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Formation of alkenyl carbenium ions by adsorption of cyclic precursors on zeolites

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Abstract

The adsorption of cyclopentene (CPE), 1-methylcyclopentene (MCPE), methylenecyclopentane (MECP), cyclohexene (CHE) and 1,3-cyclohexadiene (diene) on faujasite (Y), ZSM-5, mordenite and beta zeolites as well as on silica–alumina, was studied by in situ FT-IR and UV–VIS spectroscopies at 150–573 K. The formation of alkenyl carbenium ions, characterized by an IR band at ca. 1490–1530 cm^{-1}, were observed in a wide temperature range. UV–VIS results also confirm the formation of alkenyl carbenium ions. The ability to generate alkenyl carbenium ions on zeolites follows the sequence: $1,3\text{-diene} \geq 1\text{-MCPE} = \text{MECP} > \text{CPE} \approx \text{CHE}$. All the cyclic olefins have undergone oligomerization on zeolite Y at low temperatures, giving dimerized alkenyl carbenium ions. The formation of alkenyl carbenium ions on zeolites with small pores (like ZSM-5) was confined at low temperatures due to the inaccessibility of cyclic molecules to acidic OH groups, while the acid strength of zeolites was found to be important for stabilizing the formed carbenium ions and for producing some other species. Based on the experimental results, alkenyl carbenium ions are proposed to be formed by direct protonation of 1,3-diene, or by hydrogen transfer between alkyl carbenium ion and cyclic olefins or their corresponding oligomers.

Keywords: Cyclic olefins; Alkenyl carbenium ions; Zeolites; IR; Adsorption

1. Introduction

Hydrocarbon transformations utilizing the acidity and pores of zeolites are very important in petroleum industry [1]. The acidity of zeolites has been extensively studied by spectroscopic methods [1–7] and theoretical approaches [8,9]. Both Brϕnsted and Lewis acid sites (BAS and LAS) are found to be present on a zeolite depending on the treatment conditions. BAS exist as bridging hydroxyl groups between Al and Si atoms, and LAS are known to be generated by dehydration of BAS at high temperatures. For the reactions of olefins on zeolites, the BAS of zeolites play a critical role, and carbenium ions are assumed to be formed and act as reactive intermediates. However, unlike the case in superacid solutions [10], the formation of simple alkyl carbenium ion on zeolites has never been observed unambiguously up to now. As observed by in situ infrared (IR) [11–19] and NMR [13,20,21], adsorption of olefins usually results in the formation of hydrogen-bonded species, oligomers or alkoxy species. In some cases, alkenyl carbenium ions with resonance structures were observed [22–28].

Using in situ NMR, Haw et al. observed the formation of cyclopentenyl cations on zeolites through propene oligomerization on HY at 293 K [22], by cracking of ethene oligomers on HZSM-5 at 523 K [23], by adsorption of some cyclic precursors on HY

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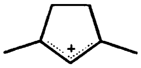
and HZSM-5 [24], and in MTO/MTG processes [25], and the cations were respectively identified to have following structures:



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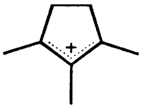

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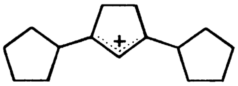

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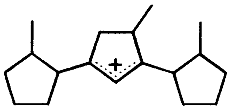

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Because the formation of alkenyl carbenium ions has strong relationship with alkyl carbenium ions and consumes a stoichiometric number of acid sites, studying their formation mechanism is of great importance for better understanding of the roles of zeolite acidity as well as the roles of simple carbenium ions.

In this work, the adsorption and reactions of some cyclic olefins on zeolites were investigated by in situ IR spectroscopy, which has been proved to be a powerful technique since it allows one to distinguish the BAS and LAS, and to look directly the interaction of hydroxyls with probe molecules (weak bases) [1]. As carbenium ions can be stabilized in cyclic structures, we expected to directly observe their formation at low temperatures. We will mainly focus on the results of zeolite Y in this paper, because faujasite zeolite has large open pores (0.74 nm × 0.74 nm) which do not limit the access of many cyclic molecules to the acidic OH groups.

2. Experimental

2.1. Sample preparation

The following samples were used: HY (JRC, Si/Al = 2.8), HZSM-5 (Asahi Chemical Industry Co. Ltd., Si/Al = 27), mordenite (JRC, Si/Al = 10), H-beta (SÜD-CHEMIE AG, Si/Al = 25), silica–alumina (Catalysts & Chemicals Ind. Co. Ltd., Si/Al = 1.9) and SiO_2 (Aerosil Nippon). Each sample was pressed into a self-supporting wafer (ca. 10 mg/cm^2) and was placed in a quartz IR cell connected to a closed gas-circulation system. Before adsorption, the samples were evacuated at 773 K for 1 h, oxidized by circulating O_2 (100 Torr, 1 Torr = 133.3 Pa) at 773 K for 1 h and evacuated at the same temperature for another 15–60 min to remove residual contaminants. Subsequently, the samples were treated with 100 Torr of H_2 or D_2 at 673 K for 1 h to get their H- or D-forms. The samples were then cooled to room temperature (RT) in the presence of H_2 or D_2, and followed by evacuation. The treatment conditions were chosen to avoid the production of LAS on the samples, and the absence of them has been confirmed by CO adsorption [3].

2.2. Reagents

Cyclopentene (CPE), 1-methylcyclopentene (MCPE), methylenecyclopentane (MECP), cyclohexene (CHE) and 1,3-cyclohexadiene (diene) were purchased from Aldrich, and were purified by vacuum distillation and freeze-pump-thaw cycles before use.

2.3. IR and UV–VIS measurements

After sample pretreatment, adsorption was performed at 150 K, and the IR cell was immediately evacuated unless otherwise indicated. The cell was then gradually warmed at a rate of ca. 6 K/min while evacuation. Only a small amount (10–40 μmol) of adsorbates was introduced. All IR spectra were recorded on a JASCO 7000 FT-IR spectrometer equipped with an MCT detector at a resolution of 4 cm^{-1}, and 64 scans were collected for each spectrum in the region 4600–400 cm^{-1}. Only differential spectra are given here, which were obtained by subtracting the spectra collected at different temperatures before adsorption. UV–VIS spectra were collected on a JASCO V-560 UV–VIS spectrophotometer and samples were treated in a similar manner as IR experiments.

