[Review Paper]

Adsorption of Hydrocarbons and Formation of Carbocations over Zeolites Studied by IR Spectroscopy

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Carbocation species are considered to be important intermediates in the reactions of hydrocarbons over zeolites, and the formation mechanism, as well as the reactivity, has been studied mainly by NMR and IR spectroscopy. The present state of knowledge obtained from these studies is summarized, and experimental details of IR methods for the investigation of solid catalysis are described. As an example of IR research on the catalysis of zeolites, recent results on the formation of alkenyl cation species by the reaction of cyclic alkenes with the acidic hydroxyl groups on zeolites are summarized. The formation of alkenyl cation species was observed by adsorption of cycloalkenes on silica–alumina, HY zeolite, mordenite, H-ZSM-5 and H-beta zeolite, and characterized by IR peaks at 1490–1530 cm^{-1} and UV-visible peaks at 290–330 nm. Formation of alkoxy groups in addition to alkenyl cations was observed on H-ZSM-5 with smaller pores and H-beta with weaker acidity zeolites in comparison with HY zeolite.

Keywords

Zeolite catalyst, IR, Alkene, Carbocation, Adsorption

1. Zeolites

The zeolites form a family of aluminosilicates with periodic porous crystal structures, and are widely applied in industrial processes because of their sorption characteristics, shape selectivity, ion exchange ability, and catalytic properties. Zeolites are particularly important catalysts in the petrochemical field, especially as cracking and reforming catalysts. In addition, the recent attention to Green Chemistry has spotlighted zeolites as waste-free and reusable solid acid catalysts, which could replace conventional homogeneous inorganic acids.

Zeolite structures consist of SiO_4 or AlO_4 tetrahedral unit cells, with each tetrahedron sharing the corner oxygen atoms with neighboring four unit cells to form the crystal lattice. The deficient charge of Al^{3+} relative to Si^{4+} requires cationic species, usually alkaline metals, to be present near the neighboring lattice oxygen atoms to achieve charge balance. Therefore, cation exchange with protons forms hydroxyl groups resulting in a bridging $\text{Si}-\text{OH}-\text{Al}$ structure¹⁾. These bridging hydroxyl groups are well known as Brønsted acid sites, with dissociation equilibria similar to acids in solution (Fig. 1)²⁾. These Brønsted acid sites are the basis for the acid catalytic properties of zeolites. The dissocia-

tion equilibrium of protons on zeolites is balanced to the associated form (hydroxyl groups) in the low temperature range and moves to the dissociated form with increasing temperature. Experiments have confirmed the presence of mobile protons hopping across lattice oxygen anions in pores³⁾.

One specific characteristic of the solid acid catalytic properties of zeolites is shape selectivity, which is attributed to the ordered porous structures with pore sizes (0.4–0.8 nm) similar to molecular sizes. The shape selectivity for any reaction over zeolites includes the effects of the pore size on both the formation rate and the selectivity of products due to the restricted size of reactant and product molecules related to the pore size. The shape selectivities over zeolites can be summarized as effects on the reactants, the products, and the transition state. Reactant shape selectivity regulates the intercalation of large reactant molecules and promotes the access of small molecules to the active sites inside the zeolite pores. Product shape selectivity encourages the diffusion of small product molecules out of the zeolite crystal, restricts the migration of large

Fig. 1 Dissociation Equilibrium of Brønsted Acid Sites of Zeolite

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Fig. 2 Lewis Acid Sites and Brønsted Acid Sites of Zeolite

product molecules from inside to outside the zeolite, and cracks larger product molecules into small molecules. Transition state shape selectivity affects the allowable shape of the transition state inside the limited space of the zeolite pores.

Brønsted acid hydroxyl groups allow the zeolite to adsorb various oxygen- and nitrogen-containing molecules by hydrogen bonding, and attract polar molecules by the electrostatic force due to the large dipole moment of the acidic hydroxyl groups. This dipole moment also attracts non-polar molecules with highly polarizable structures such as π -electrons (soft base) through induction of dipole-dipole interactions. Furthermore, non-polar alkane molecules are also adsorbed because the small molecules have similar size to the zeolite pores, resulting in high contact area and resulting dispersion force. Many catalytic reactions over zeolites are considered to depend on the various adsorption properties of zeolites.

Silanol (Si-OH) groups are present on the external surface of zeolites, which are generated by the occurrence of bond deficiencies between silicon and oxygen atoms during crystal growth. Both silanol and acidic hydroxyl groups can be clearly observed and distinguished by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The silanol groups are regarded as neutral in comparison with the Brønsted acid hydroxyl groups, but some silanol groups on ZSM-5 zeolite are weakly acidic⁴⁾.

Zeolites may also contain Lewis acid sites generated by dehydration from two acidic hydroxyl groups under vacuum at above 750 K⁵⁾. The structure of the Lewis acid sites can be explained by the presence of both Al and Si⁺, the contribution of extra-framework AlO⁺ species, or hydroxyl nests (Fig. 2)⁶⁾, but the specific details of the origin of the Lewis acid sites have not been clarified^{7),8)}.

2. Characterization of the Acidic Properties of Zeolites

2.1. NMR

¹H, ²⁹Si and ²⁷Al magic angle spin (MAS) measure-

ments are the most frequently used types of NMR spectroscopy technique for studies on zeolites, so are briefly explained below.

2.1.1. ¹H MAS NMR

The acidic hydroxyl groups on zeolites can be detected by the characteristic chemical shift on ¹H MAS NMR. Generally for H-ZSM-5 zeolites, the chemical shift of silanol groups occurs at 1.8-2.0 ppm and that of the acidic hydroxyl groups at 4.1-4.5 ppm, but these values are dependent on the type of zeolite and the Si/Al ratio. The activation energy for proton dissociation of the acidic hydroxyl groups can be estimated by the dependence of the peak width on temperature³⁾.

