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Mechanism of Decomposition of Surface Ethoxy Species to Ethene and Acidic OH Groups on H-ZSM-5

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ABSTRACT: The reaction mechanism of the decomposition of ethoxy species to ethene and acidic OH groups on H-ZSM-5 was studied by IR spectroscopy using isotope-labeled ethanol. The concerted mechanism occurring on both the ethoxy (acid) site and the counterpart lattice oxygen was suggested by GC-MS analysis of evolved d_2-ethene and IR observation of the recovery of OH s groups on acid sites from the decomposition of CH_3CD_2O- ethoxy species. The concerted mechanism was further confirmed by the estimation of activation energy for decomposition of CH_3CH_2O-, CH_3CD_2O-, and CD_3CD_2O- ethoxy species, 122 ± 3, 125 ± 3, and 140 ± 5 kJ mol^{-1}, respectively, where the kinetic isotope effect was observed for the cleavage of the CH or CD bond of the methyl group of the ethoxy species.
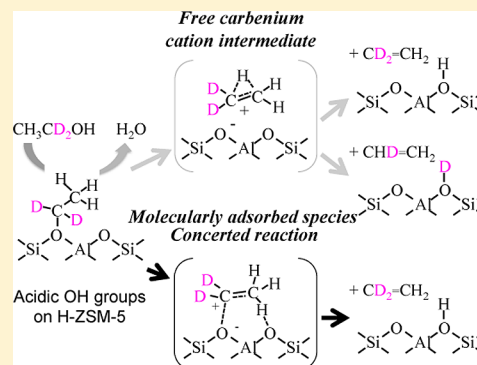
Proton-form zeolites are solid acid catalysts with microporous structure and have been widely utilized for hydrocarbon transformation reactions.[1−3] The mechanisms for these reactions are considered to involve carbocations as intermediates, which are formed by protonation of hydrocarbons from acidic OH groups bridging to Si and Al atoms in zeolite frameworks.[4−8] Carbenium ions could be formed on acidic OH groups from (1) protonation of unsaturated hydrocarbons, (2) deprotonation of saturated hydrocarbons, and (3) dehydration of oxygenates.[7] For the formation from unsaturated hydrocarbons, Kazansky suggested by a theoretical method that ethoxy species were stable intermediates formed from protonation of ethene and that adsorbed carbenium ions existed only in the transition state.[9−11] Contrary to the prediction, monomeric alkoxy species corresponding to products of protonation of light olefins (ethene, propene, and butenes) have not been identified experimentally as isolated stable intermediates[12] either by infrared (IR) spectroscopy or nuclear magnetic resonance (NMR). On the other hand, unimolecular alkoxy species were observed from the dehydration of methanol and ethanol to methoxy and ethoxy species, respectively, over acidic OH groups by IR spectroscopy[13−16] and NMR.[17−20]

These alkoxy species are regarded as the initial intermediate for the conversion of methanol[21−24] and ethanol[25−27] to olefins or ethers over zeolites with shape selectivity.[28] The dehydration mechanism of ethanol has also been studied experimentally[29−32] and by theoretical approaches.[33,34] We recently reported the formation of ethoxy species from ethanol,[35] which was the intermediate to ethene, and the activation energy of ethoxy decomposition to ethene and acidic OH groups was estimated.[36] Interestingly, intramolecular H/D exchange of CD_3CH_2OH to CHD_2CH_2OD was found to occur, which was mediated by acidic OH groups of zeolites, even at 313 K with

an activation energy of 72 ± 4 kJ mol^{-1}.[37] In this study, to get insight into the mechanism of the decomposition of ethoxy species to ethene, reaction of isotope-labeled ethoxy species was observed.

Concerning the reaction mechanism of decomposition of ethoxy species, two routes have been proposed.[25] The first mechanism proceeds via carbenium ion intermediates as a transition state on acid sites resulting from C−O bond cleavage (Scheme 1a). The structure of the formed carbenium ion is converted to the more stable symmetric species, which to C atoms are equivalent. Thus, all H or D atoms have the same probability to be left on the acid site when evolving into ethene.