3. Results and discussion

3.1. Cyclopentene adsorbed on HY

Fig. 1 shows the IR spectra of CPE adsorbed on zeolite HY. To obtain more information, the IR cell

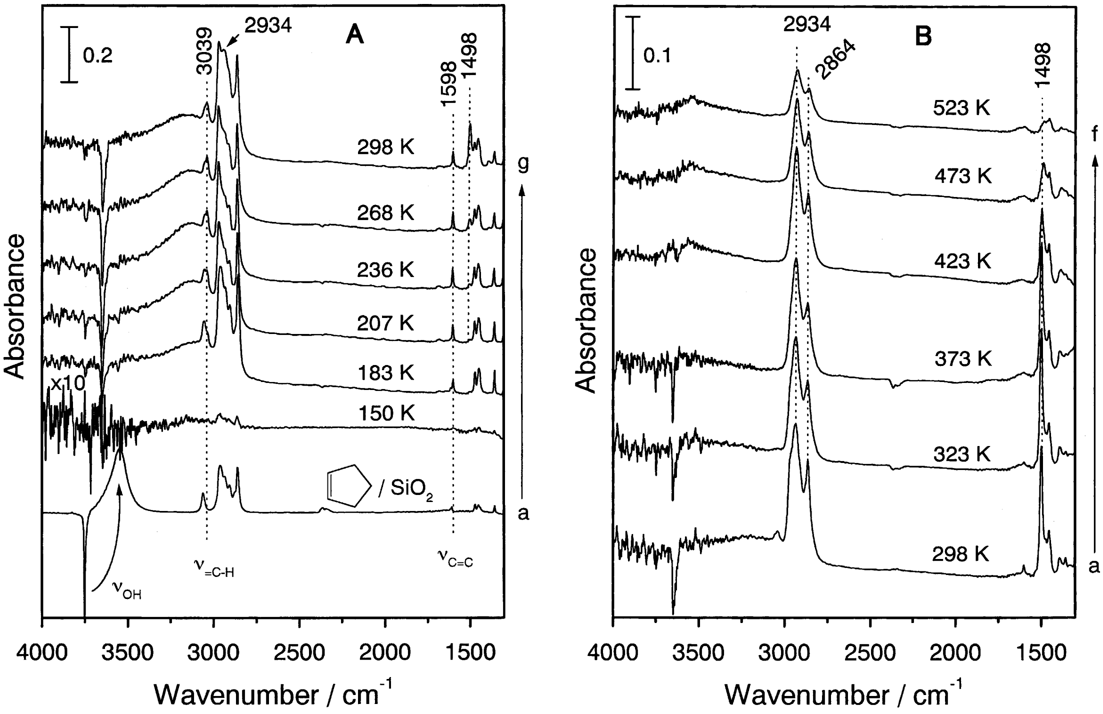


Fig. 1. (A) IR spectra of CPE adsorbed on (a) SiO_2 at 196 K; and on HY at various temperatures without evacuation: (b) 150 K; (c) 183 K; (d) 207 K; (e) 236 K; (f) 268 K; and (g) 298 K. (B) IR spectra of CPE adsorbed on HY at various temperatures under evacuation: (a) 298 K; (b) 323 K; (c) 373 K; (d) 423 K; (e) 473 K; and (f) 523 K. The reverse peaks indicate the consumption of the OH groups.

was closed at low temperatures (150–298 K, Fig. 1A) and then evacuated at high temperatures (298–523 K, Fig. 1B) after introducing CPE at 150 K. The spectrum of CPE adsorbed on SiO_2 is given in Fig. 1A, a, as a reference. CPE is only mono-molecularly adsorbed on silica, giving a similar spectrum to that of CPE free molecules. The interaction of C=C bond of CPE with silanols causes the OH stretching vibration band shifting downwards to 3550 cm^{-1}, ca. 200 cm^{-1} lower than that of free silanols, and the bands of $\nu_{=C–H}$ and $\nu_{C=C}$ appear at 3061 and 1607 cm^{-1}, respectively. When CPE was adsorbed on HY, only hydrogen-bonded species, the so-called π–OH complex [14,15], were formed at temperatures lower than 207 K. A negative band is observed at 3647 cm^{-1} due to the interaction of C=C bond with the acidic OH groups in β cages, which causes ca. 500 cm^{-1} downscale shift of ν_{OH} band (from 3647 to 3141 cm^{-1}). The bands related with the unsaturated features of CPE also shift to lower frequencies (3039 and 1598 cm^{-1}), confirming the formation of π–OH complex. At 207 K, a weak band at 1498 cm^{-1} appears. It grows in intensity with the increase in temperature, and becomes very strong at 298 K. Simultaneously, one band at 2934 cm^{-1} can be clearly observed. Upon evacuation, the bands related with molecularly adsorbed CPE disappear (Fig. 1B), and the ν_{OH} band at 3141 cm^{-1} resulting from the formation of π–OH complex cannot be seen. However, the reverse peak at 3647 cm^{-1} still remains, suggesting that the acidic OH groups are consumed. In $\nu_{=C–H}$ region, only two bands at 2934 and 2865 cm^{-1} left at 323 K, and the 1498 cm^{-1} band is the strongest one. The 1498-cm^{-1} band reduces in intensity at 423 K, and almost disappears at 523 K.

The appearance of an IR band at 1490–1530 cm^{-1} upon adsorption and reaction of small olefins and alcohols on zeolites, usually at 320–373 K, has been reported [26–33], and different interpretations were given. For example, this band has been attributed to the skeletal breathing modes of aromatics [29–31], to OCO group from surface species [32] and to the formation of “nonclassic carbenium ions” [33]. However, Deno [34] first observed a band at 1530 cm^{-1} in superacid solutions and assigned it to the asymmetric stretching vibration of the [C=C–C]$^{+}$ unit of alkenyl carbenium ions. He interpreted that the positive charge of this unit is delocalized within the three carbon atoms, therefore, its vibrational frequency situates in the region just between those of typical C–C and C=C stretching modes. Taking into account the similarities between superacid solutions and zeolites on catalytic behavior, this assignment was adopted to zeolite system by some authors [26–28], and it was supported by UV–VIS results and ab initio calculations [35].

