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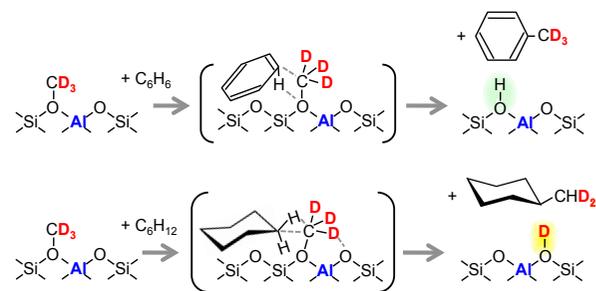
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Different mechanisms operate for reactions of methoxy species to form C-C bonds with various hydrocarbons: in methyl cation-like and carbene-like mechanisms, most probably both in concerted manner.





Journal Name

ARTICLE

Mechanisms of reactions of methoxy species with benzene and cyclohexane over H-ZSM-5 zeolites

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The first-step reaction mechanisms of d_3 -methoxy (OCD_3) species on H-ZSM-5 zeolite with benzene and cyclohexane were directly observed by infrared (IR) spectroscopy. Only toluene was produced in gas phase at the beginning simultaneously with the consumption of methoxy species on the surface at 473 K. Acidic OH groups were formed in the place of d_3 -methoxy groups for the reaction with benzene, while OD groups were recovered for the reaction with cyclohexane similarly to the case of light olefins. Thus, the presence of different methylation mechanisms of methoxy species is confirmed: CD_3 unit reacted with benzene as is the cases of amines and dimethylether, but CD_2 unit with cyclohexane and light olefins to leave one of the deuterium atoms on the zeolite. Difference of these mechanisms in activation energy is also estimated and used for the further discussion on the mechanisms.

Introduction

A variety of zeolites, a representative family of solid acid catalysts, is explored for the application to the methanol-to-olefin MTO reaction in order to selectively obtain propene, which is a vital starting material for petrochemical products.¹⁻⁵ The “hydrocarbon pool mechanism” has been well recognized as a general mechanism operating during the steady state of the MTO reaction.^{6, 7} The detailed structures of hydrocarbon species as well as the role of them for the evolution of light olefins are still under discussions, because they are strongly dependent of the pore structure of zeolites.⁸ On the other hand, less is clarified with respect to the initial elemental steps of the MTO reaction, which is of importance in order to understand similarities and differences of Brønsted acidic OH groups on solid surfaces and protons in homogeneous media. Methoxy species, which are formed by dehydration of methanol and acidic OH groups on zeolites, are accepted as the initial activated species in MTO reaction.⁹⁻¹¹ Methoxy species were found to function as methylation agent with other hydrocarbon compounds such as benzene,^{9, 10, 12, 13} cyclohexane,^{10, 11, 13} ethene^{10, 11, 15} and so on. The creation of C-C bonds between methoxy species and reacted hydrocarbons was confirmed by analysis of products and surface species using ¹³C-labeled methanol by nuclear magnetic resonance (NMR) or d_3 -methanol (CD_3OH) by infrared (IR) spectroscopy.

On the mechanism of the C-C bond formation from methoxy species, two types of intermediates have been proposed;^{5, 11} 1) carbenium cation (CH_3 unit) and 2) carbene-like (CH_2 unit) intermediates. While density functional theory (DFT)-based calculations excluded carbene-like species from

the possible intermediate for the reaction of methoxy groups,¹⁶ experimental evidences on the intermediate are still limited. The carbenium cation intermediate was verified at the early stage of the research on MTO by the decrease of the d_3 -methoxy species, which was observed by IR spectroscopy, during the reaction with benzene and by the production of d_3 -toluene in gas phase.⁹ On the other hand, carbene-like intermediate was recently found by IR observation of reactions of d_3 -methoxy species with light olefins, where consumption of d_3 -methoxy species and the concurrent recovery of OD groups occurred.¹⁷ Meanwhile, carbenium cation (CD_3 unit) intermediate was proposed for the reaction of d_3 -methoxy species with dimethylether (DME) to produce propene directly.¹⁸ In this way, the activated structure and the detailed reaction mechanisms of methoxy species with hydrocarbons have not been systematically considered. Therefore, by studying methylation reaction of benzene and cyclohexane by methoxy species, we aimed at interpreting the detailed nature of methoxy species and the unique role of Brønsted acidic sites on zeolites.