Scheme 1. Possible Mechanism of Decomposition of $CH_3CD_2−$ Ethoxy Species via (a) Ethyl Carbenium Ion Intermediate and (b) Molecularly Adsorbed Species in a Concerted Route
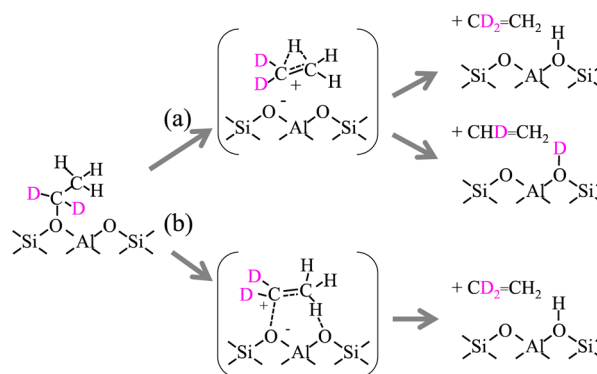
The second mechanism involves a concerted elimination of C−O and C−H bonds of ethoxy species on acid and base pair sites (Scheme 1b). Because the reaction coordinate is the dissociation of the C−H bond, the isotope effect on the activation energy for the decomposition would appear; d_3-methylated ethoxy (CD$_3$CD$_2$O− and CD$_3$CH$_2$O−) species would require higher energy than that of the d_0-methylated ethoxy (CH$_3$CH$_2$O− and CH$_3$CD$_2$O−) species. Therefore, (1) the observation of regeneration of acidic OH or OD groups in IR spectra during the reaction, (2) comparison of the activation energy among isotopes, and (3) GC-MS analysis of the produced ethene would lead to the actual mechanism for the decomposition of ethoxy species to evolve ethene on H-ZSM-5.

First, the decomposition of CH$_3$CD$_2$O− ethoxy species, which are produced from CH$_3$CD$_2$OH, is studied. When CH$_3$CD$_2$O− ethoxy species are decomposed via a carbenium ion intermediate, the acid sites can be recovered as both OH and OD groups, whereas only OH groups are regenerated if the concerted mechanism follows (b). Therefore, the observation of acidic OH or OD groups in IR spectra during the reaction would be effective for determining the reaction path. Figure 1a
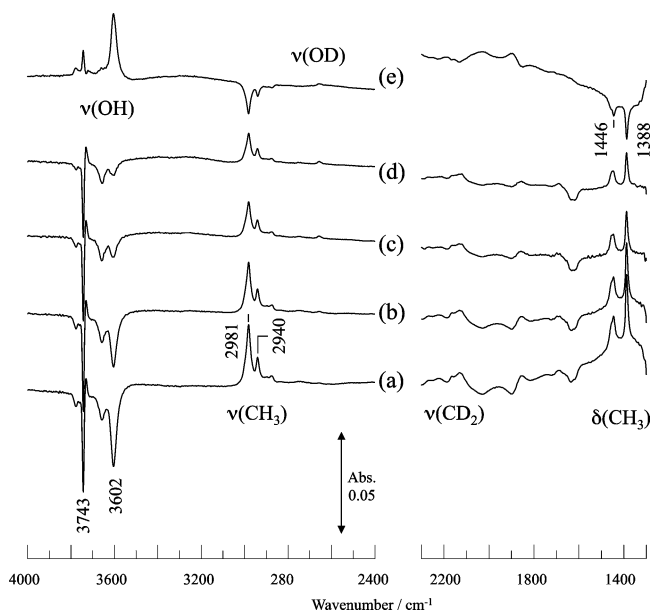

Figure 1. Time course of IR spectra of H-ZSM-5 injected CH$_3$CD$_2$OH at 473 K; after d_2-ethanol introduction for (a) 5, (b) 10, (c) 30, and (d) 60 min and (e) spectrum of (a) subtracted from (d).

shows a difference IR spectrum of H-ZSM-5 before and after CH$_3$CD$_2$OH adsorption at 473 K, followed by immediate evacuation for 5 min. Negative bands of silanol and acidic OH groups appear at 3743 and 3602 cm^{-1}, respectively, and CH$_3$ stretching (3000−2800 cm^{-1}) and bending bands (1500−1300 cm^{-1}) of CH$_3$CD$_2$O− ethoxy species are observed. Additionally, CD$_2$ stretching bands are observed at 2300−2100 cm^{-1}. The bands of CH$_3$CD$_2$O− ethoxy species and the negative band of acidic OH groups decrease in intensity with progress of evacuation time from spectrum (a) to (d) in time course (Figure 1). It should be noted that only the acidic OH groups are recovered, whereas the change of the acidic OD band (2700−2600 cm^{-1}) is negligible in the subtracted spectrum in Figure 1e. Therefore, the reaction path illustrated in Scheme 1b is more likely. The mechanism would be supported by the

decomposition of CD$_3$CH$_2$O− ethoxy species, where regeneration of only OD groups is expected. However, the rapid H/D exchange reaction of CD$_3$ and OH groups of ethanol catalyzed by acidic OH groups of H-ZSM-5[37] prior to the ethoxy formation resulted in a H/D equilibrated surface, and no information was provided.

