

# Direct Observation of Unstable Intermediate Species in the Reaction of *trans*-2-Butene on Ferrierite Zeolite by Picosecond Infrared Laser Spectroscopy

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The reaction dynamics of *trans*-2-butene adsorbed to acidic hydroxyl groups on the surface of ferrierite zeolite is examined by time-resolved spectroscopy using a tunable infrared picosecond pulse laser system. The transient absorption spectra measured by a two-color pump–probe technique at 188–243 K reveal bleaching and hot bands of the OD stretching mode 2 ps after excitation. This vibrationally excited state relaxes within 20 ps at 188 K, while the bleaching band includes a long-lifetime component that lasts for more than 100 ps at 243 K. Thus, the OD (isotope-exchanged hydroxy groups) stretching band does not entirely recover in this period and is mirrored by an analogous weakening of the CH bending band of the adsorbed *trans*-2-butene. Simultaneously, three new bands in CH stretching region were observed at 3045, 3095, and 3130 cm<sup>-1</sup>. This result suggests the presence of a short-lived intermediate formed by reaction between the acidic hydroxyl groups and adsorbed *trans*-2-butene.

## 1. Introduction

Zeolites are crystalline, microporous aluminosilicates with high internal surface area, and zeolite-based materials have been widely used in petrochemical applications. The crystallographic structure and local structure of active sites in zeolite are well-known, and acid-catalyzed reactions on zeolites have been investigated by various methods. The hydroxyl groups located between aluminum and adjacent silicon atoms on the zeolite surface represent strong Brønsted acid sites, driving many acid-catalyzed reactions.<sup>1</sup> According to the established reaction mechanisms in organic chemistry, carbenium cation species are regarded as intermediates of the catalytic reactions on zeolites. However, the results of recent quantum chemical calculations have suggested that the stable intermediate is in fact an alkoxy species,<sup>2</sup> and carbenium cations are claimed to be present in the transition state on solid acid catalysts, where stabilization by solvent molecules does not occur. Experimentally, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy have been utilized to observe the reaction intermediates, and various species have been detected as products of reactions of hydrocarbons and alcohols on zeolites. Most of the observed species are produced through a sequence of several elemental reactions at high temperatures, and the monomolecular reaction intermediates formed after the initial reaction of the adsorbed species with the acidic OH groups on zeolites remain unclear. This is most probably due to the rapid progression of subsequent reactions after protonation from the acidic OH groups, even at

low temperatures. However, these short-lived intermediate species are expected to be detectable through the use of a time-resolved spectroscopy technique.

Direct observation of short-lived intermediate species during surface reactions is one of the major goals in surface chemistry, providing insight into the various dynamic processes that occur on surfaces. Recent progress in laser technology has led to the development of lasers capable of producing ultrashort IR pulses in a tunable system as the basis for pump–probe spectroscopy, representing a powerful tool for investigating the dynamics of molecules adsorbed onto solid surfaces.<sup>3–7</sup> The transient spectra observed by excitation of a specific vibrational mode using IR pulses provide information on the structure of the transient species and the dynamics of the system represented by vibrational relaxations and reactions, offering important clues for interpretation of the fundamental aspects of catalytic reactions. Only a few studies, however, have obtained information on the surface of the adsorbates.<sup>8,9</sup> Bandara et al. succeeded in obtaining transient spectra for the thermal decomposition reaction of formate on NiO(111) surface and identified the reactive intermediate on the basis of the picosecond temperature jump induced by irradiation with intense near-infrared laser pulses.<sup>9</sup> In that study, the decomposition reaction was preceded by the transformation of stable bidentate formate to unstable monodentate formate as the reactive intermediate, and the two species were confirmed to be in equilibrium before decomposition. The frequencies of the observed species and the proposed energy diagram of the formic acid decomposition are also supported by quantum chemical calculations.<sup>10</sup> Although several picosecond vibrational studies have been performed to examine the vibrational relaxation processes of zeolite hydroxyl groups,<sup>11–16</sup> the only report in the literature treating the reaction dynamics of other species adsorbed on zeolite surfaces deals

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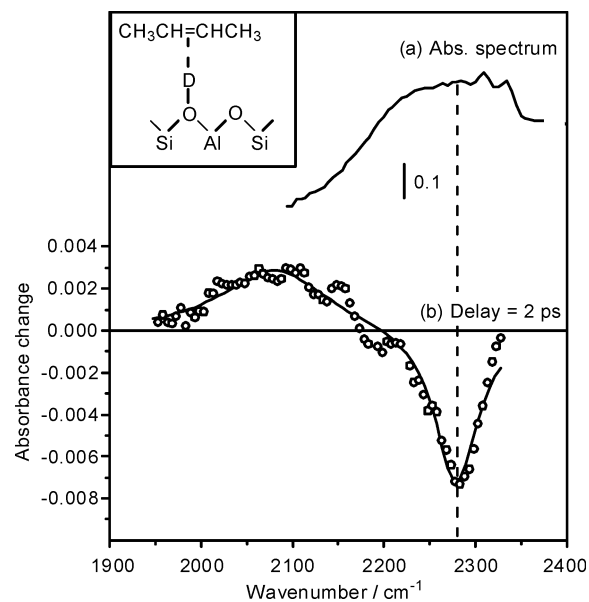
with the observation of transients in an isobutene/zeolite system.<sup>8</sup> In that study, the structural change of isobutene adsorbed on zeolite hydroxyl groups was observed on the basis of vibrational excitation of the OH stretching mode.