Experimental

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 for 1 h. Benzene (Wako Pure Chemical Industries, Inc., 99.5 %), d_6 -benzene (Merck & Co. Inc., 99.95 %), clohexane (Tokyo Chemical Industries, Co. Ltd., 99.5 %), cyclohexene (Tokyo Chemical Industries, Co. Ltd., 98.0 %), ethene (TAKACHIHO CHEMICAL INDUSTRIAL Co. Ltd., 99.9 %), dimethyl ether (Kanto Chemical Industries, Inc., 99.8 %) were used without further

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purification. For methanol three isotope samples were used; CH₃OH (Wako Pure Chemical Industries, Inc., 99.8 %), CD₃OH (Merck & Co., Inc., 99 % isotopic purity) and ¹³CH₃OH (Cambridge Isotope Laboratories, Inc., 99 % isotopic purity).

The amount of methoxy groups was adjusted to 40 % (8.8×10^{-6} mol on 60 mg sample disk) of the acidic OH groups (2.2×10^{-5} mol on 60 mg sample disk). Thus, 60 % of the acidic OH groups were coexisting with methoxy species. Then, a quarter amount of hydrocarbon to the amount of methoxy species was supplied from the gas phase. Therefore, the molar ratio of acidic OH groups, methoxy species and the reactant was set to 6 : 4 : 1, in order to extract the information on the initial reaction. IR spectra were observed at certain times, followed by the immediate collection of the gaseous molecules for analysis. IR spectra were obtained at a resolution of 4 cm⁻¹ using a Jasco 4100 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. The gaseous components were analyzed by a GC (GC-14B, SHIMADZU Corporation) and a GC-mass (Agilent Technologies, GC-7890Q and MS-5975C with Triple-Axis Detector) spectrometer with a HP plot column.

Results and discussion

Before observing the change of surface species during the reaction, the catalytic performance of the reaction of methoxy species with benzene over H-ZSM-5 at 473 K are compared with those with ethane and propene in Table 1. Note that 40 % of the total Brønsted acidic sites were exchanged to methoxy species, and that only a quarter molar amount of reactant with respect to methoxy species was introduced. Thus, introduced hydrocarbon molecules were free to be adsorbed on the isolated acidic OH groups and reacted with methoxy species several times in the time course.

The reaction of ethene was slow at 473 K and simple at the initial time to form only propene, followed by further methylation by methoxy species to produce C₄ compound, because the amount of methoxy species was 4 times of that of supplied reactant. Propene reacted much more extensively than

Table 1 Reaction of methoxy species with benzene, ethene and propene over H-ZSM-5 at 473 K

Reactant	Time / min	Conversion ^a / %	Yield / %	
			+ C1 compound ^b	+ C2 compound ^c
Benzene	30	14	12	2
	60	42	23	19
Ethene	30	0.5	0.5	0
	60	2.6	1.8	0.8
Propene	5	28	22	4.7
	10	39	29	6.2

^a Conversion of reactant

^b Toluene, propene and C₄ hydrocarbons for benzene, ethene and propene, respectively

^c Xylene, C₄ and C₅ hydrocarbons for benzene, ethene and propene, respectively

ethene under the same conditions due to the accelerated rate of the reaction by increasing the carbon number of light olefins as previously reported.¹⁷ Thus, results at short reaction times are compared. Nevertheless, C₅ (+ C₂) compound was already observed at 5 min in addition to C₄ (+ C₁) compound. The reactivity of benzene with methoxy species was an order of magnitude higher than that of ethene. Toluene was produced at the initial stage with a small amount of xylene, and methylation proceeded further at 60 min. These results agree well with previous reports.⁹⁻¹³ Next, changes of surface species were directly observed by IR spectroscopy under the same reaction conditions as those in Table 1.

