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Methanol Activation

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Evidence for a “Carbene-like” Intermediate during the Reaction of Methoxy Species with Light Alkenes on H-ZSM-5

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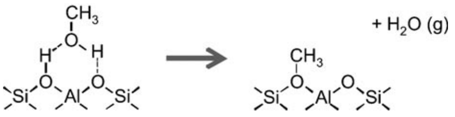
There have been various discussions of the mechanism of methanol to olefin (MTO) and methanol to hydrocarbon (MTHC) reactions specifically dealing with certain zeolite topologies of CHA,[1] MFI,[2–4] BEA,[3] TON,[5] and others, as well as general summaries.[6] One example of particular interest is the structure of hydrocarbons formed in zeolite channels, the so-called “hydrocarbon pool” (HCP).[3,4,7,8] Since the selectivity of products formed from cracking of HCP is directly affected by the porous structure of zeolites, the clarification of the structures of HCP in various zeolites is crucially important. In contrast, less research and discussion has been carried out on the initial C–C bond formation from the starting C_1 compound, methanol.[1,5,8,9] Since the initial processes of MTO and MTCH would not be affected by the porous structure because of the small sizes of the products, reaction mechanisms on a single acidic OH group of zeolites should become significant rather than zeolite topologies.

MTO and MTHC reactions start with the activation of methanol. The formation of methoxy species on zeolite upon exposure to methanol was first observed by infrared (IR) spectroscopy by Ono and Mori.[10] Later, it was reported that IR spectra of methoxy species formed on bridging sites of Si and Al and on external Si sites, compensating for the acidic OH groups and the external silanol groups, respectively, appear differently.[11] Similarly, the formation of ethoxy species from ethanol adsorption on zeolites was confirmed by IR[12] and NMR[13] spectroscopy. Thus, surface alkoxy species are regarded as the first activated species on zeolites formed from dehydration of alcohols. However, reports on the mechanism of the first C–C bond formation from methoxy species and their reactivity are still limited. Mainly two types of intermediates in mechanisms have been proposed on the first C–C bond formation from methoxy species:[6,14] 1) carbenium cations and 2) carbene-like intermediates. Although recent researches focus more on the HCP species[15–17] rather than the reactions of light hydrocarbons, there is a general agreement on the reaction of methoxy species that the C–C bond formation from methoxy groups to ethene does not occur,[2,5,9] even though ethene is formed apparently as primary product. Under such circumstances, the research group of Hunger has recently been energetically studying the reactivity of methoxy species using solid state NMR spectroscopy and has claimed that methoxy groups are active species in the MTO and MTHC reactions.[18] They have recently reported that methoxy groups work as methylation agents of cyclohexane via “carbene-like species”.[14] Recent developments in experimental techniques allow us to examine various proposals on mechanisms on MTO and MTHC; we closely investigated the reactivity of methoxy species on H-ZSM-5 as well as other zeolites by IR spectroscopy using isotopes.

Methanol molecules adsorb on the acidic OH groups of zeolites by strong hydrogen-bonding interactions as depicted in Scheme 1, and subsequently dehydrate to form methoxy groups and water at temperatures above 473 K. The formed methoxy groups remain stable after water desorption, whereas immediate formation and desorption of ethene and water occur in the case of ethanol adsorption.[12] The formed methoxy species are thermally stable under evacuation even at 673 K, and the maximum coverage is about 40 % of the number of the acidic OH groups on H-ZSM-5. The IR spectrum of methoxy groups on H-ZSM-5 at 523 K is shown in Figure 1 a, whereby a background spectrum measured before methoxy formation is subtracted from that with methoxy groups. Negative peaks in the OH stretching region are attributed to silanol (3740 cm^{-1}) and acidic OH (3600 cm^{-1}) groups, which decreased as a result of methoxy formation. Two types of methoxy groups on silanol and the acidic OH groups show CH stretching bands at slightly different frequencies: at 2980 and 2868 cm^{-1} for methoxy species on the sites of the acidic OH groups, and at lower frequency sides (2955 and 2855 cm^{-1})[11] for those on silanol sites, respectively. The band at 1457 cm^{-1} is assigned to methyl deformation band of both types of methoxy groups. The distorted baseline between 2000 and 1800 cm^{-1} is due to a false feature of combination and overtone bands of zeolite lattice vibrations.[19] Time-course spectra after the introduction of ethene to methoxy groups at the same temperature are arrayed in Figure 1 b–e, and Figure 1 f is a subtracted spec-



Scheme 1. Formation of methoxy groups from methanol adsorbed on the acidic OH groups on zeolites.