In the present study, two-color picosecond IR–IR pump–probe experiments were carried out for the *trans*-2-butene/zeolite system. *trans*-2-Butene was selected as an olefin because of its high thermodynamic stability compared to linear butene isomers, which are converted to *trans*-2-butene at considerably lower temperatures (<230 K) in the absence of proton transfer from zeolites,<sup>17,18</sup> although the detailed mechanism has not been clarified. Thus, the reaction of *trans*-2-butene with the acidic hydroxyl groups is observed at higher temperatures, where proton transfer occurs. The previously observed isomerization of *n*-butene is beyond the scope of the present study. At around 300 K, conventional Fourier transform (FT) IR spectroscopy has revealed that *trans*-2-butene molecules react on zeolites to form the dimer olefin 2,5-dimethyl-3-hexene simultaneously with isotope exchange between the olefin molecules and the OD groups of the zeolite.<sup>19</sup> Thus, species that have already reacted with another molecule after proton transfer from zeolite at around 300 K have been observed by conventional vibrational analyses. However, the short-lived monomolecular intermediates formed in the initial stage of the reaction have yet to be observed directly. Through the use of picosecond IR laser spectroscopy, transient absorption spectra for the *trans*-2-butene/zeolite system are obtained in this study in the period immediately following excitation of the OH (OD) stretching mode by application of an intense IR pulse. In addition to the extremely fast vibrational relaxation of the excited state of OH (OD) interacting with *trans*-2-butene, CH stretching bands at above 3000 cm<sup>-1</sup> belonging to a short-lived intermediate species are found here to persist for more than 100 ps following excitation. The generation of this short-lived intermediate is promoted by the local transient temperature increase induced by irradiation with a short laser pulse. As the local temperature returns to the original temperature within 100 ms, the period of heating is insufficient to allow significant diffusion of *trans*-2-butene molecules into the ferrierite pores, preventing complicating intermolecular reactions.

## 2. Experimental Section

Samples of approximately 30 mg of ferrierite zeolite (Tosoh; Si/Al = 8.5) were pressed into self-supporting disks of 20-mm diameter. The samples were placed in a quartz IR cell with a CaF<sub>2</sub> window for in-situ spectroscopy and were attached to a conventional vacuum line (10<sup>-3</sup> Torr). The ferrierite disk was pretreated with 100 Torr of oxygen at 773 K for 1 h, followed by treatment with 100 Torr of hydrogen at 673 K for 1 h. Deuteration of the acidic OH groups of ferrierite was performed by repeating the adsorption and evacuation of D<sub>2</sub>O at 473 K. *trans*-2-Butene (ca. 5 Torr) was introduced into the IR cell at 230 K, and measurements were carried out at room temperature, 188, 233, and 243 K.

For IR–IR pump–probe measurements, the output of a mode-locked Ti:sapphire laser (Mira, Coherent; central wavelength, 800 nm; pulse duration, 100 fs) pumped by a cw-Nd:YVO<sub>4</sub> laser (Verdi, Coherent; wavelength, 532 nm; output power, 5 W) was used as a seed pulse train. These pulses were successively amplified by two amplifier systems in series: a combined regenerative/multipass amplifier system (Titan-I-3p, Quantronix) and a multipass amplifier system (Titan-PA-10, Quantronix). The 800-nm output pulses from this amplifier system, each with 3-ps duration and 10 mJ/pulse energy and



**Figure 1.** (a) Linear absorption spectrum of *trans*-2-butene adsorbed onto ferrierite zeolite in the OD stretching region and (b) transient absorption spectrum 2 ps after excitation. Open circles denote experimental data and solid curve represents a least-squares fit using Lorentzian functions. (Inset) Schematics of *trans*-2-butenes adsorbed to surface hydroxyl groups ( $\pi$ -OD) of ferrierite zeolite.

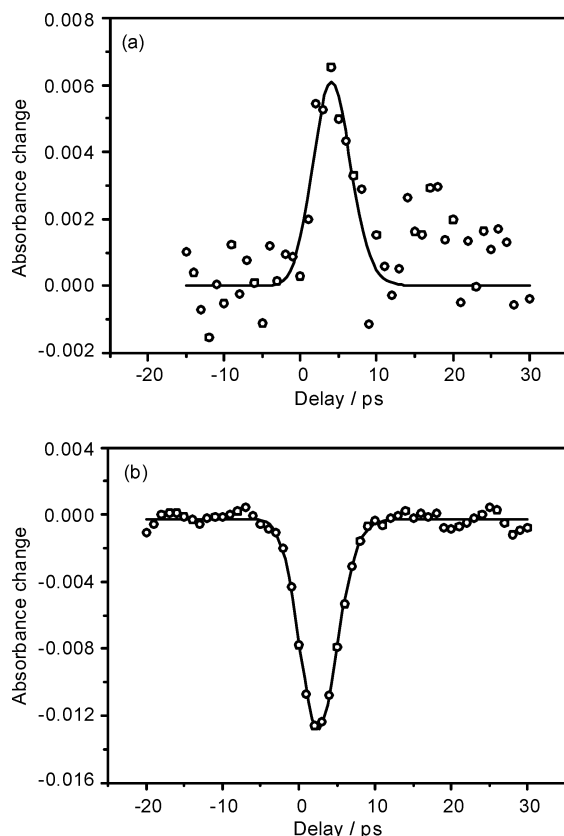
repeated at a rate of 10 Hz, were divided into two beams at an energy ratio of 4:1. Each beam was used as a light source for an optical down conversion system (TOPAS, Light Conversion) to produce two independently tunable IR pulses. The IR pulses were tunable in the range 900–3600 cm<sup>-1</sup>, with a spectral width of 13 cm<sup>-1</sup> and a pulse duration of 2 ps. The pump energy at 2278 and 2990 cm<sup>-1</sup> was ca. 40  $\mu$ J/pulse, and the energy of the probe pulses was ca. 10 and 6  $\mu$ J/pulse at 2278 and 1457 cm<sup>-1</sup>, respectively. The probe pulses were split into two beams before the IR cell, and one beam was used as a reference. The pump and probe beams were focused at the same position on the sample disk, and the reference beam was focused on a different part of the sample disk. The probe and reference beams transmitted from the sample disk were detected by mercury cadmium telluride (MCT) detectors. The signals were integrated using a boxcar averager, averaging more than 1000 pulses at each point using a personal computer. Further details on the experimental setup for the IR–IR pump–probe experiment can be found elsewhere.<sup>8</sup>

