

Dynamic Processes of Olefins Adsorbed on Hydroxyl Groups of DM20 Zeolite Excited by Picosecond Infrared Pulses: Vibrational Relaxation, Short-Lived Species and Desorption

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We have investigated olefins adsorbed on Brønsted acidic hydroxyl groups (OD) of DM20 zeolite by transient infrared absorption spectra after excitation of the OD stretching mode using picosecond infrared lasers. The olefins studied were ethylene, deuterated ethylene, propylene, and isobutene, and only isobutene was adsorbed on OD at its methyl group while the other olefins were adsorbed at their double bonds. For all the olefins except isobutene, simple vibrational relaxation of the $\nu = 1$ state was observed and the lifetimes were 2–4 ps. These lifetimes are an order faster than that of isolated OD. For isobutene, a long lifetime component lasting more than 500 ps was observed in addition to vibrational relaxation of 2 ps. The transient absorption spectra for isobutene-adsorbed zeolite at various time delays and frequencies indicated the existence of a short-lived species and a slow desorption process compared with vibrational relaxation.

I. Introduction

One of the most important applications of picosecond time-resolved infrared spectroscopy is to observe chemical processes that are accompanied by molecular structural change, such as dissociations, isomerizations, and adsorption–desorption. High-resolution time-resolved infrared spectroscopy is particularly effective for observing chemical processes on a powdered catalyst, where high inhomogeneity is inevitable. However, previous studies on this kind of system focused mainly on vibrational energy transfer without structural change.^{1–6} One of the reasons for this is that the adsorbed species studied, including rare gases, metal carbonyl, methane, and water, were too simple and too stable to undergo structural change. To examine a process where a compound undergoes structural change, we chose to examine highly reactive olefins as an adsorbate on zeolite, a widely used powdered catalyst, and studied their dynamics by picosecond infrared spectroscopy.

An olefin molecule introduced into zeolite channels at low temperature forms a 1:1 complex with Brønsted acidic hydroxyl groups.^{7–9} With an increase in temperature, the olefin undergoes dimerization, polymerization, or isomerization even at temperatures below 0 °C. These reactions have been intensively investigated not only because of their industrial importance, but also because they represent fundamental reactions carried out using zeolite as the catalyst. Nevertheless, the reaction mechanisms are still unclear.^{10–20} As an example, it is believed that reaction of isobutene in zeolite is initiated by proton transfer from Brønsted acid sites to the olefins, but there is no direct observation of this process.¹⁷

In the present study, we investigated four types of olefins adsorbed on Brønsted acidic surface hydroxyl groups of mordenite zeolite (DM20) by pump–probe experiments using picosecond infrared lasers. The olefins were ethylene ($\text{CH}_2=\text{CH}_2$), ethylene-*d* ($\text{CD}_2=\text{CD}_2$), propylene ($\text{CH}_3\text{CH}=\text{CH}_2$), and isobutene ($(\text{CH}_3)_2\text{C}=\text{CH}_2$). The infrared transient absorption spectra in the frequency region 2000–2800 cm^{-1} after excitation of the hydroxyl group were measured. At low temperature (150

K), fast vibrational energy relaxation was observed for all olefins. For isobutene, we have succeeded in making real-time observations of a short-lived species and a desorption process.

II. Experimental Section

The treatment of DM20 zeolite has been described in detail in previous papers, and we only briefly review it here.^{3,21} A zeolite of H-mordenite, JRC-Z-HM20 (Si/Al = 10), was supplied by the Catalysis Society of Japan (CSJ). The powdered sample was pressed to a self-supporting disk of 20 mm diameter and 0.1 mm thickness. The sample disk was placed inside an infrared cell attached to a conventional vacuum line (10^{-4} Torr). DM20 zeolite was produced from the HM20 sample by exchanging the surface hydroxyl group hydrogens for deuterium using heavy water pretreated to remove residual water and other impurities. Olefins (99% purity) were supplied by Takachiho Trading Co., Ltd., and were purified by vacuum distillation and freeze–pump–thaw cycles. Olefin vapor (about 4 Torr) was introduced into the infrared cell cooled at 110 K, and the experiments were carried out in this atmosphere. Under these conditions, the sample temperature was about 150 K, by calibration using a plastic disk with a thermocouple introduced in the cooled cell.

