# An Ethoxy Intermediate in Ethanol Dehydration on Brønsted Acid Sites in Zeolite

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Acid-catalyzed ethanol dehydration on zeolite is shown to proceed via a covalent ethoxy group ($C_2H_5O$) as a stable intermediate, which was directly observed by IR spectroscopy.

## Introduction

Zeolites are microporous crystalline aluminosilicates with high internal surface area and are widely used in the petrochemical industry.[1] As the crystallographic structure and the local structure of active sites are well-known, many acid-catalyzed reactions on zeolites have been investigated. The hydroxyl groups located between aluminum and adjacent silicon atoms have been shown to be strongly Brønsted acidic, and to drive many acid-catalyzed reactions.[2] According to the established reaction mechanisms in organic chemistry, carbenium cation species have been regarded as intermediates of the catalytic reactions on zeolites. However, recent quantum chemical calculations have revealed alkoxy groups to be a more stable intermediate than carbenium cation species.[3] Carbenium cations have been claimed to be present in the transition state on solid acid catalysts, where stabilization by solvent molecules does not occur on zeolites. Experimentally, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy has been utilized to observe the reaction intermediates, and various species have been detected by reactions of hydrocarbons and alcohols on zeolites.[4,5] Most of the species observed to date are produced via several elemental reactions at relatively high temperatures. However, the monomolecular reaction intermediates formed after the initial reaction between the adsorbed species and acidic OH groups on the zeolite remain unclear, most probably due to the rapid onset of subsequent reactions after protonation from the acidic OH groups even at low temperature. As it is difficult to observe the reactions of olefin molecules on zeolites, which are complicated by rapid dimerization, oligomerization, and polymerization, in this study the dehydration of alcohol on zeolite was observed in an attempt to identify the reaction intermediate by careful selection of the experimental conditions.

## Experimental Section

Mordenite zeolite, JRC-Z-HM20 (Catalysis Society of Japan, Si/Al = 10), was pressed into a self-supporting disk (20 mm

diameter, 20–30 mg) and placed in an IR cell attached to a conventional closed circulation system. The sample was pretreated by circulating $O_2$ (100 Torr; 1 Torr = 133.322 Pa) at 773 K with a liquid nitrogen trap for 1 h followed by evacuation ($10^{-3}$ Torr) at the same temperature for 15 min to remove residual contaminants. The sample was then treated with circulating $H_2$ (100 Torr) at 673 K for 1 h, followed by evacuation while cooling to room temperature. Although zeolites are known to have both Brønsted and Lewis acid sites, the pretreatment conditions were chosen so as to eliminate Lewis acid sites, and the absence of such sites was confirmed by CO molecular probe. The IR spectra were obtained at a resolution of 4 cm$^{-1}$, using a Jasco 7300 Fourier transform IR (FT-IR) spectrometer equipped with a mercury cadmium telluride (MCT) detector. A total of 64 scans were averaged for each spectrum. The IR spectra of the clean disk were recorded under evacuation at various temperatures as background spectra. Background-subtracted IR spectra showing adsorbed species are presented throughout this paper. Ethanol was introduced onto the sample surface in a quantity equivalent to no more than 30% of the Brønsted acid sites. The IR cell was immediately evacuated after ethanol addition.

## Results and Discussion

A typical IR spectrum for mordenite zeolite with pores of $0.70 \times 0.65$ nm$^2$ after pretreatment is shown in Figure 1 together with the schematic structure, where each stick represents an Si–O–Si unit. When Si is replaced with Al, a proton compensates for the charge imbalance by generating an acidic OH group. The IR absorption band of the acidic OH groups is observed at 3610 cm$^{-1}$, and the silanol band appears at 3747 cm$^{-1}$. As the acidic OH groups monitored in the IR spectra are responsible for various acid-catalyzed reactions on zeolites, IR study is considered suitable for observing both active sites and adsorbed molecules on zeolites.