## 3. Results and Discussion

### 3.1. Transient Absorption Spectrum of Deuterated Hydroxyl Groups of Ferrierite Interacting with *trans*-2-Butene.

The linear absorption spectrum of *trans*-2-butene adsorbed onto ferrierite at 188 K in the OD stretching region is shown in Figure 1a. This spectrum was measured by scanning the frequency of the probe pulse. A broad absorption band centered around 2278 cm<sup>-1</sup> can be observed, assigned to the stretching mode of ferrierite acidic OD  $\pi$ -hydrogen-bonded to the C=C bond of *trans*-2-butene.<sup>19–21</sup> This  $\pi$ -hydrogen-bonded structure ( $\pi$ -OD) is the most stable structure on zeolites (including ferrierite) at low temperatures, where protonation from acidic OD (OH) groups to alkene molecules does not occur.<sup>19</sup> The structure of  $\pi$ -OD is illustrated in the inset of Figure 1. The two upward peaks in the vicinity of 2340 cm<sup>-1</sup> represent the contribution from CO<sub>2</sub> gas in air.

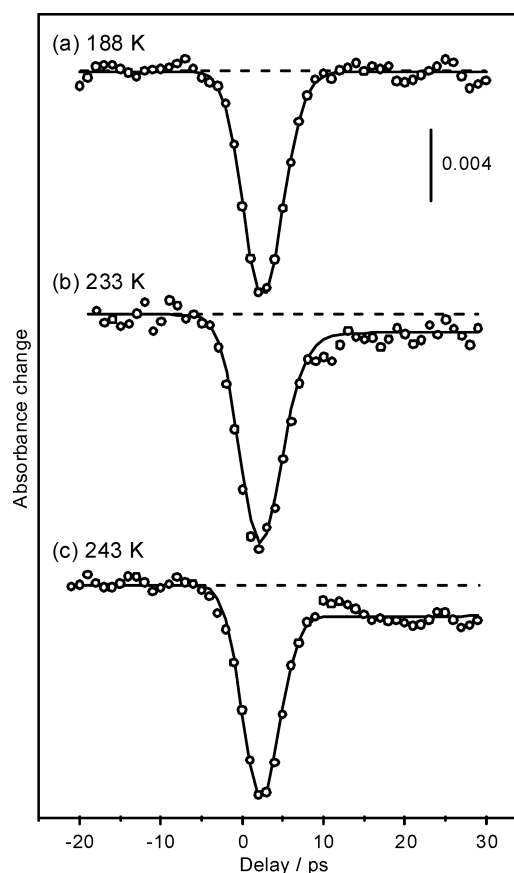
The transient absorption spectrum obtained 2 ps after IR pulse excitation of the  $\pi$ -OD band at 2278 cm<sup>-1</sup> is shown in Figure



**Figure 2.** Temporal absorbance change at (a) 208  $\text{cm}^{-1}$  and (b) 2278  $\text{cm}^{-1}$  for excitation at 2278  $\text{cm}^{-1}$ . Open circles denote experimental data and solid curves were derived by a least-squares fit (see text).

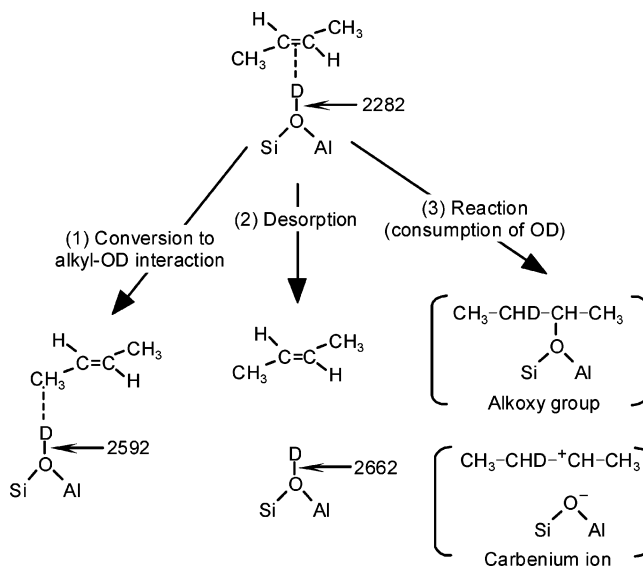
1b. A dip can be observed at 2278  $\text{cm}^{-1}$ , corresponding to the pump frequency, and a broad transient absorption band centered around 2081  $\text{cm}^{-1}$  emerges. These bands are assigned to transient saturation of the transition between the  $v = 0$  and  $v = 1$  states (bleaching band) and transient absorption from  $v = 1$  to  $v = 2$  (hot band) of the  $\pi$ -OD stretching mode, respectively. The solid curve drawn through the data points is a least-squares fit using two Lorentzian functions.