The optical setup of the infrared–infrared pump–probe experiments for powdered catalysis has also been described previously.⁵ Two independently tunable (900–3600 cm^{-1}) infrared pulses were generated by two combination systems of OPG/OPA (optical parametric generation and amplification) and DFG (difference frequency generation). These systems were pumped by the output (800 nm, 6 ps, 10 mJ/pulse) of a regenerative and multipass amplifier system equipped with a Ti:sapphire oscillator. Both infrared pulses had a pulse width of 4 ps and a spectral width of 10 cm^{-1} . The energies of the pump and probe pulses were 30 $\mu\text{J}/\text{pulse}$ and 2 $\mu\text{J}/\text{pulse}$, respectively. These pulses were focused and overlapped on the disk by a BaF_2 lens (focal length = 120 mm). The frequencies of these two infrared pulses were calibrated during experiments using absorption bands of isolated OD groups of the zeolite, CO_2 , and a polystyrene film.

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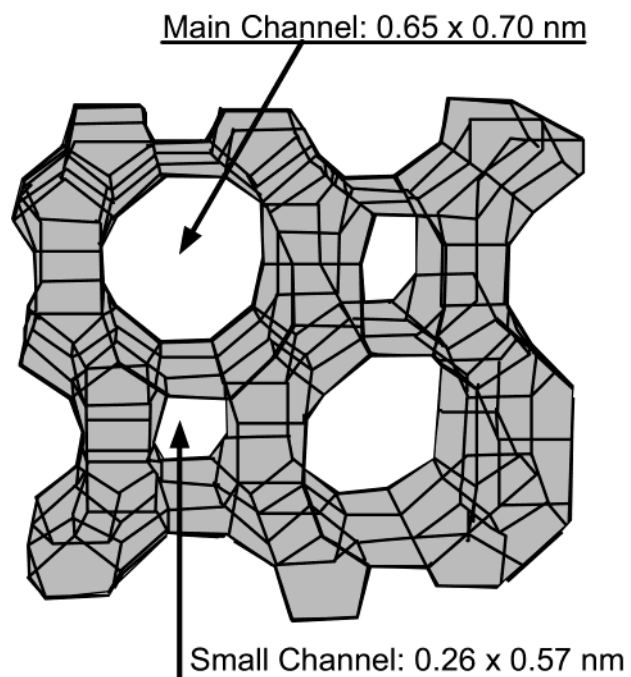


Figure 1. Skeletal structure of mordenite zeolite. Corners represent Si or Al atoms, and O atoms are located at the middle of solid lines.

Since the output of the DFG process is less stable spatially and temporally compared with the OPG/OPA process, which is the conventional method to generate mid-infrared pulses, a large number of accumulations were required to obtain a good signal-to-noise (S/N) spectrum. We collected signals at each frequency over several thousand pulses. For further improvement of the S/N ratio, some spectra shown here are the averaged results of several days of measurements under the same conditions, after reproducibility was confirmed. Thus, the maximum averaged number at each point reaches 10^4 . When the sample temperature was kept at 150 K, the spectrum of the olefin-adsorbed zeolite did not change even after 12 h of pump pulse irradiation.

III. Results and Discussion

III. 1. Vibrational Relaxation of Olefin-Adsorbed Hydroxyl Group. Zeolite is crystalline aluminosilicate ($\text{SiO}_2 \cdot n\text{Al}_2\text{O}_3$) containing many molecular-size pores. Mordenite zeolite is one kind of zeolite that has two types of channels called main and small channels, as shown in Figure 1, whose cross-section sizes are 0.65×0.70 nm and 0.26×0.57 nm, respectively. The size of an ethylene molecule, as estimated from atomic distances and van der Waals radii, is $0.49 \times 0.42 \times 0.24$ nm. This size is very similar to the size of the small channel, and thus it is difficult for ethylene molecules to enter the small channel and easier to enter the main channel. The other olefins we investigated are larger in size than ethylene, so they would be introduced into only the main channel.

The zeolite's Brønsted acid sites are surface hydroxyl groups bridged between Si and Al atoms. Since the Si/Al ratio of the sample used in our study was 10, each olefin molecule could interact with at most only one Brønsted acidic hydroxyl group. Infrared spectroscopy shows two characteristic absorption forms when an olefin molecule is adsorbed on a hydroxyl group. Infrared spectroscopy shows two characteristic absorption forms when an olefin molecule is adsorbed on a hydroxyl group.^{7–20} The band observed around 2600 cm^{-1} is assigned to a hydroxyl group interacting with the methyl group of an olefin molecule (methyl adsorption), whereas the band around 2300 cm^{-1} is assigned to a hydroxyl group interacting with the double bond of the olefin (π -adsorption).