2.1.2. ²⁹Si MAS NMR

The coordination of Si to Al through oxygen atoms can be estimated by the value of chemical shift of ²⁹Si MAS NMR, which shifts to lower magnetic field by 5 ppm with each increase in coordination number n ($n=0-4$). Therefore, the Si/Al ratio can be roughly estimated from the ratio of the integrated intensity of the peaks⁹⁾. Since the chemical shift is also affected by the bond angle of Si-O-T (T=Si or Al), assignment of peaks should be carefully considered^{9),10)}.

2.1.3. ²⁷Al MAS NMR

The coordination state of Al can be evaluated by the chemical shift on ²⁷Al MAS NMR. Peaks due to tetra- and penta-coordinated Al occur at 50-60 ppm and 20-30 ppm, respectively. The peak of hexa-coordinated extra-framework Al appears at around 0 ppm. Tri-coordinated Al has not yet been identified by ²⁷Al MAS NMR, but the presence of tri-coordinated Al on mordeinite after evacuation at above 675 K was detected by X-ray absorption near edge structure (XANES) spectroscopy¹¹⁾.

2.2. IR Spectroscopy

2.2.1. IR Absorption of Acidic Hydroxyl Groups

Acidic hydroxyl and silanol groups on zeolites are detected as absorption bands at 3650-3550 and at around 3750 cm⁻¹, respectively, by IR spectroscopy. The lower absorption energy of the acidic hydroxyl groups relative to that of the silanol groups is attributed to the decrease in electron density of the O-H bond due to the donation of electrons from the oxygen of the

Fig. 3 Polarization by Electron Donation from O to Al

acidic hydroxyl groups to the adjacent Al atom (**Fig. 3**). This donation is the origin of the Brønsted acidity of the acidic hydroxyl groups of zeolites¹⁾. Since the acid strength is also dependent on the steric factors represented by the bond angle of Si-O-Al, simple comparison of the frequency of the IR absorption bands cannot indicate the acid strength^{12),13)}. The energy difference between the associated and the dissociated acidic hydroxyl groups can be estimated from the dependence of the integrated peak intensity on temperature²⁾.

2. 2. 2. Characterization of Acid Sites by Using Probe Molecules

IR spectroscopy can be used for the characterization of acidity and adsorption features through the investigation of adsorbed probe molecules. Pyridine is a typical probe molecule for IR characterization. Pyridine adsorbed on Lewis acid sites shows a CH in-plane bending mode at around 1450 cm^{-1} , whereas protonation by Brønsted acid sites forms pyridinium ions with a characteristic band at around 1540 cm^{-1} ^{14),15)}. Therefore, the presence or absence of these two types of acid sites on zeolites can be shown by IR observation of adsorbed pyridine. Another typical probe molecule is CO. CO molecules adsorbed on Brønsted and Lewis acid sites shows a stretching absorption band at $2150\text{--}2190\text{ cm}^{-1}$. CO probes for IR characterization have long been used for metal and metal oxide surfaces as well as cation-exchanged zeolites¹⁶⁾, and are now applied for proton-type zeolites. One of the advantages of the CO probe over the pyridine probe is the smaller molecular size, which enables adsorption in the small pores of zeolites. However, CO is only weakly basic compared with strongly basic pyridine, so interaction and consequently detection is only possible with strongly acidic sites^{7),17)~20)}. Other probe molecules, such as N_2 , O_2 , H_2 , Ar, Kr, Xe and others, are also used^{7),13),18)~22)}.

3. Experimental IR Spectroscopy Systems for Solid Catalysis

IR spectroscopy is widely used to study solid catalysis including zeolites and provides various types of information. The changes in hydroxyl groups bridging between Si and Al, which are responsible for zeolite acid catalysis, can be observed clearly by IR spectroscopy simultaneously with the changes in adsorbed reactant, product, and intermediate species. Various *in-situ* measurements have been devised for the investigation of catalytic reactions over zeolites. Some examples of

Fig. 4 IR Cell

Fig. 5 Closed Circulation System

experimental set-up and method are described below.

3. 1. *In-situ* IR Cell and Closed Gas-circulation System²³⁾

In-situ IR measurements provide a wide variety of information since real time observation of the catalytic reactions is possible by using Fourier transform (FT) IR. The types of information include the state of the adsorbed species, and the changes in functional groups of the surface species, which are closely related to the reaction mechanisms over solid catalysts. A schematic illustration of an *in-situ* IR cell is shown in **Fig. 4**. The temperature, which is monitored by a thermocouple attached near the sample, is controlled by cooling with liquid nitrogen flow in a stainless steel tube and electrical heating around the cell in the range between 90 and 900 K. Connection of the IR cell to the closed gas-circulation system, as illustrated in **Fig. 5**, allows evacuation and exposure of the catalyst to molecules in the gas phase.

Scheme 1 Proposed Mechanism of Formation of Alkenyl Cation in the Oligomerization of Propene Catalyzed by HY

3. 2. Sample Preparation for the Transmission Method^{(24),(25)}

3. 2. 1. Disk Preparation

A sample of a powder catalyst can be easily prepared as a disk together with an alkaline halide binder (ratio 1 : 100 to 1 : 300) in an oil-press for transmission IR measurements. This method requires only a small amount of sample. The spectra of the catalysts can be compared, but this method is not suitable for the observation of catalytic reactions. Additionally, the observation of surface hydroxyl groups on the catalysts is hindered by presence of water in the sample disks because alkali halides are highly hygroscopic.

