis site from two Brønsted sites. This theoretical model shows the presence of two Lewis acid sites (trigonal Al species and positive Si^+) and a Lewis basic site (tetrahedral negative Al species). Actually, the structure reorganizes and an aluminum ion leaves the framework, compensating for the negative charge on the adjacent aluminum as AlO^+. Jacobs and Beyer suggested this extraframework AlO^+ species to be the true Lewis acid site.[27]

Acids with a Hammett constant $-H_o > 12$, i.e., with a value referring to 100% sulfuric acid, are regarded as superacids in solution. The strength of Brønsted acids can be increased by chemical modification, e.g., by replacing hydroxyl groups for fluoride; for H_2SO_4, the stronger derivative is HSO_3F ($-H_o$=15). The second method consists of the mixing a strong Lewis with a weaker Brønsted acid such as

$$2HF + SbF_5 = H_2F^+ + SbF_6^-$$

where the Hammett constant depends on the ratio of the components. The second method can be easily applied for zeolites. The acidity of Brønsted centers can be enhanced by modification of their local environments via introducing Lewis acid centers into adjacent positions. Superacidity can arise from a synergetic interaction between both types of acid sites. A simplified representation of this is as follows:



The generally used techniques to characterize zeolite acidity are temperature-programmed desorption (TPD) of preadsorbed bases, particularly ammonia or pyridine, the indicator method, microcalorimetry, and IR spectroscopy of adsorbed probe molecules such as pyridine, CO, or H_2. The various techniques of multinuclear NMR spectroscopy become a more frequently applied method as well. From the TPD pattern, the concentration of acid sites can be determined and their strength characterized by the temperature of the desorption peak maximum.[28] In the indicator method, bases of suitable size are used to neutralize the acid sites while the change in the color of indicators shows the equivalence of the acid−base pairs.[28] Microcalorimetry gives quantitative data of the number and strengths of acid sites.[29,30] IR spectroscopy is used to examine either the variation of the OH stretching frequency of different zeolites or the influence of adsorption on characteristic frequencies of base molecules interacting with Brønsted and Lewis acid sites.[31−33] The disadvantage of this technique is that the accurate determination of the extinction coefficients necessary for quantitative analysis is not free from difficulties.

Multinuclear NMR identifies the different OH groups either directly by ^{1}H NMR or indirectly using ^{13}C, ^{15}N, and/or ^{31}P NMR of adsorbed bases, such as pyridine, ammonia, acetonitrile, carbon monoxide, nitrous oxide, trimethyl phosphine.[34−39] Recently, new, highly sophisticated NMR techniques have been used for the quantitative determination of zeolite acidity. From the CPREDOR (cross-polarization rotational echo double resonance) spectra, the molecular surrounding of strong and weak acid sites has been determined. It was found that protons of strong Brønsted sites are located near Q^4(nAl) sites where $n = 1$, while near those where $n > 1$ bonds protons of the weak acid sites.[40−42] The ^{1}H/^{27}Al, ^{15}N/^{27}Al, or ^{31}P/^{27}Al TRAPDOR (transfer of population in double resonance) NMR spectroscopic studies led to the more precise determination of zeolite acidity and bond distances between aluminum and the corresponding atom of the adsorbed base molecule.[43−45]

In the discussion of zeolite acidity, the results of theoretical calculations have become increasingly important. From proton mobility calculations, the acid strength,[46,47] from density functional studies the acidity order of isomorphously substituted zeolites,[48] have been determined. A part of the theoretical works aimed at the description of the interaction of water with the acid sites.[49−54] From these studies, an atomic description of the mechanism of proton mobility, in accordance with the experimental results, was suggested. Summarizing, we conclude that there is still room for improving both the experimental techniques and the theoretical methods in order to describe the actual acidity of a zeolite catalyst operating around 700 K in an industrial reactor.

IV. Experimental Techniques for Detection of Alkenyl Carbenium Ions in Zeolites

A. IR Spectroscopy

Of the battery of physical methods, infrared spectroscopy has proved to be a very powerful and, therefore, most frequently applied technique for the characterization of zeolites and the pursuit of processes on their internal surface. Being of vibrational origin, IR spectroscopy provides primarily structural data such as molecular symmetry, geometry, and bonding. In time-resolved experiments, transient surface species can be monitored, with possible intermediates detected that are involved in the transformations of adsorbed molecules.

Infrared spectroscopy is especially advantageous in surface studies as (i) due to its rather high-energy resolution, the measurements of small frequency shifts and band shape analysis become feasible, (ii) the frequency of adsorbed species is highly sensitive to the kind of interaction with the surface, (iii) there is a rigorous correlation between the spectra of adsorbed species and of molecules of a similar well-known structure, and (iv) the experiments can be carried out over a wide range of pressures, i.e., the system can be studied under realistic conditions.

From the various techniques, the transmission technique is most widely applied, accomplished by simply measuring the transmittance of infrared radiation passing through a self-supported sample disk of about 5−8 mg/cm^2 thickness. On one hand, IR spectroscopy allows the direct observation of the hydroxyl groups in the range from 3750 to 3500 cm^{-1}, mostly responsible for the Brønsted acidity and their attack by basic molecules. On the other hand, due to the strong framework vibrations of the zeolite, the range <1200 cm^{-1} with the exception of some ‘optical windows’ in the far-infrared is nearly completely obscured. In general, transmission of finely divided solids means performing spectroscopy at low signal level is still not routine and requires much more effort compared to ordinary samples. The transmission technique in the presence of finely divided solids suffers from the disadvantage that the zeolite sample is subjected to a quite drastic compression which might lead to serious damage of the structure.

A less frequently applied alternative is diffuse-reflectance infrared spectroscopy. This technique is favored when strongly scattering samples are analyzed. In this case, from the backscattered radiant flux using the Schuster−Kubelka−Munk function a spectrum is obtained. In most cases, this qualitatively resembles an absorbance spectrum. Compared to transmission, according to the Kubelka−Munk theory, diffuse scattering is more sensitive in the near-infrared range while its advantage in the fundamental region is not so great.

A second alternative is infrared photoacoustic spectroscopy where the absorption of modulated light is converted by nonradiative processes to heat pulses, resulting in a pressure wave within the sealed cell, which is detected by a sensitive microphone. The advantage of this method, in general, is the simple way of sample preparation, and it is the last resort to record spectra of opaque samples which cannot be obtained by other techniques. The disadvantage is that special care and efforts have to be taken during spectral acquisition.

Only rarely applied is infrared emission spectroscopy which requires the sample to be at higher temperature than the detector and suffers from experimental difficulties such as very low energy, spurious radiation, temperature gradients, etc. The preferred application would be in situ experiments with samples at higher temperatures.

Examining the plethora of methods, it might be stated that none of these techniques is ideal for all problems. A method has to be selected to fit the problem, the detailed experimental conditions, the sample type, and the information desired. In any case, the application of several complementary methods is recommended.

The spectrometer design for running spectra is not of crucial importance. Dispersive or Fourier transform instruments may be used. The latter are superior due to (i) the throughput or Jacquinot advantage, i.e., the larger light gathering power on account of the lack of slits, (ii) the multiplex or Fellgett advantage, i.e., the simultaneous recording of all frequencies resulting in an improvement of the signal-to-noise, and (iii) the Connes advantage, i.e., the high wavelength accuracy. To our knowledge, today no instrument manufacturer offers dispersive IR spectrometers.

Infrared spectra are recorded using homemade optical cells furnished with infrared transparent windows allowing (i) the pretreatment of the sample usually in high vacuum at elevated temperature and (ii) monitoring the adsorbate pressure and temperature. For transmission experiments, both glass and all-metal cells are customary. For the pretreatment of the sample in the glass cell, a self-supporting wafer of about 5−8 mg/cm^2 thickness is lifted from the optical part into a compartment surrounded by a hinged tubular oven, while in the metal cell the sample holder is inserted into a cylindrical heating coil.[55] Examples of cell constructions can be found in some older monographs and reviews[56−59] or in the actual literature. A review of UHV infrared cells has been published elsewhere.[60] Suitable commercial cells are only available for the diffuse reflectance technique.[61]

For the formation of carbocations, the presence of surface acid centers is a prerequisite. While Brønsted sites give rise to the formation of carbonium ions from paraffins, alkyl carbenium ions from olefins and alkenyl carbenium ions from dienes, on Lewis acid sites alkyl carbenium ions from paraffins, and alkenyl carbenium ions from olefins are generated by hydride ion abstraction. By means of IR spectroscopy, the Brønsted sites can directly be observed in the OH stretching range, although more favorably sensitized by probe molecules. The Lewis centers can only be determined by using suitable probes, mainly fairly strong or weak bases such as pyridine, ammonia, quinoline, pyrrole, pyrrolidine, carbon monoxide, hydrogen, and nitrogen.[62−64] Combined with TPD or calorimetry, the different acid centers may be distinguished and their amount and acid strength estimated.

B. UV−vis Spectroscopy

In general, electronic spectroscopy should be superior to infrared spectroscopy for the observation of surface species due to the larger absorptivity and the lack of interfering adjacent bands. But a serious drawback is that only electronic transitions can be traced, and rovibrational fine structure frequently remains unresolved. Therefore, no structural information can be extracted from such spectra.

The principal prerequisite is the presence of chromophores with transitions in the spectral ranges accessible to commercial spectrometers. This excludes, e.g., alkylcarbocations from spectral observation, while unsaturated carbenium ions can be detected due to their $\pi-\pi^*$ transitions.

Although, in principle, Fourier transform spectrometers are applicable to the UV−vis region, there is not much use of them in this spectral region as some FT advantages get lost, e.g., the multiplex advantage is canceled in the case of shot noise and actually becomes a multiplex disadvantage in the case of flicker noise.[65] On the other hand, the less structured broad bands do not require the high resolution and the high wavelength accuracy provided by interferometers. Thus, in the UV−vis region, exclusively dispersive spectrometers are used.

Nowadays by means of computers, modern spectrometers have become substantially improved, e.g., by facilities such as microprocessor control, self-checking routines, rapid scanning, and visual display systems as well as opportunities for data processing. Today this follow-up treatment of acquired data has become an essential part of the necessary efforts. Baseline corrections, band sharpening by deconvolution, and signal-to-noise enhancement are some examples. Overlapping bands, weak sidebands, and shoulders can be detected and localized by forming the derivatives of the spectrum.[66] The same is valid for the infrared range.

On powdered samples, scattering causes severe losses in transmittance. According to theory, the scattered light increases with the fourth power of the wavenumber. Therefore, in the UV−vis range it should be more advantageous to replace the transmission by the reflectance method. However, from comparison of both methods, using zeolites Sendoda et al.[67] gave a preference to the transmission mode, followed by other research groups.[68,69] The advantages of the transmission technique are a demand for a lower amount of sample, an easier sample handling concerning degassing and admission of adsorbate, no need for an extra diffuse reflectance accessory, and the omission of data conversion into the Schuster−Kubelka−Munk function. The typical experimental equipment for transmission studies on zeolites is shown in Figure 1.[68]

The zeolite powders are applied as self-supporting wafers as mentioned for IR spectroscopy, placed in a gold foil frame, and inserted into a quartz cell fused to a Conflat flange and connected to a vacuum/dosage system. Heat treatment is accomplished by surrounding the cell by a tubular oven while the spectra are recorded at room temperature.

The majority of zeolite systems has been investigated applying diffuse reflectance spectroscopy (DRS). In the case of both scattering and absorption, both

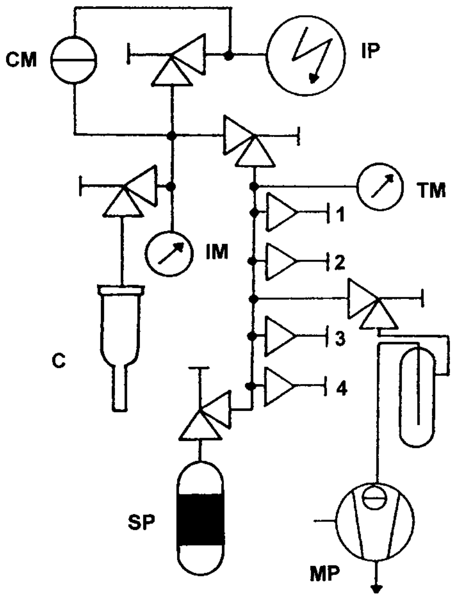


Figure 1. Schematic representation of the experimental equipment. C, quartz cuvette; IM, ionization gauge; CM, capacitance manometer; IP, ion pump; TM, thermocouple gauge; SP, sorption pump; MP, mechanical pump; 1−4 inlet valves. (Reprinted with permission from ref 68. Copyright 1983 The Royal Society of Chemistry.)

effects have been unified in the Schuster−Kubelka−Munk equation which replaces the Bouguer−Lambert−Beer law.

For performing DRS, a diffuse reflectance accessory has to be applied, the heart of which is an integrating sphere coated with a highly reflective material which collects the scattered radiation and leads it to the detector. As with IR spectroscopy, the sample cells must allow outgassing of the zeolite at elevated temperatures and controlling the admission of adsorbates. With the already mentioned exception, they are exclusively homemade, the constructions of which can be found in the respective literature.[70,71]

As an alternative in UV−vis, photoacoustic spectroscopy has also been applied to zeolite systems, but up to now not to the observation of carbenium ions.

C. In Situ NMR Spectroscopy

In situ NMR spectroscopic experiments are performed on real catalyst samples using sufficiently high temperatures, pressures, and reactant loadings.[72] In the absence of high concentrations of paramagnetic species or metal particles with magnetic properties, high-resolution magic-angle-spinning spectra of adsorbed species are easy to obtain. The basic NMR spectrometer for an in situ study differs little from a standard instrument for solids.[72] Suitable NMR experiments were used to probe the structures of organic adsorbates (^{13}C), Brönsted acidic sites (^{1}H), nuclei associated with active sites (e.g., ^{27}Al), other nuclei composing the framework (e.g., ^{29}Si or ^{31}P), or cations ion-exchanged into the catalyst or present as promoters.[72−77]

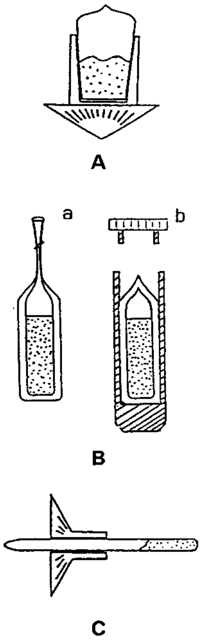
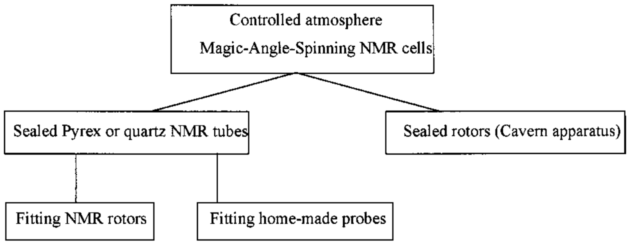


Figure 2. NMR probes. (A) NMR cell designed to fit Andrew-Beams rotors. (B) NMR tube insert incorporating sample (a), sealed NMR cell fitting double-bearing MAS NMR rotor. (C) NMR cell fitting directly into homemade probes. (Reprinted with permission from ref 112. Copyright 1994 Elsevier Science.)