Figure 2a shows the linear infrared absorption spectrum of ethylene-adsorbed zeolite at 150 K (sample temperature). In the spectrum, one broad band centered at 2380 cm^{-1} was observed and is a typical absorption band assigned to the stretching mode of a π -adsorption hydroxyl group. Similar bands at 2380 and 2300 cm^{-1} were observed for ethylene-*d*- and propylene-adsorbed zeolite, respectively, and these bands are also assigned to the π -adsorption hydroxyl group (spectra not shown). Absorption bands of isobutene-adsorbed zeolite at 150 K were different from those of the other olefins, and are shown in Figure 3a. The two bands located at 2590 and 2670 cm^{-1} are assigned from their frequencies to methyl-adsorption hydroxyl groups and isolated surface hydroxyl groups, respectively.

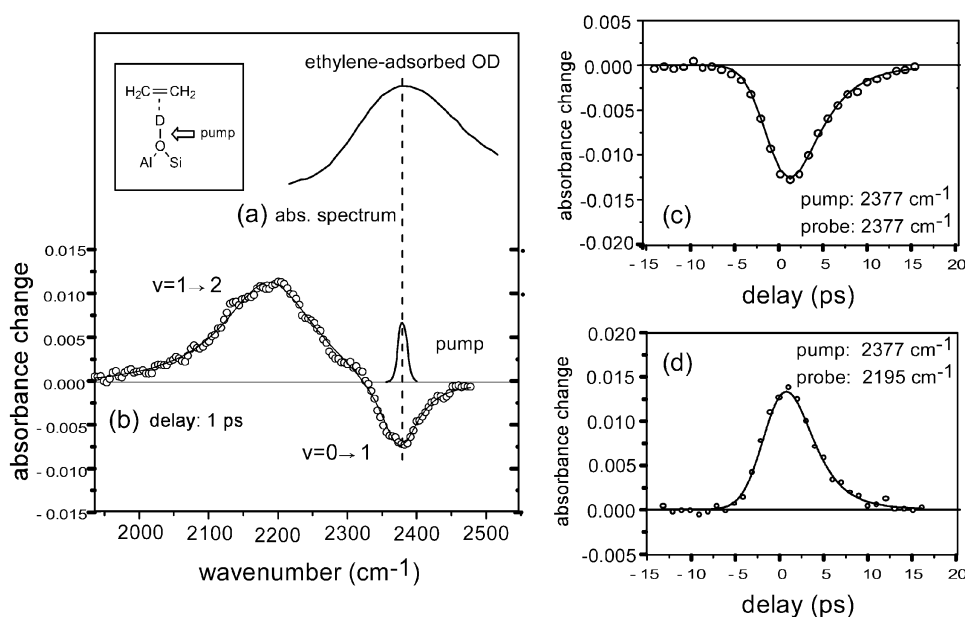


Figure 2. Linear and transient absorption spectra of ethylene-adsorbed hydroxyl groups of DM20 zeolite. (a) Linear absorption spectrum (arbitrary units). (b) Transient absorption spectrum at 2 ps delay time after excitation at 2377 cm^{-1} . (c, d) Temporal absorbance changes at 2377 and 2195 cm^{-1} , respectively, for excitation at 2377 cm^{-1} . Open circles are experimental data, and solid curves are derived by least-squares fits. Inset shows the structure of an ethylene-adsorbed hydroxyl group (π -adsorption) before excitation. The shape of the pump pulse is also illustrated.