Figure 2a and b shows the absorbance changes for probing at 2278  $\text{cm}^{-1}$  (bleaching band) and 2081  $\text{cm}^{-1}$  (hot band) as a function of delay time (from  $-20$  to  $30$  ps) at a pump frequency of 2278  $\text{cm}^{-1}$ . The delay of  $0$  ps corresponds to the exact superposition of pump and probe pulses. To estimate the lifetimes from these decay curves, the parameters of a convolution function between a single-exponential function and a Gaussian function representing the laser pulse were optimized by a least-squares fit. The optimized convolution functions are shown as solid lines in Figure 2. The bleaching band weakens abruptly upon excitation compared to free OD (ca.  $\tau = 50$  ps at  $188$  K), and this feature decays exponentially with a time constant of ca.  $\tau = 2$  ps. It has been reported that the presence of an adsorbate hydrogen-bonded to OD (OH) on the zeolite surface shortens the vibrational lifetime of the OD (OH).<sup>15,16,22–24</sup> A complementary strengthening of the hot band is also observed, relaxing with an identical time constant of ca.  $\tau = 2$  ps. It is inferred from these observations that relaxation from the  $v = 1$  state proceeds directly to the  $v = 0$  ground state at  $188$  K without the involvement of other intermediate states. In practice, the energy input of  $40 \mu\text{J}/\text{pulse}$  causes local heating of about  $+40$  K through the relaxation of lattice vibrations,<sup>25</sup> resulting in estimated local temperatures of  $230$ – $240$  K. No reaction should take place in this temperature range between *trans*-2-butene and the OD (OH) groups.<sup>19</sup>

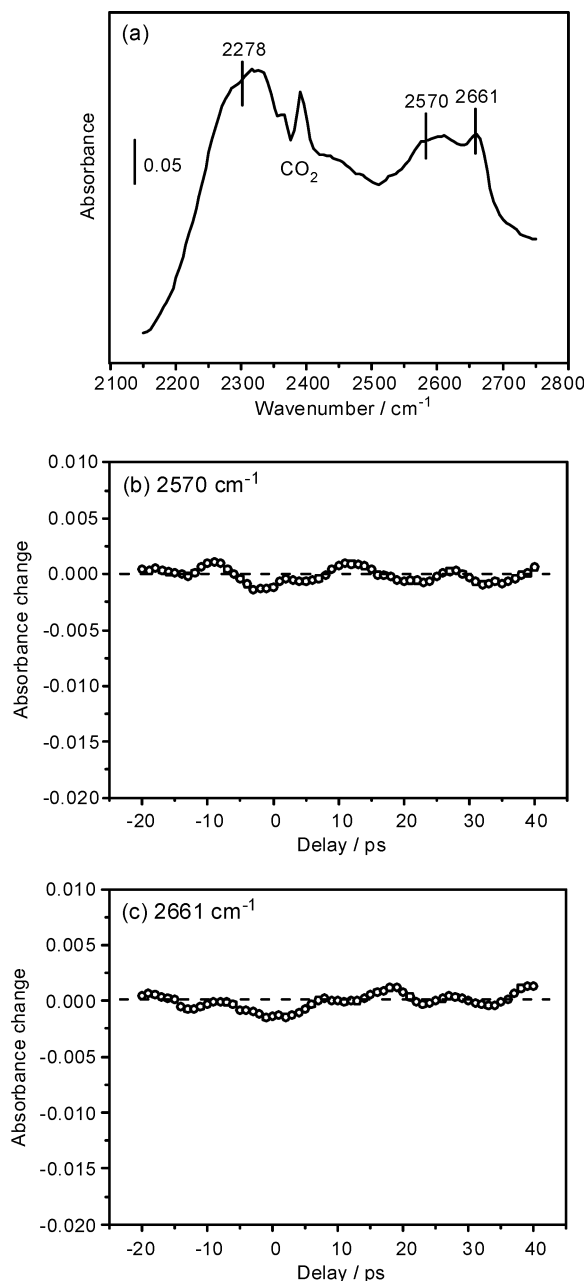


**Figure 3.** Temporal absorbance change at 2278  $\text{cm}^{-1}$  for excitation at 2278  $\text{cm}^{-1}$  and substrate temperatures of (a)  $188$  K, (b)  $233$  K, and (c)  $243$  K. Open circles denote experimental data and solid curves were derived by a least-squares fit (see text).

### SCHEME 1: Schematic Description of Possible Origins for the Decrease of Hydrogen-Bonded OD Band in Intensity

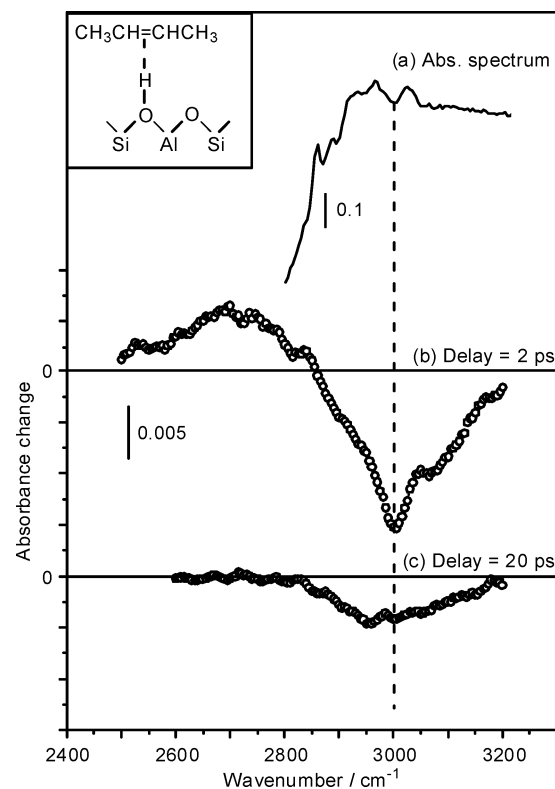


**3.2. Temperature Dependence of Recovery Profiles of the Transient Bleach Band.** Figure 3 shows the temperature dependence of the temporal absorbance changes when probed at 2278  $\text{cm}^{-1}$  (bleaching band) with a pump frequency of 2278  $\text{cm}^{-1}$ . As the substrate temperature was increased, a component with a lifetime of longer than  $100$  ps after excitation emerged in the time profile of the bleaching band, representing an unrecovered part of the absorbance of the bleaching band (Figure