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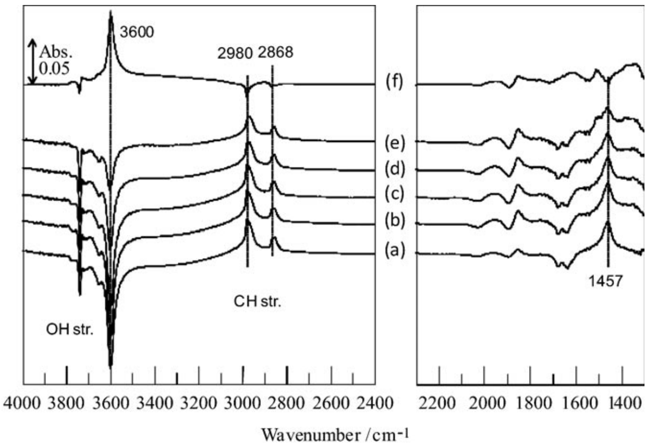


Figure 1. Time course of IR spectra of surface species during the reaction of methoxy species with ethene at 523 K on H-ZSM-5: a) before ethene introduction and after b) 5 min, c) 10 min, d) 30 min, and e) 60 min; f) subtracted spectrum of (a) from (e).

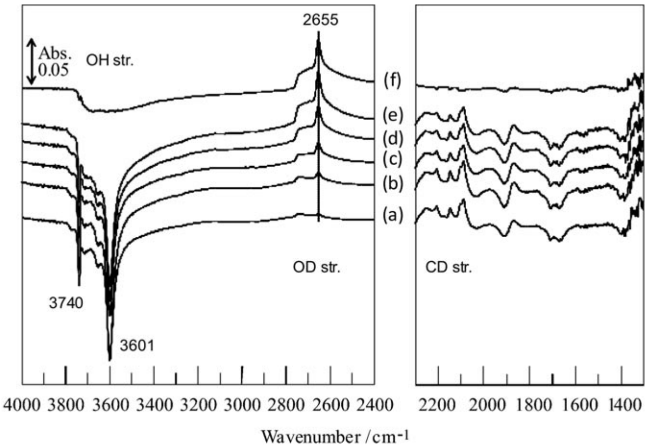


Figure 2. Time course of IR spectra of surface species during the reaction of methoxy (OCD_3) species with ethene at 523 K on H-ZSM-5: a) before ethene introduction and after b) 5 min, c) 10 min, d) 15 min, and e) 20 min; f) subtracted spectrum of (a) from (e).

trum of (a) from (e). The decrease in three bands of methoxy groups (dotted lines) and the recovery of the band of the acidic OH groups are clearly observed in Figure 1 f, indicating that methoxy groups on the sites of the acidic OH groups are consumed by the reaction with ethene.

The products of the reaction in Figure 1 are listed in Table 1. The bottom row indicates that there was no reaction of ethene alone on H-ZSM-5 in the absence of methoxy groups after 60 min. Thus, neither methoxy species nor ethene molecules react individually at 523 K. In contrast, methoxy species react with ethene first to propene, and carbon chain elongation seems to proceed in the time course: propene molecules react with methoxy species to form C_4 products, which further react with methoxy species to produce C_5 compounds. When propene is treated with methoxy groups under the same reaction conditions,[20] gradual carbon chain growth occurs in the time course of reaction products such as ethene, and similar IR spectra to those in Figure 1 are observed. Thus, methoxy groups are regarded as methylation reagents of light alkenes as well as cyclohexane and toluene.[21]

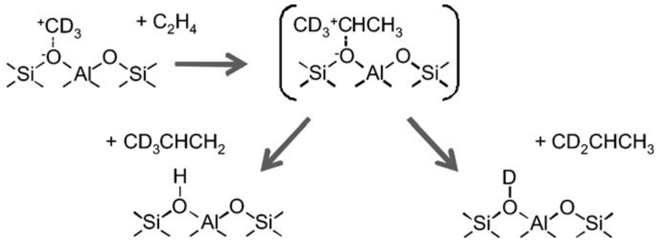
Table 1: Reaction of ethene with methoxy species on H-ZSM-5 at 523 K.[a]

Reaction time [min]	Conversion [%][b]	Yield [mol %] $C_3^=$	C_4	C_5	C_6
5	0.8	0.8	0	0	0
10	2.3	1.9	0.4	0	0
30	12.3	8.2	3.4	0.5	0.3
60	16.3	8.3	6.6	1.0	0.3
60[c]	0	–	–	–	–

[a] Reaction conditions: catalyst: 60 mg; ethene: ca. 15 Pa; $T = 523$ K. [b] Conversion of ethene. [c] No methoxy species present.