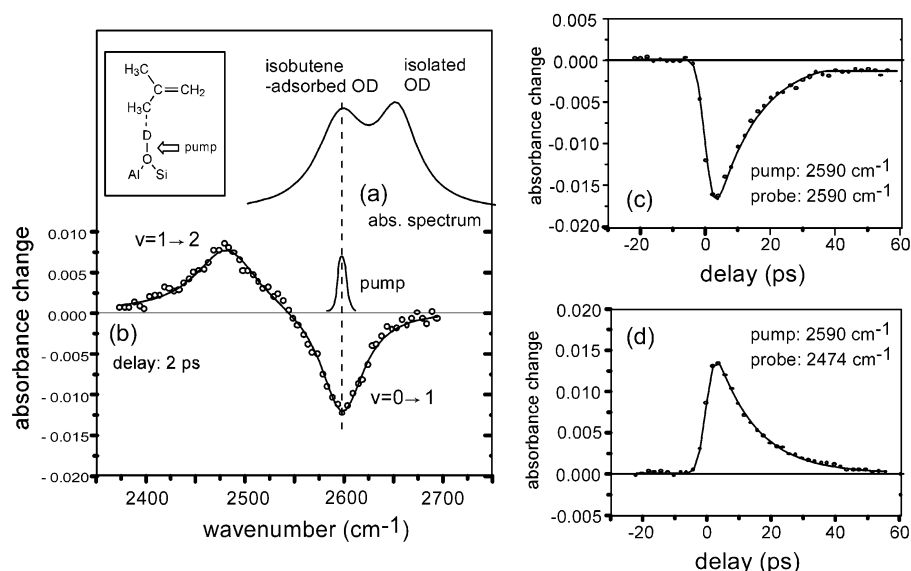


Figure 3. Linear and transient absorption spectra of isobutene-adsorbed hydroxyl groups of DM20 zeolite. (a) Linear absorption spectrum (arbitrary units). (b) Transient absorption spectrum at 2 ps delay time after excitation at 2950 cm^{-1} . (c) and (d) Temporal absorbance changes at 2590 and 2474 cm^{-1} , respectively, for excitation at 2590 cm^{-1} . Open circles are experimental data, and solid curves are derived by least-squares fits. Inset shows the structure of an isobutene-adsorbed hydroxyl group (methyl adsorption) before excitation. The shape of the pump pulse is also illustrated.

We measured transient absorption spectra after excitation of these olefin-adsorbed Brønsted acidic hydroxyl groups by picosecond infrared pulse. In Figures 2b and 3b, open circles are the transient spectra for ethylene- and isobutene-adsorbed hydroxyl groups, respectively, measured at 2 ps after the pump pulse. In the spectra, solid curves through the data points were derived by a least-squares fit using two Lorentzian functions, and the position and width (fwhm = 10 cm^{-1}) of the pump pulse are shown by the solid curve labeled “pump.” For ethylene-*d*- and propylene-adsorbed hydroxyl groups, very similar transient spectra were obtained. In these transient spectra, decreases and increases in transient absorption were observed at the same frequency as the pump pulse and at lower frequency than the pump pulse, respectively. This feature is typical of a transient absorption spectrum when a fundamental tone of an isolated vibrational mode is pumped by the infrared pulse, and the decrease is due to saturation between $\nu = 0$ and $\nu = 1$ states (bleaching band), while the increase is due to transient absorption from $\nu = 1$ to $\nu = 2$ (hot band).⁵

Figures 2c,d and 3c,d are temporal profiles probed at the two different transient bands, namely, the bleaching band and the hot band. These temporal profiles, except the one shown in Figure 3c, seem to be represented by a single-exponential function, whereas the temporal profile of the bleaching band of isobutene-adsorbed hydroxyl groups in Figure 3c exhibits a long lifetime component as explained in the next section. Least-squares fits were carried out to determine the decay time components. A double exponential function, whose longer time component was fixed at 1 ns, was applied to Figure 3c, and a single-exponential function was used for the other temporal profiles. The laser pulse width was taken to be a Gaussian function of fwhm = 4 ps. The curves derived from these fits are represented in the respective figures by solid curves on the experimental data points. All curves were well consistent with the experimental data, and the derived lifetimes are summarized in Table 1.

The lifetimes of the bleaching and hot bands are the same within each system as shown in Table 1, implying that the observed decay behavior originates from decay of the same vibrational excited state. This result supports the contention that saturation between $\nu = 0$ and $\nu = 1$ accounts for the transient

TABLE 1: Lifetimes of Hydroxyl Groups of DM20 Adsorbed with Various Olefins at 150 K^a

adsorbed species	$\nu = 0 \rightarrow 1$ (ps)	$\nu = 1 \rightarrow 2$ (ps)
none	75 (2)	
ethylene (π)	4 (1)	4 (1)
ethylene- <i>d</i> (π)	4 (1)	4 (1)
propylene (π)	2 (1)	2 (1)
isobutene (methyl)	12 (2)	12 (2)

^a Values in parentheses denote the estimated error limit.

absorption decrease and the transition from $\nu = 1$ to $\nu = 2$ accounts for the transient absorption increase. The derived decay times correspond to the vibrational relaxation time (T_1) of $\nu = 1$ to $\nu = 0$, and there is no other relaxation path.