The following block diagram illustrates the different experimental sets well for measuring adsorbed reactants, intermediates, and reaction products under static conditions:



The first experiments were carried out in sealed capsules fitting NMR rotors. The sets for Andrew−Beam rotors and the high-speed double-bearing MAS rotors are illustrated in Figure 2a and b.[78−80]

In all these sets the tubes have to be perfectly balanced, and hence, the sealing has to be extremely carefully done. Homemade probes are also used, the advantage of which is that the heavy spinner can accommodate a less balanced NMR tube and, hence, the sealing does not have to be carefully done (Figure 2c).[80−82] The disadvantage of this system is that the spinning rate is usually lower (2.5−4 kHz).

Two general experimental protocols are followed. If the sample is sealed in a glass ampule, it is possible to alternate sample heating steps outside the probe with spectroscopic characterization steps at room temperature.[72,79,82] The second general protocol uses variable-temperature MAS probes to observe the reaction while in progress.[72,83] Commercial probes are available from several vendors with temperature ranges from 77 to 523 K or higher.

A possible disadvantage of glass ampules is that they cannot be reopened for the subsequent addition or removal of reagents and products in more elabo-

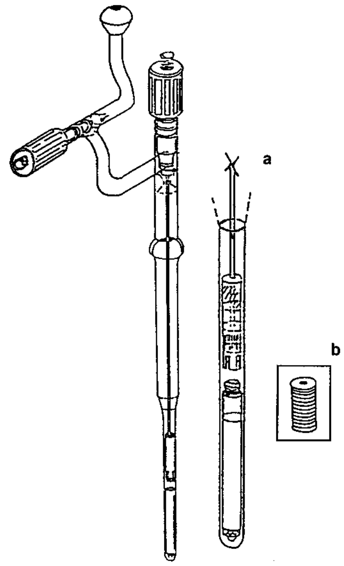


Figure 3. Second-generation CAVERN (cryogenic adsorption vessel enabling rotor nestling) apparatus: left diagram shows the CAVERN apparatus prior to capping; right diagram shows an enlarged view of the apparatus lower section after capping (a) and of Kel-F cap used for sealing the sample at cryogenic temperatures (b). (Reprinted with permission from ref 112. Copyright 1994 Elsevier Science.)

rate in situ protocols. Figure 3 shows a simple preparation device, the CAVERN apparatus,[72,84] which permits the rotor to be sealed or unsealed in the vacuum line to facilitate multiple reagent adsorption stages.

The rotor design depicted in Figure 2 is based on a zirconia tube which tolerates temperatures between 77 and 673 K and plastic components on either end that are kept close to ambient temperature during high- or low-temperature experiments.[72,84]

Very recently a novel method has been reported on NMR studies of heterogeneous catalysis providing information on surface species generated under actual reaction conditions. The pulse–quench catalytic reactor operates as a standard microreactor with provision for continuous and/or pulse introduction of reactants and GC analysis of volatile products leaving the reactor.[85,86] The most significant feature is the provision for rapidly switching (in 100–200 ms) the gas stream flowing over the catalyst bed to cryogenically cooled nitrogen. The catalyst cooled to room temperature is transferred into the zirconia rotor in a drybox, followed by sealing and recording the NMR spectrum. The advantages of this method are (i) it tests exclusively the adsorbed phase since no reactive gas is present in the rotor and (ii) the volatile product formed over the catalyst is simultaneously analyzed by GC. However, very careful experimental work is required to exclude contamination of the catalyst by air.

For quantitative measurements, NOE (nuclear Overhauser effect) suppressed spectra (obtained by so-called inverse gated experiments) are required, because ^{13}C MAS NMR is customarily performed with ^{1}H decoupling to remove line broadening arising from heteronuclear dipolar coupling. For very mobile physisorbed species, it is sometimes possible to observe scalar coupling patterns in the absence of decoupling.[87]

One characteristic of in situ NMR experiments is that there is typically a wide range of correlation times characterizing molecular motion. Some species will be essentially immobile as a result of strong chemisorption on the catalyst surface or physical entrapment.[72] Other species may reside exclusively in the gas phase or may be partitioned into adsorbed and gas-phase populations in slow exchange on the NMR time scale owing to diffusion constraints. One of the practical consequences of this wide variation in dynamics is that ^{1}H–^{13}C cross-polarization (CP)[88] spectra may reflect a corresponding distribution of enhancements and thus may be only semiquantitative.[72] The use of ^{13}C-labeled compounds does not necessitate the CP enhancement, and so these difficulties can be avoided.

The accuracy of ^{13}C chemical shifts may be established to within 1 ppm or better by external referencing, and this figure may be further improved sometimes by adding a suitable internal standard, such as methane, which is not strongly adsorbed by the catalyst.[72,89] The volume magnetic susceptibility corrections due to the use of an external reference are small and can be frequently neglected. This is, however, not the case for ^{1}H chemical shifts, as the chemical shift range of protons is much smaller.[89] The ^{13}C MAS line widths of species bound to the framework of zeolites are usually not more than 5 ppm. Weakly adsorbed species typically have line widths of 1 ppm or less.[72] The ^{13}C isotropic chemical shifts of adsorbates in zeolites are generally within 3 ppm of their corresponding values in solution. Thus, in many cases, one can use ^{13}C chemical shifts from solution to assign MAS NMR spectra of products formed during in situ experiments.[72,89]

V. Generation and Transformations of Alkenyl Carbenium Ions in Zeolites

A. Alkenyl Carbenium Ions from C_2 Hydrocarbons

Generation of alkenyl carbenium ions over zeolites from ethane should take place at high temperature since these ions are assumed to be the intermediates in the low-paraffin-to-aromatics process.[90] Experimental observation of these ions in this transformation is very difficult due to the high temperature (above 573 K the IR spectra of the adsorbed species are obscured very much by the self-emission of the zeolite pellet or powder). Actually, their formation requires the previous formation of C_4 intermediates, and for formation of an allyl carbenium ion, a carbon chain of at least three carbon atoms is necessary.

Ethene transforms to primary carbenium ions on acidic solids involving the generation of hydrogen-bonded complexes as a first step.[91,92] This complex can be identified by OH bands generally shifted into the 3200–3300 cm^{-1} range.[93–95] The carbenium ions formed take part in fast oligomerization reactions with further ethene molecules giving ionic surface species with C_4, C_6, or C_8 carbon chains.[96] These surface alkyl species can leave the surface as olefins with back-donation of the proton to the solid. This

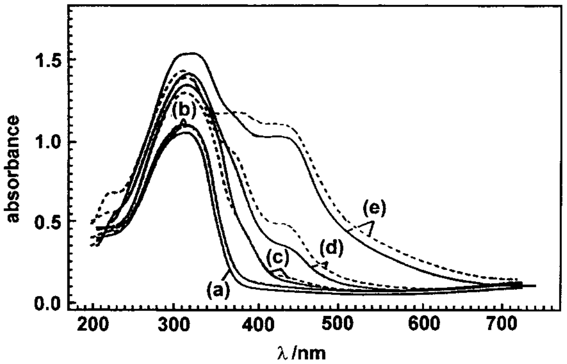


Figure 4. UV−vis difference spectra of ethene-loaded zeolite HZSM-5 (denoted as CAZ 49, thickness of the wafer is equal to 10.0 mg cm^{-2}, reactant stream 20 cm^3 min^{-1} of ethene (5 vol. %) in nitrogen; time on stream 1 h. Reaction temperatures: (a) room temperature; (b) 373 K; (c) 473 K; (d) 523 K; and (e) 573 K; (−) in situ, (- - -) ex situ measurements (where the volatile products were analyzed). (Reprinted with permission from ref 100. Copyright 1992 The Royal Society of Chemistry.)

reaction route leads to compounds of straight or branched carbon chains, which is determined by the pore structure of the zeolite. Not exclusively alkyl but also alkenyl type carbenium ions may be formed in secondary reactions that parallel the main transformations even at room temperature, as shown independently by Laniecki and Karge and Kazanskii et al. for ethene adsorbed on dealuminated mordenite (this means that the aluminum content of mordenite was decreased, preserving the structure) and HZSM-5 zeolites, respectively, where UV−vis bands characteristic of them around 300 nm increased in intensity with contact time.[97,98] The simplest alkenyl carbenium ion, the allyl cation, has three carbon atoms in the chain. Therefore, ethene first should be oligomerized to form a carbenium ion of this type. This was first proved by Garbowski and Praliaud.[99] With increasing temperature, additional bands were found at 375 and 440 nm, as can be seen on the spectra of ethene adsorbed on zeolite HZSM-5 by Melsheimer and Ziegler (Figure 4).[100]

The explanation of the secondary transformations of ethene including oligomerization, aromatization, and cracking at moderate and high temperature is a point of discussion even for authors using the same type of zeolite.[101−103] Melsheimer's discussion accounts not only for carbenium ions of open chain but also for diphenyl−methyl and/or alkylcyclohexadienyl-type species.[100] On the other hand, Zecchina et al. concluded no space is available for species larger than "*tert*-butyl residues" and that they might be accommodated only in the channel intersections.[104] The average carbon number for the oligomers in the channels of HZSM-5 zeolites varies over a wide range, and the role of Brønsted and Lewis acid sites is also unclear, although Derouane et al., using ^{13}C NMR measurements, showed that oligomerization takes place fast even below room temperature.[105,106]

Adsorption and reactions of acetylene over HZSM-5 zeolite were recently studied by Zecchina et al.[107] The authors suggest that both the formation of $C_2H_3^+$ ions and the polymerization of acetylene are slow processes at room temperature. For $[C_{2n}H_{2n+1}]^+$ (n = 1,2,...) carbenium ions, when $n = 1$ this moiety has no unpaired electrons and the positive charge is localized. When $n = 2$ or larger, the charge is delocalized. The authors assigned the IR bands due to the double bond as follows: bands at 1702, 1640, 1580, and ca. 1500 cm^{-1} are characteristic for monomer, dimer, trimer, and polymer species, respectively. The IR spectra presented show a very intense and broad band around 1500 cm^{-1} characteristic of polymeric carbenium ions. The UV−vis spectra of the adsorbed species exhibit highly intense bands around 500 nm and only weak absorptions around 300 nm attributed to the monoenyl carbenium ions.[97] The spectrum taken 5 min after loading the sample with acetylene at room temperature shows the presence of polymeric carbenium ions absorbing around 500 nm. On the basis of this experiment, a slow polymerization step is hardly understandable.

Haw et al. came to the opposite conclusion on the basis of ^{13}C in situ solid-state NMR studies.[108] They found that acetylene did not react at room temperature. The temperature had to be raised to more than 473 K in order to find any transformation. Accordingly, they propose vinyl alkoxy species, not carbenium ions, are formed during chemisorption of acetylene on both HY−FAU- and HZSM-5-type zeolites.

Gorte's group concluded from static and MAS ^{13}C NMR spectra of acetylene chemisorbed and reacted over HZSM-5 zeolite that the surface species containing aliphatic and olefinic carbon atoms characterized by resonances at 35 and 135 ppm, respectively, were relatively immobile and their formation was associated with the Brønsted acidity of the zeolite.[109] An opposing opinion is that of Dutta and Puri, who assumed Lewis acid sites to be required for polymerization of acetylene over transition metal ion-exchanged faujasite-type zeolites.[110]

From the discussion, it is clear that the experimental findings, as well as their interpretations, are ambiguous as to formation of carbenium ions, oligomerization, or polymerization of acetylene over acidic zeolites.

B. Alkenyl Carbenium Ions from C_3 Hydrocarbons on Various Zeolites

Activation of propane over zeolites generally requires high temperatures above 673 K even if dehydrogenation components are present on the catalyst. In this process, dehydrogenation or cracking takes place as the first elementary reaction, as suggested by Olah.[6] Over acidic zeolites olefins formed in this first reaction step may undergo oligomerization or inter- and intramolecular hydride transfer leading to di- and/or polyenes, the further transformation of which results in the appearance of aromatics. This reaction route operates in the Cyclar process for the conversion of inferior C_3−C_4 paraffins into aromatics and hydrogen.[111] As previously mentioned for ethane, the detection of alkenyl carbenium ions at high temperature is difficult; consequently, there are no in situ experimental data either by UV−vis−IR or NMR spectroscopy to indicate their formation. Ivanova and Derouane carried out in situ ^{13}C NMR measurements and found that over gallium-modified

HZSM-5 (Ga/HMFI, zeolite was prepared by heat treatment of the intimate mixture of Ga_2O_3 and HZSM-5) zeolite, a scrambling of the carbon atoms of propene took place after 5 min of reaction at 573 K. The result was interpreted by the formation of a pseudocyclopropane intermediate.[112] Resonances appearing in the 120−140 ppm range were assigned to alkylaromatic compounds. Although for the mechanism formation of alkyl carbenium ions via dehydrogenation steps was proposed, no experimental evidence was found for their existence in the zeolite pores.

Numerous data have been published in the literature on the transformation of propene in zeolites, and a wide variety of experimental techniques have been applied to produce detailed information about the elementary steps of this reaction.[93,94,113] The conclusions can be summarized as follows: (1) Upon adsorption of propene on zeolites, a π complex is formed involving the C=C bond of propene and the acid site of the zeolite.[114,115] (2) Chemisorption of propene takes place on both Brønsted and Lewis acid sites, generally present in zeolites, resulting in the formation of $C_3H_7^+$ and $C_3H_5^+$ carbocations as primary surface species.[116,117] (3) Oligomerization of propene is a very fast process in which both types of acid sites are involved. However, the role of Brønsted acid sites is more important.[118−125] (4) Desorption and/or decomposition of oligomers, formed from several C_3 units and consisting of more or less branched carbon chains, are detected above 400 K, leading to a paraffin-rich mixture of hydrocarbons larger than C_3.[126−130] (5) Depending on the reaction temperature, formation of aromatics and/or polynuclear aromatic compounds are detected or assumed, and it is also supposed that these transformations produce coke, resulting in the deactivation of zeolite catalysts.[119,131−133] (6) In some papers the formation of radicals and/or radical ions have been reported upon interaction of propene with zeolites.[134−136] (7) The generation, detection, and role of alkenyl carbenium ions in oligomerization as well as in hydrocarbon transformation is still a contraversial subject. Detection of alkenyl carbenium ions by direct observation of the $\pi-\pi^*$ transitions in the UV−vis region without disturbing adjacent bands makes this type of spectroscopy more attractive than IR spectroscopy. However, information which can be obtained only by the IR technique is indispensable for deriving the structure of the surface species. As has been shown, oligomerization of alkenes can be followed by monitoring the disappearance of the C=C double bond or the formation of CH_2 and/or CH_3 groups.[93,137] The frequency of the C=C stretching mode of propene is sensitive to the type of the nonframework cation and has been observed in the range 1610−1650 cm^{-1}.[138] On HZSM-5, a weak band at 1641[139] or 1628 cm^{-1} [104] could be observed in the spectra recorded subsequently upon contact with propene while this band was absent in those taken after longer contact times or after thermal treatment. It is likely that oligomeric carbenium ions with chains of six and nine carbon atoms are present in the zeolite pore system, as suggested by Grady and Gorte, who found no propene in the desorption product of surface species formed from adsorbed propene.[140] Provided the surface is covered by oligomers, present as carbenium ions, and when it is true that the bands in the 1500−1540 cm^{-1} range are due to intermediate surface-alkene π complexes,[141] this band should have been observed shortly after propene admission, which was not the case.