Time courses of IR spectra measured during reaction of methoxy species on H-ZSM-5 with benzene at 473 K are shown in Figure 1. A background spectrum measured after pretreatment of H-ZSM-5 was subtracted from the spectrum of methoxy-formed sample (spectrum (a)) and those measured after the supply of benzene (spectra (b)-(f)). Thus, a negative band of acidic OH groups at around 3610 cm⁻¹ is attributed to consumed OH groups by the formation of methoxy species upon dehydration. Bands attributed to methoxy species were observed at 2950-2800 cm⁻¹ in spectrum (a) (CH₃ stretching bands of methyl group). Time course of spectra were measured until 30 min after the reaction started (spectra (b)-(f)). Since adsorptions of benzene superimposed the spectral change at 1 min, subtracted spectrum of (b) from (f) is arrayed on top in order to find the differences of the surface species between 30 and 1 min after the reaction. The adsorption of a part of benzene is found by weak CH stretching bands above 3000 cm⁻¹ (dotted curve in Figure 1). In difference spectrum (f)-(b) the increase of acidic OH groups and the decrease of methoxy species in amount are confirmed by an upward OH band at 3610 cm⁻¹ and downward CH₃ stretching bands of methoxy species, respectively. Therefore, acidic OH groups were recovered on the site of methoxy species after the reaction with benzene. Above observation is in consistent with the results of reactions

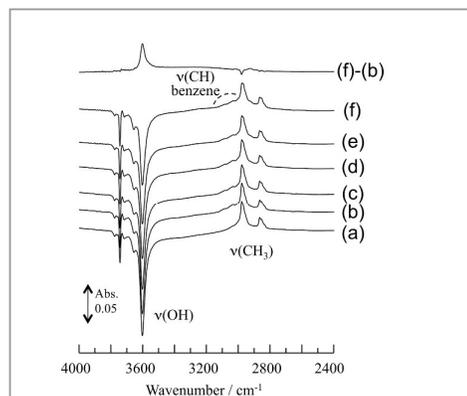


Fig. 1 Time course of IR spectra measured during reactions of methoxy species with benzene. Spectrum (a) was measured before introduction of cyclohexane or benzene, and (b) 1 min, (c) 5 min, (d) 10 min, (e) 20 min and (f) 30 min after starting the reaction. Top spectra were obtained by subtraction of (b) from (f)

shown in Table 1.

For the understanding of the detailed reaction mechanism, d_3 -methoxy (OCD_3) species were employed for the same reactions (Figure 2). Spectra in Figure 2 are background-subtracted as described in Figure 1. The presence of d_3 -methoxy species is recognized by their CD_3 stretching bands appearing at $2300\text{--}2000\text{ cm}^{-1}$. A small amount of adsorbed benzene was found in spectra (b)–(f) by the CC stretching band at around 1500 cm^{-1} in addition to CH stretching bands observed clearer than those in Figure 1 due to the absence of CH_3 stretching bands of methoxy species in Figure 2. In the subtracted spectrum of (b) from (f) consumption of methoxy species and adsorbed benzene are confirmed by the decrease of stretching bands of CD_3 ($2300\text{--}2000\text{ cm}^{-1}$) and CC (around 1500 cm^{-1}) to produce toluene and so on (Table 1). The regeneration of the OH band assigned to the acidic OH groups of H-ZSM-5 was also clearly observed in the spectrum of (f)–(b). While residual OD groups were observed in spectra (a)–(f) in Figure 2, no OD groups were formed during the reaction of d_3 -methoxy groups with benzene as found in the top spectrum in Figure 2. Thus, methoxy species reacted as CD_3 units to form C–C bonds with benzene molecules, which left H atoms from one of their CH bonds. This result supports the reported mechanism, which was evidenced by the observation of CD_3 -toluene formed from benzene (C_6H_6) and d_3 -methanol