Samples of zeolites for observation of *in-situ* catalysis are prepared as self-supporting disks for the transmission IR method. By knowing the weight of the catalyst, the surface area of the disk, and the size of the IR beam spot, quantitative analysis of the surface and the adsorbed species is possible. However, some samples of high silica zeolites are difficult to form into disks, and some structured materials collapse in the oil-press. In such cases, the adhesion method is more suitable.

3. 2. 2. Adhesion Method

Catalyst powders can be stabilized on the same substrates (CaF_2 , Si and so on) as sample disks by adhesion after dispersion in solvents. Iso-propanol was originally used⁽²⁶⁾, but acetone and ethers have also been used recently. Catalyst powders should be well ground to achieve homogeneous dispersion of the samples, and to avoid scattering and loss of the IR beam. Grooves in the substrate and oblique positioning of the substrate plate in the cell may help with sample stabilization.

3. 3. Diffuse Reflectance IR Spectroscopy (DRIFT)⁽²⁵⁾

DRIFT is superior to the conventional transmission method because no special sample preparation is necessary: powder catalysts can be measured simply by placing in a sample cup. Some types of commercially available *in-situ* sample holders can be adjusted for FT-

IR sample rooms. However, careful attention should be paid for the quantitative interpretation of the results because the intensity and shape of absorption bands are dependent on the particle size of the sample and the space density in the sample cup. In addition, DRIFT increases the intensity of the signals from the adsorbed species by several multiples of ten compared to the transmission method for catalysts with small specific surface area^{(27)~(29)}.

4. Investigation of Intermediates in Reactions of Hydrocarbons over Zeolites

Reaction mechanisms and intermediates in the reactions of hydrocarbons on zeolites have been intensively studied, and some intermediate structures have been proposed.

4. 1. Alkenyl Cation Intermediates

Alkenyl cation is formed by hydride subtraction from alkenes, proton addition to alkenes, and dehydration of carbenium cations. Experimentally, the formation of alkenyl cation was observed using ^{13}C variable temperature (VT)-MAS NMR during propene oligomerization over HY zeolite⁽³⁰⁾. The cyclopentenyl cation was formed by intermolecular addition of propene and dehydration of the conjugated diene species, which formed a ring *via* intermolecular hydride transfer to form the cyclopentenyl cation (**Scheme 1**). Cyclopentenyl cation was also produced by cracking of ethene oligomer on H-ZSM-5 zeolite⁽³¹⁾. In addition, alkenyl cations can be formed by protonation of conjugated dienes, α , β -unsaturated ketones, allyl alcohols, and so on at Brønsted acid sites (**Scheme 2**)⁽³²⁾. The characteristic signals of the alkenyl cations are observed at 250 ppm by ^{13}C MAS NMR, 1490-1530 cm^{-1} by IR, and 300-330 nm by UV spectroscopy. Only the electron-delocalized hydrocarbon cation species are experimentally observed, and no electron-localized hydrocarbon cations have been reported. This suggests the requirement of significant stabilization by intramolecular electron-delocalization in the highly nucleophilic pore

Scheme 2 Formation of Alkenyl Cation Catalyzed by Brønsted Acid Site

Fig. 6 Carbenium Ion and Carbonium Ion

spaces of zeolites³⁰⁾.

4.2. Carbenium Cation and Alkoxy Intermediates

Alkenyl cations are the stable intermediate of reactions of hydrocarbons and alcohols over zeolites, which are formed *via* multi-step reactions, whereas carbenium cations (**Fig. 6**) are the initial intermediates formed immediately after protonation by the acidic hydroxyl groups on zeolites following the reaction mechanisms in homogeneous acid catalysis. Carbonium cations have also been proposed as intermediates of reactions of saturated hydrocarbons^{33),34)}. Carbenium cation intermediates were formed *via* the carbonium ion transition state (**Fig. 6**) during *n*-alkane cracking to lighter hydrocarbons, based on the superacidity of zeolites. This mechanism explains the observation that branched cracking products are preferentially produced. However, no experimental observation of carbenium cation has been reported, so only indirect experimental data represented by product analysis are available.

One proposal is that zeolites are not superacids but that the skeletal structure is more important to stabilize the intermediate, which continues the idea that the conventional estimation of the acid strength of zeolites is over-estimated and that acid strength is not the only factor involved in the catalytic activity³⁰⁾. Solvation is generally accepted to be important to stabilize carbenium cations in homogeneous systems. Solid catalysis was distinguished from homogeneous catalysis based on the presence and absence of solvation by quantum chemical calculations of the reaction intermediates of alkenes and zeolitic protons: addition of a proton from the acidic hydroxyl groups of zeolite to an alkene (ethene) resulted in an alkoxy (ethoxy) group *via* a carbenium (ethyl) cation as a transition state³⁵⁾. The calculation results suggested that the intermediate structure on zeolites was different from that in liquid phase due to the absence of solvation. Therefore, simple monomeric ionic compounds, which are generally considered, are not stabi-

lized on zeolites. This concept also explains the experimental results of product selectivity for branched alkanes by adopting the semi-empirical rule that a more stable intermediate has a more stable transition state. The alkoxy groups are intermediate because carbenium cation $[\text{Si}-\text{O}^--\text{Al}]\text{R}^+$ would react rapidly to form the alkoxy group $[\text{Si}-\text{OR}-\text{Al}]$ due to the high nucleophilicity of the zeolite pore spaces^{30),32)}.

These investigations of mechanisms and intermediates provide valuable information to consider the reaction conditions for practical processes. Therefore, we have been studying the adsorption and reactions of hydrocarbons on zeolites by direct observation using IR spectroscopy. Our findings on the reactions of cyclic alkenes, alcohols and ethers on zeolites are described below.