**Figure 4.** (a) Linear absorption spectrum of *trans*-2-butene adsorbed onto ferrierite zeolite in the OD stretching region and temporal absorbance changes at (b) 2570  $\text{cm}^{-1}$  and (c) 2661  $\text{cm}^{-1}$  after excitation at 2278  $\text{cm}^{-1}$  and 233 K. Open circles denote experimental data and solid curves were derived by a least-squares fit (see text).

3b and c). Since there was no baseline shift during these measurements, as indicated by the absorbance in the negative delay region, the absorbance can be understood to have recovered within 100 ms (10 Hz repetition rate). The lifetimes were estimated from this decay behavior by obtaining a least-squares fit of the parameters of a convolution function between a single- or double-exponential function and a Gaussian function representing the laser pulse. The optimized convolution functions are shown as solid lines in Figure 3. The recovery time for the shorter component at all temperatures was ca.  $\tau = 3$  ps, while the recovery time for the longer component was more than 1 ns. These results appear to suggest that structural change of the *trans*-2-butene  $\pi$ -OD bond or desorption of adsorbed *trans*-2-butene occurs following vibrational relaxation of the  $v = 1$  state.



**Figure 5.** (a) Linear absorption spectrum of *trans*-2-butene adsorbed onto ferrierite zeolite in OH stretching region and transient absorption spectrum (b) 2 ps and (c) 20 ps after excitation. (Inset) Schematics of *trans*-2-butene adsorbed to surface hydroxyl groups ( $\pi$ -OH) of ferrierite zeolite.

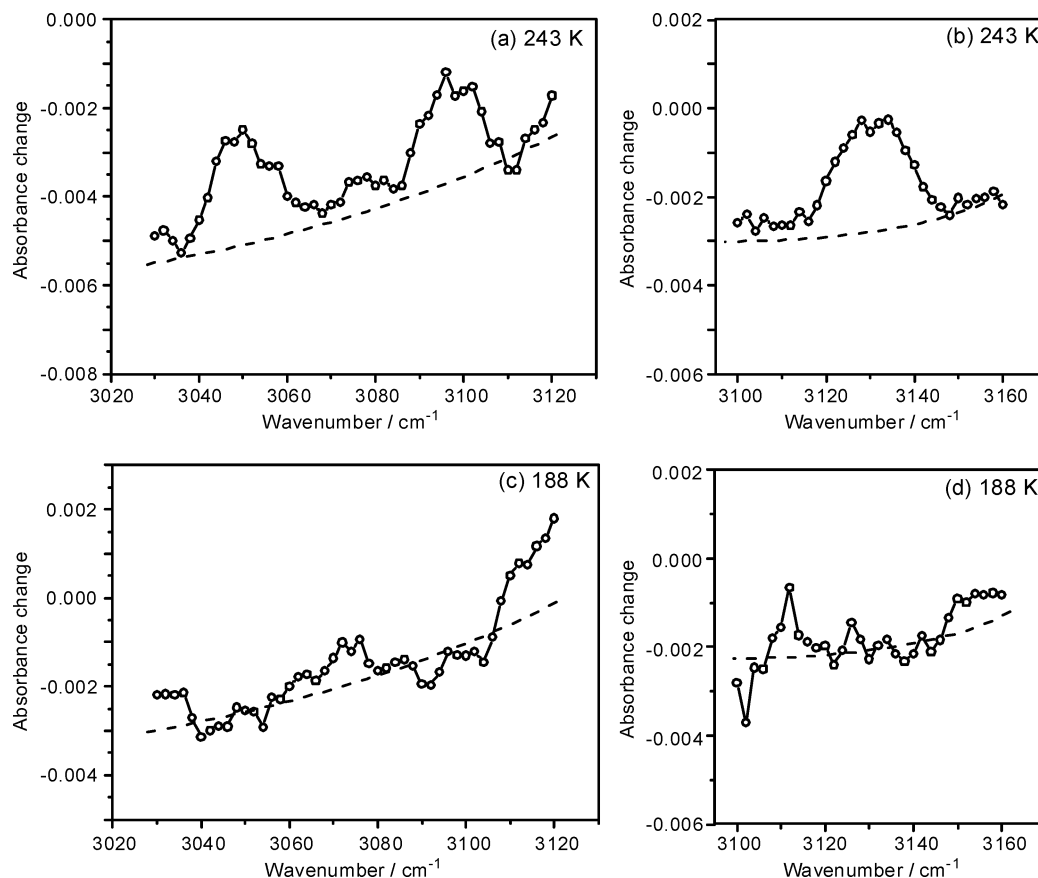
Similar results were obtained for isobutene-adsorbed zeolite systems in previous experiments.<sup>8</sup>

The unrecovered part of the absorbance may originate from (1) structural change of adsorbed *trans*-2-butene, (2) desorption, or (3) consumption of adsorbed *trans*-2-butene by reaction, as schematically illustrated in Scheme 1.