An IR spectrum for mordenite measured immediately following ethanol adsorption at 333 K is shown in Figure 2a. The OH band of the acidic OH groups at 3612 cm$^{-1}$ is negative due to the conversion of free atmospheric OH to hydrogen-bonded OH. The band due to hydrogen-bonded OH extends from 3000 to below 1300 cm$^{-1}$ (indicated by an arrow), and has a complex absorption structure. Briefly, the stretching band is perturbed by two fundamental bending modes ($\delta$ and $\gamma$) and
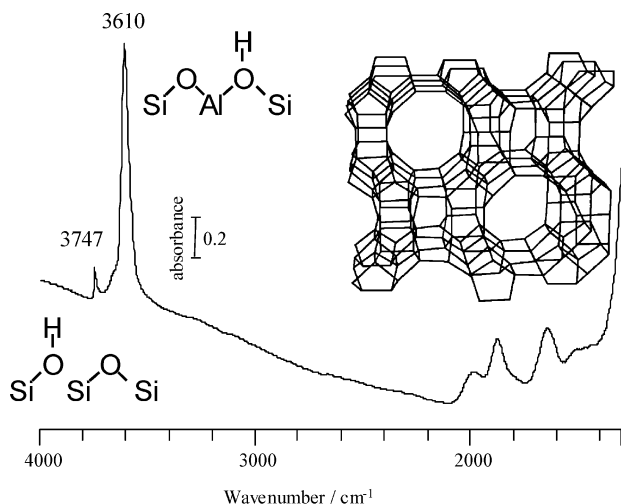
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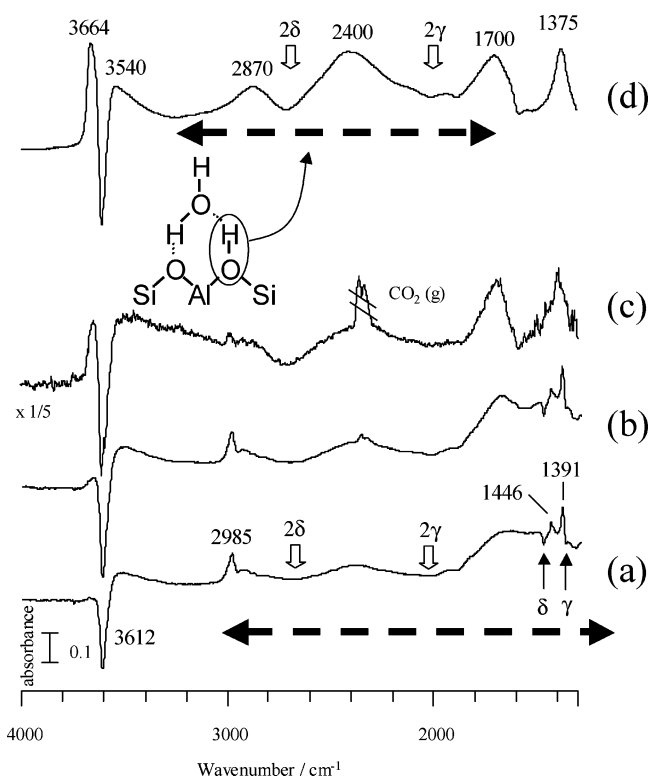† Tokyo Institute of Technology.
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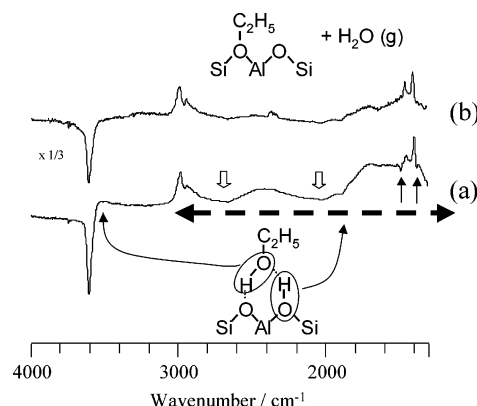⊥ The University of Tokyo.