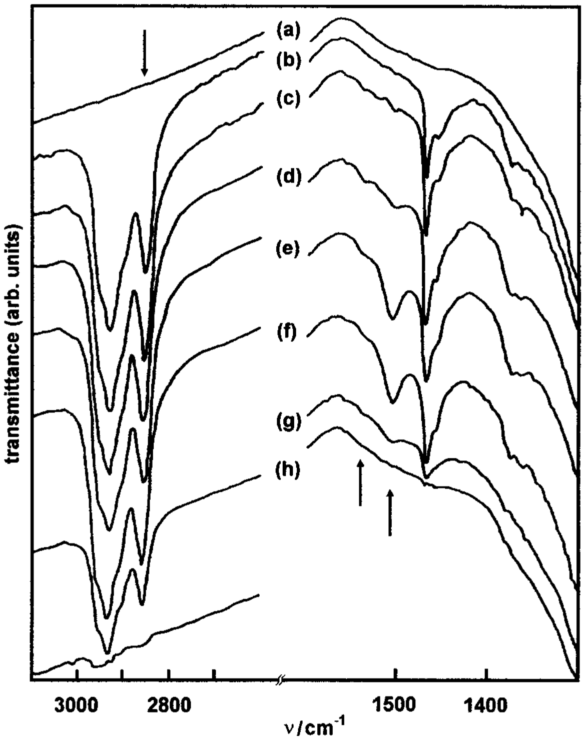


Figure 5. Infrared spectra of propene adsorbed on zeolite HZSM-5/870: (a) background, (b) 5 min after admission of 1.33 kPa of propene at beam temperature, (c) 3 h at 340 K, (d) 1 h at 370 K, (e) 1 h at 420 K, (f) after evacuation at 370 K, (g) at 470 K, (h) at 570 K for 1 h each. (Reprinted with permission from ref 155. Copyright 1988 The Royal Society of Chemistry.)

Zecchina's group published two papers on the adsorption of propene on HZSM-5 and H-mordenite.[104,142] They were able to record the IR spectra very quickly, and the FTIR technique allowed them to detect below room temperature a band at 3100 cm^{-1}. This band was assigned to the stretching mode of the OH bond perturbed by propene. They observed a downscale shift ($-\delta v = 15$ cm^{-1}) of the C=C stretching band of adsorbed propene compared to the gas phase attributed to a hydrogen bonded complex. This hydrogen-bonded complex proved to be stable only between 100 and 180 K.

The C$\underline{\ -\ }$C$\underline{\ -\ }$C stretching mode of alkenyl carbocations should also be detectable by IR spectroscopy, leading to the appearance of a band in the region between those typical of the C−C and C=C stretching modes. In superacid solution, this band was observed by Deno at 1530 cm^{-1}, characteristic of symmetrically substituted allyl carbocations.[11] Therefore, a band emerging around 1510 cm^{-1} should be attributed to the C$\underline{\ -\ }$C$\underline{\ -\ }$C stretching mode of alkenyl carbocations, as proposed recently (see Figure 5).[138,143]

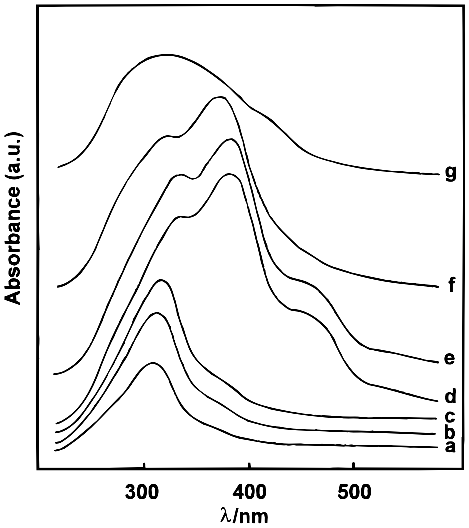


Figure 6. Transmission electronic spectra of zeolite HNaY exposed to 1.33 kPa of propene at room temperature after (a) 5 min, (b) 1 h, (c) 2 h; (d) at 320 K after 1 h; (e) after evacuation for 1 h at room temperature, (f) at 470 K, and (g) at 570 K. (Reprinted with permission from ref 272. Copyright 1988 Elsevier Science.)

The good agreement between the UV−vis and IR spectroscopic results supports the idea that stable alkenyl carbenium ions are formed from propene interacting with zeolite HZSM-5. IR bands are only clearly observed upon heat treatment, indicating the very low surface concentration of these species at room temperature. The results of Bezouhanova et al., in which the 1520 cm^{-1} band was not observed after benzene or cyclohexane admission,[141] and those of Grady and Gorte, where no aromatic compound could be detected by TPD,[140] corroborate the assignment of this band to alkenyl carbenium ions rather than to aromatic compounds. Representative UV−vis spectra of propene adsorbed on HNaY−FAU zeolite under different conditions are shown in Figure 6.

Monoenyl carbocations can be formed either from propene or from oligomers upon re-adsorption and hydride ion abstraction, as described in detail elsewhere.[139] It has been assumed that a mixture of monoenyl carbenium ions (absorbing around 310 nm) with various chain lengths is present, and therefore, a narrow band cannot be expected for these compounds. The simplest monoenyl carbenium ion, the allyl carbocation, is theoretically predicted to absorb at 293 nm.[144] Although there is some evidence for its origination in zeolites, definite proof is still lacking.

For the formation of di- and trienyl carbocations, surface species with carbon chains of at least five or seven carbon atoms are necessary; the bands observed at 380 and 450 nm should be assigned to the di- and trienyl carbenium ions. The disappearance of these bands at higher temperatures follows the following sequence: first trienyl species at 470 K and then dienyl compounds at 570 K, in good agreement with the enhanced probability of cracking shorter carbon chains with increasing temperature. To summarize, the bands observed at ca. 320, 380, and 450 nm are assigned to mono-, di-, and trienyl carbenium ions,[145] but it should be mentioned that electronic spectra only yield information on the degree of unsaturation, while the detailed structure still remains uncertain.

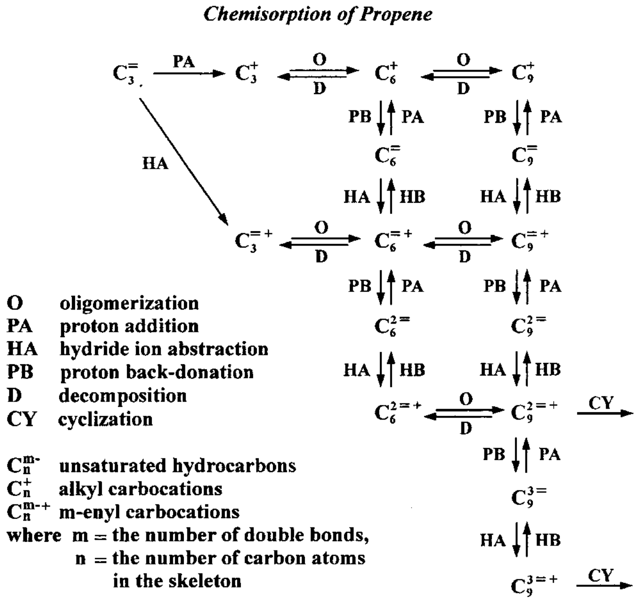
Besides IR and UV−vis spectroscopic evidences, ^{13}C NMR results are useful supplements to the detection of unsaturated carbenium ions formed from propene in zeolites.[78] Initially, only three types of long-lived carbenium ions could be unambiguously identified using ^{13}C solid-state MAS NMR. [118,146−149] They all are characterized by unusually large ^{13}C NMR chemical shifts. Haw's group found that cyclopentenyl carbenium ions were generated after completing the oligomerization of propene over HY−FAU zeolite at room temperature. They concluded that alkyl-substituted cyclopentenyl carbenium ions are present, and due to the delocalization of their positive charge, these ions are long-lived entities in zeolites. This work underlines the importance of oligomerization for the generation of unsaturated carbenium ions, since it is the prerequisite for the formation of the sufficiently long carbon chains. Cyclopentenyl cations are formed in several zeolite structures from a variety of olefins and their precursors.[146,147,150] On the other hand, the stable trityl cation, $(C_6H_5)_3C^+$, was identified on HY−FAU and Hβ-BEA zeolites.[150,151] Using the pulse−quench catalytic reactor, Haw's group recently has isolated the 1,2,4,6-pentamethylbenzenium cation obtained as an intermediate in the reactions between benzene or toluene and methanol.[152] This was possible since the reaction product water was eliminated from the zeolite. The presence of 1,3-dimethylcyclopentenyl ion was shown using the same technique in various methanol-to-gasoline reactions. However, this carbenium ion seems to be a side product rather than a true intermediate.[153,154]

The generation of di- and trienyl carbocations from propene is influenced by temperature rather than by time of contact. From both the UV−vis and IR spectra it is evident that below 340 K, owing to fast oligomerization, the surface transformations of adsorbed propene are complete within 2 h. At higher temperatures, further oligomerization and formation of more unsaturated carbocations are observed. During these subsequent reactions, intermolecular hydride ion abstractions and consecutive adsorption−desorption steps may occur, resulting in the formation of dienes and/or trienes as very reactive surface intermediates. The lack of bands in the IR spectra of polyenes demonstrates their extremely high reactivity. Taking into account the observation that only C_6 and C_9 alkenes and no aromatic compounds were found in the desorption product[140] and that (besides Brønsted centers) an appreciable number of Lewis acid sites are present in the zeolite (Note: the carbenium ion itself acts as a Lewis acid site!), the generation of alkenyl carbenium ions is assumed to proceed via the elementary steps shown in Scheme 1.[155]

As the UV−vis band position is influenced by the number and structure of the substituents attached to the resonance-stabilized structural unit, giving rise to a red shift with increasing substitution,[11,156] a similar behavior should be expected in the IR range.

Transformation of cyclopropane to propene is a widely used test reaction to monitor the surface acidity of catalysts.[157] In the carbocationic mechanism

Scheme 1. Formation of Alkenyl Carbenium Ions from Propene



of this transformation, nonclassical carbenium ions (edge-protonated cyclopropane) and isopropyl carbenium ions play the dominant role. In the side reactions leading to the formation of carbonaceous deposits, alkenyl-type carbenium ions are also generated. On acidic zeolites, alkenyl carbenium ions appear only after transformation of cyclopropane to propene, i.e., the detection of alkenyl carbenium ions from cyclopropane in acidic zeolites requires thermal treatment. In Figure 7 the UV−vis spectra of adsorbed cyclopropane and propene on zeolite HZSM-5 are shown.

The spectra taken at different stages of pretreatment in the presence of the adsorbate become similar and after treatment for 30 min at 320 K become almost identical (compare the spectra denoted c). IR spectroscopic measurements performed under the same experimental conditions reveal that no cyclopropane is present, rather it was completely transformed to propene. Therefore, the direct formation of alkenyl carbocations from cyclopropane is unlikely, as already assumed on the basis of the spectral changes observed.[139] For the transformation of carbocations generated from cyclopropane and propene, a probable mechanism was assumed and experimentally confirmed.[142]

Unsaturated carbenium ions are easily formed from both methylacetylene and allene on Brønsted acidic zeolites. Zecchina et al. describe the main spectral changes that occur upon methylacetylene adsorption on zeolite HZSM-5.[142] The first adsorption step gives rise to a band at 1950 cm^{-1}, assigned to the vibration of the hydrogen bond formed between the acidic OH group and the C≡C triple bond. The fast disappearance of this band indicates a fast carbenium ion formation. The interaction of the C≡C triple bond with silanol groups results in an absorption at 2115 cm^{-1}, and for the physisorbed species, the C≡C stretching vibration of $CH_3-C\equiv CH$ is found at 2126 cm^{-1}. The rate of development of bands attributed to carbocationic species is observed as follows: 1515 > 1626 > 1680 cm^{-1}. Oligomerization of methylacetylene results in pentamers as the species of maximum carbon chain length. The rate of the development of the UV−vis bands is as follows: the fastest is that of the band around 300 nm, followed by that at 360 nm, and finally by that around 420 nm. These bands are attributed to monomeric, dimeric, and trimeric unsaturated carbenium ionic species.

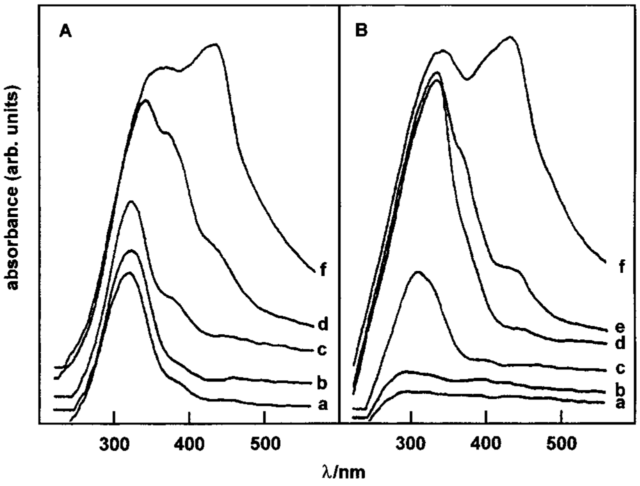


Figure 7. Transmission electronic spectra of surface species formed upon adsorption of (A) propene and (B) cyclopropane in HZSM-5/770: (a) 5 min, (b) 1 h after loading the sample with 1.33 kPa of hydrocarbons at 290 K, (c) after heating at 320 K for 1 h, (d) at 370 K for 1 h, (e) at 420 K for 1 h, and (f) at 470 K for 0.5 h. (Reprinted with permission from ref 155. Copyright 1988 The Royal Society of Chemistry.)

Stucky et al. report that the ^{13}C NMR spectra showed two resonances at 30.1 and 128.0 ppm relative to TMS, corresponding to methyl and vinyl or aryl carbons, respectively. Their UV−vis spectroscopic results proved differences due to the zeolite structure.[158]

Adsorption of allene on acidic zeolites is an irreversible process.[159] Over A-type zeolites (Brønsted acid-free), allene transforms to methylacetylene without oligomerization. On the other hand, it forms oligomers in acidic samples. In the IR spectra, a band generally appears around 1510 cm^{-1}, being assigned to the unsaturated carbenium ions. This is hardly observed due to the very fast oligomerization of allene.