Xu and Haw studied the adsorption of cyclopentanol on HY by using NMR [24]. They found that water was eliminated at moderate temperatures and then CPE and its oligomers were formed. The latter further forms trimerized carbenium ions like **3** at 323–393 K. Since CPE was directly used as adsorbate on HY in our case, it is expected that alkenyl carbenium ions can be formed easier compared with its corresponding alcohol. From the NMR results [24] and the above-mentioned assignments of the band at 1490–1530 cm^{-1}, we assigned the band at 1498 cm^{-1} to the formation of alkenyl carbenium ions. Since this band has been observed at 207 K, it means that alkenyl carbenium ions has already formed at such a low temperature.

3.2. 1-MCPE and MECP adsorbed on DY

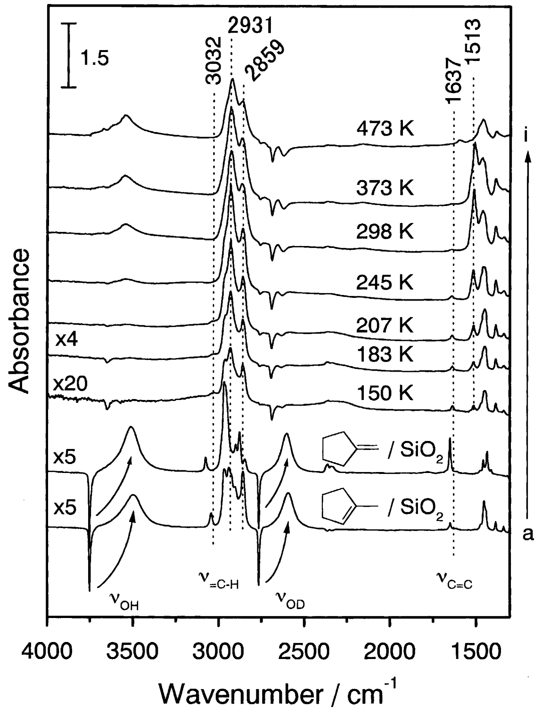


Fig. 2. IR spectra of 1-MCPE or MECP adsorbed on DY at various temperatures: (c) 150 K; (d) 183 K; (e) 207 K; (f) 245 K; (g) 298 K; (h) 373 K; and (i) 473 K. The two isomers gave the same results upon adsorption on zeolite Y. The spectrum of 1-MCPE adsorbed on SiO_2 at 215 K (a); and MECP adsorbed on SiO_2 at 210 K (b) are given as references. The reverse peaks indicate the consumption of the OH and OD groups.

Fig. 2 shows the IR spectra of 1-MCPE and MECP adsorbed on DY zeolite (the same results were obtained by using HY). As shown in Fig. 2a and b, both olefins are mono-molecularly adsorbed on SiO_2, and the spectra are respectively identical to these of the two olefins in liquid phase [36,37]. By comparing Fig. 2a and b, it can be clearly seen that the spectra of the isomers are totally different in high- and low-frequency regions. The $\nu_{=C–H}$ and $\nu_{C=C}$ bands of 1-MCPE appear at 3043 and 1650 cm^{-1}, respectively, while those of MECP appear at 3075 and 1654 cm^{-1}. However, for the adsorbed species formed after their adsorption on DY, exactly the same spectra were obtained (Fig. 2, spectra c–i), suggesting that double bond migration (from MECP to 1-MCPE) proceeds very fast and the same reaction products were formed. As shown in Fig. 2c, dramatic changes have occurred in the ν_{CH} vibrational region (3100–2800 cm^{-1}) as soon as introducing 1-MCPE or MECP at 150 K. The obtained spectrum is different from those of the isomers. For both isomers, the most intensive band is at ca. 2960 cm^{-1}, while the band at 2931 cm^{-1} shows the strongest intensity after adsorption. The band at 2960 cm^{-1} only appears as a very small shoulder, it further decreases in intensity with the elevation of temperature, and can hardly be seen at 298 K. At 150 K, the olefinic C–H stretching band at 3032 cm^{-1} and the $\nu_{C=C}$ band at 1637 cm^{-1} (23 cm^{-1} lower than that of 1-MCPE free molecules) can still be observed, suggesting the presence of molecularly adsorbed species, i.e. π–OH complex. In the low-frequency region (1600–1300 cm^{-1}), a new band at 1513 cm^{-1}, which has been attributed to the formation of alkenyl carbenium ions, appears soon after introducing the adsorbate at 150 K. With increasing temperature, the bands at 2931, 2859 and 1513 cm^{-1} grow in intensity, and the band at 3032 cm^{-1} due to olefinic C–H stretching almost disappears at 245 K due to desorption and/or reaction of the molecularly adsorbed species at higher temperatures. Upon heating to 373 K, the 1513 cm^{-1} band reaches maximum intensity, and disappears with further increase in temperature. Only the bands at 2931, 2859, 1465 and 1382 cm^{-1} remain at 473 K. Meanwhile, a band at 1600 cm^{-1} due to the formation of aromatic compounds appears.

Compared with the case of CPE, alkenyl carbenium ions were formed at much lower temperature due to the presence of a tertiary carbon in 1-MCPE or MECP. It is worth noting that the increase of the 1513-cm^{-1} band was accompanied by the consumption of the OD bands. This suggests that the formation of alkenyl carbenium ions is coincident with the consumption of a stochiometric number of acidic hydroxyl groups. However, owing to the low IR absorption coefficient, the stretching vibrational modes of C–D bond were not clearly observed at low temperatures.