5. Direct Observation of Reactions of Cyclic Alkenes on Zeolites by IR Spectroscopy^{36)~40)}

5.1. Detailed Experimental Procedure

5.1.1. Sample Preparation

The following catalysts were used: HY (JRC, Si/Al = 2.8), H-ZSM-5 (Ashahi Chemical Industry Co., Ltd., Si/Al = 27), mordenite (JRC, Si/Al = 10), H-beta (SÜDCHEMIE AG, Si/Al = 25), silica-alumina (Catalysts & Chemicals Ind. Co., Ltd., Si/Al = 19) and silica (Aerosil Nippon). Each sample was pressed into a self-supporting disk ($10 \text{ mg} \cdot \text{cm}^{-2}$) and was placed in the center of an IR cell, which was connected to a closed gas-circulation system. The sample was pretreated in the *in-situ* cell, first by oxygen at 773 K for 1 h, then by evacuation for 10-60 min, followed by hydrogen (deuterium) for 1 h at the same temperature. The temperature was then decreased under hydrogen (deuterium) to room temperature, and the gas phase was evacuated at room temperature. This series of pretreatments does not produce any Lewis acid sites¹⁸⁾. All organic reagents were purchased from Aldrich and were used as received.

5.1.2. IR Measurement

Spectra were measured after adsorption of 10-40 μmol of organic compounds at 150 K onto the pretreated catalysts followed by evacuation, unless otherwise mentioned. Typical measurements were conducted during gradual heating ($6 \text{ K} \cdot \text{min}^{-1}$) under evacuation with a JASCO 7000 FT-IR equipped with an MCT detector at 4 cm^{-1} resolution. Spectra were obtained by subtracting the background spectrum measured before hydrocarbon adsorption after pretreatment. Therefore, decreases in species appear as negative peaks and increases in species as positive peaks in spectra.

5.1.3. UV-visible Diffuse Reflectance Spectroscopy

UV-visible diffuse reflectance spectra were measured after the introduction of organic compounds at liquid nitrogen temperature followed by gradual warming to

Negative peaks indicate consumption of the OH groups.

Fig. 7 (A) IR Spectra of CPE Adsorbed on (a) SiO_2 at 196 K; and on HY at Various Temperatures without Evacuation: (b) 150 K; (c) 183 K; (d) 207 K; (e) 236 K; (f) 268 K; and (g) 298 K
(B) IR Spectra of CPE Adsorbed on HY at Various Temperatures under Vacuum: (a) 298 K; (b) 323 K; (c) 373 K; (d) 423 K; (e) 473 K; and (f) 523 K

room temperature for 30 min.

5. 2. Reactions of Cyclic Alkenes over Zeolites

5. 2. 1. Reaction of Cyclopentene (CPE) Adsorbed on HY Zeolite

IR spectra measured after adsorption of CPE at 150 K and immediate evacuation followed by gradual warming under vacuum are shown in **Fig. 7**. The reference spectrum (a) in **Fig. 7A** shows CPE adsorbed on the silanol groups of silica with hydrogen-bonding interaction. The band of the free silanol groups (3750 cm^{-1}) present before adsorption of CPE was converted to the broad band ($3800\text{--}3300\text{ cm}^{-1}$) of the hydrogen-bonded groups after adsorption of CPE with its $\text{C}=\text{C}$ bond, resulting in a negative peak of the former and the positive peak of the latter. The frequencies of all absorption bands at lower frequency than 3300 cm^{-1} in **Fig. 7A** (a) are identical to those of free CPE⁴¹⁾. The olefinic feature of CPE is shown by the CH stretching band of $=\text{CH}$ groups at 3061 cm^{-1} and $\text{C}=\text{C}$ stretching band at 1600 cm^{-1} . Other bands observed at $3000\text{--}2700$ and below 1550 cm^{-1} are attributed to CH_2 stretching and bending vibration modes, respectively. In the case of HY zeolite, the negative peak of the acidic hydroxyl groups was observed at 3647 cm^{-1} and alternative broad hydrogen-bonded band centered at 3141 cm^{-1} . The larger shift from the isolated to the hydrogen-bonded hydroxyl band of the acidic sites in comparison with silanol groups is attributed to the stronger interaction of the adsorbed CPE with the acidic hydroxyl groups than with silanol groups, as confirmed by the $=\text{CH}$ (3039 cm^{-1}) and $\text{C}=\text{C}$ (1598 cm^{-1}) stretch-

ing bands of the adsorbed CPE both occurring at lower frequencies on HY zeolite than on silica.

With increasing temperature, two bands at 2934 and 1498 cm^{-1} appeared and increased in intensity. Spectra measured after further heating in vacuum are shown in **Fig. 7B**. All bands had lower intensity than in **Fig. 7A** (see scales), indicating the desorption of considerable amounts of CPE by heating in vacuum. The characteristic bands of adsorbed CPE (olefinic $=\text{CH}$ and $\text{C}=\text{C}$ stretching bands) disappeared at 323 K , whereas CH stretching and other bands were observed at $2700\text{--}3000$ and $1300\text{--}1600\text{ cm}^{-1}$. Simultaneously, the negative peak of the free acidic hydroxyl bands remained, while that due to the hydrogen-bonded species disappeared, indicating the consumption of acidic hydroxyl groups in the reaction of the adsorbed species, and the observed bands in **Fig. 7B** at 323 K were assigned to the reaction product. The negative peak at 3647 cm^{-1} disappeared with further heating to 473 K , followed by gradual decrease in intensity of all peaks up to 523 K . A broad peak centered at around 3500 cm^{-1} was observed at above 423 K , which was attributed to the acidic hydroxyl groups hydrogen bonded with alkyl groups of the hydrocarbon oligomeric species formed by the reaction⁴²⁾. On the other hand, the peak at 1498 cm^{-1} in CH bending absorption region increased in intensity up to 373 K in **Fig. 7B**, then decreased gradually during heating, and disappeared at 523 K .