C. Alkenyl Carbenium Ions from Longer Chain Aliphatic Hydrocarbons

Hydrocarbons with chains of four or more carbon atoms can undergo cracking in which the β-C−C bond (with respect to the positive charge) is ruptured. In the cracking of butanes and larger paraffins, alkenyl carbenium ions may be formed by secondary reactions, and in most cases, these processes lead to catalyst deactivation by formation of carbonaceous deposits. Alkenyl carbenium ions are not detected upon adsorption of butane and 2-methyl-propane.[160]

Reactions of butenes over zeolites have been exhaustively investigated by many research groups.[137,161−167] Due to the different surface complexes formed during adsorption on basic and acidic catalysts, the *cis/trans* ratio, obtained from isomerization of 1-butene to *cis*- and *trans*-2-butenes, is used to characterize the acid−base properties of solid catalysts. On acidic zeolites, fast oligomerization of butenes takes place even below room temperature.[168] Above 373 K, the decomposition of oligomers starts, which results in the transformation to paraffins, which release from the catalyst surface, and polyenes which remain trapped in the zeolite pores. Polyene intermediates are regarded as the carbenium ion species.[169,170] Alkenyl carbenium ions generated from butenes on various acidic zeolites have been investigated by UV−vis, IR, and ^{13}C NMR spectroscopies, and the following general conclusions have been unanimously drawn: monoenyl carbenium ions are instantly formed in the zeolite cavities after admission of butenes at room temperature, while at longer contact times or at elevated temperatures, polyenyl carbenium ions are generated.[68,99,171] UV−vis bands characteristic of these ions appeared around 310, 360, and 460 nm, very close to those wavelengths detected for ethene and propene.

Adsorption and reaction of isobutylene on HY and HZSM-5 zeolites were studied by Haw et al. using variable-temperature in situ MAS ^{13}C NMR spectroscopy.[172] They found that the C1 and C3 labels of isobutylene were scrambled, in contrast to propene adsorption where such a process was not observed. Another difference in the behavior of propene and isobutylene is the absence of silyl ether species on the zeolite surface in the presence of isobutylene. Corma et al. performed ab initio MO calculations to differentiate between the protonation of propene and isobutylene. They found, however, both the reaction mechanism and the properties of the transition states to be practically the same irrespective of the increased branching of isobutylene.[173]

As protonation of butadiene gives rise to the formation of alkenyl carbenium ions, due to their very high reactivity, their detection is not free of difficulties. Reaction of butadiene with Brønsted acid sites of zeolites is accompanied by coke formation via oligomerization.[174] An almost identical conclusion was drawn by Haw et al. on the basis of ^{13}C NMR measurements in which they could not detect any reactive intermediate due to its very low steady-state concentration in the zeolite.[175]

Upon adsorption of butadiene on zeolite ZSM-5, the band assigned to the C_−_C_−_C part of the alkenyl carbenium ions was observed around 1500 cm^{-1} in the IR spectra taken at different loadings.[132] In the UV−vis spectra, with increasing the adsorbed amount of butadiene, bands appeared at 310, 350−380, 430−450, 520−570, and 630−660 nm attributed to alkenyl carbenium ions of growing unsaturation. Medin et al. proved the difference between the reactivity of ethene and butadiene on ZSM-5 zeolite.[98] As shown by the spectra in Figure 8, immediately after butadiene adsorption at room temperature, several bands appear in the UV−vis spectrum while for ethene a heat treatment at 473 K is required for the development of three bands.

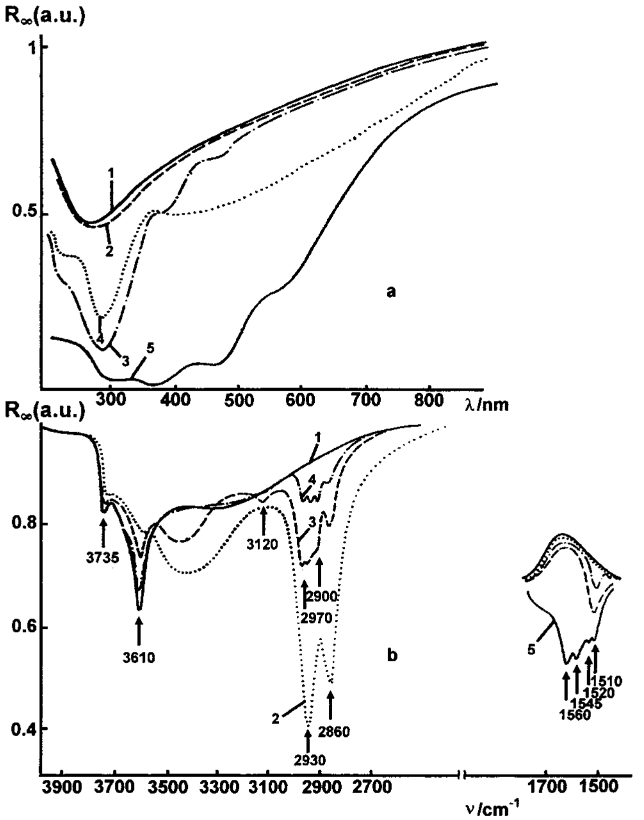


Figure 8. (a) UV−vis and (b) IR spectra of HZSM-5 zeolite: (1) after activation in vacuum at 773 K, (2) after adsorption of ethene at 300 K, after evacuation at (c) 473 K and (4) 573 K, (5) after adsorption of butadiene-1,3 on the activated sample (1) at 300 K. (Reprinted with permission from ref 98. Copyright 1989.)

It is interesting to note that the positions of the bands assigned to monoenyl (300 nm), dienyl (360 nm), and trienyl (460 nm) carbenium ions are approximately identical regardless of the source, indicating the generation of similar surface intermediates from different substrates. The formation of the alkenyl carbenium ions has also been detected by IR spectroscopy, indicated by the bands at 1510, 1520, 1545, and 1560 cm^{-1} shown in the inset of Figure 8.

Adsorption of higher olefins, e.g., pentenes, hexenes, and heptenes, was studied by Bezouhanova et al. in detail.[176−178] The band generally observed in the IR spectra at 1520 cm^{-1} was assigned to the intermediate formed upon adsorption of olefin on the acid site of the zeolite. Either a π complex or a carbenium-ion-like structure was suggested for the surface intermediate formed in this way. Förster and Kiricsi assumed the formation of similar alkenyl−carbenium-ion-type surface intermediates from propene and hex-1-ene in HZSM-5 zeolite on the basis of UV−vis spectroscopic studies.[155]

D. Carbocations from Cyclic C_6 Hydrocarbons

Formation of surface species from cyclohexane, cyclohexene, cyclohexadiene, and benzene upon interaction with acidic forms of zeolites has been investigated by several research groups. IR spectroscopic investigations show that the adsorption of

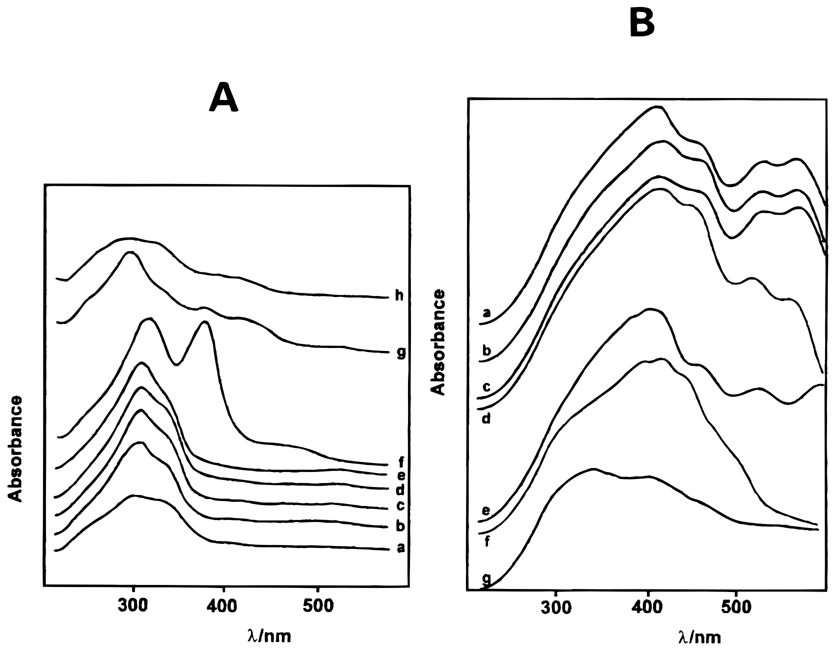


Figure 9. Transmission electronic spectra of zeolite HZSM-5 loaded with 666 Pa cyclohexene (Figure A) and 133 Pa cyclohexadiene (Figure B): (A) at room temperature immediately (a) after admission of cylohexene, (b) after 1 h, (c) after 2 h, and (d) after 3 h. After evacuation for 1 h at (e) room temperature, (f) 370 K, (g) 470 K, and (h) 570 K; (B) shortly (a) after admission at room temperature, (b) after 30 min, (c) after 1 h. After evacuation for 1 h at (d) room temperature, (e) 370 K, (f) 470 K and (g) 570 K. (Reprinted with permission from ref 182. Copyright 1989 Elsevier Science.)

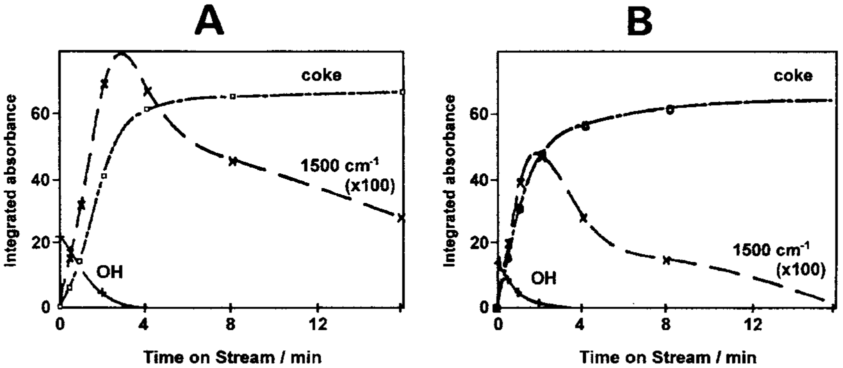


Figure 10. Variation of the intensity of some characteristic IR bands with time on stream: (A) HY_I and (B) HY_{SA} zeolite. (Reprinted with permission from ref 185. Copyright 1994 Elsevier Science.)

cyclohexene gives rise to the appearance of a band at 1532 cm^{-1}, which may be attributed to alkenyl carbenium ions.[179] This band has also been assigned to aromatic compounds formed on the zeolite surface.[180,181] It was observed exclusively on the acidic sample (LaHNaY−FAU) but not on NaY−FAU. After adsorption of cyclohexane, this band was observed on neither LaHNaY− nor NaY−FAU zeolites. UV−vis spectroscopic investigations confirmed the absence of any band in the near UV region upon cyclohexane adsorption on zeolites.

The spectra of surface species formed from cyclohexene and cyclohexadiene, however, exhibit several bands as shown in Figure 9. These spectral features develop much faster for cyclohexadiene than for cyclohexene. The precise structure of the surface species is still not known. However, reaction pathways were assumed that may explain the reactions.[182]

Lavalley's group carefully studied the transformation of cyclohexene over acidic zeolites.[183−185] They observed a band at 1500 cm^{-1} in the IR spectra of adsorbed cyclohexene and assigned it to unsaturated carbenium ions. The intensity of this band passed through a maximum when the absorption of the Al−OH groups disappeared. The situation is shown in Figure 10.

They suggested an intermolecular hydride ion abstraction from olefins by carbenium ions to be more probable than the direct hydride ion abstraction by a Lewis acid site of the zeolite. The two alternative explanations are very similar since a carbenium ion, due to its electron-deficient structure, generally acts as a Lewis acid site.

Upon adsorption of benzene, only very weak bands emerged in the UV−vis region.[186] It can be concluded that the UV−vis bands of hydrocarbons adsorbed on solid surfaces might be compared to the spectra of unsaturated carbenium ions observed in superacid solutions. This is the most advantageous way for attributing bands to distinct ionic species, since carbocation formation has been very extensively studied in superacids.[1] Comparison of the spectra of cyclohexadiene and cyclohexene proved that the ion-forming capability of cyclohexadiene was superior to that of cyclohexene. From the spectroscopic investigations of these hydrocarbons, it can be inferred that the generation of ions decreases in the sequence cyclohexadiene > cyclohexene > cyclohexane ≈ benzene.

E. Alkenyl Carbenium Ions from Alcohols

Alcohols may be dehydrated over zeolite catalysts to ethers and olefins. The product distribution is determined by the reaction conditions, particularly by the reaction temperature.

Adsorption of methanol on acidic zeolites has been investigated by various experimental[187−192] and theoretical[193−197] methods. The first reaction steps of methanol interacting with the acid sites of the zeolite are very complex, in which trimethoxonium ions,[198] physisorbed as well as chemisorbed methanol and methoxyl groups bound to the silanol groups,[199] and ion-pair complexes with a second adsorbed methanol or water molecule were assumed as intermediates.[200,201] Some authors debated the presence of methoxy groups on the basis of ^{13}C NMR spectroscopic results.[202] The role of the Lewis acidity in this reaction was investigated by a few groups.[203,204]

The mechanism of the methanol-to-gasoline process proved to be very complex. Mechanisms involving key components of different chemical characters have been assumed. The main proposals for the mechanism may be classified by the nature of reactive intermediates as follows: traditional carbene-type intermediates,[205,206] radicals,[207] oxonium ions,[208−210] carbon pool mechanism,[211−213] and carbocations.[214] As being concerned with the role of the alkenyl carbenium ions in the methanol-to-gasoline process, we should only consider the carbocationic mechanism. The mechanism of the reaction was investigated in detail by Derouane et al.[215,216] Their work reports for the first time the carbenium ionic mechanism of this reaction, tracing it back to the formation of ethene as the product of dehydration of dimethyl ether. Methanol transforms over zeolite HZSM-5 via several dehydration, oligomerization, hydride transfer, and dehydrogenation steps to a gasoline fraction containing aromatic hydrocarbons as one of the main components. Their UV−vis spectroscopic studies showed that, contrary to the adsorption of ethene and propene, methanol does not react at room temperature. UV−vis bands were only proved after treatment of the zeolite in the presence of methanol at elevated temperatures, as shown in Figure 11.

At 473 K, two strong bands at 290 and 365 nm appeared. Upon heating at 523 K, the intensity of the band at 365 nm increased. After treatment at 573 K, the color of the sample turned brown and a broad spectral pattern with several maxima around 600, 500, 420, 330, 270, and 240 nm was observed (see spectrum e in Figure 11). The spectral changes observed below 523 K were similar to those generally found for olefin adsorption. These bands were attributed to unsaturated carbenium ions. From this, it follows that olefins are the reactive intermediates in the transformation. Analysis of the spectral changes led to the mechanism suggested for the formation of aromatics shown in Scheme 2.