3.3. CHE adsorbed on DY

Fig. 3 gives the IR results of CHE adsorbed on DY. The $\nu_{=\mathrm{C-H}}$ and $\nu_{\mathrm{C=C}}$ bands of adsorbed CHE on silica appear at 3026 and 1651 cm^{-1}, respectively (Fig. 3a). At low temperatures (below 207 K), CHE is molecularly adsorbed on DY, and two kinds of hydrogen-bonded species, alkyl–OH and π–OH complexes [14,15], can be confirmed to exist by the appearance of doublet bands at 3020, 3002 cm^{-1} and 1651, 1636 cm^{-1}, respectively. The formation of alkenyl carbenium ions, characterized by a band at 1529 cm^{-1}, was observed at 207 K and above. This band can be stable up to 373 K, and disappears at 473 K. It is noted that three bands at 2928, 2858 and 1451 cm^{-1} were accompanied by the 1529-cm^{-1} band.

It is well known that cyclohexyl cation is less stable than 1-methylcyclopentyl cation, and can easily rearrange to the latter in superacid solutions [10,38]. In fact, skeletal rearrangement of six-membered rings to methyl-substituted five-membered rings is thoroughly established on an acidic catalyst at high temperatures [39,40]. The NMR results of Xu and Haw [24] suggested that cation **4** was formed at 373 K by adsorption of cyclohexanol on HZSM-5. However, the IR spectra shown in Figs. 2 and 3 are different in low-frequency region (1600–1300 cm^{-1}), although they are similar in $\nu_{\mathrm{C-H}}$ region. Also the band characterized for alkenyl carbenium ions situates at different positions (1513 and 1529 cm^{-1}, respectively). Therefore, skeletal rearrangement is not supposed to happen under our experimental conditions, namely, the formed species have structures like cyclohexenyl cation rather than methylcyclopentenyl structures like cation **4**.

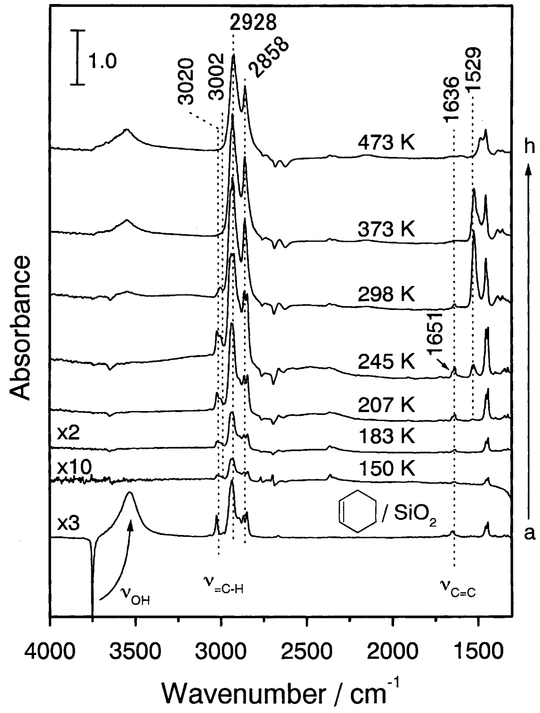


Fig. 3. IR spectra of CHE adsorbed on (a) SiO_2 at 196 K; and on DY at various temperatures: (b) 150 K; (c) 183 K; (d) 207 K; (e) 245 K; (f) 298 K; (g) 373 K; and (h) 473 K.

3.4. 1,3-Diene adsorbed on DY

Alkenyl carbenium ions can be formed by direct protonation of dienes. When 1,3-diene was adsorbed on DY at 150 K, immediate appearance of a band at 1529 cm^{-1} was observed (Fig. 4b), suggesting that alkenyl carbenium ions can be formed readily by protonation of 1,3-diene. At 183 K, another new

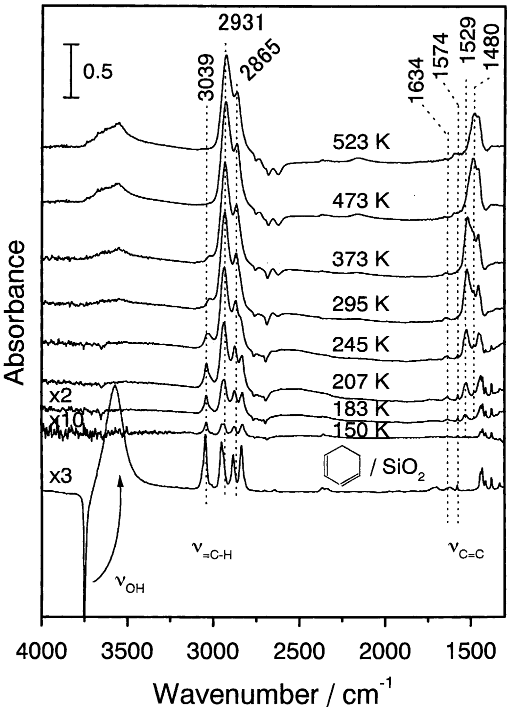


Fig. 4. IR spectra of 1,3-diene adsorbed on (a) SiO_2 at 207 K; and on DY at various temperatures: (b) 150 K; (c) 183 K; (d) 207 K; (e) 245 K; (f) 298 K; (g) 373 K, (h) 473 K; and (i) 523 K.

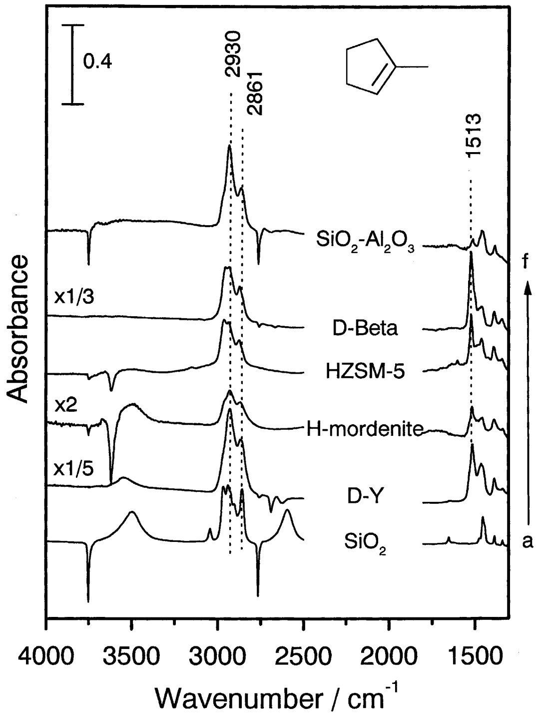


Fig. 5. IR spectra of 1-MCPE adsorbed on (a) SiO_2 at 215 K; and on (b) DY; (c) H–mordenite; (d) HZSM-5; (e) D-beta and (f) silica–alumina at 298 K. The adsorbate was introduced at 150 K followed by evacuation.

band at 1480 cm^{-1} appears. This band also grows progressively with the elevation of temperature, and it replaces the 1529 cm^{-1} band to become the predominant band in low-frequency region at 473 K. As will be discussed later, this band can be assigned to the formation of poly-enylic carbenium ions.