Next, activation energies of decomposition of ethoxy species (CH$_3$CH$_2$O−, CH$_3$CD$_2$O−, and CD$_3$CD$_2$O−) were estimated.[36] Arrhenius plots using the rate constants shown in Figure 2 were fit to linear correlations, and the activation
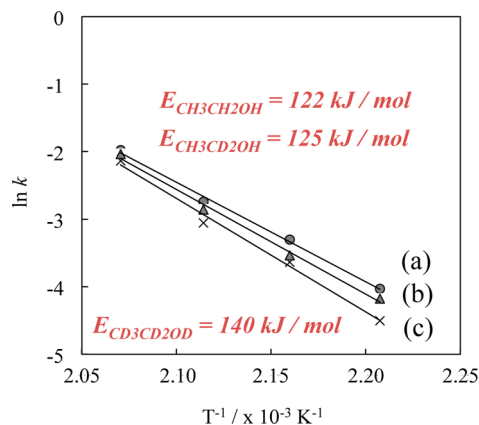
Figure 2. Arrhenius plots for the decomposition of ethoxy species: (a) CH$_3$CH$_2$O−, (b) CH$_3$CD$_2$O−, and (c) CD$_3$CD$_2$O−.

energies of ethoxy species (CH$_3$CH$_2$O−, CH$_3$CD$_2$O−, and CD$_3$CD$_2$O−) were estimated at 122 ± 3, 125 ± 3, and 140 ± 5 kJ mol^{-1}, respectively. CH$_3$CH$_2$O− and CH$_3$CD$_2$O− ethoxy species were decomposed with similar activation energies, and only CD$_3$CD$_2$O− ethoxy species required higher energy than the others. The difference can be realized in terms of the isotope effect, where the energy for the cleavage of the CD bond appears higher than that of CH. The difference of CH$_3$CH$_2$O− and CD$_3$CD$_2$O− in activation energy (18 kJmol^{-1}) resulted in the exponential term of the rate eq 1 at measured temperatures to unity.

$$\frac{k_{CH}}{k_{CD}} = \frac{A_{CH}}{A_{CD}} \exp\left(-\frac{E_{CH}^{\neq} - E_{CD}^{\neq}}{RT}\right) \qquad (1)$$

Thus, the difference in the pre-exponential factors is regarded as predominant to k_{CH}/k_{CD}, which was 1.595−1.172 at 453−483 K. The k_{CH}/k_{CD} estimated from the difference in zero-point energy difference assuming the complete cleavage of CH and CD is known to be 6.5−7.0 at 298 K and 3.31 at 473 K. The obtained k_{CH}/k_{CD} (1.37 at 473 K) is far less, supporting the concerted mechanism, where cleavages of both C−O and C−H or C−D simultaneously proceed. Thus, the contribution of the C−H or C−D bond is less than the complete cleavage mechanism, although the presence of an observable isotope effect confirms the inclusion of C−H or C−D bond cleavage in the rate-determining step. Therefore, ethene is formed from the decomposition of ethoxy species on the basis of a concerted mechanism.

The crucial evidence of the above-suggested mechanism is the analysis of the evolved ethene. The products from the decomposition of ethoxy species were analyzed by GC-MS. The spectrum of ethene produced from CH$_3$CD$_2$O− species is compared with that from CH$_3$CH$_2$O− ethoxy species