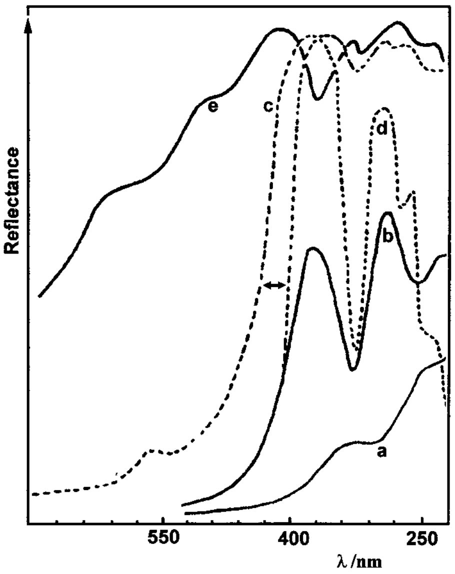


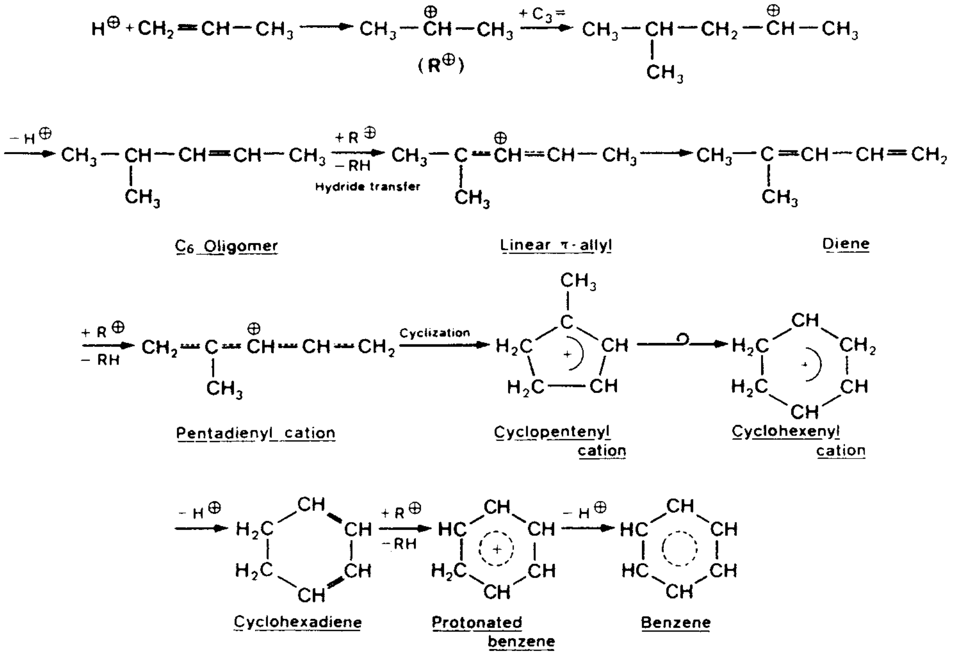
Figure 11. UV−vis spectra of LaHY−FAU used in a batch reactor for 7 h with (standard conditions) $T_{act} = 623$ K, feed = 1-butene/isobutane = 1/9, $T_{react} = 353$ K, $P = 30$ bar, and LSHV = 4.07 h^{-1} unless stated otherwise. (I): T_{react} = 353 K (A) and 373 K (B). (II): LSHV = 2.27 (A), 3.86 (B), and 4.07 h^{-1} (C). (III): T_{act} = 523 (A), 623 (B), 673 (C), and 773 K (D). (Reprinted with permission from ref 261. Copyright 1995 Elsevier Science.)

It should be mentioned that, in this case, at higher temperatures carbonaceous deposits are also formed. Therefore, the role of alkenyl carbenium ions generated up to 473 K is determining, i.e., aromatic hydrocarbons are formed via these ions. However, at higher temperatures, their role becomes more disadvantageous, leading to side reactions such as the formation of deposits.

Reaction of ethanol over zeolite ZSM-5 gave ethene as the main product.[217] Aromatic hydrocarbon formation was supposed to proceed via cyclopolyene intermediates.[21846] At relatively low temperatures (around 423 K), an inhibitor effect of water on the oligomerization of ethene as the primary product from ethanol was assumed.[219]

Transformations of 1-propanol and 2-propanol over acidic zeolites are very fast processes, and thus, carbenium ions cannot be observed due to their fast reaction with the olefins, released from other acid sites, resulting in polymers of ionic character. This was proved by ^{13}C MAS NMR experiments,[220] TPD-IR techniques,[140,221] and catalytic test reactions.[222,223] Förster et al. investigated the adsorption of 2-propanol on H− and HNa−mordenites by means of UV−vis−NIR spectroscopy.[139] They found an instant development of UV−vis bands at 295 and 380 nm after adsorption of 2-propanol on H−mordenite, while on the less acidic HNa−mordenite it was slower. The formation of unsaturated carbenium ions was accompanied by the production of water, evidenced by the $2v_{1,3}$ band of adsorbed water at 1410 nm (see Figure 12). The authors concluded that unsaturated carbenium ions are generated via propene as the primary product of 2-propanol dehydration.

Scheme 2. Assumed Mechanism for the Formation of Aromatic Hydrocarbons from Propene over Acidic Zeolites (Reprinted with permission from ref 214. Copyright 1980 Elsevier Science.)



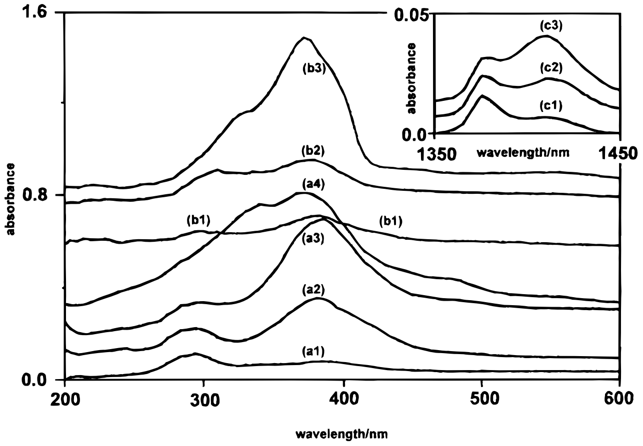


Figure 12. Transmission electronic spectra of (a) H− and (b) NaH−mordenite loaded with 133 Pa of 2-propanol. (a1) immediately after admission at room temperature, (a2) 1 h at room temperature, (a3) 18 h at room temperature, (a4) 1 h at 370 K; (b1) 4 h after exposure at room temperature, (b2) 1.5 h at 350 K, (b3) 1 h at 370 K. (c) Near-infrared spectra of NaH−mordenite loaded with 2-propanol (inset at top right side), conditions (c1−c3) same as (b1−b3). (Reprinted with permission from ref 139. Copyright 1987 The Royal Society of Chemistry.)

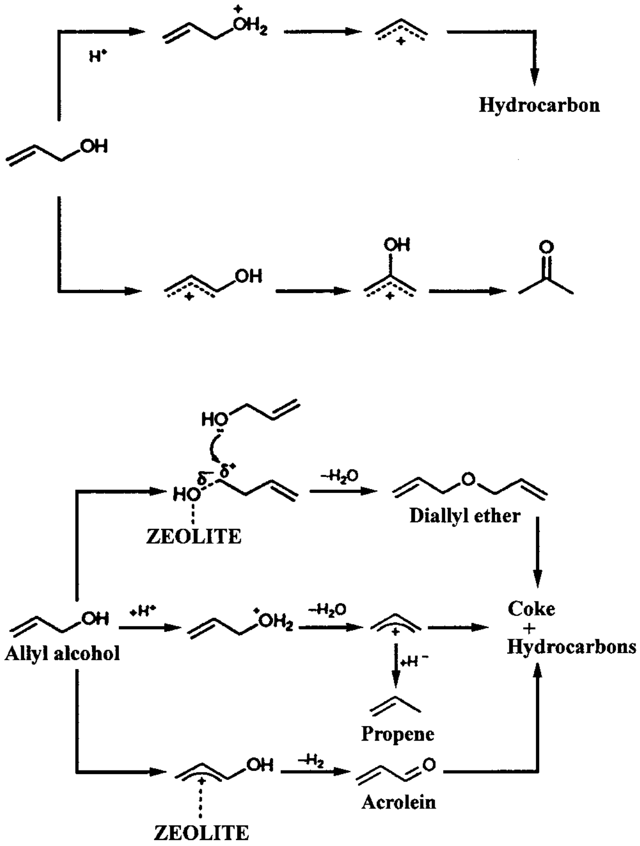
The reaction of butanols over acidic zeolites results in *tert*-butyl carbenium ions as short-lived intermediates.[224−227] Kazansky et al. came to the same conclusion from the results of an in situ ^{13}C NMR investigation of *tert*-butyl alcohol interaction with sulfuric acid.[228] Kavalchev et al. found a new IR band at 1510 cm^{-1} upon admission of butanol to HZSM-5 zeolite.[229] The band intensity passed through a maximum with contact time, allowing the authors to assign this band to a π complex as surface intermediate formed by interaction of the C=C bond with Brønsted acid sites. Others attributed this band to alkenyl carbenium ions, as indicated and will be discussed later.

When unsaturated alcohols, such as allyl alcohol, are adsorbed on acidic zeolites, the IR spectral changes are as follows: (i) the OH bands shift to lower wavenumbers, (ii) the C=C bond cannot be observed, and (iii) an intense band at 1510 cm^{-1} appears.[230,231] Hutchings et al. studied the transformation of allyl alcohol over zeolites.[232,233] They first suggested a two-path mechanism for the formation of hydrocarbons or acetone and later a three-path mechanism (see Scheme 3) for the formation of diallyl ether, hydrocarbons, and acrolein.

It should be mentioned that Bezouhanova observed acrolein instead of acetone as the product.[234] Mechanistically the proton can attack either the C=C bond or the oxygen atom of the alcoholic OH group. Which of them is more negatively charged?

Depending on the proton attack, two different types of carbenium ions may be formed. When the proton interacts with the oxygen atom, an oxonium ion is generated, the further reaction of which gives water and an unsaturated (allyl) carbenium ion bound to the surface. When the proton attacks the C=C bond, a saturated (hydroxypropyl) carbenium ion is formed. Only the former form is UV−vis active. Gorte et al. performed a combined TPD-IR study and concluded that 1:1 surface complexes were formed from allyl alcohol and Brønsted acid sites.[233] These species easily dehydrated to allyl cations and water. The authors suggest a detailed mechanism for this reaction. It seems to us that the challenge to give an experimental proof of the allyl carbenium ion is one of the roots initiating a number of excellent papers on adsorption and transformation of allyl alcohol over acidic zeolites in the past few years.[235−241] The most important points of these papers are as follows: (i) NMR spectra show resonances which may be attributed to unsaturated carbenium ions, (ii) in the IR spectra a band appears generally in the 1505−1550 cm^{-1} range, (iii) mainly olefins were identified

Scheme 3. Suggested Reaction Schemes for the Transformation of Allyl Alcohol (Reprinted with permission from refs 231 and 232. Copyright 1990 and 1991 Royal Society of Chemistry and Elsevier Science.)



as products, (iv) formation of acetone is unlikely since the rearrangement of $CH_3-CH^+-CH_2-OH$ to $CH_3-C^+(OH)-CH_3$ proceeds via the primary carbenium ion, (v) hydride ion donation to an allyl carbenium ion to form propene can only occur from olefins since no paraffinic hydrocarbon is within the system, but in this reaction neither allyl cations nor propene are consumed, (vi) formation of acrolein may be explained rather by transformation over basic sites, rather than acid sites, involving a hydrogen release due to dehydrogenation.

Kiricsi et al. investigated the adsorption of allyl alcohol on HZSM-5 zeolite.[242,243] Alkenyl carbenium ions were detected instantly after admission of the alcohol at room temperature, as shown in Figure 13.

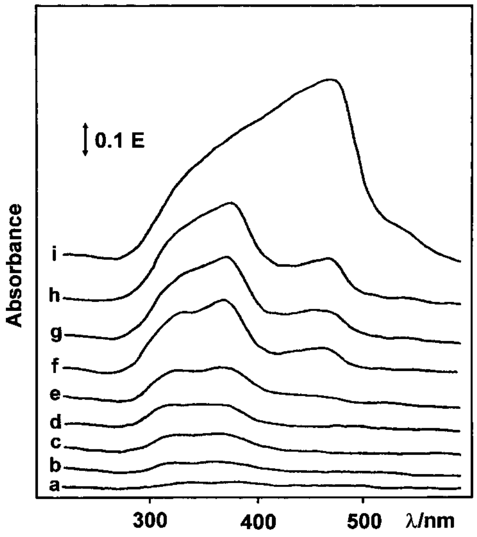
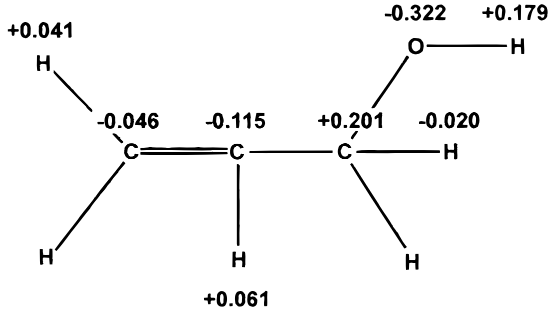


Figure 13. UV−vis spectra recorded at room temperature after activation of zeolite HZSM-5 (SiO_2:Al_2O_3 = 28) at 400 °C: (a) initial sample, (b) after introduction of 100 Torr of CH_3OH at room temperature and heating at 200 °C for 1 h, (c) heating overnight at 200 °C, (d) expansion of c and zero suppressed, (e) after heating at 250 °C for 1 h. (Reprinted with permission from ref 214. Copyright 1980 Elsevier Science.)

Scheme 4. Partial Charges of the Atoms in Allyl Alcohol Calculated by the MNDO Method (Reprinted with permission from ref 243. Copyright 1990 Elsevier Science.)



Almost simultaneously the formation of both mono- and dienyl carbenium ions, absorbing at 310 and 380 nm, starts. After 3.5 h, a nearly “explosive” enhancement of mono- and dienyl carbenium ions took place, and a sudden rise of trienyl ions was detected after 5 h at room temperature. It is known that allyl alcohol exhibits outstanding reactivity in either substitution or elimination reactions due to S_N1 or E1 mechanisms. Such unimolecular transformations occur via a carbenium-ion-like intermediate, which for allyl alcohol should be the allyl cation.[244] Therefore, a high probability of dehydration of allyl alcohol can be expected as the main reaction in acidic media. Allene as the product of this reaction is unable to leave the zeolite channels due to its very high reactivity under acidic conditions. It rather reacts further to oligomers of polyenyl type. These observations indicate that the transformation of allyl alcohol proceeds via a carbocationic mechanism in which the proton attacks the oxygen atom with high probability rather than the double bond of allyl alcohol. This reaction leads to the formation of mono- and dienyl carbenium ions, as experimentally observed.

The molecular electrostatic potential map (MEP) of allyl alcohol was calculated using the MNDO method.[243] It was found that the largest negative charge is located near the oxygen atom. Therefore, it should be regarded as the most probable site for protonation. The partial charges calculated in the same approximation gave the same result, as can be seen in Scheme 4 and Figure 14.