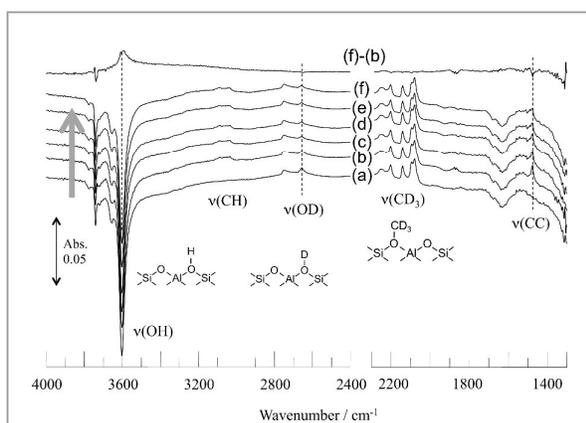


Fig. 2 Time course of IR spectra measured during the reaction of d_3 -methoxy species with benzene at 473 K. Spectrum (a) was measured before introduction of benzene, and (b) 1 min, (c) 5 min, (d) 10 min, (e) 20 min and (f) 30 min after starting the reaction. Top spectra were obtained by subtraction of (b) from (f).

(CD_3OH) over H-ZSM-5.⁹

The reaction mechanism of methoxy species with benzene, which was confirmed by observation of surface species, is different from that with light olefins. In the case of the reaction of d_3 -methoxy species with ethene, acidic hydroxy groups were recovered as OD, indicating that methoxy species reacted with ethene as CD_2 unit. IR spectra observed during this reaction under the same conditions as those in Table 1 and Figures 1 and 2 are shown in Figure 3. No bands of ethene were observed due to very small amount of adsorbed species at 473 K, but bands of d_3 -methoxy species and consumed acidic OH groups were

observed. In the time course of the reaction, the gradual recovery of OD band at around 2650 cm^{-1} is clearly observed accompanied with the decrease of CD bands of d_3 -methoxy species, which is the evidence of the reaction of d_3 -methoxy

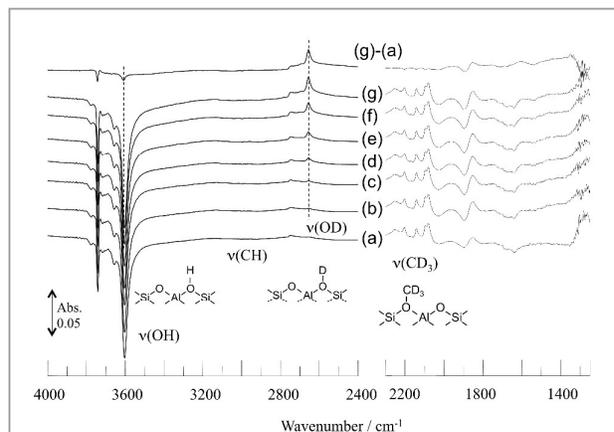


Fig. 3 Time course of IR spectra measured during the reaction of d_3 -methoxy species with ethene at 473 K. Spectrum (a) was measured before introduction of ethene, and (b) 5 min, (c) 10 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min after starting the reaction. Top spectra were obtained by subtraction of (a) from (g)

species as CD_2 unit with ethene.¹⁷

Methylation of cyclohexane with methoxy species over zeolites are reported to proceed under similar reaction conditions.^{10, 11, 13} Although we attempted the simultaneous analysis of gaseous molecules and surface species, the dilute molecules in gas phase prohibited any precise quantifications. On the other hand, IR observation of surface species provided important information on the reaction mechanism from clear spectral changes. Therefore, IR results are shown for the reaction of methoxy species with cyclohexane. d_3 -Methoxy species were also reacted with cyclohexane under the same conditions. The time course of spectra measured during the reaction of d_3 -methoxy species with cyclohexane at 473 K is