3.5. 1-MCPE adsorbed on various zeolites and silica–alumina

The IR results of 1-MCPE adsorbed on SiO_2, silica–alumina and several zeolites at 298 K are shown in Fig. 5 (1-MCPE was introduced at 150 K followed by evacuation). It can be seen that the characteristic band at 1513 cm^{-1}, due to the formation of alkenyl carbenium ions, was developed on all the acidic samples, i.e. zeolites and silica–alumina, although the intensity on the latter is rather low. At high-frequency region, similar spectra were obtained on zeolite Y, mordenite and silica–alumina, that is, two strong bands appear at 2930 and 2861 cm^{-1}, and the former is stronger. However, different spectra were obtained for ZSM-5 and beta zeolites in $\nu_{C–H}$ region, suggested that other species may co-exist with alkenyl carbenium ions. Details on this point will be reported elsewhere.

Table 1 lists the lowest temperatures at which the characteristic band at ca. 1490–1530 cm^{-1} can be

Table 1
The lowest temperatures at which the characteristic band at 1490–1530 cm^{-1} can be detected

Adsorbate	Zeolite (K)			
	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	–

detected on zeolites upon adsorption of cyclic olefins and diene in our study. It seems that 1,3-diene has the highest ability to generate the alkenyl carbenium ions. The presence of a tertiary carbon can also accelerate their formation. Since ZSM-5 has a smaller pore size (open apertures: 0.53 nm × 0.56 nm), the access of cyclic molecules to its acidic OH groups was confined, and alkenyl carbenium ions cannot be formed at temperatures as low as on faujasite (Y). Taking into account the fact that alkenyl carbenium ions were formed on all the acidic samples, one can deduced that acidity is critical in the formation of alkenyl carbenium ions. On the other hand, the acid strength of zeolites is found to be important in stabilizing the formed carbenium ions and in producing some other species.

3.6. UV–VIS results

The formation of alkenyl carbenium ions was confirmed by using UV–VIS spectroscopy, and the results are shown in Fig. 6. Various adsorbates were introduced on HY at liquid nitrogen temperature. Then the samples were warmed to RT, and UV–VIS spectra were recorded as a function of adsorption time and temperature. After the sample was kept at RT for 30 min, two bands at 315 and 390 nm appear upon adsorption of CPE (Fig. 6a), while 1-MCPE adsorbed on HY gives two strong bands at 323 and 400 nm, and a small shoulder at ca. 480 nm. For CHE, only one broad band at ca. 345 nm was observed. In the case of 1,3-diene, the spectrum is very complicated (Fig. 6d). Besides two bands at 345 and 408 nm, other four bands are also observed at 256, 458, 518 and 573 nm.

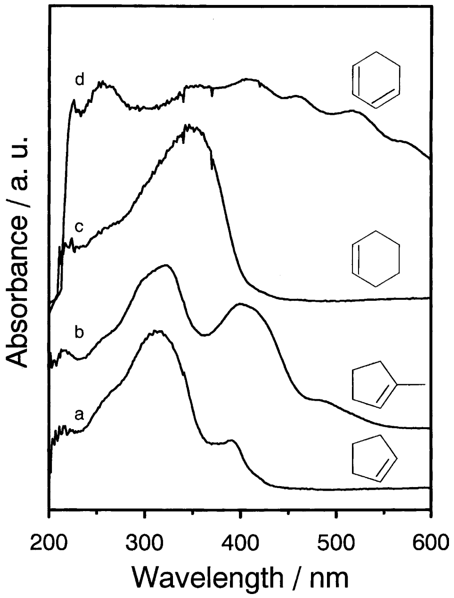


Fig. 6. UV–VIS spectra of CPE (a); 1-MCPE (b); CHE (c); and 1,3-diene (d) adsorbed on HY at liquid nitrogen temperature and then warmed to RT and kept for 30 min.

The UV–VIS bands observed in the range 280–330, 360–380 and 430–470 nm have been attributed to π–π^* transitions of mono-, di-, and tri-enylic carbenium ions based on experience with superacid solutions, and the formation of branched, i.e. alkyl-substituted, carbenium ions causes slight red-shift of these bands [26,27]. Therefore, the bands observed in our case can be assigned accordingly. Since the band at 300–350 nm was observed in all cases, it is clear that mono-enylic carbenium ions are formed on zeolite Y upon adsorption of cyclic olefins and diene, in consistent with our IR results.

For CHE, only mono-enylic carbenium ions were formed on HY at RT (345 nm). However, a small amount of di-enylic carbenium ions (390 nm) were also formed together with mono-enylic ones after adsorption of CPE, and a considerable amount of di-enylic ones and a small amount of tri-enylic ones are present on HY in the cases of 1-MCPE and 1,3-diene (ca. 400 and 480 nm). Aromatics and poly-enylic carbenium ions were also formed when 1,3-diene adsorbed on HY even at RT, as indicated by the bands at 256 and 450–600 nm, respectively.

If the di-enylic or poly-enylic carbenium ions exist, an IR band should be observed at frequencies lower than 1510 cm^{-1}. In Fig. 4, a new band appears at 1480 cm^{-1} since 183 K on the adsorption of 1,3-diene. Compared with UV–VIS results (Fig. 6d), this band can be easily assigned to the formation of di- and poly-enylic carbenium ions. For the adsorption of 1-MCPE, a broad band does appear at 1465 cm^{-1} at higher temperatures (e.g. Fig. 2g). This band must relate with the formation of di- and tri-enylic carbenium ions, although it may be composed by several overlapped bands. The results of 1-MCPE adsorbed on DY at RT confirm this point (vide infra).