The consumption of acidic hydroxyl groups between 298 and 373 K is considered to form alkoxyl groups or carbenium cations accompanied by proton transfer from

the acidic hydroxyl groups. The band at 1498 cm^{-1} , which appeared with increasing temperature, was attributable to the reaction product. Similar bands at $1490\text{--}1530\text{ cm}^{-1}$ were observed for the reaction products of light alcohols and alkenes over zeolites at $320\text{--}373\text{ K}$ ^{43)–49)}, and assigned to aromatic ring breathing^{45)–47)}, OCO stretching or CC stretching of conjugated structures of $[\text{H}-\text{C}=\text{C}^+]$ and $[\text{H}^+-\text{C}=\text{C}]$ groups⁴⁹⁾. The band at 1530 cm^{-1} observed by the reaction of dienes in superacid solution was attributed to the $[\text{C}=\text{C}-\text{C}]^+$ asymmetric stretching mode, as the band of $[\text{C}=\text{C}-\text{C}]^+$ appeared in between typical C–C stretching ($1200\text{--}800\text{ cm}^{-1}$) and C=C stretching ($1680\text{--}1620\text{ cm}^{-1}$) due to the delocalization of electrons⁵⁰⁾. This assignment was supported by several research groups because of the similarity of superacids and zeolites in acidity^{28),43),44)}. Theoretical calculations and UV-visible spectra of allyl cations also supported this interpretation⁵¹⁾.

NMR observation of the reaction of cyclopentanol adsorbed on HY zeolite indicated that the formation of CPE and its oligomerization accompanied by dehydration occurred with heating to form alkenyl species with peaks at 250 and 150 ppm at $323\text{--}393\text{ K}$ ³¹⁾. In the present study, the alkenyl cation is considered to be produced at lower temperatures due to the initial CPE reactant. Thus, we assigned the observed band at 1498 cm^{-1} to alkenyl cation as previously³¹⁾, as well as the assignment of the band at $1490\text{--}1530\text{ cm}^{-1}$ ⁵⁰⁾.

5.2.2. Reactions of 1-Methylcyclopentene (1-MCPE) and Methylenecyclopentene (MECP) Adsorbed on DY Zeolite

A series of temperature dependent IR spectral changes were measured after adsorption of 1-MCPE and MECP on DY (deuterated Y) zeolite; both resulting in the same spectra at the same temperatures, as shown in **Fig. 8** (c–i). Spectra (a) and (b) in **Fig. 8** correspond to adsorbed 1-MCPE and MECP on deuterated silica, respectively, and are identical to 1-MCPE and MECP in the liquid phase^{41),52)}. Olefinic =CH and C=C stretching bands of 1-MCPE and MECP appeared at different frequencies due to the different molecular structures. The negative peaks of the H- and D-form silanol groups shifted to lower broad frequencies, indicating the direct interaction of the silanol groups with the C=C bonds of 1-MCPE and MECP. Because deuteration of silica and HY zeolite was not complete under the present conditions, considerable amounts of H-form silanol and acidic hydroxyl groups remained. In contrast to silica, both 1-MCPE and MECP adsorption on DY zeolite resulted in the same spectra due to the rapid isomerization of MECP to the more stable 1-MCPE at 150 K, so the =CH and C=C stretching bands were observed at similar positions to those of 1-MCPE on silica. However, the intensity of the olefinic bands was much weaker than those on silica in

The two isomers gave the same results after adsorption on zeolite Y. Spectra of 1-MCPE adsorbed on SiO_2 at 215 K (a); and MECP adsorbed on SiO_2 at 210 K (b) are given as references. The negative peaks indicate consumption of the OH and OD groups.

Fig. 8 IR Spectra of 1-MCPE or MECP Adsorbed on DY at Various Temperatures: (c) 150 K; (d) 183 K; (e) 207 K; (f) 245 K; (g) 298 K; (h) 373 K; and (i) 473 K

comparison with other bands. In addition, some bands, which were absent for 1-MCPE and MECP on silica, were observed at 2931 and 1513 cm^{-1} in **Fig. 8** (c). These two bands increased in intensity with increasing temperature accompanied by decrease in intensity of the olefinic bands. In addition, the negative peak of acidic OD groups persisted above 245 K, at which alkene was absent. Therefore, the adsorbed species with bands at 2931 and 1513 cm^{-1} are regarded as reaction products of 1-MCPE with the acidic hydroxyl groups of DY zeolite. The product is most probably carbenium cation formed by protonation of the alkene. However, the band at 1513 cm^{-1} is characteristic of alkenyl species as discussed above for the CPE reaction. The details of the reaction mechanism are discussed below, but the formation of alkenyl cation accompanied consumption of the acidic hydroxyl groups. The involved D atoms were considered to form C–D bonds, but no CD stretching bands were observed due to the small absorption coefficient.

The reaction product with bands at 2931 and 1513 cm^{-1} disappeared with further increases temperature to 473 K, where peaks at 2931, 2859, 1465 and 1382 cm^{-1} remained. Simultaneously, a band at 1600 cm^{-1} due to the C=C stretching mode and a broad band at 3500 cm^{-1} appeared. The former band indicates the formation of olefinic species, and the latter the H–D isotope exchange between the acidic OD groups and the adsorbed hydrocarbon species. In other

For comparison, 6.81 mmol 1-methylcyclopentene ($0.18 \text{ mmol} \cdot \text{g}^{-1}$ catalyst) was also introduced on HY at 235 K. If monomeric species are formed, the consumption of acid sites should occur on the dotted line.