Figure 4a shows the linear absorption spectrum of *trans*-2-butene-adsorbed zeolite in the OD stretching region. This spectrum was measured at 233 K by scanning the frequency of the probe laser. The broad absorption band centered around 2278  $\text{cm}^{-1}$  is assigned to  $\pi$ -OD, as seen in Figure 4a. Another broad absorption band centered around 2570  $\text{cm}^{-1}$  is assigned to the stretching mode of zeolite OD hydrogen-bonded by a methyl ( $\text{CH}_3$ ) group to *trans*-2-butene (methyl-OD), representing another quasi-stable adsorbed structure.<sup>20</sup> A band due to the stretching mode of an isolated acidic OD (free-OD) on ferrierite zeolite is also observed at 2661  $\text{cm}^{-1}$ .<sup>21</sup>

On the basis of mechanisms 1 and 2, transient absorbance changes at 2570  $\text{cm}^{-1}$  or 2661  $\text{cm}^{-1}$  should be observed following pump-pulse excitation. Figure 4b and c shows the transient absorbance changes when probed at 2570  $\text{cm}^{-1}$  (methyl-OD) and 2661  $\text{cm}^{-1}$  (free-OD) at 233 K as a function of delay time (from -20 to 30 ps) using a pump frequency of 2278  $\text{cm}^{-1}$ . No transient absorbance changes were observed for either methyl-OD or free-OD groups for up to 40 ps in these experiments, demonstrating that neither change of the adsorbed structure nor desorption of *trans*-2-butene occurred on ferrierite under IR pump-pulse irradiation. This result is quite different from that obtained in the previous study of isobutene adsorption on mordenite zeolite, where desorption was observed.<sup>8</sup> Thus, the possibilities of a change of the adsorption structure and desorption of *trans*-2-butene can be discounted as the main





**Figure 6.** Transient absorption spectrum 20 ps after excitation of *trans*-2-butene adsorbed onto OH for substrate temperatures of (a, b) 243 K and (c, d) 188 K.

sources of the unrecovered part of the absorbance change observed at 233 and 243 K (Figure 3b and c). These experimental results instead suggest that mechanism 3, the consumption of adsorbed *trans*-2-butene by reaction induced by irradiation with IR pump pulses, is responsible for the unrecovered part of the absorbance change.

Previous FT-IR measurements of the same system have shown that H/D isotope exchange between zeolite OD and C–H bonds in *trans*-2-butene occurs at substrate temperatures above ca. 270 K.<sup>20</sup> This reaction can be easily confirmed by the weakening of the  $\pi$ -OD band centered around 2278  $\text{cm}^{-1}$  and simultaneous strengthening of the  $\pi$ -OH band centered around 2990  $\text{cm}^{-1}$ . The absorption spectra in the region of these  $\pi$ -OD and  $\pi$ -OH bands obtained before and after 30 min IR pump–pulse irradiation at 2278  $\text{cm}^{-1}$  and 233 K reveal a weakening of the  $\pi$ -OD band and strengthening of the  $\pi$ -OH band (data not shown). Thus, it is reasonable to conclude that IR pump–pulse irradiation induces H/D isotope exchange. As mentioned above, this is due to the energy input causing local heating, which induces a transient temperature increase of ca. 40 K.<sup>25</sup> Therefore, the occurrence of a reaction at an apparent temperature of 233 K is considered to correspond to the transient temperature of 273 K, which is in agreement with our previous FT-IR study.<sup>19</sup>

The H/D isotope exchange reaction is generally conceived as being mediated by either the carbenium or alkoxy species.<sup>26</sup> One of the main goals of this study was to directly observe such short-lived intermediated species produced in these surface reactions. However, the H/D isotope exchange reaction consumes the  $\pi$ -OD signal because of conversion of  $\pi$ -OD to  $\pi$ -OH during extended IR pump–pulse irradiation. Therefore, to make the system reversible, experiments were performed using the

H-form, that is, *trans*-2-butene adsorbed via  $\pi$ -OH (2990  $\text{cm}^{-1}$ ), to detect the reaction intermediates during the H/H exchange reactions occurring after IR pump–pulse irradiation. These experiments make it possible to measure small signal changes that can only be detected by prolonged accumulation of each data point, meaning that it should be possible to confirm any desorption or change in the adsorption structure of *trans*-2-butene. However, as the frequency region of the free-OH stretching mode is beyond the frequency tunable region of the present laser system, the *trans*-2-butene/OD system was used in the first stage of these experiments.

**3.3. Transient Absorption Spectrum of Adsorbed *trans*-2-Butene.** **3.3.1. C–H Stretching Region.** The linear absorption spectrum of *trans*-2-butene adsorbed on ferrierite at 243 K in the  $\pi$ -OH stretching region is shown in Figure 5a, with the  $\pi$ -OH structure illustrated in the inset. This spectrum was measured by scanning the frequency of the probe IR laser pulse. The broad absorption band centered around 2990  $\text{cm}^{-1}$  can be assigned to the  $\pi$ -OH stretching mode on the basis of the findings of previous FT-IR measurements.<sup>21</sup> An olefinic C–H stretching band of adsorbed *trans*-2-butene can also be observed at 3050  $\text{cm}^{-1}$ , together with other C–H stretching bands at 2860 and 2960  $\text{cm}^{-1}$ .<sup>27</sup> The band at 2990  $\text{cm}^{-1}$  because of  $\pi$ -OH, corresponding to the peak of the broad  $\pi$ -OH stretching band observed in the FT-IR spectrum (not shown), is excited by the IR pulse irradiation and exhibits transient features that can be seen by comparing the spectra captured at 2 and 20 ps (open circles in Figure 5b and c). At 2 ps, the absorption at 2990  $\text{cm}^{-1}$ , corresponding to the frequency of the pump pulse and representing transient saturation of the transition between the  $v = 0$  and  $v = 1$  states (bleaching band), becomes as a negative band, while the broad absorption centered around 2700  $\text{cm}^{-1}$ ,

