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Ethene oligomerization on H-ZSM-5 in relation with ethoxy species

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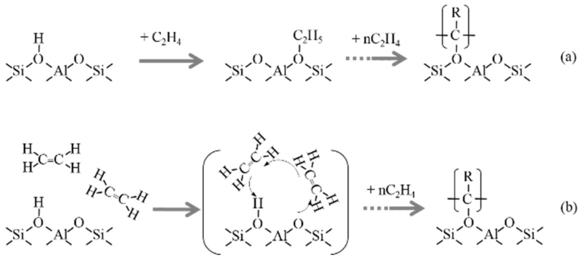
The oligomerization of ethene over H-ZSM-5 was studied by infrared (IR) spectroscopy. The possibility of ethoxy intermediate for the ethene oligomerization was investigated. Ethene oligomerization was found to proceed on the basis of a concerted mechanism with plural ethene molecules, and not by a stepwise mechanism with ethoxy intermediate.

Dimerization and oligomerization of light olefins are available routes for the production of liquid fuels,[1-5] and elementary reactions in methanol to hydrocarbons (MTH) reaction.[6,7] The interaction of light olefins with acid sites occurs with donating π-electron from olefins to form "π-complexes". As a result of protonation of olefins, alkoxy species bonding to lattice Si and Al atoms on zeolites were suggested to form as stable intermediates by early theoretical studies, [8,9] while alkyl cation intermediates were identified in homogeneous system during reactions. The stabilization of the intermediate by formation of covalent bond between protonated species and framework atoms compensates for the absence of solvation effect on gas-solid interface. While the π-complexes are experimentally observed, no monomeric alkoxy species formed from further protonation from OH groups to light olefins have not been identified either by infrared (IR) spectroscopy nor Nuclear Magnetic Resonance (NMR). On the other hand, the mechanism and the structure of intermediate for ethene protonation on acidic OH groups of zeolites have been discussed by theoretical approaches. Svelle et al. theoretically explored the ethene dimerization through two different mechanisms using a 4T cluster; stepwise and concerted mechanisms (Scheme 1).[10] In the stepwise mechanism, surface ethoxy group is first formed through the protonation of an adsorbed ethene on an acidic OH group, and then C-C bond is formed between the ethoxy specie and another ethene molecule. On the other hand, in a concerted mechanism, an adsorbed ethene on an acidic OH group is activated and reacted simultaneously with another adjacent ethene. On the basis of the calculated activated barriers, the concerted reaction was concluded to be favourable in the ethene dimerization.[10] Namuangruk et al. also investigated ethene dimerization by using a 84T FAU zeolite model.[11] In this case, the activation energy of the rate-determination step, which is the formation of ethoxy species from ethene, in the stepwise mechanism was lower than that of the concerted mechanism. Recently, Chu et al. studied the influence of Brønsted acid strength and pore confinement on the ethene dimerization, and concluded that the concerted mechanism was preferred on weak acid sites, but that two mechanisms became competitive with strong acid sites.[12] In this manner, the mechanism of ethene dimerization have been controvertibly discussed by theoretical methods with much less information from experimental results.[13-15]



Scheme 1 Ethene oligomerization on the basis of (a) the stepwise and (b) the concerted mechanisms.

The formation of ethoxy species from ethene has not been observed so far due to the rapid oligomerization of ethene, while ethoxy species were observed from the dehydration of ethanol over acidic OH groups by using IR spectroscopy and NMR.[16-18] Accordingly, a simple question arises: whether ethoxy species act as intermediates in the ethene dimerization and oligomerization. In order to clarify this point, ethene adsorption and reactions including other olefins was studied in detail.