The lifetimes for the olefin-adsorbed hydroxyl groups are about 1 order of magnitude shorter than that of isolated hydroxyl groups. The values observed are also much smaller than those of hydroxyl groups adsorbed by other species studied previously.^{1–6} These fast relaxations indicate that the adsorption of olefin molecules strongly influences the vibrational relaxation process. The relaxation rate of population decay ($\gamma = 1/T_1$) in solid phase is generally expressed by the equation^{22,23}

$$\gamma = \gamma_0 \frac{\exp(\eta\omega_0/kT) - 1}{[\exp(\eta\omega_\nu/kT) - 1]^N}, \quad \gamma_0 = |G_{\{v\}}|^2 \rho_{\{v\}} \quad (1)$$

where $G_{\{v\}}$ is the matrix element of anharmonic coupling, $\rho_{\{v\}}$ is the density of states, T is the temperature of the system, and k is the Boltzmann constant. The subscript $\{v\}$ denotes a set of accepting modes. This equation assumes that the energy dissipation process from a vibrational mode of frequency ω_0 to N quanta of the accepting mode of ω_ν ($\omega_0 = N\omega_\nu$) is the rate-determining step.

On the basis of this theory, the terms representing anharmonic coupling ($G_{\{v\}}$) and the density of states ($\rho_{\{v\}}$) are the origins of a change in lifetime when the temperature of the system is constant. These terms, especially the anharmonic coupling term, strongly depend on the potential shape of the vibrational mode excited by a pump pulse. Our results showing that short lifetimes accompanying olefin adsorption imply that adsorption of an

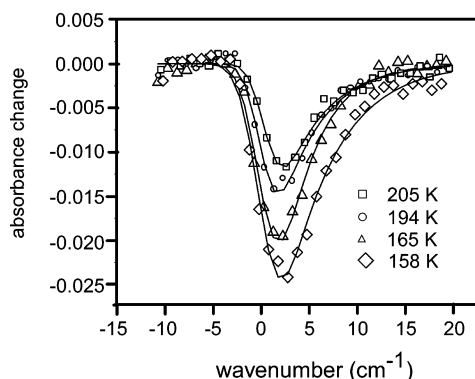


Figure 4. Temperature dependence of temporal absorbance change when pumped and probed at 2377 cm^{-1} , for ethylene-adsorbed hydroxyl groups. The number of accumulations is smaller than in Figure 2 because of faster measurement.

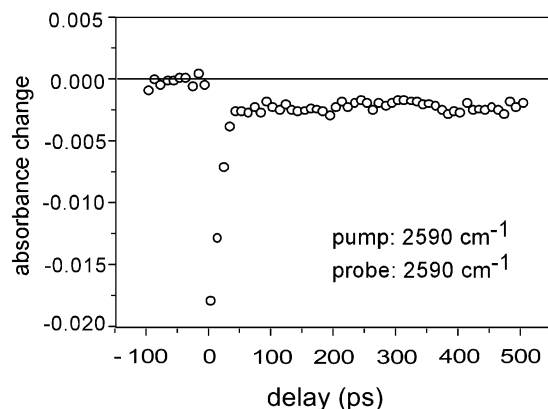


Figure 5. Longer temporal absorbance changes for isobutene-adsorbed hydroxyl groups under the same conditions as in Figure 3c.

olefin strongly distorts the potential of the hydroxyl group, and the magnitude of distortion due to π -adsorption is stronger than that due to methyl adsorption. On the other hand, the result that ethylene-*d* and propylene showed lifetimes similar to that of ethylene indicates that neither mass (isotope) nor vibrational modes of the adsorbed species strongly influence vibrational relaxation.

We also measured the temperature dependence of the transient spectra in anticipation of reaction of the olefins. However, the absorbance decreased as temperature increased without any change in relaxation time T_1 , and the signal disappeared around 200 K, which is significantly lower than the temperature where reaction and desorption occur (about 230 K). One example of the temperature-dependent data for ethylene is shown in Figure 4, although the quality is poor because the number of accumulation was small due to rapid measurements. The decrease in absorbance with the increase in temperature was reproduced for all temperatures examined, and absorbance recovered as the temperature decreased. We made sure that linear infrared absorbance was constant in this temperature region. Thus, there appears to be a process that does not influence T_1 of ethylene-adsorbed hydroxyl groups but does change the dephasing time (T_2).

III. 2. Short-Lived Species and Desorption of Adsorbed Isobutene. Only for isobutene-adsorbed hydroxyl groups did the time profile of the bleaching band deviate from simple single-exponential decay. This deviation implies that reaction, desorption, or some other dynamic is induced by the infrared pulse. To confirm this, we measured the temporal profile for the hydroxyl groups up to 500 ps, as shown in Figure 5. The change in absorbance became constant at 40 ps and this constant level lasted to 500 ps, and the absorbance change recovered to