To gain insight into the reaction mechanism, deuterated methoxy groups were produced from [D$_3$]methanol (CD_3OH) and allowed to react with light olefins. Figure 2 a shows the spectrum of deuterated methoxy groups formed on H-ZSM-5. As in the case of Scheme 1, a decrease in silanol and the acidic OH groups is shown by negative peaks at 3740 and 3601 cm^{-1}, respectively, and CD stretching bands are observed between 2300 and 2000 cm^{-1}. The methyl deformation band is absent in Figure 2 a because of the isotope shift below the low-frequency limit of the IR spectra.[22] Upon the introduction of ethene under the same conditions as those in Figure 1, the CD stretching bands decrease in intensity and acidic OD band at 2655 cm^{-1} appear and increase in intensity. It should be noted that only the acidic OD groups recover, whereas the acidic OH band at 3600 cm^{-1} is negligible in the subtracted spectrum in Figure 2 f. This result indicates that the hydrogen atom of the acidic hydroxy groups can be only provided by methoxy groups and not from ethene molecules. In other words, C−C bond formation between [D$_3$]methoxy groups and ethene molecules does not proceed with the CD_3 unit. Only two deuterium atoms are included in the product as a CD_2 group, leaving one deuterium atom as an acidic OD group.

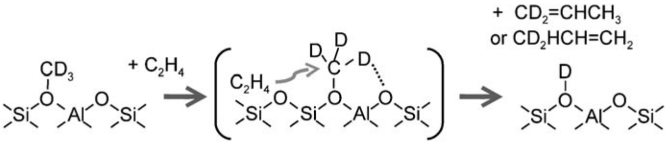
The alkoxy groups formed on zeolite surfaces were proposed to react as carbenium cations in transition states in early theoretical studies.[23] In addition, methoxy groups were supposed to migrate in the form of methyl cations in a similar manner to the motion of protons of acidic OH groups.[10,24] This methyl cation formation reaction from methoxy groups is supported by DFT calculations.[25,26] Assuming the carbenium cation mechanism for the reaction observed in this study, in which [D$_3$]methoxy species react with ethene as CD_3^+ groups, the 2-propyl cation ($CD_3CH^+CH_3$) would be present as an intermediate (Scheme 2). Otherwise, such a cationic form may be the transition state and the 2-propoxy group would be the stable form. For the conversion of 2-propyl cation to propene and Brønsted acid site, two possible pathways exist: one results in the formation of $CD_3CH{=}CH_2$ and an OH group, and the other $CD_2{=}CHCH_3$ and OD. Even considering the isotope effect between hydrogen and deuterium, the absence of the recovery of the acidic OH groups cannot be explained by the



Scheme 2. Mechanism of the reaction of a methoxy group with ethene to propene via an isopropoxy group (or isopropyl cation).

carbenium cation mechanism. Another possible route is proposed by a recent theoretical calculations, suggesting the stabilization of 1-propyl cation ($^+CH_2CH_2CH_3$) from the reaction of methoxy groups and ethene.[26] Following this scheme, $^+CH_2CH_2CD_3$ cation is expected to form from [D_3]methoxy group and ethene, which results in releasing hydrogen for Brønsted acid site and evolving [D_3]propene ($CH_2{=}CHCD_3$). Thus, the methyl carbenium cation mechanism is not applicable in any case.

From the NMR observation of the production of [^{13}C]methylcyclohexane from [^{13}C]methoxy groups and cyclohexane, a carbene-like intermediate for the reaction of methoxy groups is proposed through C–H bond activation of the methoxy group with lattice oxygen (Scheme 3).[14] DFT-based calculations excluded carbene-like species from the possible intermediate for the reaction of methoxy groups.[9] However, in the case of present study, a carbene-like intermediate is the most likely from the fact that deuterium originally present in the [D_3]methoxy group is the source of the recovered Brønsted acid site (Scheme 3). This reaction probably proceeds in a concerted manner as proposed by Hunger et al., whereby a lattice oxygen atom would attract one of the deuterium atoms in the [D_3]methoxy group. Concurrently, adsorbed ethene in equilibrium with gaseous molecules reacts with the activated [D_3]methoxy group. If the C=C double bond is directly formed between methoxy groups and ethene molecules, $CD_2{=}CHCH_3$ would be produced. The other possibility is the generation of $CD_2HCH{=}CH_2$ if hydrogen transfer occurs from ethene molecules to methoxy groups.