First, the oligomerization of ethene was observed at 303 K by IR spectroscopy for contirmation.[13-15] Time course of spectra measured after introduction of ethene to H-ZSM-5 zeolite at 303 K are arrayed in Fig.1. There spectra were measured after the exposure to ethene with the same moles equivalent to the number of acidic OH groups. Since a background spectrum measured before ethene supply is subtracted, a negative band due to the isolated acidic OH groups, appeared (3612 cm^{-1}) is converted to hydrogen-bonded ones (3207 cm^{-1}). IR spectra of adsorbed ethene on acidic OH groups are observed at 3100 and 2900 cm^{-1} (stretching of CH groups), 1612 cm^{-1} (stretching of C=C bond) and 1442 cm^{-1} (bending of CH group).[13] It should be noted that the C=C stretching of ethene is IR inactive but observable due to the direct involvement to adsorption. A band at 2989 cm^{-1} is attributed to CH stretching band of gaseous ethene (spectra (a) and (b)). Both the shift to the OH stretching band and the C=C stretching band (Raman band of gaseous ethene at 1623 cm^{-1}) suggests the interaction of the π-electron of ethene with acidic OH groups. The formation of saturated methyl and methylene groups was confirmed by the appearance and increase of bands associated to ν(CH_3) at 2959 cm^{-1} and ν(CH_2) at 2936 and 2862 cm^{-1} with the progress of time. Two δ(CH) bands in saturated hydrocarbons were also observed at 1469 and 1382 cm^{-1}. These results suggest that the protonation and oligomerization from ethene molecular occurs at 303 K. The negative band of acidic OH groups almost disappeared after evacuation of gaseous ethene (Fig. 1(e)) because of the removal of mono-molecular ethene adsorption. However, it did not completely recovered due to the consumption of some sites by the formation of oligomers, which is probably surface alkoxy species (the remained species observed in Fig. 1 (e)). Therefore, the rapid oligomerization of ethene was confirmed at 303 K.

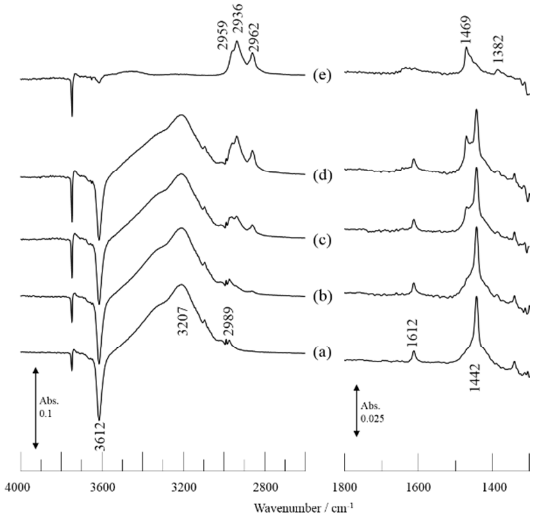


Fig. 1 Time course of IR spectra of H-ZSM-5 interacted with ethene at 303 K; after ethene introduction for (a) 1 min, (b) 10 min, (c) 30 min and (d) 60 min, and (e) after evacuation of gaseous phase.

Next, the role of ethoxy species for the ethene oligomerization was studied. This confirms the presence or absence of the stepwise mechanism. Ethene was injected at 303 K after ethoxy species were produced from ethanol at 473 K.[16,17] Fig. 2(a) shows the spectrum of ethoxy species formed on H-ZSM-5. Decrease of isolated silanol and acidic OH groups is shown by negative peaks at 3747 and 3612 cm^{-1}, respectively, and CH stretching bands of ethoxy species were observed at 3000-2850 cm^{-1}. Bands at 1447 and 1395 cm^{-1} is attributed to CH bending bands of ethoxy species.[16,17] The coverage of ethoxy species in Fig. 2(a) is 30 % of the number of the acidic OH groups on H-ZSM-5. Ethene with 0.7 moles equivalent to the number of acidic OH groups, corresponding to the number of vacant acidic OH groups, was supplied to ethoxy species at 303 K. In Figs. 2(b) and 2(c), isolated acidic OH groups is converted to hydrogen-bonded OH groups with ethene after the injection of ethene in the same manner as that in Fig. 1. No evident spectral changes were formed by comparing spectra (b) and (d) in Fig. 2 during the time course for 60 min after ethene supply. Therefore, a subtracted spectrum was calculated to clearly observe the difference. In spite of conditions for oligomer formation on the bare H-ZSM-5 (Figure 1), the amount of ethoxy species was not changed, which was found by the absence of any negative bands of ethoxy species in Fig. 2(e). Therefore, ethoxy species are regarded as spectators: ethoxy species do not act as intermediates for ethene oligomerization at 303 K (Scheme 2(b)). In other words, ethene oligomerization at 303 K proceed not via stepwise mechanism but probably via concerted mechanism. Additionally, the formation of ethoxy species with a spectrum in Figure 2(a) from ethene was not observed either in Figs. 1 and 2 (Scheme 2(a)). This experimental conclusion supports the mechanism proposed by Svelle et al.[10] Furthermore, the stepwise mechanism is expected on the basis of suggestions reported by Chu et al.[12], since H-ZSM-5 is analogous to strongly acidic zeolites. However, it was not the case in the present study. The effects of acid strength and the pore confinement for the selection of the reaction routes for ethene reactions are to be further studied using various zeolites with different topologies and acid strength and density.