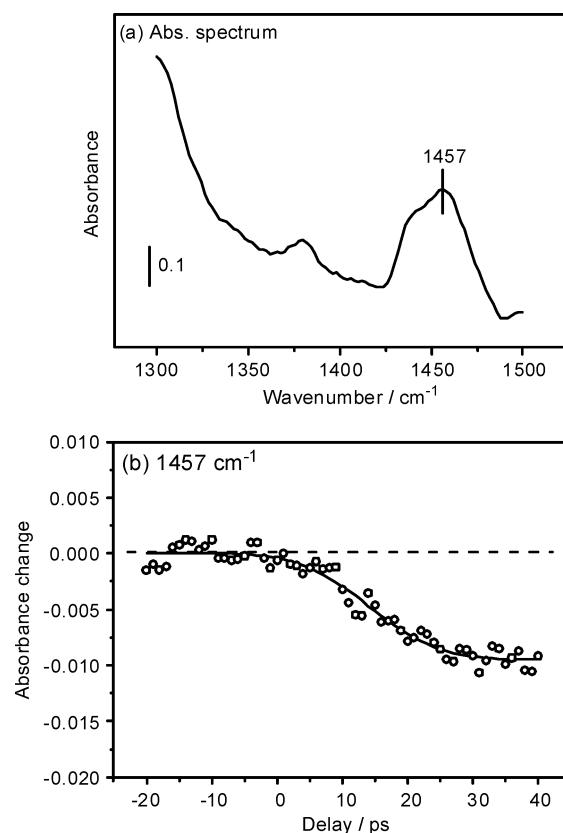
assigned to transient absorption of the  $\pi$ -OH stretching mode from  $v = 1$  to  $v = 2$  (hot band), becomes apparent. At 20 ps, the hot band absorption at  $2700\text{ cm}^{-1}$  is no longer present, while the transient bleaching band at around  $2990\text{ cm}^{-1}$  persists. This temporal behavior agrees well with the results obtained using OD groups (Figure 3b and c) and indicates that the vibrational relaxation of  $\pi$ -OH is completed within 20 ps. These results suggest that the origin of the unrecovered part of the bleaching band observed at 20 ps is due to the consumption of adsorbed *trans*-2-butene by proton transfer from zeolite to adsorbed *trans*-2-butene under IR pump-pulse irradiation, resulting in transient local heating of ca. +40 K.<sup>25</sup>

As the C-H stretching modes of adsorbed *trans*-2-butene and the  $\pi$ -OH stretching mode overlap in the same IR spectral region as shown in Figure 5a, the transient C-H stretching absorptions of the adsorbed *trans*-2-butene are obscured. The transient spectrum above  $3000\text{ cm}^{-1}$  at 20 ps (Figure 5c) was therefore examined in more detail by increasing the accumulation time for each data point.

Figure 6 shows the transient spectra of adsorbed *trans*-2-butene in the C-H stretching region ( $3030\text{--}3120$  and  $3100\text{--}3160\text{ cm}^{-1}$ ) 20 ps following excitation of the  $\pi$ -OH band at  $2990\text{ cm}^{-1}$  by IR pump pulses. At 243 K (Figure 6a and b), three upward peaks at approximately  $3045$ ,  $3095$ , and  $3130\text{ cm}^{-1}$  were observed above the broad bleaching background recognized in Figure 5c. At 188 K (Figure 6c and d), however, only the broad bleaching background was observed. From the temperature dependence of the transient bleaching band observed in Figure 3, the IR pump-pulse irradiation is considered to induce proton transfer at temperatures higher than 233 K. Thus, these three transient peaks observed at 243 K in Figure 6a and b are expected to represent transient species produced by irradiation with IR pump pulses, that is, reaction intermediates generated during the H/H exchange reaction. While the assignment of the transient peaks observed at 243 K is discussed in more detail in conjunction with quantum chemical calculations elsewhere, this is the first observation of the short-lived quasi-stable intermediate species formed by protonation of an olefin from the acidic OH groups on zeolite.

**3.3.2. C-H Bending Region.** The presence of transient species was also confirmed by the temporal profiles of the C-H bending modes of adsorbed *trans*-2-butene obtained after excitation with IR laser pulses. Figure 7a shows the linear absorption spectrum of *trans*-2-butene adsorbed on ferrierite at 243 K in the C-H bending region. The absorption band at  $1457\text{ cm}^{-1}$  is assigned to the C-H bending modes of the  $\text{CH}_3$  groups of *trans*-2-butene,<sup>27</sup> while the strong absorbance below  $1400\text{ cm}^{-1}$  is due to the ferrierite substrate. Figure 7b shows the transient absorbance change when probed at  $1457\text{ cm}^{-1}$  as a function of delay time (from  $-20$  to  $30\text{ ps}$ ) with a pump frequency of  $2290\text{ cm}^{-1}$ . Absorbance in the  $1457\text{ cm}^{-1}$  band weakens over this time period, suggesting the generation of an unstable intermediate species on the ferrierite surface by proton transfer from the acidic OH groups to *trans*-2-butene because of transient local heating induced by IR pump-pulse irradiation.