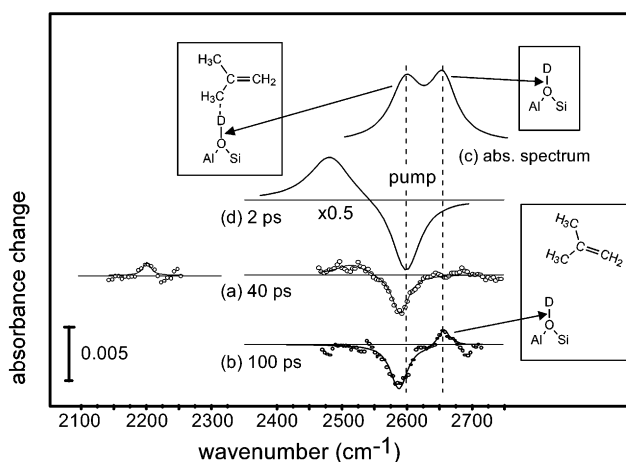


Figure 6. Transient absorption spectra of isobutene-adsorbed hydroxyl groups at (a) 40 and (b) 100 ps delay time after excitation at 2950 cm^{-1} . (c) Linear absorption spectrum and (d) transient absorption spectrum at 2 ps delay time are also shown for comparison (the same data as in Figure 3). Open circles are experimental data, and solid curves are derived by least-squares fits. Insets are predicted structures for each band.

zero after 100 ms because no baseline shift was observed in the 10 Hz operation.

The longer lifetime component, lasting longer than the time it takes for vibrational relaxation to be almost complete (about 40 ps), suggests that some kind of structural change takes place over this longer time period. Structural change can be demonstrated through measurements of transient absorption spectra at longer delay times. We measured transient absorption spectra at delay times of 40 and 100 ps, as shown in parts a and b, respectively, of Figure 6. The linear absorption spectrum (Figure 6c) and the transient spectrum at 2 ps delay time (Figure 6d) with its intensity reduced by a factor of 2 are also shown for comparison.

It was reported that the time profile showing an unrecovered baseline results from increase in lattice temperature by the pump pulse.^{24,25} This possibility is also excluded by measurement at longer delay times. For the baseline shift by lattice temperature increase, the transient absorption spectrum measured after vibrational relaxation is complete, about 40 ps for our case, no longer correlates to the population prepared by the pump pulse, and thus a broad peak similar to the original linear absorption bands would be observed. In our study, we observed a narrow, Lorentzian-like single peak, which is rather similar to the peak made by hole burning of the pump pulse even after 40 ps. This result proves that the transient peaks after 40 ps originate from the population prepared by the pump pulse. Moreover, for a baseline shift originating from a lattice temperature jump, it was also reported that the time profile is very sensitive to the frequency of the pump pulse.²⁵ In our investigations, the isobutene-adsorbed hydroxyl groups always showed the baseline recovering even when the pump frequency was changed by about 20 cm^{-1} . Also, isolated hydroxyl groups and the hydroxyl groups with the other olefins (ethylene, ethylene-*d*, propylene) adsorbed did not show nonrecovery of the baseline under the same experimental conditions.

The temperature increase was estimated from the heat capacity of SiO_2 ,²⁶ the measured density of the zeolite disk, the transmittance of the isobutene-adsorbed OD stretching band, and the pulse energy per area. The temperature increase was calculated to be approximately 5 K. However, this estimation largely depends on the area of the pump pulse on the sample. The spatial mode of the infrared pulse generated by DFG for

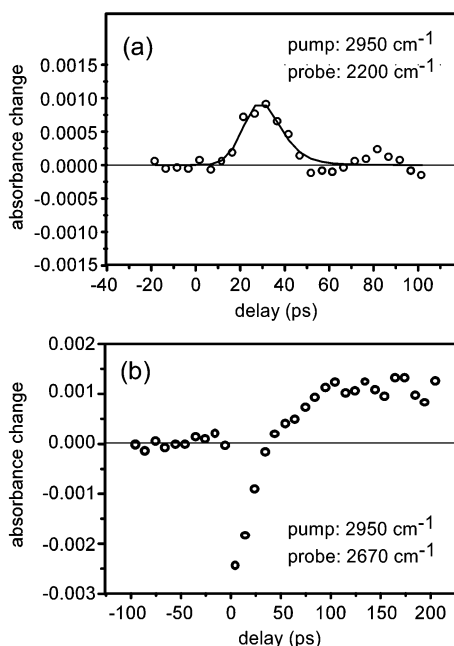


Figure 7. Temporal absorbance changes probed at (a) 2200 and (b) 2670 cm^{-1} for excitation of isobutene-adsorbed hydroxyl groups at 2950 cm^{-1} . The solid curve in (a) serves as a guide.

this experimental setup is not as good as that generated by only an OPG/OPA process, and the shape of the focal point is far from a Gaussian-like profile; thus, the area of the pump pulse is larger than the estimated value (a circle of 0.1 mm diameter). Therefore, the actual temperature increase is probably smaller than the estimation of 5 K.