**Figure 1.** IR spectrum and schematic illustration (inset) of mordenite zeolite.



**Figure 2.** IR spectra of ethanol adsorbed on mordenite at 333 K (a) immediately following ethanol adsorption and (b) 60 min later. (c) Difference spectra and (d) reference spectrum of water adsorbed on mordenite at the same temperature.
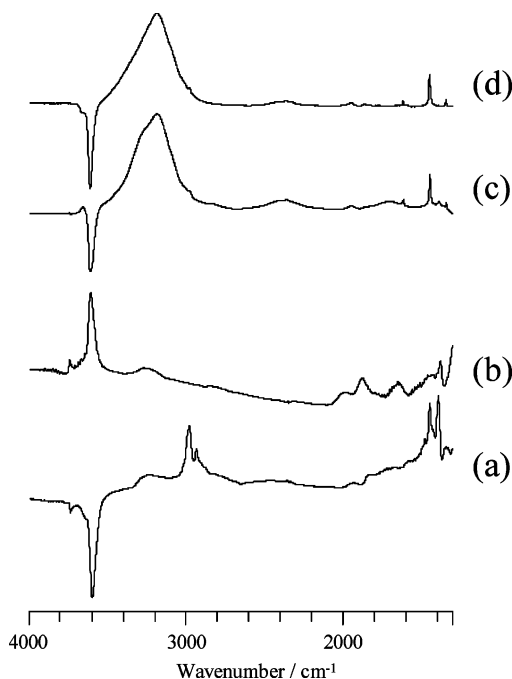


**Figure 3.** IR spectra of ethanol adsorbed on mordenite at 453 K (a) immediately following ethanol adsorption and (b) 10 min later.

Therefore, the hydrogen-bonding character of free acidic OH groups evolves over time after exposure to ethanol at 333 K. The most probable reaction for this evolution is the dehydration of ethanol to produce water, where the generated water molecules adsorb onto the acidic OH groups on the zeolite surface. Thus, the IR spectrum of water adsorption at the same temperature is shown for comparison in (d). In the case of water adsorption, a broad band due to hydrogen-bonded OH on zeolite ($3300-1700$ cm$^{-1}$, indicated by an arrow) is perturbed by overtones of the bending modes but not by bending fundamentals, as the fundamental bending modes in this case are present below 1300 cm$^{-1}$ due to the weaker interaction of the acidic OH groups with water than with ethanol.[6] A comparison of the spectra in (c) and (d) reveals the generation of water from the adsorbed ethanol over time at 333 K. As the absorption structures are similar for OH groups hydrogen bonded to both ethanol and water, and considering the lack of distinct bands appearing after 60 min, the counterpart of water, thought to be an ethyl cation or ethoxy group, was not identified by the results in this study.

For the purpose of identifying the dehydrated intermediate, the adsorption and dehydration of ethanol were observed at higher temperature. The spectral change over time was monitored at 453 K. The spectra measured 1 and 10 min after ethanol introduction are compared in Figure 3. At this temperature, water desorption occurs and the amount of adsorbed ethanol decreases accompanying ethanol dehydration. As the absolute intensity of the absorption bands in the spectra differs, they were normalized such that the CH stretching bands were equivalent in intensity. Figure 3a is almost the same as Figure 2a, showing ethanol adsorbed on the acidic OH groups in the structure shown in the inset. Figure 3b is again similar to Figures 2a and 3a except for the absence of the complex absorption structure of hydrogen-bonded acidic OH groups in Figure 3b. This suggests that ethanol and water molecularly adsorbed onto the acidic OH groups have disappeared. The negative band for isolated acidic OH groups is still present in Figure 3b, attributed to the consumption of acidic protons on zeolite. In the same spectrum, CH stretching and bending bands very similar to those of ethanol (Figure 3a) remain, indicating the presence of ethyl groups on the zeolite surface. Based on the facts that (1) water produced by ethanol dehydration is absent, (2) the acidic OH groups are consumed, and (3) ethyl groups are present, the stable intermediate for ethanol dehydration on zeolite, as observed in Figure 3b, is identified as an ethoxy group.

The identification of an ethoxy group as an intermediate for ethanol dehydration to ethylene was confirmed as follows. The

the corresponding overtones ($2\delta$ and $2\gamma$), as illustrated by arrows in the inset of Figure 3a.[6] Bands attributable to the adsorbed ethanol are observed at $3700-3200$ cm$^{-1}$ (stretching of OH hydrogen bonded to acidic OH groups), 2985 cm$^{-1}$ and below (CH stretching), 1446 cm$^{-1}$ (CH$_3$ degenerate bending), and 1391 cm$^{-1}$ (CH$_3$ symmetric bending). The CH$_2$ bending modes are too weak to be detected clearly. Figure 2b was measured 60 min after ethanol adsorption. In comparison to Figure 2a, the spectral features differ slightly in the ranges $3700-3400$ and $1800-1300$ cm$^{-1}$. The difference spectrum subtracting (a) from (b) is shown in (c). The difference spectrum exhibits a complex absorption structure similar to that for the hydrogen-bonded OH stretching band in (a). The band due to free acidic OH groups decreased further and is observed as a negative band in (c).