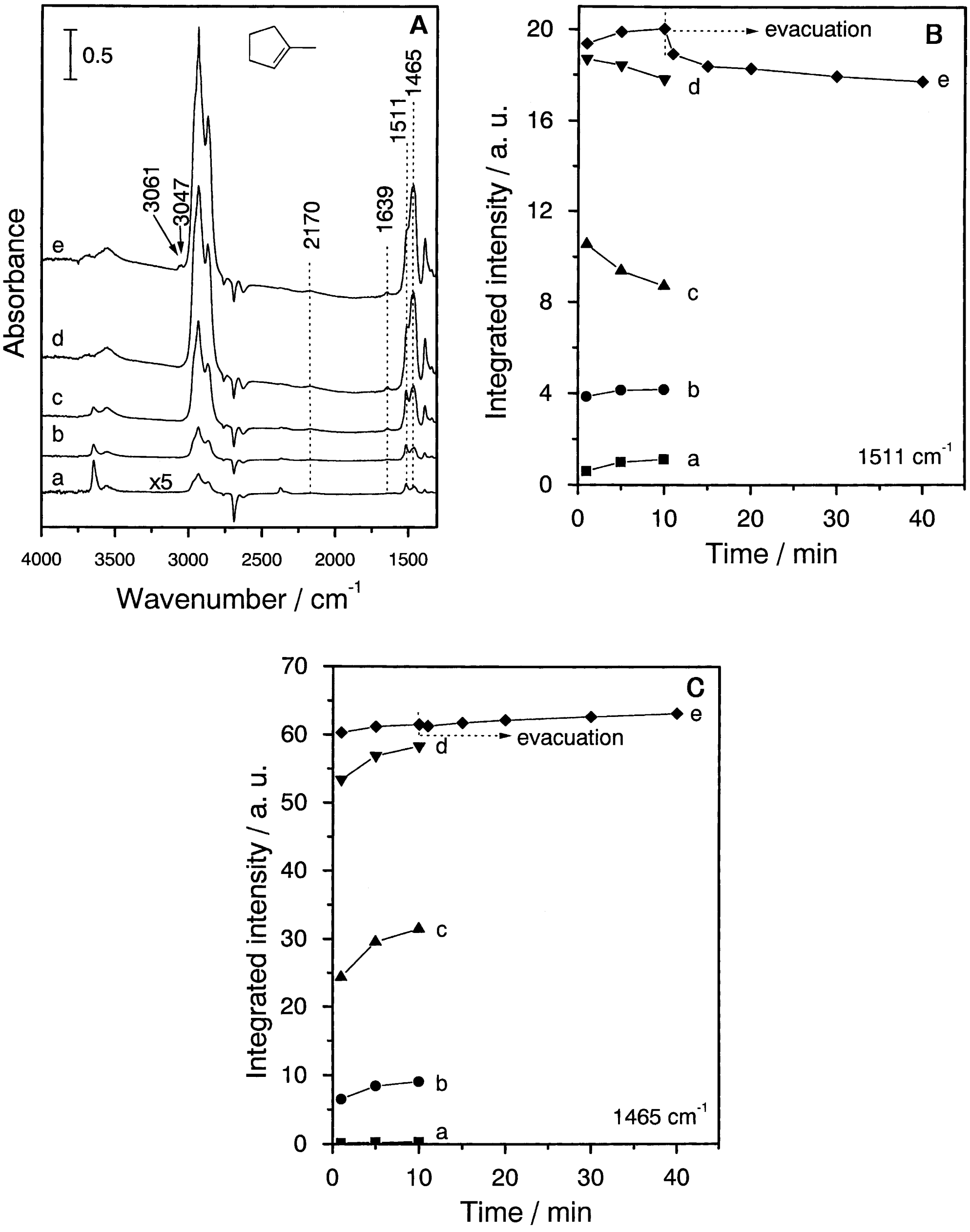


Fig. 7. The 1-MCPE adsorbed on DY at RT. (A) IR spectra; (B); and (C) integrated intensity of the bands at 1511 and 1465 cm^{-1} as a function of time. The dosing amount of adsorbate on DY is: (a) 0.04 mmol/g; (b) 0.24 mmol/g; (c) 0.64 mmol/g; (d) 1.44 mmol/g; and (e) 3.04 mmol/g.

3.7. 1-MCPE and CHE adsorbed on DY at RT

To investigate how mono- and poly-enylic carbenium ions are formed, 1-MCPE and CHE were adsorbed on DY at RT. The IR spectra as a function of the amount of olefin and adsorption time are shown in Figs. 7 and 8. When very little amount (0.04 mmol/g cat.) of 1-MCPE was dosed to the sample, a band