From these considerations, dehydration is the most probable first step of allyl alcohol conversion, resulting in allene bound as an allyl carbenium ion to the surface and adsorbed water. The very reactive allene takes part in oligomerization reactions, while water converts the Lewis acid to Brønsted acid sites making them able to attack further allyl alcohol molecules,

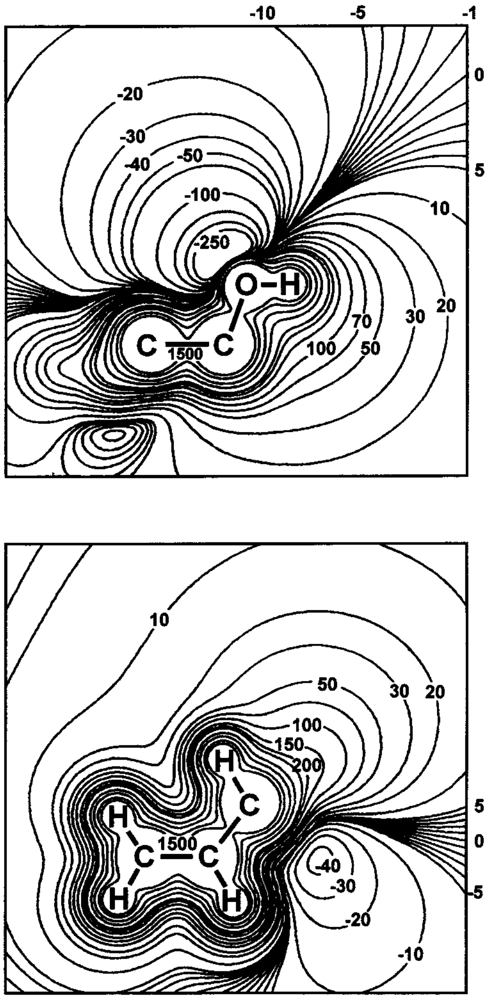


Figure 14. Electronic spectra of allyl alcohol adsorbed on zeolite HZSM-5 pretreated at 773 K in high vacuum. Spectra were recorded (a) immediately after loading the sample with 532 Pa of allyl alcohol at room temperature, (b) after 1 h, (c) after 1.5 h, (d) after 2 h, (e) after 2.5 h, (f) after 3.5 h, (g) after 4 h, and (h) after 5 h. Spectrum i was obtained after heating the system at 320 K for 0.5 h. (Reprinted with permission from ref 243. Copyright 1990 Elsevier Science.)

thereby enhancing the rate of the formation of unsaturated carbenium ions, similar to an autocatalytic reaction, which was observed by UV−vis spectroscopy. With increasing number of Brønsted acid sites, the concentration of allyl carbenium ions increases but then the probability of oligomerization of allene inside the channels is also enhanced, which results in the generation of polyenyl carbenium ions, as evidenced by the spectral changes. Thus, generation and transformation of alkenyl-type carbenium ions could be proved from the adsorption of allyl alcohol on acidic zeolites.

VI. Influence of Acidity on the Generation and Transformations of Alkenyl Carbenium Ions in Zeolites

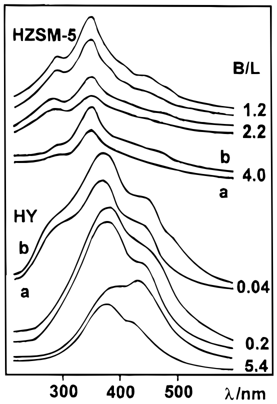


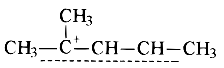
Figure 15. Electrostatic potential map of allyl alcohol in the CCO (A) and CCC planes (data are given in kJ mol^{-1}). (Reprinted with permission from ref 243. Copyright 1990 Elsevier Science.)

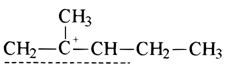
The influence of the acidity of the zeolite on the formation of alkenyl carbenium ions has been investigated by several authors.[100,103,139] All authors agree, the acidity of the zeolite plays a dominant role. Förster et al. showed that generation of mono-, di-, and trienyl carbenium ions from allene, cyclopropene, propene, 2-propanol, and acetone slowed in the sequence of decreasing Brønsted acidity on H−mordenite > HNa−mordenite > Na−mordenite.[139]

The common feature in the spectra of adsorbed propene and allene is the shift of the UV−vis band to higher wavelengths with contact time and its reversion upon evacuation. This observation can be explained by assuming the band position of monoenylic carbenium ions (observed generally in the 275−320 nm range in superacidic solution) is sensitive to the substituent groups.[11,144,145] While the insertion of an additional double bond gives rise to a frequency jump of about 60 nm, the extension of the carbon chain or formation of branched oligomers, accomplished by consecutive reactions (both propene and allene oligomerize very fast at room temperature over acidic zeolites), results only in a continuous shift of the maximum. Quantum chemical calculations show that the lowest vertical singlet excitation energies (LVSEE) for methyl-substituted allyl carbenium ions decrease with growing methyl substitution. For that case, there should be an equilibrium mixture of monoenyl carbenium ions, the common feature of which is a C_6 backbone absorbing at different frequencies.

$CH_3-CH-CH^{+}-CH-CH_2-CH_3$

$CH_2-CH^{+}-CH-CH_2-CH_2-CH_3$


$CH_3-\overset{CH_3}{\overset{|}{C^{+}}}-CH-CH-CH_3$


$CH_2-\overset{CH_3}{\overset{|}{C^{+}}}-CH-CH_2-CH_3$

From spectroscopic measurements performed on zeolites with different B/L ratios, although it is accepted that the Brønsted acid sites play the dominant role in oligomerization of olefins, the participation of Lewis centers in this reaction cannot be neglected.[117,137] It follows that the higher the amount of Brønsted acid sites, the more pronounced the oligomerization of olefins, and consequently, the alkenyl carbenium ions, formed during reaction, absorb at higher wavelengths, as observed for both propene and allene on both types of zeolites, HZSM-5 and HY (see Figures 15 and 16).

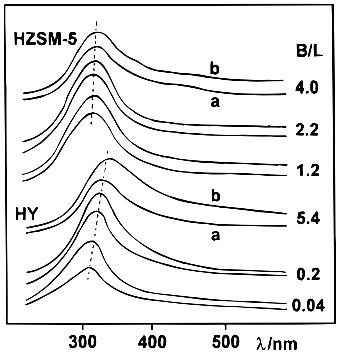
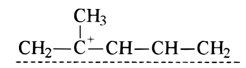


Figure 16. UV−vis spectra of allene adsorbed on HY−FAU and HZSM-5 zeolites of different Brönsted/Lewis acidity ratios (indicated on the right side of the spectra), spectrum (a) was recorded shortly after adsorption while (b) was after 1 h. (Reprinted with permission from ref 273. Copyright 1991 Elsevier Science.)

In the spectra of adsorbed allene, the prevailing band is found in the range 359−380 nm, characteristic of dienyl carbenium ions. From allene, the generation of increasingly unsaturated carbenium ions should be expected.

$$\underline{CH_2{-}CH{-}\overset{+}{CH}{-}CH{-}CH}{-}CH_3$$



$$\underline{CH_2{-}\overset{\overset{CH_3}{|}}{C^+}{-}CH{-}CH{-}CH_2}$$

The idea is that if the number of Brønsted acid sites in the zeolite sample is decreased by dehydroxylation instead of lowering the degree of ammonium ion exchange,[139] the existence of even simpler monoenyl carbenium ions should be observed by UV−vis spectroscopy, since with increasing dehydroxylation the strength of Brønsted acid sites probably also increases, thereby promoting the stability of a given carbenium ion. As shown in Figure 16, this expectation is true: the lower the B/L ratio the more pronounced a band emerged at ca. 290 nm on both zeolites.

Accepting the explanation for the shifts of the UV−vis bands to higher wavelengths detailed above, one would interpret the reverse displacement occurring upon evacuation of the sample at increasing temperatures as follows: At about 400 K or higher, the oligomers formed undergo cracking and/or desorb, thereby having carbenium ions (including the alkenyl types) of shorter carbon chain length, thus absorbing at higher frequencies.

The absorption maximum of the allyl cation as the simplest monoenyl carbenium ion is predicted to appear at 293 nm as a result of LCAO-MO calculations.[145] The lowest vertical singlet excitation (LVSE) energies calculated by the CNDO/S and MNDO−HE methods and the standard heats of formation $\Delta H_f°$ by MNDO computations are listed in Table 2.

It becomes obvious that higher substituted monoenyl and dienyl carbenium ions should absorb at higher wavelengths. Furthermore, the stability of the carbenium ions under study also increases with increasing methyl substitution. These results are in good accordance with the experimental observations discussed above. According to the results of quantum chemical calculations, the assignment of a given UV−vis band to a well-defined alkenyl ion seems to be rather difficult. The observation of a band only indicates a group of alkenyl ions.

The lower the B/L ratio of a zeolite, the higher should be the frequency of the alkenyl carbenium ions formed from propene and allene on different zeolites. This can be explained by the preferred formation of monoenyl carbenium ions absorbing at 280−310 nm. This fact might be due to an increase of the strength of the Brønsted acid sites with decreasing concentration (as a result of dehydroxylation), thereby promoting the stability of the monoenyl carbenium ion formed from allene. The higher the B/L ratio of the sample, the more enhanced the formation of oligomers giving rise to bands at lower frequencies.

VII. Assignment of the Bands Generally Observed in the UV−vis Spectra between 280 and 500 nm and around 1510 cm−1 in the IR Spectra

UV−vis spectroscopic studies of the adsorption of olefins prove the creation of unsaturated carbenium ions in acidic zeolites. The bands observed in the ranges 280−330, 360−380, and 430−470 nm have been attributed to $\pi-\pi^*$ transitions of mono-, di-, and trienylic carbenium ions. It has already been stated that these wavelengths, characteristic of alkenyl carbenium ions formed in zeolites, agree well with those calculated by Sorensen's equation describing the frequency dependence of polyenylic carbenium

Table 2. Lowest Vertical Singlet Excitation Energies and Standard Heats of Formation Obtained by Semiempirical Quantum Chemical Methods

	LVSE energies/nm			$\Delta H_f°$/kcal•mol^{-1}		
carbocation	CNDO/S (absolute)	MNDO (relative)	MNDO-HE (absolute)	MNDO (relative)	MNDO (absolute)	MNDO (relative)
allyl	220	0	281	0	221.4	0
isopropylallyl	237	17	289	8	200.0	−21.4
n-propylallyl	237	17	289	8	195.8	−25.6
1-ethyl-2-methylallyl	253	33	314	33	195.2	−26.2
1-ethyl-3-methylallyl	234	14	300	19	187.0	−34.4
1,1,3-trimethylallyl	241	21	313	32	185.4	−36.0
pentadienyl	286	0	299	0	219.8	0
1-methylpentadienyl	290	4	306	7	207.3	−12.5
2-methylpentadienyl	297	11	311	12	214.7	−5.1
1,1,3,5-tetramethylpentadienyl	305	17	328	29	188.7	−31.1
1,1,5,5-tetramethylpentadienyl	325	37	330	31	182.8	−37.0

ions as a function of the number of conjugated double bonds in the respective ion.[139] Furthermore, the ability to form alkenyl ions of different hydrocarbons and their derivatives follows the same sequence as that observed in superacid solutions.[245] The bands formed at ambient temperature are assigned to $\pi-\pi^*$ transitions of alkenyl carbenium ions, while those developing at higher temperatures might be attributed to substituted benzyl and/or polyalkylaromatic ions.[103,246] These investigations reveal very close similarities to events in superacidic solution. Sorensen's equation proves suitable for specification of the absorption maxima of mono-, di-, and trienylic carbenium ions.[145,245] Furthermore, the capability of adsorbates for alkenyl carbenium ion generation followed the same sequence found by Rosenbaum and Symons in superacids.[8] It has also been reported that both the overall as well as the Lewis acidity of the zeolites plays an important role in the course of alkenyl ion formation.[16,139] Characteristic red shifts of the UV−vis bands were also observed in the case of zeolites and attributed to the formation of branched, i.e., alkyl-substituted, alkenyl carbenium ions. This finding has been supplemented by semiempirical quantum chemical calculations.[247]

The band, often appearing in the 1505−1530 cm^{-1} range upon adsorption of small olefins and alcohols at 320−370 K (in some cases even at ambient temperature), is attributed by different authors to substantially different surface species. The great variety of substrates, the adsorption of which leads to the emergence of this band, indicate that it belongs to a group of surface intermediates rather than to a given compound of well-defined structure.

Adsorbates, the adsorption of which results in the development of this band, are endowed with an enhanced capability of generating carbenium ions upon interaction with acid sites of zeolites. An additional common feature is that this band cannot be observed after adsorption of the substrates on less acidic or nonacidic zeolites nor on samples poisoned by strong bases. Consequently, surface acidity is the basic requirement for the appearance of this band. The stability of the surface species responsible for this band proved to be only slightly dependent on the structure of the parent compounds. Generally after evacuation above 550 K these surface compounds vanish.

As was discussed previously, the transformations of olefins and alcohols show fundamental similarities when comparing their behavior in zeolites and in superacidic solution. This fact has frequently been utilized for the interpretation of the experimental results obtained on zeolites, since the chemistry of hydrocarbons and hydrocarbon derivatives in superacidic solution has been clarified.[1] From experiments described in the literature, one should be able to give a more accurate assignment to the band under discussion.

One group has attributed this band to a π complex formed between the double bond of olefins and the Brønsted acid sites of zeolites. The same intermediates, which are formed from olefins as the result of alcohol dehydration, have also been proposed for alcohol adsorption. The frequency of the C=C mode of olefins adsorbed on nonframework cations of zeolites was found to be dependent on the nature of the cations.[167] Since on acidic zeolites the adsorption of olefins is accompanied by fast oligomerization, their C=C stretching fundamental can hardly be observed. Bands appearing between 1613 and 1650 cm^{-1} are assigned to terminal C=C double bonds of olefins interacting with Brønsted acid sites. In the case of propene adsorption on protonated zeolites, Gosh showed that the C=C fundamental appeared at 1633 cm^{-1} and the high-frequency band of the Brønsted acidic OH groups of HY was shifted to 3200 cm^{-1}.[123] On HZSM-5, two distinct C=C vibrational bands of adsorbed propene were observed at 1646 and 1632 cm^{-1}, while the OH bands at 3745 and 3610 cm^{-1} were displaced to 3710 and 3460 cm^{-1}. In the case of H−mordenite, the C=C stretching vibration of adsorbed propene could not be detected due to its very fast oligomerization. The downscale shift of the C=C stretching band of adsorbed propene is commensurate with that observed by others. From this observation, it follows that Gosh's explanation for the C=C bond of olefins interacting with protons of Brønsted sites would seem to be preferred to that given by Bezouhanova et al., who attributed the band at 1510−1530 cm^{-1} to this intermediate.[141,176−178] Very recently, it was found in low-temperature adsorption of 1-butene on HZSM-5 zeolite that the π complex formed between the double bond and the Brønsted acid site absorbs only several 10 wavenumbers lower than the C=C mode of the gas-phase molecule.[248−251]

A second group assigned this band to aromatic or the precursors of aromatic compounds. As far as the assignment of the band at 1505−1530 cm^{-1} to aromatic compounds is concerned, the observations are inconsistent. Some noticed this band but did not detect aromatic compounds in the products desorbed at increasing temperatures,[125,140,141,177] while others succeeded in observing both the band in question as well as the formation of aromatics, although the latter were generally formed above 573 K.[91,101,180,203,224] In several papers dealing with the adsorption of olefins on acidic zeolites at low and intermediate temperatures, this band was neither discussed nor was the formation of aromatic compounds reported.[93,94,117,137,252] For the assignment of the band near 1510 cm^{-1} to aromatic compounds, its appearance upon adsorption of aromatics serves as unambiguous evidence, but this is not the case. Adsorption of benzene and toluene gives rise to bands at 1478 and 1496 cm^{-1} on acidic zeolites.[186,253]

In 1994 Schleyer's group reported the simulated IR spectrum of the allyl cation (CISD/6-31G** level), predicting the asymmetric $\mathrm{C}\underline{-}\mathrm{C}\underline{-}\mathrm{C}$ stretching vibration at 1558 cm^{-1}.[254] This theoretical value was in agreement with the experimental one, when allyl chloride was co-deposited with SbF$_5$ on a NaCl crystal in a vacuum at 130 K (see Figure 17).