In the transient spectrum at 40 ps, Figure 6a, a weak absorption decrease was observed at 2580 cm^{-1} , a decrease of 10 cm^{-1} from the bleaching band at the 2 ps delay time. Around 2500 cm^{-1} an absorption increase appears with a much weaker intensity than that of the absorption decrease at 2580 cm^{-1} . This feature is completely different from that of the spectrum at 2 ps delay time. The difference in the area under the absorption decrease and increase bands indicates that the population of the excited mode vanishes. We measured the transient spectra over a wider frequency range and found a weak transient absorption increase at 2200 cm^{-1} , as shown at the left of Figure 6a. We also found that this band increased just after the pump pulse and lasted a few tens of picoseconds (Figure 7a). This emergence of a new band indicates that a short-lived species is produced in this time period. The 10 cm^{-1} red shift of the absorption decrease band was not an experimental artifact and always reproduced. The cause of this shift is not obvious, but a certain dynamic might occur in this time region. A transient decrease located at 2690 cm^{-1} was not reproduced, and it was ignored.

It is difficult to assign the observed short-lived species only from these data, but fortunately several candidate species can be identified because there are few vibrational modes in this frequency region (around 2200 cm^{-1}). The C–D stretching mode usually has an absorption around 2200 cm^{-1} ; for example, the C–D stretching mode of deuterated ethylene (CD_2CD_2) is 2251 cm^{-1} .²⁷ Candidate species containing a C–D bond which can be produced from the isobutene-adsorbed hydroxyl group are an alkoxy group (Figure 8a) and a carbenium ion (Figure 8b). Another candidate is an OD stretching mode bonding with an olefin through a double bond, i.e., a π -bonded hydroxyl group (Figure 8c). This species is normally stable, however, so it is not likely to be the short-lived species. To determine the structure of the species producing this absorption, it is necessary

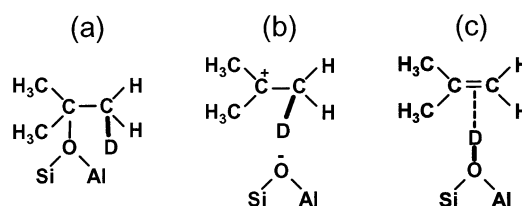


Figure 8. Candidates of short-lived species: (a) alkoxy group like species, (b) carbenium ion like species, and (c) π -bonded hydroxyl group.

to carry out further experiments measuring the lower energy region and/or performing theoretical calculations to predict the structure.

As shown in Figure 6b, the shape of the transient absorption decrease at 2580 cm^{-1} in the spectrum at 100 ps is almost the same as in the spectrum at 40 ps, but a new band emerges at 2670 cm^{-1} . Since the frequency and shape of the new band are the same as for isolated hydroxyl groups, this band originates from desorption of an isobutene molecule from a hydroxyl group. The fact that no band was observed around this frequency (2670 cm^{-1}) in the spectrum at 40 ps indicates that desorption has not started at 40 ps. This is clearly seen in Figure 7b, which shows the temporal profile with the probe pulse fixed at 2670 cm^{-1} . After bleaching around 2 ps, the transient absorption increase started at 40 ps and became constant at 100 ps.

We concluded from these data that desorption of isobutene occurs only after vibrational relaxation of the first state ($T_1 = 12$ ps) has almost finished and that direct energy transfer from the hydroxyl group to the weak bond between isobutene and the hydroxyl group does not lead to the desorption of isobutene. Since the temperature increase when the system reaches thermal equilibrium is estimated to be only 5 K or less, desorption does not take place at thermal equilibrium. Thus, isobutene molecules must start to desorb when the energy provided by the pump pulse dissipates to only limited vibrational modes that probably couple to the first excited mode more strongly than the other modes. This process of desorption of isobutene induced by the infrared pulse is illustrated in Figure 9.

Ebata et al. found a similar temporal profile for dissociation of isolated hydrogen bonded clusters using a picosecond infrared pulse.²⁸ They excited by infrared pulse the hydroxyl group of phenol dimer prepared by supersonic jet, and observed dissociated phenol molecules by REMPI (resonance enhanced multiphoton ionization) using a UV pulse. The bond breakage of the hydrogen bond between two phenol molecules take place after 5 or 14 ps vibrational relaxation, which is called intramolecular vibrational redistribution (IVR) in an isolated system, and the time scale of the dissociation was 55 or 89 ps. Dissociation taking place not directly but after vibrational relaxation seems to be a general phenomenon in a large system.