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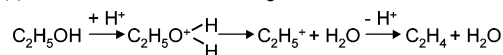*J. Phys. Chem. B, Vol. 109, No. 21, 2005* **10971**



**Figure 4.** IR spectra of (a) ethoxy-adsorbed mordenite, (b) ethoxy-desorbed mordenite, (c) mordenite after adsorption of desorbed species at 213 K, and (d) ethylene-adsorbed mordenite at 213 K.
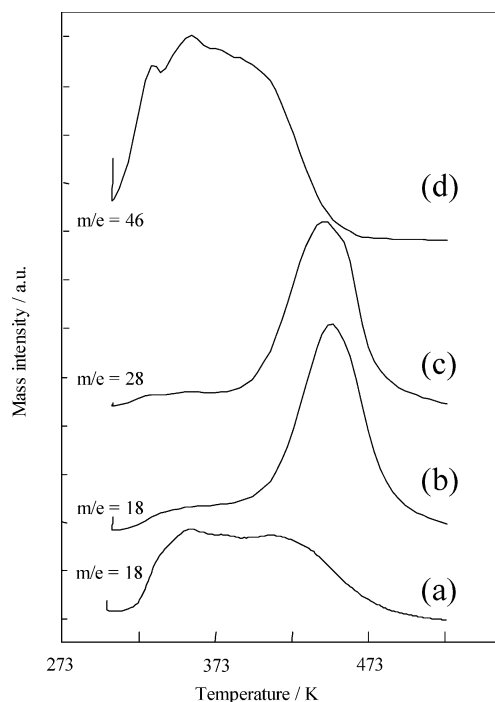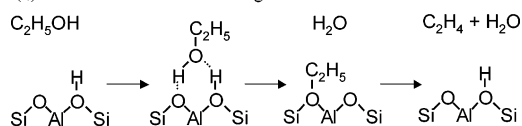


**Figure 5.** TPD spectra of (a) water (*m/e* 18) from water-adsorbed mordenite, (b) water (*m/e* 18), (c) ethylene (*m/e* 28), and (d) ethanol (*m/e* 46) from ethanol-adsorbed mordenite.



**Figure 6.** Comparison of mechanisms of ethanol dehydration (a) in acidic solutions and (b) on zeolites.



**Figure 7.** Change of IR spectra by incremental $d_6$-ethanol ($C_2D_5OD$) adsorption on (A) ethanol-adsorbed and (B) ethoxy-adsorbed mordenite surfaces: (a) before $d_6$-ethanol adsorption, and after (b) first, (c) second, (d) third, (e) forth, and (f) fifth dosage of $d_6$-ethanol adsorption. The broad band at <2650 cm$^{-1}$ is attributed to hydrogen-bonded OD groups in $d_6$-ethanol corresponding to OH groups in $d_0$-ethanol in Figure 3a.