**3.3.3. Mechanism of the Formation of Short-Lived Species.** The mechanism of the IR pump pulse-induced reaction of *trans*-2-butene with the acidic OH groups of ferrierite can be explained as follows. The OH stretching mode of *trans*-2-butene-adsorbed ferrierite ( $\pi$ -OH) is excited from  $v = 0$  to  $v = 1$  by irradiation with an intense IR pulse ( $40\text{ }\mu\text{J/mol}$ ). This excited state relaxes with a lifetime of ca. 2 ps, leading to local heating (ca. 40 K),<sup>25</sup> although the system takes longer to reach thermal equilibrium. As a result of this local transient increase in surface temperature,



**Figure 7.** (a) Linear absorption spectrum of *trans*-2-butene adsorbed onto ferrierite zeolite in the C-H bending region and temporal absorbance changes at (b)  $1444\text{ cm}^{-1}$  and (c)  $1457\text{ cm}^{-1}$  after excitation at  $2999\text{ cm}^{-1}$ . Open circles denote experimental data and solid curves were derived by a least-squares fit (see text).

*trans*-2-butene starts to react with surface OH groups at an apparent temperature 243 K but not at 188 K. As the temperature 100 ms after excitation (heating) is much less than 1% of the original temperature increase, as estimated by the heat-diffusion equation,<sup>28</sup> the sample effectively cools back to the initial temperature before irradiation of the next pump pulse (100 ms). This phenomenon is therefore completely reversible under a 10 Hz cycle.

The real temperature of the sample after irradiation increases by about 40 K,<sup>25</sup> and thus the reaction takes place at slightly below room temperature. This is in agreement with the previous FT-IR results, where H/D exchange between *trans*-2-butene and the OD groups of zeolite evidently occurred at ca. 300 K.<sup>20</sup> FT-IR observations have previously revealed the simultaneous formation of the olefin dimer as a stable hydrocarbon product. If this dimer species were to be formed under the present conditions, the stable product would not decompose to the original *trans*-2-butene and the absorbance would not recover within 100 ms. However, the *trans*-2-butene molecules cannot diffuse sufficiently in such a short time to react with other *trans*-2-butene molecules in the ferrierite pores.<sup>21,29</sup> Thus, the reaction products identified here, which are reversible to the adsorbed *trans*-2-butene, are regarded as short-lived intermediate species that occur in local minima of the potential energy surface.

## 4. Conclusions

Transient absorption spectra for *trans*-2-butene adsorbed on the Brønsted acidic hydroxyl groups of ferrierite zeolite were successfully measured using a two-color picosecond infrared-infrared pump-probe technique. At a substrate temperature of

188 K, the transient spectrum obtained 2 ps after irradiation revealed bleaching and hot bands of the OD stretching mode with extremely fast vibrational relaxation times of ca. 3 ps. At a higher substrate temperature of 243 K, the absorbance of the bleaching band did not fully recover within ca. 3 ps but was completely recovered within 100 ms accompanied by a transient decrease in absorbance of the C–H deformation band of *trans*-2-butene adsorbed on the ferrierite. Additional CH stretching bands at 3054, 3095, and 3130 cm<sup>-1</sup> also emerged 20 ps after excitation of hydrogen-bonded OH stretching band at the higher substrate temperature. These results are considered to reflect the formation of a short-lived intermediate by reaction between *trans*-2-butene and acidic hydroxyl groups. The reaction would be caused by the local transient temperature increase induced by IR pulse irradiation. The intermediate was shown to be reversible to *trans*-2-butene within 100 ms. Thus, the transient IR spectra of a short-lived intermediate species formed from the reaction of *trans*-2-butene with acidic OH groups of zeolite were experimentally observed for the first time.

**Note Added in Proof:** After we completed the manuscript, density functional theory (DFT) calculations on protonation of isobutene on H-ferrierite was reported.<sup>30</sup> According to the results,  $\pi$ -bonded species is the most stable, and the Gibbs energy increases in the order carbenium ion < *iso*-butoxy < *tert*-butoxy. Thus, the recovery of the presently observed short-lived species to the original  $\pi$ -bonded structure is supported from the DFT calculations. However, since the calculated vibrational frequencies of the protonated species and the alkoxy groups appear quite similar, the absolute structure of the observed short-lived species needs further examination.

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## References and Notes

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- (25) Local heating of  $40 \pm 10$  K was estimated on the basis of the heat capacity of SiO<sub>2</sub> ( $0.47 \text{ J g}^{-1} \text{ K}^{-1}$ ), the sample weight (14 mg), thickness (ca. 0.1 mm), diameter (ca. 20 mm), and the beam diameter at the sample (ca. 0.25 mm). The local temperature increase was also estimated on the basis of the assumption that the  $\pi$ -OH vibrational energy of 2990 cm<sup>-1</sup> ( $5.939 \times 10^{-20} \text{ J}$ ) dissipates over the volume determined by the density of vibrationally excited  $\pi$ -OH groups through vibrational relaxation from  $\pi$ -OH groups to low-frequency phonon modes. In the ferrierite sample used in this study, the density of Brønsted acidic sites was about  $0.1 \text{ Å}^{-3}$ , and the number ratio of  $\pi$ -OH groups to Brønsted acidic sites was estimated to be about 0.3 from the FT-IR spectrum. The number ratio of vibrationally excited  $\pi$ -OH groups to total  $\pi$ -OH groups was about 0.003, as estimated from the FT-IR and transient bleaching spectra. Thus, the density of vibrationally excited  $\pi$ -OH group was estimated to be  $3 \times 10^{-4} \text{ Å}^{-3}$ . The estimated local temperature increase based on this estimation is in agreement with that determined by the first method within acceptable error.
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