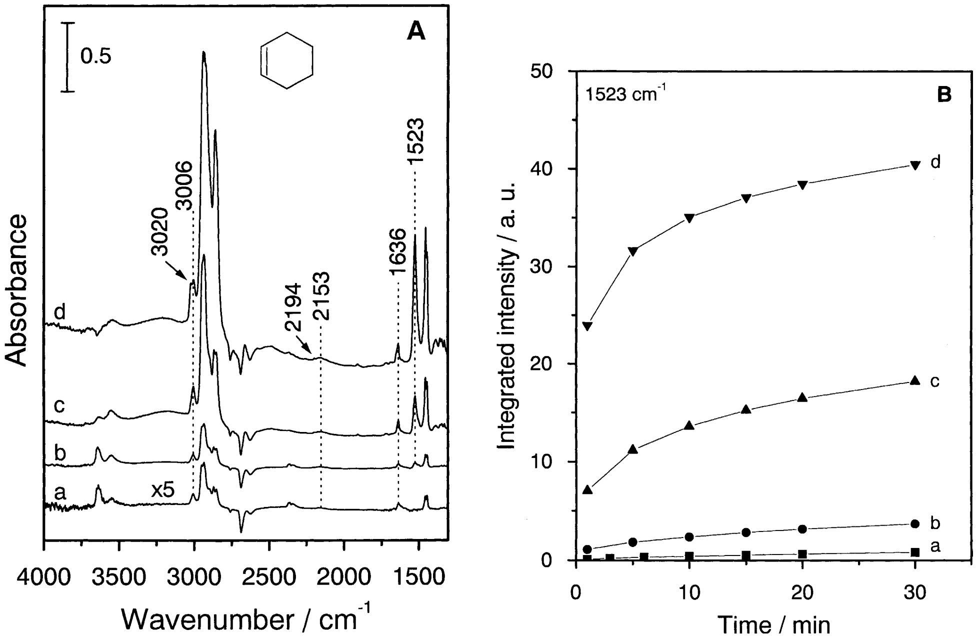


Fig. 8. CHE adsorbed on DY at RT. (A) IR spectra; (B) integrated intensity of the band at 1523 cm^{-1} as a function of time. The dosing amount of adsorbate on DY is: (a) 0.03 mmol/g; (b) 0.18 mmol/g; (c) 0.48 mmol/g; and (d) 1.08 mmol/g.

at 1511 cm^{-1} appears at once, and the bands due to $\nu_{=C-H}$ and $\nu_{C=C}$ cannot be observed (Fig. 7A, a). Meanwhile, in ν_{OH} region, two bands at ca. 3642 and 3556 cm^{-1} appear, which are attributed to the stretching vibration of OH groups of zeolite Y in β and α cages, respectively. This suggests that 1-MCPE and/or the formed species have high mobility at RT. They can undergo H/D exchange with OD groups resulting in the formation of OH groups and C–D bonds (2170 cm^{-1}). With increasing dosing amount, the 1511 cm^{-1} band increases, and a band at 1465 cm^{-1} also grows and finally overlaps with the 1511 cm^{-1} band. Compared with UV–VIS results, the band at 1465 cm^{-1} can be attributed to the formation of di- and tri-enylic carbenium ions.

Fig. 7B and C shows the integrated intensity of the bands at 1511 and 1465 cm^{-1} as a function of adsorption time. At low coverages (0.04 and 0.24 mmol/g cat.), the 1511 cm^{-1} band increases in intensity with time. However, it decreases with time at high coverages of 1-MCPE (Fig. 7B, c and d). When the sample is over saturated (3.04 mmol/g, Fig. 7B, e), three peaks related with the unsaturated features of olefins can be observed at 3061, 3047 and 1639 cm^{-1}. Since the spectrum shows no similarity to that of 1-MCPE (Fig. 2a) but is similar to those of oligomers [13], it is safe to say that oligomers have been produced at this time. In this case, the 1511-cm^{-1} band gains intensity with time again. Upon evacuation, its intensity slightly decreases with time. On the other hand, the 1465-cm^{-1} band grows in intensity with adsorption time regardless of the olefin amount. It grows even under evacuation, indicating that there is a reservoir, which can continuously supply its precursors. After a comparison of Fig. 7B and C, correlation between the two bands at 1511 and 1465 cm^{-1} can be easily established. Recalling that these two bands can be respectively assigned to the formation of mono- and di- or tri-enylic carbenium ions, it can be deduced that mono-enylic carbenium ions are formed first from 1-MCPE and/or oligomers, and then they transform to di- and tri-enylic carbenium ions by losing more hydrogen atoms.

Fig. 8 shows the results of CHE adsorbed on DY at RT. Since only mono-enylic carbenium ions were formed at RT basing on the UV–VIS result (Fig. 6c), it is possible to see clearly the influence of olefin amount

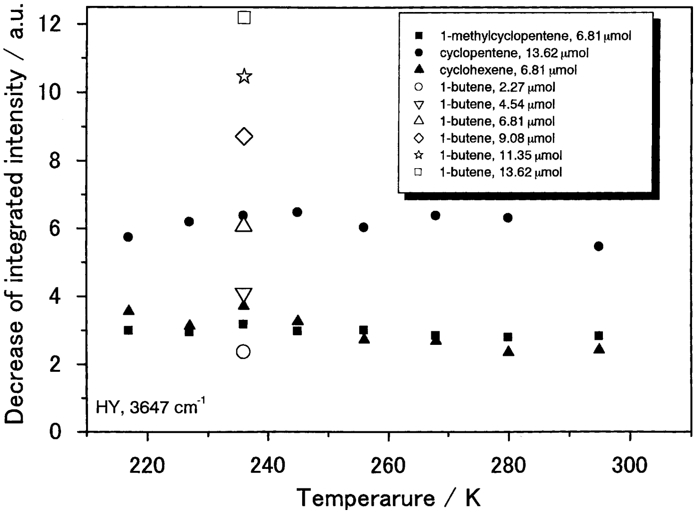
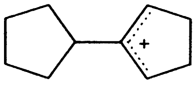


Fig. 9. Consumption of acid sites of HY by dosing different amount of olefins (see text for explanation).

and time on their formation by monitoring the band at ca. 1529 cm^{-1}. As shown in Fig. 8A, a, no band at 1490–1530 cm^{-1} appeared in the beginning. However, one band at ca. 1523 cm^{-1} was developed soon and it continuously increased with time and olefin amount, suggesting that the formation of mono-enylic carbenium ions is also dependent on time and olefin amount.

3.8. *Identifying the structure of the formed species*

It is well known that small olefins can be adsorbed mono-molecularly on the acidic hydroxyls of zeolites at low temperatures to form 1:1 π–OH complex [14,15], and the acid sites of zeolites can be calibrated at designated temperatures by selecting suitable olefin. The 1-butene is believed to be a suitable molecule for probing the acid sites of zeolite Y since only its acidic hydroxyls in supercages were found to participate in the adsorption of 1-butene [14]. Also oligomerization of 1-butene does not occur on zeolite Y at temperatures below 250 K [14]. Therefore, 1-butene was used to calibrate the acid sites of HY at 235 K in order to identify the structure of the formed species for the adsorption of cyclic olefins. A controlled amount of 1-butene (2.27 μmol, 0.06 mmol/g cat.) was introduced to the IR cell. An IR spectrum was collected after 3–5 min of the dosage, and then other doses were given, until saturated adsorption. By measuring the decrease of the integrated intensity of the 3647-cm^{-1} band (stretching vibration of OH groups in supercages), the correlation between the OH band intensity (represents the amount of acid sites) and the dosage of 1-butene was obtained (Fig. 9). In separate experiments, fixed amount of CPE, 1-MCPE and CHE was dosed to the sample and the weakening of the 3647-cm^{-1} band versus temperature is plotted. If the formed species are monomeric, the consumption of acid sites should be the same as dosing the same amount of 1-butene. However, only about half of the acid sites were consumed, suggesting that the formed species are dimerized, e.g.