Fig. 9 Calibration of Acid Sites of HY Using 1-Butene at 235 K

Scheme 3 Proposed Mechanism of Formation of Alkenyl Cation in the Reaction of 1-MCPE Catalyzed by HY

words, some hydrogen atoms were released from the acidic OH groups to form alkene molecules. The 3500-cm^{-1} band due to the acidic OH groups formed by isotope exchange appeared at frequencies corresponding to the groups hydrogen bonded with alkyl groups⁵³. Thus, intermolecular reaction to form oligomeric alkene molecules, which formed hydrogen-bonding interactions with the acidic OH groups through their alkyl groups, should be considered. The formation of alkenyl cation from 1-MCPE was observed at lower temperatures range than from CPE, due to the stability of the tertial carbenium intermediate for the formation of the alkenyl cation from 1-MCPE.

In order to estimate the amount of acidic hydroxyl groups consumed by the formation of alkenyl cation, 1-butene adsorption was quantified at 235 K, where 1-butene and conversion of the isolated acidic hydroxyl groups to the hydrogen-bonded groups with 1-butene show a linear correlation (Fig. 9)⁵³. By using the calibration line, the integrated intensity of the reverse band

of the isolated acidic hydroxyl groups can be measured. The time course of the integrated intensity of the reverse band of the isolated acidic hydroxyl groups after adsorption of $6.81 \mu\text{mol}$ of 1-MCPE at 235 K is also shown in Fig. 9. The reaction of 1-MCPE was stable at 235 K from Fig. 9, and the formed species was the alkenyl cation from Fig. 8. The amount of consumed acidic sites was half of the 1 : 1 ratio, reflecting the dimeric reaction. Elimination of hydride is necessary for the direct formation of monomeric alkenyl cation, which seems unlikely because hydride elimination requires any electrophile as an acceptor. Thus, the reaction mechanism as described in Scheme 3 is proposed. The carbenium cation formed by proton transfer from zeolite donates hydride to an alkene molecule adsorbed on the acidic hydroxyl group to form an alkane molecule and an alkenyl cation. The alkane molecule is released from the acid site due to its small heat of adsorption in comparison with alkene molecules, so only one acidic hydroxyl group is consumed for the reaction of two alkene molecules. Thus, only half the number of acid sites is required, compared to the number of reactant molecules. This mechanism is compatible with the stability of carbenium and alkenyl cations: the electron-delocalization of alkenyl cation is more favorable, and the energy difference of carbenium and alkenyl cations induces the hydride transfer.

5.2.3. Reaction of 1-MCPE Adsorbed on H-ZSM-5 Zeolite

The changes of IR spectra of adsorbed 1-MCPE on H-ZSM-5 with temperature are shown in Fig. 10A (b-g) together with a reference spectrum of adsorbed 1-MCPE on silica at 215 K. The reference spectrum (h) in Fig. 10A is of methylcyclopentoxo species formed by adsorption of methylcyclopentanol (MCPOH) on zirconia at 393 K⁵⁴. The adsorbed 1-MCPE on silica is only desorbed by increasing temperature in vacuum, and was assigned to adsorbed species with the C=C bond interacting with the silanol group. In spectra (b-g) in Fig. 10A, two C=C stretching peaks were observed at 1660 and 1634 cm^{-1} , which are attributed to 1-MCPE adsorbed on the acidic hydroxyl groups with alkyl groups and C=C bond, respectively^{53,55}. The smaller pore size of H-ZSM-5 compared with that of HY zeolite inhibited the direct interaction of the C=C bond of 1-MCPE molecules with the acid sites especially at low temperatures. A new band appeared at 1520 cm^{-1} from 196 K, which was assigned to alkenyl cation for the same reason as that for the adsorbed species on HY zeolite as described above. The 1520-cm^{-1} band increased in intensity and reached the maximum at 373 K, then shifted to 1510 cm^{-1} with decreasing intensity at 473 K, and disappeared at 623 K.

The CH stretching region of Fig. 10A is expanded in Fig. 10B with an additional reference spectrum of

Spectra of 1-methylcyclopentene adsorbed on DY at 298 K (to form dimerized alkenyl carbenium ions) and 1-methylcyclopentanol adsorbed on ZrO_2 at 398 K (to form 1-methylcyclopentoxo) are given as references.

Fig. 10 IR Spectra of 1-Methylcyclopentene Adsorbed on SiO_2 at 215 K and on H-ZSM-5 at Various Temperatures: (A) 4000-1300 cm^{-1} region and (B) 3200-2700 cm^{-1} region

1-MCPE on DY zeolite at 198 K (spectrum (i)). 1-MCPE on silica showed main peaks at 3043, 2969, 2940 and 2856 cm^{-1} with additional two shoulder peaks. 1-MCPE on H-ZSM-5 showed a weaker 3043- cm^{-1} peak at the same temperature, and disappeared at 295 K together with the peak at 2856 cm^{-1} . The series of spectra in **Fig. 10B** of 1-MCPE on H-ZSM-5 are different from that of 1-MCPE on DY zeolite (**Fig. 10B** (i)). The CH stretching bands of the adsorbed species derived from 1-MCPE on DY zeolite were observed at 2930 and 1860 cm^{-1} , which were attributed to alkenyl cation. On the other hand, any other species seem to be involved in the spectra of adsorbed species on H-ZSM-5. The most probable reaction product is alkoxyl groups formed by proton transfer and C-O bond formation between the carbenium cation and a lattice oxygen. A reference spectrum of methylcyclopentoxo species on zirconia (spectrum (j) in **Fig. 10B**) shows CH stretching bands at 2970 and 2879 cm^{-1} , and the spectrum of the final product of 1-MCPE on H-ZSM-5 at 295 K can be reproduced by the sum of alkenyl cation (spectrum (i) in **Fig. 10B**) and methylcyclopentoxo species (spectrum (j) in **Fig. 10B**). Therefore, both alkenyl cation and methylcyclopentoxo species are probably formed in the small pores of H-ZSM-5.