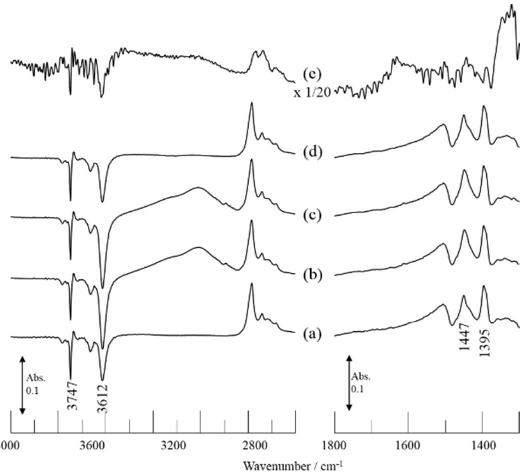
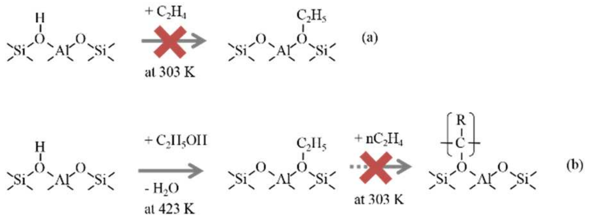


Fig. 2 Time course of IR spectra of ethoxy species on H-ZSM-5 interacted with ethene at 303 K; (a) before ethene introduction, after ethene introduction for (b) 1 min and (c) 60 min, and (d) after evacuation; (e) subtracted spectrum of (a) from (d).

In the same manner, the formation of C_3 and C_4 alkoxy species from propene and butenes have not been observed also due to the formation of oligomers from propene[19] and dimers from butenes.[20] On the other hand, C_5 and C_6 olefins, which cannot be dimerize in the restricted pore space of H-ZSM-5, produced monomeric C_5 and C_6 alkoxy species at 223 K.[21]

In summary, ethene oligomerization on H-ZSM-5 at 303 K proceeds via a concerted mechanism. Ethoxy species were formed by ethanol adsorption and dehydration on acidic OH groups, but were not formed from ethene adsorption (Scheme 2 (a)). Additionally, ethoxy species did not react with ethene at 303 K (Scheme 2(b)).

While the concerted mechanism was supported in the present study at 303 K, the stepwise mechanism in the ethene oligomerization cannot be ruled out. Ethoxy species would be able to react with ethene at high temperatures because methoxy species, which is probably lower reactivity than ethoxy species, react with ethene at above 473 K.[22] However, ethene oligomerization cannot be observed experimentally at high temperatures because ethoxy species are decompose at 453 K, and because the formation and decomposition oligomers become equilibrium at high temperature range under the present experimental conditions.[16,17] On the other hand, some hydrocarbons species were observed by ethene flow condition on H-ZSM-5 at 573 K,[23] where concentration of ethene was extremely higher than that in present study. Nevertheless, the formation of such hydrocarbon species cannot be directly attributed to the stepwise mechanism of ethene oligomerization because the contribution of reactions of other hydrocarbons than ethene, which were formed by decomposition of oligomers, cannot be negligible. Therefore, the presence of the stepwise mechanism is not confirmed experimentally.



Scheme 2 Stepwise mechanism: (a) ethoxy species did not formed from ethene at 303 K, and (b) ethoxy species, which formed form ethanol, did not react with ethene at 303 K.

Conclusions

Ethene oligomerization over H-ZSM-5 at 303 K proceed not via stepwise mechanism with ethoxy intermediate, but on basis of a concerted mechanism, where plural ethene molecules are simultaneously activated.

Experimental section

H-ZSM-5, JRC-Z5-90H (Si/Al = 45), was provided by Catalysis Society of Japan. Ethene (99.9%, Takachiho Chemical Industries, Inc.) and ethanol (99.8%, Wako Pure Chemical Industries, Ltd.) were used. The self-supporting disk of H-ZSM-5 was place 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 its temperature for one hour. 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 paper.

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