We estimated the proportion of isobutene-adsorbed hydroxyl groups that are converted into isolated OD as a result of desorption. The relative populations of each species can be estimated from the integrated absorbance intensity of each band and the relative absorption coefficients at 100 ps. The absorption coefficients of the isobutene-adsorbed hydroxyl band and the isolated hydroxyl group band were estimated from the temperature dependence of the Fourier transform infrared spectra. The intensity ratio of absorption decrease of the isobutene-adsorbed band to the absorption increase of the isolated hydroxyl group was estimated to be 3–4 from the transient spectrum at 100 ps (Figure 6b). However, the absorption coefficient of an isobutene-adsorbed hydroxyl group is only 2 or 3 times larger than that of an isolated hydroxyl group. This estimation indicates that

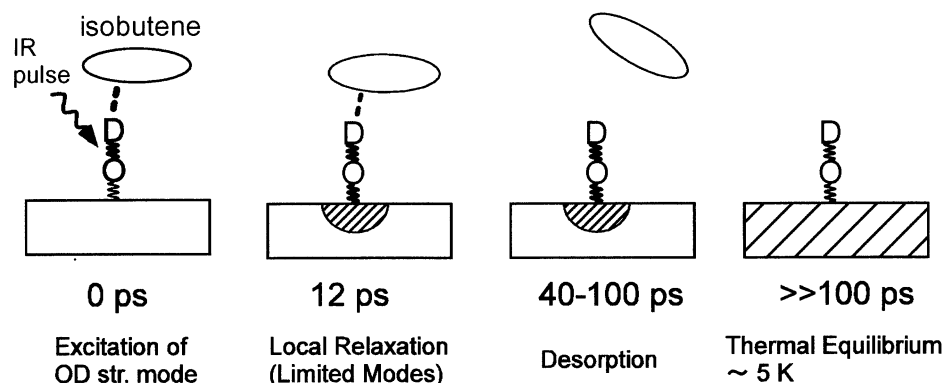


Figure 9. Proposed mechanism for isobutene desorption process after excitation of an isobutene-adsorbed surface hydroxyl group (OD) by a picosecond infrared pulse. The isobutene molecule is shown as an ellipse.

50%–100% of the decrease in the population of isobutene-adsorbed hydroxyl groups is attributable to conversion to isolated hydroxyl groups as a result of desorption. Thus, there is a possibility that another path of energy transfer exists besides desorption. The band appearing at 2200 cm^{-1} in the transient spectra at 40 ps may represent a candidate for an alternative path.

IV. Conclusion

We measured transient absorption spectra of olefin-adsorbed Brønsted acidic hydroxyl groups of DM20 zeolite at 150 K by picosecond infrared–infrared pump–probe experiments. The adsorbed olefins were ethylene, ethylene-*d*, propylene, and isobutene, and their adsorption forms are methyl adsorption for isobutene and π -adsorption for the other olefins. The features of the transient spectra observed for surface hydroxyl groups with adsorbed olefins (except isobutene) showed typical vibrational relaxation from $\nu = 1$ to $\nu = 0$. The derived lifetime (T_1) was 12 ps for isobutene and 2–4 ps for the other olefins. The lifetime strongly depends on the adsorbed structures (π - or methyl adsorption) and does not depend on the structure and mass of the adsorbate. The temperature dependence of the temporal profile of the bleaching band was also measured for ethylene-adsorbed hydroxyl groups. The signal disappeared around 200 K, which is significantly lower than the desorption or reaction temperature, and little change in T_1 was observed at the temperatures we measured.

It was found that the temporal profile for an isobutene-adsorbed hydroxyl group has a long lifetime component lasting more than 500 ps. From the measurements of transient absorption spectra after vibrational relaxation at 40 and 100 ps, the dynamics of an isobutene-adsorbed hydroxyl group was revealed, as follows. The population of the $\nu = 1$ state decays with a lifetime of 12 ps. At 40 ps after the pump pulse, a percentage of the isobutene-adsorbed hydroxyl groups transforms into a different structure. This short-lived species has a transition frequency of 2200 cm^{-1} and exists for only a few tens of picoseconds. The isobutene gradually desorbs from the hydroxyl group from 40 to 100 ps. This time scale indicates that the desorption takes place after the end of the vibrational energy relaxation and before thermal equilibrium. The isobutene-adsorbed hydroxyl group recovers completely within 100 ms.

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