They observed the development of new bands at 1577 and 1547 cm^{-1} parallel to the disappearance of the C=C vibration of allyl chloride at 1641 cm^{-1}. Upon warming the system, the band at 1577 cm^{-1} vanished while that at 1547 cm^{-1} became more

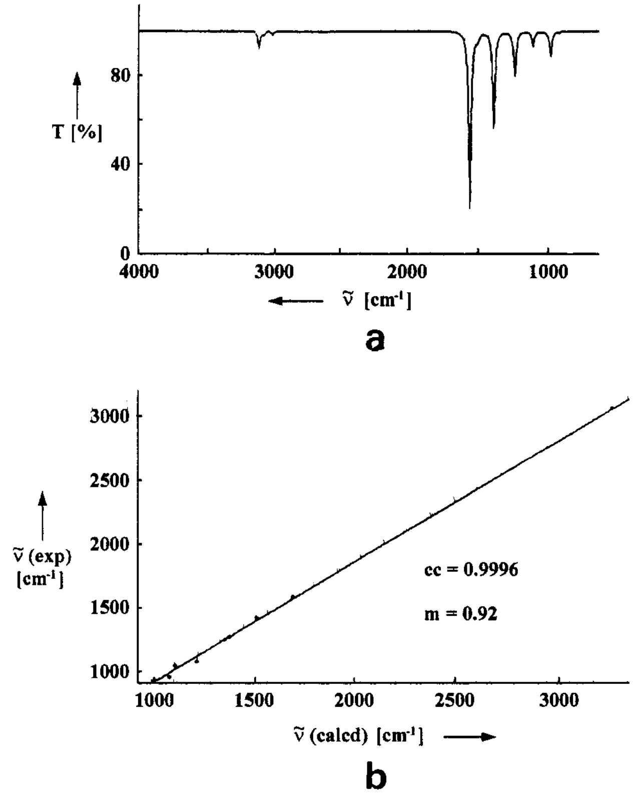


Figure 17. UV−vis spectra of propene adsorbed on HZSM-5 and HY zeolites. (For conditions, see Figure 15.)

intense. At 250 K, the band at 1578 cm^{-1} attributed to the C—C—C vibration of the allyl cation was almost completely replaced by an absorption at 1535 cm^{-1}. The authors assigned this band to a polymeric species. In these experiments Schleyer's group was the first to observe the allyl cation as the smallest long-lived carbenium ion in a solid SbF_5 matrix, proving the formation of this ion under cryogenic conditions.

Later Schleyer et al. reported the results of empirical force field and ab initio calculations of the structural parameters and thermodynamical characteristics of allyl and substituted allyl carbenium ions.[255] From this work, a complete theoretical description of the alkenyl carbenium ions is available.

Combined UV−vis−IR spectroscopic investigations aimed at the identification of surface species formed from olefins on zeolites at low temperatures show a good correlation between the appearance of the UV−vis absorption near 310 nm, observed in both superacids and zeolites and assigned to monoenyl carbenium ions, and the IR band at ca. 1510 cm^{-1}. According to Deno, symmetrically substituted allyl carbenium ions have a sharp band at 1530 cm^{-1} with a large absorption coefficient in strong acidic solutions.[11] Taking into account the experimental evidence obtained by UV−vis and IR spectroscopy and the similar behavior of olefins and alcohols in superacids and zeolites, Deno's assignment given for the band at 1530 cm^{-1} can be adopted for zeolites too. Therefore, this band must be due to alkenyl carbenium ions developed in zeolites.

These unsaturated carbenium ions may be formed at low temperature by (i) hydride ion abstraction on Lewis acid sites, or (ii) intermolecular hydride ion abstraction from olefins by alkyl carbenium ions, or (iii) conjunct polymerization at medium temperature or by (iv) cracking of oligomers. For the formation of the allylic carbenium ion, mechanism (ii) may be favored as zeolites usually contain more Brønsted than Lewis sites. For the generation of di- and trienylic carbenium ions and their further transformation, a detailed reaction scheme has been proposed by Vedrine et al.[214] According to this suggestion, alkenyl carbenium ions may be regarded as the precursors of aromatic compounds which are formed at higher temperatures.

VIII. Role of Alkenyl Carbenium Ions in Solid Acid Catalyzed Reactions

A. Role of Unsaturated Carbenium Ions in Alkylation with Olefins

1. Alkylation of Benzene with Propene

Alkylation reactions proceed via alkyl carbenium ions formed from an olefin reacting with aromatic molecules.[256] Depending on the reactant ratios, side reactions olso occur. For the isopropyl carbenium ion generated from interaction of propene with a Brønsted acid site, there are two main reaction routes to byproducts: (i) reactions with a second propene molecule (present in the zeolite channels or cages) resulting in oligomeric carbenium ions or (ii) hydride ion abstraction to form unsaturated carbenium ions. Both transformations may run into the formation of carbonaceous deposits. Increasing benzene concentration in the feed suppresses the side reactions since it converts isopropyl carbenium ions into alkylate. Recently, a theoretical model of the *n*-propylbenzene formation in isopropylation of benzene with propene over zeolites was suggested.[257] It is concluded that the byproduct *n*-propylbenzene forms in the reaction of benzene with protonated isopropylbenzene. This assumption is in accordance with the general stability order of carbenium ions, i.e., formation of primary carbenium ions is unlikely due to its very low stability.

Ivanova and Derouane carried out in situ ^{13}C MAS NMR experiments[112] and Flego et al. IR−UV−vis studies[258] of the alkylation reaction, finding the role of propene as discussed above. Both groups arrived at the same conclusions: (i) the NMR signals depicted in Figure 18 prove that the surface species, the isopropyl carbenium ions, are partially localized on the surface since the mobility of one of the methyl groups is restricted while the IR spectra in Figure 19 reveal the formation of alkenyl carbenium ions, furthermore, (ii) in excess benzene, only slow oligomerization of propene has been detected.

As reported,[258] the carbenium ion-forming capabilities of propene, benzene, and cumene are different. Benzene was found to be less reactive than propene or cumene. Formation of alkenyl carbenium ions from propene takes place easily even at room temperature. UV−vis spectra of the self-supporting wafers show no bands in the case of a sample used after benzene adsorption and its color remained white, while on the

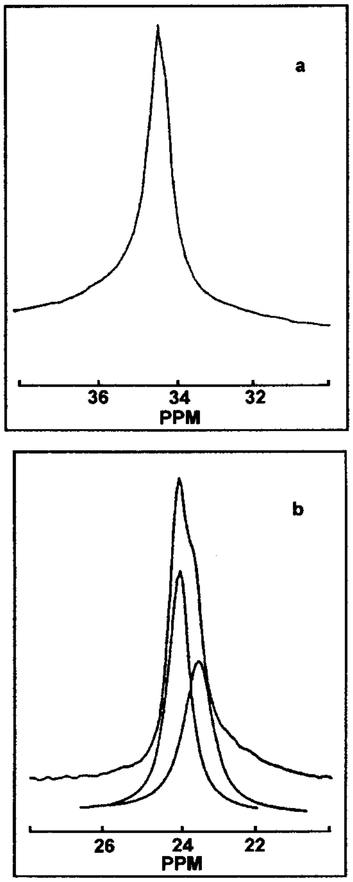


Figure 18. Calculated spectrum of allyl carbenium ion (a) and the correlation between the calculated and experimental spectra of allyl carbenium ions (b). (Reprinted with permission from ref 254. Copyright 1994 VCH.)

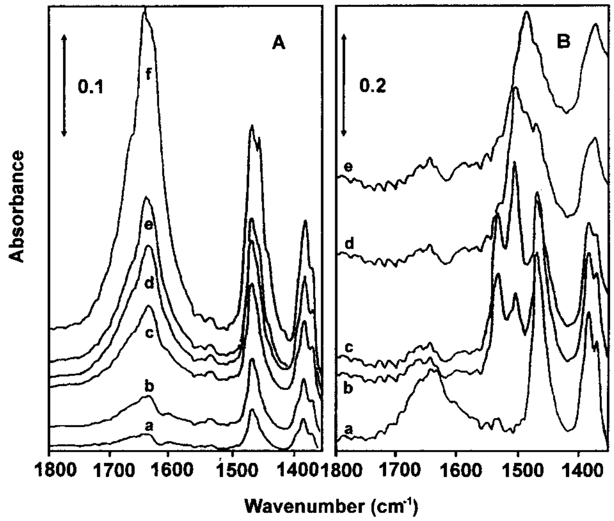


Figure 19. Aliphatic regions of ^{13}C MAS NMR spectra observed immediately after adsorption of 1 molecule/UC of (a) propene-2-^{13}C or (b) propene-1-^{13}C and 9 molecule/UC of benzene over HZSM-11 at 298 K. (Reprinted with permission from ref 112. Copyright 1994 Elsevier Science.)

other specimen two intense bands appeared accompanied by a brownish-yellow coloring.

2. Alkylation of Isobutane with Butenes

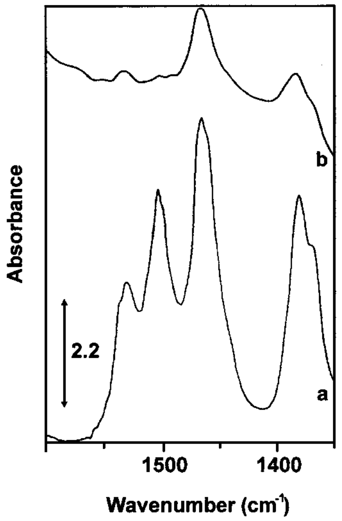


Figure 20. Difference IR spectra of H-beta zeolite after loading (A) with increasing amounts of propene (0.1−1 Torr, a−f) at 295 K and desorption (B) at 295 K (a), 373 K (b), 423 K (c), 473 K (d), and 523 K (e) for 30 min. (Reprinted with permission from ref 258. Copyright 1995 Elsevier Science.)

In 1993, Corma reviewed the factors affecting the yield of alkylates such as reaction temperature, acidity of the solid catalyst, space velocity of the reactants, reactant ratios, and time on stream in the alkylation of isobutane with 1-butene.[259] The influence of the reaction temperature on the activity of zeolite catalysts and deactivation was investigated by Weitkamp and Maixner by applying CP/MAS ^{13}C NMR spectroscopy.[260] Recently, the role of 1-butene in the alkylation reaction was studied by IR−UV−vis spectroscopy.[160] Flego et al., operating under various experimental conditions, found that the amount of alkenyl carbenium ions present in the zeolite catalyst correlates with the concentration of carbonaceous deposits formed on the catalysts.[261] The conclusions of these papers may be summarized as follows.

The amount of alkylate (paraffin) in the reaction product changes for oligomers (olefin) with time on stream and the catalyst deactivates rapidly. On the Brønsted and Lewis acid sites of the zeolite catalyst, the oligomerization of butenes may proceed on both sites with participation of alkyl and alkenyl carbenium ions. The generation of alkenyl carbenium ions is enhanced by increase of temperature and contact time. However, in the presence of isobutane, the generation of alkenyl carbenium ions is almost completely suppressed due to the enhanced hydride ion donor property of isobutane, see the difference of the intensity of bands around 1500 cm^{-1} in the spectra shown in Figure 20. This reaction to alkylate may contribute to lowering of the rate of catalyst deactivation since the olefin takes part in the alkylation but not in the oligomerization reaction.

The chemical nature of low-temperature coke from isobutane/1-butene alkylation is essentially paraffinic. With increasing reaction temperature, it becomes olefinic and/or aromatic. In the low-temperature deposits, a small amount of unsaturated species (H/C ratio below 2) is also present, as demonstrated by elemental analysis. These materials were not detected by NMR spectroscopy. Recently, Parker

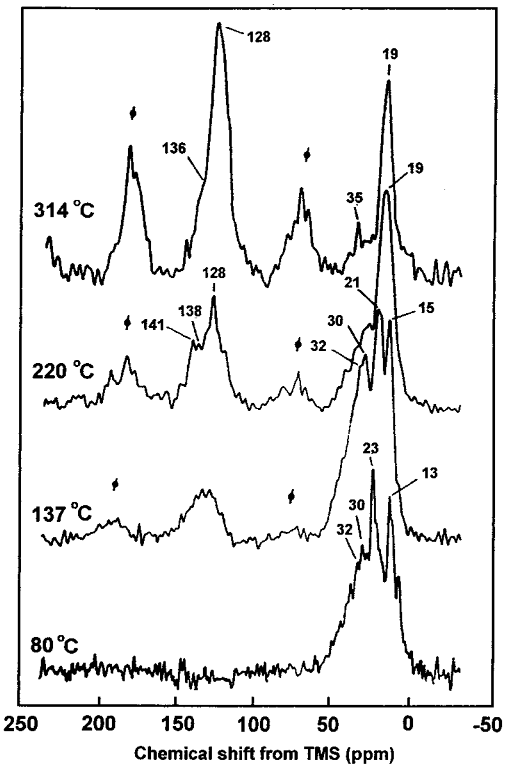


Figure 21. IR spectra of La-beta after loading of 1.33 kPa of (a) 1-butene and (b) 1-butene/isobutane mixture at 353 K for 1 min, followed by evacuation at room temperature. (Reprinted with permission from ref 160. Copyright 1995 Elsevier Science.)

published the spectrum of the trimethyl cyclopentenyl carbenium ion formed from 1-butene in triflic acid solution.[168] Representative spectra published by Maixner et al. are shown in Figure 21.

Using UV–vis spectroscopy, the presence of alkenyl carbenium ions was evidenced in the catalyst samples used in reactor experiments under various experimental conditions. It was proven that with increasing reaction temperature, the band due to the dienyl carbenium ions increased. Prolonging the residence time of the reactant yielded a used catalyst containing more unsaturated residues. By raising the activation temperature of the catalyst prior to reaction, i.e., increasing the Lewis acidity of the zeolite, the formation of polyenyl carbenium ions was enhanced, as shown in Figure 22.

From the results discussed above, the dominant role of the olefins and the reaction conditions in the formation of alkenyl carbenium ions is evident.

B. Role of Alkenyl Carbenium Ions in the Formation of Carbonaceous Deposits

For the design of the appropriate catalytic activity of zeolites, including the suppression of catalyst deactivation, an understanding of the reactions leading to the formation of deposits is necessary. For the deactivation process, a characteristic role was attributed to the alkenyl carbenium ions.