5. 2. 4. Formation of Alkenyl Cation from 1-MCPE Adsorbed on Various Zeolites and Silica-alumina

IR spectra of adsorbed species on various catalysts, which were formed by adsorption of 1-MCPE at 150 K followed by evacuation and gradual heating to 298 K in vacuum, are compared in **Fig. 11**. The band at

The adsorbate was introduced at 150 K followed by evacuation.

Fig. 11 IR Spectra of 1-MCPE Adsorbed on (a) SiO_2 at 215 K; and on (b) DY; (c) H-mordenite; (d) H-ZSM-5; (e) D-beta and (f) silica-alumina at 298 K

1513 cm^{-1} characteristic of the alkenyl cation was observed for all solid acid catalysts, but the intensity was weaker on silica-alumina in comparison with other catalysts. The spectral features of the reactant on mordenite and silica-alumina were similar to that on D(H)Y zeolite with bands at 2930 and 2861 cm^{-1} . On the other hand, an additional band was observed at 2960 cm^{-1} on D(H)-beta zeolite, similar to H-ZSM-5. Thus, both

Table 1 Lowest Temperatures at Which the Characteristic Band at 1490-1530 cm^{-1} Can Be Detected

Adsorbate	Zeolite			
	Faujasite (Y)	Mordenite	ZSM-5	Beta
CPE	207	—	RT	—
1-MCPE	150	155	183	150
MECP	150	155	183	150
CHE	207	217	RT	—
1,3-Diene	150	150	150	—

Fig. 12 IR Spectra of CHE Adsorbed on (a) SiO_2 at 196 K; and on DY at Various Temperatures: (b) 150 K; (c) 183 K; (d) 207 K; (e) 245 K; (f) 298 K; (g) 373 K; and (h) 473 K

alkenyl cation and methylcyclopentoxo species were formed on D(H)-beta zeolite, whereas alkenyl cation species were dominant on mordenite, silica-alumina and D(H)Y zeolite.

Table 1 summarizes the lowest temperatures, at which the characteristic band at 1490-1530 cm^{-1} was detected by adsorption of various alkenes on various zeolites. Comparison of the molecules found that 1,3-cyclohexadiene (1,3-diene) formed alkenyl cation at lower temperature than the others, followed by 1-MECP and MECP with tertiary carbons. Based on the types of zeolite, reactions occurred at higher temperature on H-ZSM-5 than the others, probably due to the difficult access of molecules to the acidic hydroxyl groups on H-ZSM-5 due to the smaller pores and radius of curvature than the other zeolites.

5. 2. 5. Reaction of Adsorbed Cyclohexene (CHE) Adsorbed on DY Zeolite

The changes in the IR spectra of CHE adsorbed on DY zeolite at 150 K followed by evacuation and heating are shown in **Fig. 12** (b-h) with that of adsorbed species on SiO_2 . The adsorbed species show peaks of =CH and C=C stretching at 3026 and 1651 cm^{-1} ,

Compound 1

respectively. For adsorbed species of CHE on DY zeolite, two peaks of =CH stretching at 3020 and 3002 cm^{-1} and two of C=C stretching at 1651 and 1636 cm^{-1} were observed below 207 K. The peaks at higher frequencies (3020 and 1651 cm^{-1}) are attributed to CHE adsorbed on DY zeolite with its alkyl groups, and the other peaks (3002 and 1636 cm^{-1}) to CHE adsorbed with the C=C bond directly interacting with the acidic hydroxyl groups of DY zeolite^{53),55)}. A band assigned to alkenyl cation was observed at 1529 cm^{-1} above 207 K, which increased gradually in intensity, reached the maximum at 298 K, and disappeared at 473 K. The bands at 2928 and 2858 cm^{-1} in the CH stretching region and that at 1451 cm^{-1} in the CH deformation region increased in intensity with the increased intensity of the 1529- cm^{-1} peak. Therefore, these peaks are also attributable to the alkenyl cation species formed by CHE adsorption on DY zeolite.

Cyclohexyl cation formed by proton addition to CHE in superacid solution rearranges to the more stable 1-methylcyclopentyl cation^{56),57)}. ^{13}C -NMR of cyclohexanol on H-ZSM-5 showed that a compound (**Compound 1**) was formed at 373 K³¹⁾. However, in the present study, the skeletal rearrangement from cyclohexyl groups (CHE) to cyclopentyl groups represented by **Compound 1** was not confirmed based on the different spectral appearance of **Fig. 12** (cyclohexyl groups) and **Fig. 8** (cyclopentyl groups) in the CH deformation region (1600-1300 cm^{-1}). Therefore, cyclohexenyl cation was presumably formed from CHE on DY zeolite in the present study.