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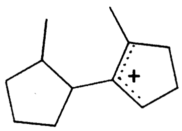

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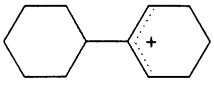

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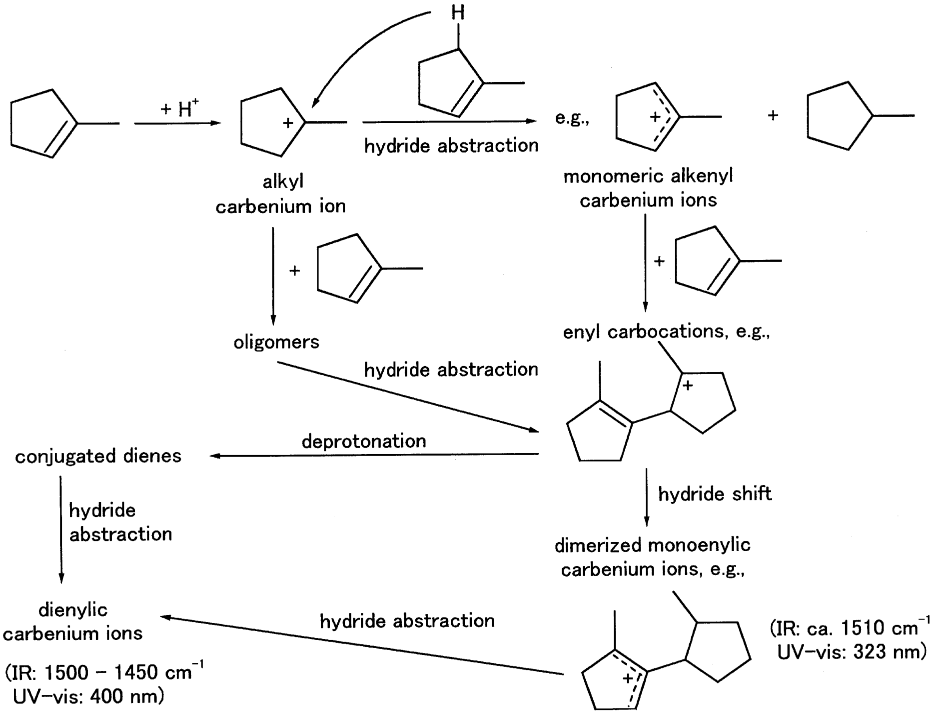

Scheme 1. Possible pathways for the formation of alkenyl carbenium ions upon adsorption of 1-MCPE on zeolite Y.

These results are similar to those of Xu and Haw [24], who detected the formation of trimerized carbenium ions like **3** at 323–393 K by adsorption of cyclopentanol on HY using NMR. Obviously, a similar conclusion can be drawn from our study, that is, the cyclic olefins undergo dimerization very fast on zeolite Y even at low temperatures. As a result, monomeric species cannot be observed, but only dimerized carbenium ions were detected.

3.9. Formation mechanisms of alkenyl carbenium ions

For 1,3-diene, alkenyl carbenium ions can be formed by direct protonation of the molecules, and this process is supposed to be quite easy according to the theoretical calculation results of Haw et al. [25]. While for olefin, alkenyl carbenium ions can be formed by hydride transfer between olefin and carbenium ion, or through hydride abstraction from olefin by LAS [27]. As mentioned above, hydride abstraction by LAS of zeolite, to form alkenyl carbenium ions, is unlikely owing to the absence of LAS on our samples. Hence, alkyl carbenium ions may act as LAS and abstract hydride from olefin or oligomers to form alkenyl carbenium ions. Scheme 1 shows the possible pathways for the formation of alkenyl carbenium ions from 1-MCPE, in which alkyl carbenium ions are proposed to play an important role in the formation of alkenyl carbenium ions. Mono-enylic carbenium ions are formed through hydrogen transfer between alkyl carbenium ions and 1-MCPE and its oligomers. Then they lose more hydrogen atoms to form di- and tri-enylic carbenium ions. The formed carbenium ions are stabilized in the cyclic structure and are particularly stable.

4. Conclusions

Alkenyl carbenium ions were formed by adsorption of CPE, 1-MCPE, MECP, CHE and 1,3-diene on silica–alumina and on faujasite (Y), mordenite, ZSM-5 and beta zeolites, and the main points are summarized as follows.

1. The formation of alkenyl carbenium ions is characterized by an IR band at 1490–1530 cm^{-1} and a UV band at 290–350 nm, and are influenced by temperature, adsorbate amount and adsorption time.
2. The ability to generate alkenyl carbenium ions ordered in the following sequence: $1,3$-diene $\geq$ 1-MCPE $=$ MECP $>$ CPE $\approx$ CHE. For 1-MCPE, MECP and 1,3-diene adsorbed on zeolite Y, the IR band at 1490–1530 cm^{-1} can be developed at temperatures as low as 150 K. The band increases in intensity with the elevation of temperature, and can be stable up to 373 K.
3. The formed species on HY are identified as dimerized alkenyl carbenium ions due to the rapid dimerization of the cyclic olefins, and monomeric adsorbed species were not observed.
4. Although alkenyl carbenium ions were formed on all the acidic samples upon adsorption of cyclic olefins, different species may co-exist on HZSM-5 and H-beta zeolites, which have smaller pores and stronger acidity than those of faujasite (Y). Also the small pores of zeolites like ZSM-5 can confine the access of cyclic molecules to acidic OH groups at low temperatures.

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