Due to its major importance, deactivation of zeolite catalysts in hydrocarbon reactions was investigated by several techniques such as ^{13}C NMR,[112,262–264] electron microscopy and EELS (electron energy loss spectroscopy),[265] in situ IR spectroscopy,[252,266] reactor and/or kinetic experiments,[267–270] and also with the combination of these techniques.[100]

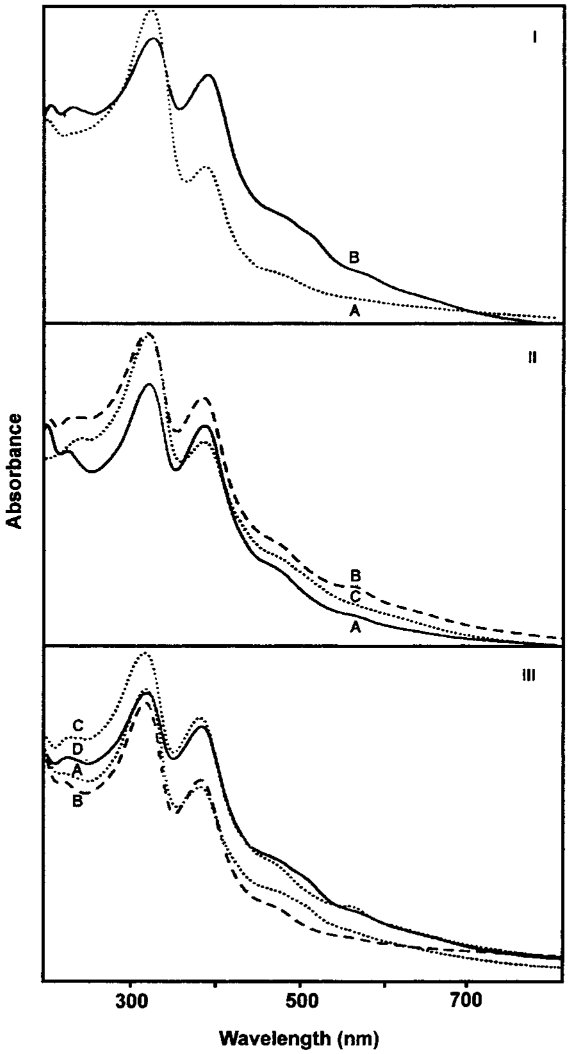


Figure 22. CP/MAS ^{13}C NMR spectra of the carbonaceous deposits from the conversion of isobutane and 1-butene on LaNaY zeolite at different temperatures. (Reprinted with permission from ref 262. Copyright 1987 Elsevier Science.)

It has been established that formation of carbonaceous deposits is also influenced by the zeolite structure, i.e., the pore geometries of the given zeolite. The deposit formation is very pronounced on zeolites of one-dimensional pore structure or large cavities with small openings. As the deactivation is a shape-selective process, its rate and selectivity depends not only on its pore structure but also on the size ratio of the cages to the precursor of the deposits. The difference between the diffusion rate of the precursors and the reactants and products is regarded as an additional factor.

Dimon et al. showed that cokes formed from propene at 393 and 723 K on USHY (USHY denotes an *u*ltrastabilized HY(–FAU) zeolite prepared by steaming of HY–FAU zeolite at high temperature in order to remove some aluminum from the framework) and HZSM-5 zeolites possessed very different H/C ratios.[269] Independent of the zeolite type, this ratio is close to 2 at the lower temperature and much

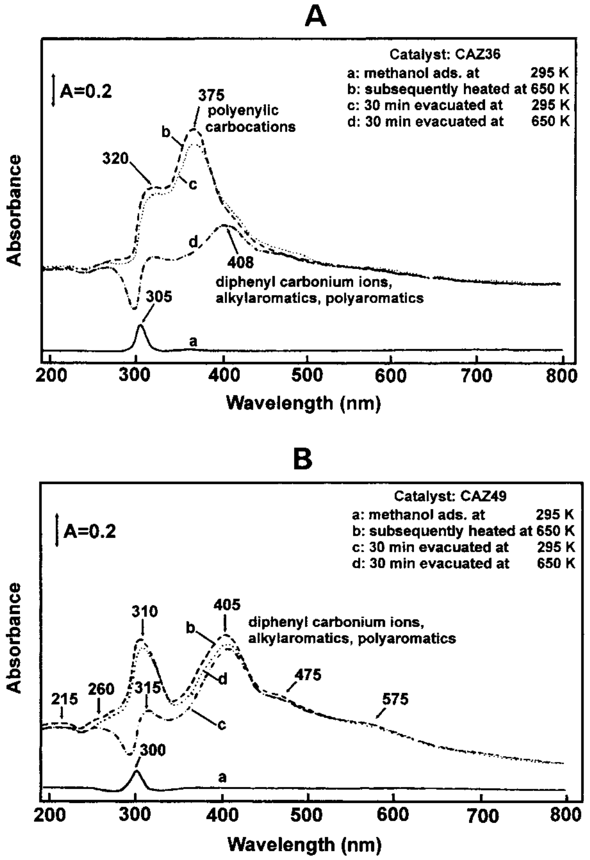


Figure 23. UV−vis difference spectra of a ZSM-5 based catalysts (denoted as CAZ 36, Figure A and CAZ49, Figure B) coked via the methanol reaction prior and after evacuation (RT or 650 K, 10^{-5} Pa, 40 min). (Reprinted with permission from ref 103. Copyright 1989 Elsevier Science.)

smaller than 1 at higher temperature. Maixner et al. came to a similar conclusion in their NMR study of adsorption and reaction of 1-hexene over LaY zeolite.[262] Guisnet suggested a coking reaction mechanism in which both alkenyl and alkylaryl carbenium ions were involved.[271]

The coke formation from methanol over HZSM-5 zeolite was investigated in more detail by Karge et al.[103] These authors pointed to several important factors such as the acidity of the catalyst, the reaction temperature, and the morphology of the catalyst influencing the formation of carbonaceous deposits. Two representative sets of spectra are shown in Figure 23.

In both cases, deposits were generated by 1 h of heating the zeolite in the presence of methanol at 650 K. This procedure was followed by evacuation at increasing temperature. Evacuation at room temperature did not bring about remarkable changes in the spectra. At higher temperatures, evacuation removes the volatile surface components being responsible for the bands at 310 and 315 nm. These bands are assigned to π-allyl and cyclohexenyl cations. Such a treatment leaves the bands of bulky aromatic compounds practically unchanged. The comparison of the two sets of spectra clearly shows the differences between the two zeolite samples. It was concluded that these differences arise from the influence of the different acidity and morphology of the samples.

IX. Some Remarks on the Radical and Radical Ion Generation

Although the generation and transformations of radicals and radical ions are not the subject of this review, we should touch on this topic since they are also assumed to be reactive intermediates in hydrocarbon reactions over solid catalysts.[274−277]

First, Kasai and Bishop summarized the results accumulated at that time in the application of ESR spectroscopy in zeolite chemistry and catalysis.[278] The most interesting question, the nature of active sites that are able to generate radicals, has been discussed in detail, in those cases when γ- or X-rays or UV irradiation have been applied at low temperature (generally at 77 K). They concluded that superoxide ions (O_2^-) associated with the exchange cations (generally Na^+), or framework aluminum, or interstitial aluminum species, or electron holes trapped by framework oxygen, or excess electrons trapped by trigonally coordinated aluminum are the potential active sites. The concentration of these sites is strongly influenced by the pretreatment condition of the zeolite. More than 20 years ago, these authors wrote “The most persistent difficulty encountered in the study of irradiated zeolites appears to be its reproducibility, especially among different laboratories”. Furthermore, the generation of reactive intermediates by irradiation in the industrial application of zeolites as catalysts is unknown. However, effort should be invested to discover the conditions of their formation. Summarizing, (i) alkali (or alkali earth) metal ion forms of zeolites are frequently used for these studies. (ii) Radical ions may be generated even from paraffins at rather low temperature. (iii) The presence of O_2 or treatment of the zeolite in O_2 or air at high temperature are general prerequisites of the formation of radicals or radical ions. From this follows that these surface species behave completely different from those of alkenyl carbenium ions, since (i) sodium forms of zeolites are generally inactive (or show extremely low activity) in alkenyl carbenium ion formation, (ii) alkenyl carbenium ion formation from paraffins has been observed only after their secondary transformation (cracking, dehydrogenation) via olefins, (iii) alkenyl carbenium ions can be generated at room temperature or above, (iv) oxidation centers or oxygen treatment of zeolites are not obligatory prior to adsorption of hydrocarbons, and (v) the active sites for ion formation are known, they are either Brønsted or Lewis acid centers.

As far as the spontaneous generation of radicals or radical cations is concerned, it is generally accepted that these surface species may easily be formed from hydrocarbon molecules having a low (less than 10 eV) ionization potential, such as aromatic and polyaromatic compounds.[279−281] However, free radical formation from saturated hydrocarbons has also been detected.[282] Radical ion generation was found for adsorption of small olefins such as ethene and propene[134,135,136,283,284] for dimethylacetylene[285] and for 3,3-dimethyl-1-butene and 2-butyne.[286] Shih assumed a so-called “solid-state defect site” as the active center in HZSM-5 zeolite which was able to generate radical ions.[286]

Recently, an excellent review was published by Rhodes and Hinds on the identification of organic cation radicals in zeolites.[287] The authors reported their own results of the reinvestigation of the spontaneous radical ion formation from several hydrocarbons including paraffins, olefins, dienes, and also acetylene derivatives, and they compared these data to those found in the literature. Looking over the possible and assumed active sites including the superoxide species, paramagnetic sites (iron and transition metal ion impurities), solid state defect sites, and oxidizing centers associated with aluminum, it turned out that Lewis acid sites are the most likely centers to generate radical ions spontaneously. It has been emphasized that oxidative pretreatment favors the formation of radical ions from both olefinic and aromatic hydrocarbons. However, according to the authors, there is little evidence that radical cations are involved in heterogeneous catalysis by zeolites. Obviously, as UV−vis spectra are quite sensitive to both alkenyl carbenium ions and the corresponding potential radical cations, more extensive work is needed using NMR and ESR technique additional to UV−vis spectroscopy to differentiate between surface species formed from hydrocarbons.

A quite new research area has being widened, dealing with intrazeolitic photochemistry. In these photochemically initiated transformations of hydrocarbons over zeolites, both radical ions[288−292] and carbocations[293,294] are assumed to be formed as reactive surface intermediates. However, Corma showed that a photoinitiated reaction can occur via either ionic or radical cationic mechanisms.[295]

On proton and electron-transfer reactions occurring in zeolites, a feature article was published recently.[296] The authors describe the generation of carbocations and cation radicals from quite large polyaromatic molecules. These bulky surface intermediates probably play an important role in catalyst deactivation by coking. Indeed, Gutsze et al. demonstrated that even from small olefins, like ethene and propene, the radical formation is in connection with coking of the zeolite.[283,284] From the combined ESR and ^{13}C NMR spectroscopic results, they could differentiate between two types of coke: low-temperature coke below 500 K while above high-temperature coke characterized by a “single-line coke spectrum” with $g = 2.0024$ present. Lewis acid centers are assigned as active sites for the generation of radical ions.

Zeolites are generally used as catalysts in Friedel−Crafts reactions, in which there is not enough space for cation radicals.[297] However, agreeing with Rhodes and Hind[287] about the generation, nature, and transformations of radical cations in zeolites, it should be emphasized that “an exciting area is predicted”.

X. Conclusions

Nowadays, the presence of carbocations in acid-catalyzed reactions is widely accepted, although due to their mostly short lifetimes and/or low concentrations, their presence is more easily postulated than proved by spectroscopic methods. The spectral proof of carbocations requires the existence of so-called key bands, i.e., characteristic group frequencies for IR and chromophoric groups for UV−vis absorption.

Zeolites, modified by synthesis or postsynthesis treatment to solid acids, are important catalysts in hydrocarbon transformations. The acidity of zeolites is usually characterized by TPD, calorimetry, the indicator method, IR, and/or NMR spectroscopy. Despite many similarities between superacid solutions and acidic zeolites, there are also differences, e.g., different proton transfer energies, weaker complexation energies, and steric constraints like molecular sieving and shape-selective effects in the case of the latter. Formation of carbocations takes place by protonation of Brønsted acid sites (B sites), assisted by the Lewis base oxygens, or hydride ion abstraction on Lewis acid sites (L sites). Both processes may occur in parallel due to the simultaneous presence of B and L sites in zeolites. The ability for generation of unsaturated carbenium ions, to which this review is essentially devoted, follows the same sequence dienes > olefins > alcohols > paraffins as found by Rosenbaum and Symmons for superacid solutions. Once formed, they may undergo consecutive reactions such as (i) charge or hydride transfer, (ii) skeletal isomerization, (iii) chain increase/shortening, or (iv) cyclization.

Alkenyl carbenium ions can be generated from a multitude of different compounds such as alkanes, alkenes, alkynes, di- and polyenes with conjugated double bonds, cycloalkanes, cycloalkenes, aromatic hydrocarbons, alcohols, ketones, etc., by applying different temperatures, acidities, and time of contact. The ion-forming capability varies from case to case.

While the development of the first alkenyl carbenium ions is unequivocal, their secondary transformations are still controversial. Sometimes the experimental findings, the intermediates, and the interpretations are ambiguous, as in the case of acetylene oligomerization. Frequently, the structure of the surface species is still unknown.

Electronic spectroscopy in the UV−vis region accessible to commercial spectrometers is a valuable tool for the detection of alkenyl carbenium ions. While alkyl carbenium ions due to their high-frequency absorptions are excluded from spectral proof, alkenyl carbenium ions can be observed by their $\pi-\pi^*$ transitions which, according to Woodward’s rule, upon alkyl substitution undergo a minor bathochromic displacement. An increase in the number of conjugated double bonds decreases the HOMO−LUMO distance, thus resulting in a more pronounced red shift together with an increase in intensity. On this basis, the degree of unsaturation of alkenyl carbenium ions can be assigned by the Sorensen and Hafner relations, while the band position is also sensitive to branching. The simplest monoenyl carbenium ion, the allyl carbocation, is supposed to give a band near 293 nm; the bands at 320, 380, and 450 nm are attributed to mono-, di-, and trienyl carbenium ions. The smooth downscale shift of the band upon evacuation at increasing temperatures might be due to species chain length shortened by cracking.

In the IR range, the assignment of bands between 1505 and 1530 cm^{-1} has been discussed either as (i) a π complex between the C═C bond and a B site, (ii) precursors to aromatic compounds, or (iii) the C_−_C_−_C stretching mode of alkenyl carbenium ions. From the parallel appearance of this band together with UV−vis bands between 280 and 500 nm, QC calculations, and experiments in cryogenic matricies, the latter assigment is more likely.

The involvement of alkenyl carbenium ions in a number of technical processes such as alkylation of aromatics or MTG underlines their importance, as, unfortunately, via side reactions they also give rise to coke formation. Attempts to suppress such reaction pathways is a worthwhile goal for further investigations.

XI. References

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