decomposed and desorbed species from ethoxy groups were trapped and re-adsorbed on the zeolite at low temperatures. After obtaining the spectrum in Figure 3b, which is reproduced in Figure 4a, the temperature was increased and the desorbed molecules were trapped until all the adsorbed species had been removed from the surface. The zeolite surface is recovered after the removal as shown in Brgure 4b. The desorbed molecules were then re-adsorbed at low temperature (213 K). The IR spectrum of the final product observed in Figure 4c is identical with that of ethylene adsorbed on mordenite at the same
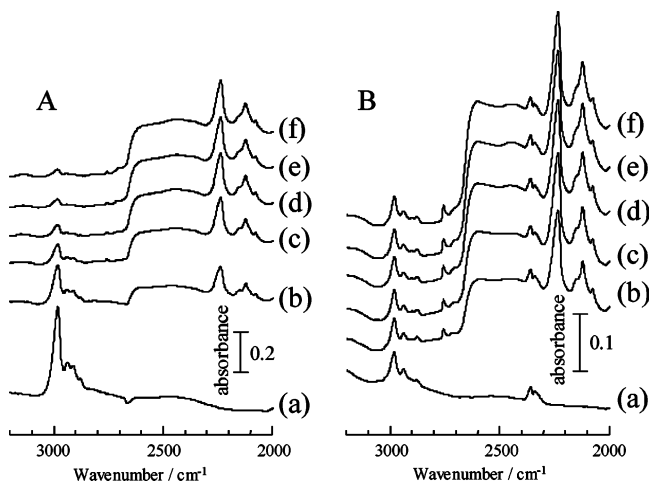
temperature (Figure 4d), confirming that the observed ethoxy groups are the intermediate for ethylene formation from ethanol dehydration. Temperature-programmed desorption (TPD) of the ethanol-adsorbed sample (Figure 5) revealed that water desorption begins at ca. 320 K and peaks at 450 K, while ethylene desorption starts from ca. 390 K with a maximum at 443 K. As the adsorbed water desorbed at much lower temperature (Figure 5a), and as the ethylene molecules adsorbed at low temperature have been shown to desorb below room temperature under evacuation,[7] the desorption of ethylene at such high temperatures is certainly attributable to alkoxy decomposition. Furthermore, oligomerization of the product ethylene is absent due to the unstable adsorption of ethylene molecules at high temperature. In the case of propanol and butanol dehydration, because the desorption temperatures of the product propylene and butene isomers are higher than that of ethylene, oligomerized hydrocarbon species were also observed, possibly formed from olefin adsorption.[8]

The mechanisms for these two intermediates, the conventional cationic intermediate and the proposed covalent intermediate, are compared in Figure 6. The alkoxy group was identified in the present study by IR spectroscopy to be a stable intermediate in ethanol dehydration on zeolite as a representative solid acid. While cationic intermediate is stabilized by solvation, such species are unstable at solid−gas interface in the absence of solvent. Thus, formation of covalent bonds would stabilize the surface species, which is in line with some theoretical conclusions.[3]

Although ethanol and ethoxy species give almost the same spectral features, the difference was observed in their behavior for $d_6$-ethanol adsorption. Incremental $d_6$-ethanol adsorptions
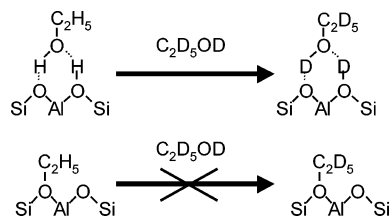
**Figure 8.** Schematic illustration of $d_6$-ethanol adsorption on ethanol-adsorbed and ethoxy-adsorbed mordenite surfaces.

on ethanol- and ethoxy-preadsorbed mordetinte surfaces were carried out. Ethanol-preadsorbed surface was prepared by adsorption of ethanol at 298 K followed by evacuation for 180 min, and ethoxy-preadsorbed surface was made by adsorption of ethanol at 423 K followed by evacuation for 180 min at the same temperature. About 10 $\mu$mol of $d_6$-ethanol was introduced each time onto respective mordenite surfaces at 298 K (Figure 7). While preadsorbed $d_0$-ethanol molecules (CH stretching bands at $2800-3050$ cm$^{-1}$) were gradually replaced by $d_6$-ethanol (CD stretching bands at $2000-2300$ cm$^{-1}$) as shown in Figure 7A, preadsorbed ethoxy groups (CH stretching bands at $2800-3050$ cm$^{-1}$) remained stably during incremental $d_6$-ethanol adsorption (Figure 7B). As summarized in Figure 8, the different behavior of alcohol and alkoxy species for adsorption of isotope-labeled alcohol further confirms the presence of stable alkoxy intermediate for alcohol dehydration on zeolite.

## Conclusion

In conclusion, a covalent ethoxy group ($C_2H_5O$) on a zeolite was directly observed during ethanol dehydration on Brønsted acidic sites as a stable intermediate by IR spectroscopy. Although IR spectra of adsorbed ethanol and ethoxy species were very similar, their stabilities for post-adsorption of $d_6$-ethanol adsorption appeared quite different.

## References and Notes

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