(reference as C_2H_4) in Figure 3. The cracking pattern of C_2H_4 in Figure 3B indicates signals of mass numbers at 27 and 26
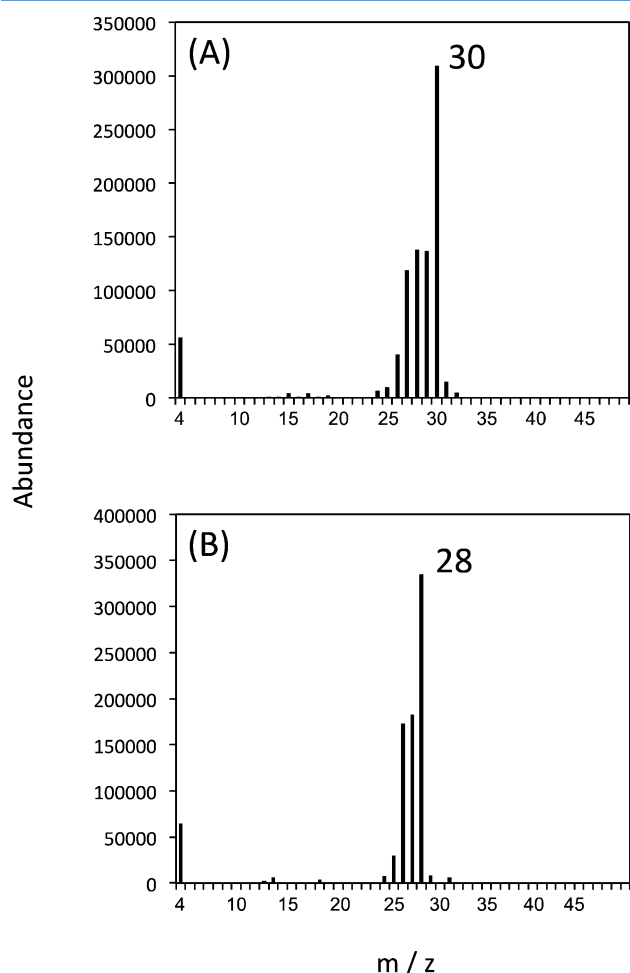
Figure 3. GC mass spectra of ethene in collected gas evolved from decomposition of (A) CH_3CD_2O- ethoxy and (B) CH_3CH_2O- ethoxy species at 523 K.

with about a half-intensity of the parent (28). Thus, species deficient in one or two H atoms are notable in addition to the parent C_2H_4. Because the parent molecule is a species with mass number 30 for the decomposition product of CH_3CD_2O- ethoxy species, desorbed ethene was identified as $C_2H_2D_2$. When $C_2H_2D_2$ loses one or two hydrogen atoms, mass numbers of the species become 29 (C_2HD_2) and 28 (C_2H_2D) or 28 (C_2D_2), 27 (C_2HD), and 26 (C_2H_2), respectively. Therefore, the broader distribution of the signals in Figure 3A in comparison with that of Figure 3B is well explained. The mass analysis of the evolved ethene formed from CH_3CD_2O- ethoxy species clarified the involvement of two D atoms.

The above results confirm that the hydrogen atom of the acidic hydroxyl groups can be only provided by the methyl group and not by methylene of CH_3CD_2O- ethoxy species. In conclusion, the mechanism of decomposition of ethoxy species was clarified using isotope-labeled ethanol to proceed through concerted mechanism, and it was shown that the reaction coordinate of the transition state is the cleaved product of one of the C−H bonds in the methyl group of the ethoxy species. A concerted mechanism in acid-catalyzed reactions using acid− base pair sites has been regarded as unique for solid acid

catalysts and is suggested to operate over various solid acid catalysts represented by zeolites. Discussions on mechanisms over zeolite catalysts are often made by theoretical calculation methods, and experimental evidence is far less sufficient. Therefore, results in the present study would be also an aid to discuss and to understand zeolite chemistry.

■ EXPERIMETAL METHODS

H-ZSM-5, JRC-Z5-90H (Si/Al = 45), was provided by the Catalysis Society of Japan. Three ethanols, CH_3CH_2OH (99.8%, Wako Pure Chemical Industries, ltd.), CH_3CD_2OH, and CD_3CD_2OD (98 and 99.5%, Sigma-Aldrich Co. LLC.), were used. The self-supporting disk of H-ZSM-5 was placed in a quartz cell, attached to a conventional closed gas circulation system. The sample was heated up to 773 K under evacuation and was maintained at its temperature for 1 h. FT-IR spectra were recorded using a Jasco 4100 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector at a resolution of 4 cm^{-1} and a typical average of 64 scans. FT-IR spectra of the pretreated disk recorded at several temperatures were used as background spectra. Background-subtracted IR spectra showing adsorbed species are presented throughout this Letter. Ethoxy species were formed by exposing H-ZSM-5 to the same amount of ethanol molecules as the number of acidic OH groups of the H-ZSM-5 used at indicated temperatures, followed by evacuation. Prior to CD_3CD_2OD adsorption for the estimation of the activation energy, acidic OH groups were exchanged to OD for precise quantification because intramolecular H/D isotope exchange mediated by acidic OH groups occurs if the CD_3 group is involved in adsorbed ethanol.[37] The rate (k) of decomposition of ethoxy species was obtained by measuring the time course of the recovery of the amount of isolated acidic OH or OD groups.[36] The products were analyzed by a GC-MS (Agilent Technologies, GC-7890Q and MS-5975C with triple-axis detector) instrument with an HP Plot column.

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Notes

The authors declare no competing financial interest.

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