5. 2. 6. Reaction of 1,3-Diene (1,3-cyclohexadiene) Adsorbed on DY Zeolite

Since alkenyl cations are known to be formed by proton addition to conjugated dienes, the adsorption and reaction of 1,3-Diene on DY zeolite were observed for confirmation of the above assignment. 1,3-Diene was adsorbed at 150 K and evacuated at the same temperature. Then, the sample was heated gradually under vacuum to 523 K (**Fig. 13**). The IR spectrum of 1,3-Diene molecularly adsorbed on silanol groups on silica is also shown in **Fig. 13** (a). Comparison with spectrum (a) shows that the adsorbed 1,3-Diene was present on DY zeolite at low temperatures. In addition, a peak at 1529 cm^{-1} was also observed. At 183 K, an additional peak at 1480 cm^{-1} appeared, which increased in intensity with decrease in intensity of the band at 1529 cm^{-1} . The 1480- cm^{-1} band was attributed to polyenyl cation species as described below.

Fig. 13 IR Spectra of 1,3-Diene Adsorbed on (a) SiO₂ at 207 K; and on DY at Various Temperatures: (b) 150 K; (c) 183 K; (d) 207 K; (e) 245 K; (f) 295 K; (g) 373 K, (h) 473 K; and (i) 523 K

5.2.7. UV-visible Diffuse Reflectance Spectra (DRS) of the Intermediates

For confirmation of the assignment of the alkenyl cation species, UV-visible DRS of adsorbed species on DY zeolite were measured (Fig. 14). These spectra were observed at room temperature after adsorption of each molecule at liquid nitrogen temperature followed by gradual warming. The adsorbed species of CPE showed two peaks at 315 and 390 nm, and 1-MCPE showed three peaks at 323, 400 and 480 (shoulder) nm, respectively. CHE showed one large peak centered at 345 nm, whereas 1,3-Diene showed a very complicated band structure including six peaks at 256, 345, 408, 518 and 573 nm. All observed peaks were attributed to the π - π^* transition of alkene or alkenyl cations.

The wavelength of the peaks in UV-visible spectra assigned to the π - π^* transition depends on the length of the conjugated hydrocarbon chain, and that peaks at 280-330, 360-380, and 430-470 nm are assigned to monoethyl, dienyl and trienyl carbenium cations, respectively^{43,44}. The alkyl-substitution moves these peaks to lower frequencies^{43,44}. The present observation that all species observed in Fig. 14 contained a peak at 300-350 nm leads to the conclusion that mono- enyl cations were formed in all cases, which agrees with IR results. Only a mono- enyl cation was formed in the case of CHE, but dienyl cation was also generated in the case of CPE. Trienyl cation was also produced in addition to mono- enyl and dienyl cations in the case of 1-MCPE, and 1,3-Diene further produced polyenyl carbenium cation species (450-600 nm) and aromatic compounds (256 nm).

Fig. 14 UV-VIS Spectra of CPE (a); 1-MCPE (b); CHE (c); and 1,3-diene (d) adsorbed on HY at liquid nitrogen temperature and then warmed to RT and kept for 30 min

Dienyl and polyenyl cations should be observed in IR spectra as peaks at lower frequencies than 1510 cm⁻¹. In fact, a peak appeared at 1480 cm⁻¹ from 183 K in Fig. 13, which was assigned to any dienyl or polyenyl cations based on the UV-visible spectrum (Fig. 14). In the case of 1-MCPE, the broad band at 1465 cm⁻¹ in Fig. 8 (g) could be attributed to dienyl and trienyl cations.

6. Conclusion

Research methods for investigation of the intermediate species formed from hydrocarbons on zeolites were briefly introduced. Especially, detailed experimental conditions for IR measurements of zeolites were described, and example IR results of reactions of cyclic alkenes on zeolites were shown. The findings are summarized as follows.

- (1) Alkenyl cation species were formed by adsorption of cycloalkenes on silica-alumina, H(D)Y zeolite, mordenite, H(D)-ZSM-5 and H(D)-beta zeolite.
- (2) Alkenyl cation species were characterized by IR peaks at 1490-1530 cm⁻¹ and UV-visible peaks at 290-330 nm.
- (3) Activation energy for the formation of alkenyl cation species follows the order.
1,3-Diene $\leq$ 1-MCPE = MECF < CPE $\approx$ CHE
On H(D)Y zeolite, 1,3-Diene, 1-MCPE and MECF had already reacted at 150 K, and the peak intensities increased up to 373 K.
- (4) Alkoxy groups in addition to alkenyl cations were formed on H(D)-ZSM-5 with smaller pores and H(D)-beta with weaker acidity zeolites in comparison with

H(D)Y zeolite.

FT-IR studies have high potential for the investigation of catalysis.

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要 旨

IR 法によるゼオライト上での炭化水素の吸着とカルボカチオンの生成に関する研究

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カルボカチオン種はゼオライト上での炭化水素の反応中間体としてしばしば提唱されており, その生成機構や反応性に関しては主に IR や NMR と呼ばれた手法が用いられてきた。本稿ではまず, これらの手法を用いてこれまでに明らかにされてきた結果を要約し, 次に IR を用いた測定手法の詳細について紹介した。IR を用いた最近の研究例として, ゼオライト上への環状アルケンの吸着によるアルケニルカチオン種の生成について記した。

環状アルケンがシリカアルミナ, HY, モルデナイト, H-ZSM-5, H-ベータに吸着すると, 酸性水酸基との反応によってアルケニルカチオン種を生成した。これは, IR スペクトルでは $1490 \sim 1530 \text{ cm}^{-1}$ に, 紫外可視吸収スペクトルでは $290 \sim 330 \text{ nm}$ に特徴的な吸収バンドを有することで確認された。さらに, 他のゼオライトと比較して細孔径の小さい H-ZSM-5 や酸強度の弱い H-ベータでは, アルケニルカチオン種に加えてアルコキシド種も生成することが分かった。

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