Scheme 3. Proposed mechanism of the reaction of methoxy group with ethene to propene via carbene-like species.

For further understanding of the reaction, [^{13}C]methanol was employed to generate [^{13}C]methoxy groups, to which ethene was supplied under the same conditions to analyze the product by gas chromatography (GC) mass spectroscopy.[27] The cracking pattern of ethene in the collected sample was exactly the same as that of the pure ethene reference (Figure S1 in the Supporting Information), whereas it was not the case for propene: peaks in the cracking pattern of propene in the product appeared in similar intensity ratios as those of pure propene but increased in mass number by one (Figure S2; $m/e = 36$–45). This result clarifies the involvement of one ^{13}C atom in propene formed by the reaction between a [^{13}C]methoxy group and ethene. Similarly, the cracking pattern of the C_2 component in the mass spectrum of produced propene increased in mass number from the pattern of reference propene (Figure S2; $m/e = 26$–29). The result implies that ^{13}C is in an sp^2 environment as a result of cleavage of propene to $^{13}CH_2{=}CH$ ($m/e = 28$) and C_1 components, assuming that a C–C single bond is split more easily than a C=C double bond. Thus, production of $CD_2{=}CH{-}CH_3$ from [D_3]methoxy groups and ethene seems more likely than that of $CD_2H{-}CH{=}CH_2$ in Scheme 3. ^{13}C NMR analyses of propene produced by the reaction of [^{13}C]methoxy groups and ethene were attempted by accumulating products from the reaction more than 10 times, but reliable results were not obtained because of the lack of satisfactory intensity of the signals.

The possibility of a reaction pathway of the methoxy groups in methyl unit was considered. It was reported that methoxy species react as methyl cations with strongly basic molecules to form $(CH_3)_nNH_{(4-n)}{}^+$ ($n = 1$–4) from ammonia and $C_5H_5N{-}CH_3{}^+$ from pyridine.[28] We also confirmed that IR spectra measured after the reaction of methoxy groups and ammonia and those of methylamine adsorbed were identical. Thus, the methoxy groups react with strong bases in the methyl unit, whereas they react via carbene-like species with light alkenes.

As the results above were all obtained using H-ZSM-5 (Si/Al = 45), other zeolites as well as H-ZSM-5 samples with different aluminum contents were compared for the reaction of [D_3]methoxy groups and ethene. First, H-ZSM-5 samples (Si/Al = 25 and 150) showed the same IR results with good signal to noise (S/N) ratio and similar selectivity as those over the sample with silicon to aluminum ratio of 45, whereas the yield of propene was dependent on the aluminum content. For H-ZSM-5 with much higher silicon to aluminum ratios (Si/Al = 270 and 350), conversion of ethene was too low to obtain good S/N ratios of the IR spectra, although the absence and presence of the recovery of OH and OD groups were confirmed, respectively. Similar results were obtained over mordenite (MOR, Si/Al = 45) and SSZ-13 (CHA, Si/Al = 45) over the same temperature range, but at a slightly higher temperatures over HY (FAU, Si/Al = 5.5). Thus, the reaction mechanism shown in Scheme 3 is experimentally evidenced on various zeolites. Further experiments using methanol isotopes and DFT calculations are underway.

Experimental Section

The hydrogen form of ZSM-5 (JRC-Z5-90H, Catalysis Society of Japan, Si/Al = 45) was pressed into a self-supporting disk (20 mm diameter, 60 mg) and placed in an IR cell attached to a conventional closed-gas circulation system. The sample was pretreated by evacuation at 773 K with a liquid nitrogen trap for 1 h. IR spectra were obtained at a resolution of 4 cm^{-1} using a Jasco 4100 FTIR 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 Communication. The gaseous components were analyzed by a GC (GC-14B, Shimadzu Corporation) and a CG–MS (Agilent Technologies, GC-7890Q and MS-5975C with Triple-Axis Detector) instrument with a HP plot column. Ethene (Takachiho Chemical Industrial Co. Ltd., 99.9%) and three methanol samples were used: CH_3OH (Wako Pure Chemical Industries, Inc., 99.8%), CD_3OH (Merck & Co., Inc., 99% isotopic purity), and $^{13}CH_3OH$ (Cambridge Isotope Laboratories, Inc., 99% isotopic purity). The amount of methoxy groups was adjusted to be 40% (8.9×10^{-6} mol on 60 mg sample disk) of the acidic OH groups (2.2×10^{-5} mol on 60 mg sample disk), and ethene (2.2×10^{-6} mol), corresponding to a quarter of methoxy groups and one tenth of the acidic OH groups, was supplied from the gas phase.

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