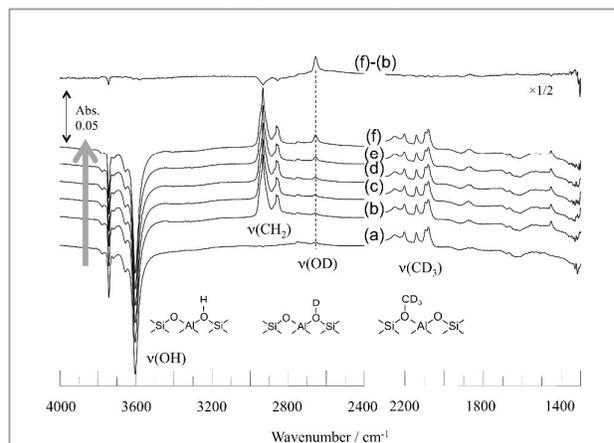
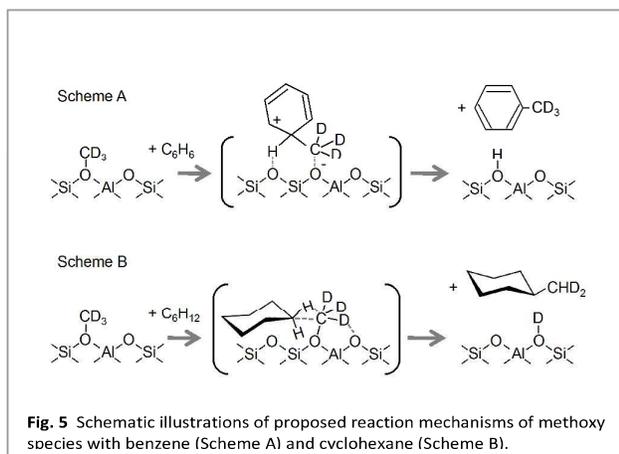


Fig. 4 Time course of IR spectra measured during the reaction of d_3 -methoxy species with cyclohexane at 473 K. Spectrum (a) was measured before introduction of benzene, and (b) 1 min, (c) 5 min, (d) 10 min, (e) 20 min and (f) 30 min after starting the reaction. Top spectra were obtained by subtraction of (b) from (f).

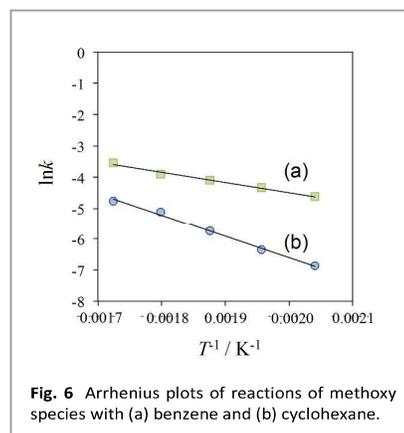
shown in Figure 4. In the case of cyclohexane, intense bands attributed to CH_2 stretching of adsorbed cyclohexane were observed at $3000\text{--}2800\text{ cm}^{-1}$ with a weak CH_2 deformation band at around 1450 cm^{-1} . The adsorption of cyclohexane is in equilibrium with gaseous molecules, since the adsorbed cyclohexane was completely removed by evacuation. The top spectrum in Figure 4, indicating the change of adsorbed species, is only explained for simplicity. The decrease of CH_2 stretching bands in intensity due to the decrease of the amount of cyclohexane is clear in the spectrum in addition to negative bands of d_3 -methoxy species. In the light of the recovery of the acidic sites, they appeared as OD groups and the acidic OH band at 3610 cm^{-1} was silent; d_3 -methoxy species reacted in CD_2 units with cyclohexane leaving one of their D atoms on the acid sites similarly to the case of the reaction with light olefins.¹⁷ Since only ^{13}C -labelled methanol was used as a methylation agent of cyclohexane for NMR analysis¹¹ so far, this new information has been found for the first time by using d_3 -methoxy species for IR analysis.

The reaction mechanisms of methoxy species with benzene and cyclohexane are compared by illustration in Figure 5. Benzene substitutes a H atom with more electrophilic (cationic) methyl groups to generate CD_3 -toluene probably using two sites (Scheme A), similarly to reactions of amines^{11, 17} and dimethylether.¹⁸ This is in analogous to so-called carbenium cation route, where CD_3 groups in d_3 -methoxy species are maintained. On the other hand, the same methoxy species form C-C bonds with cyclohexane to evolve methylcyclohexane ($\text{C}_6\text{H}_{11}\text{-CHD}_2$) and OD groups through carbene-like intermediate most likely in a concerted manner (Scheme B). In the case of cyclohexene (cyclic olefin), the reaction followed Scheme B leaving OD groups from d_3 -methoxy species,



because cyclohexene is less electro-donative than benzene.

The rate of the reaction was measured by using the increase of recovery of the integrated peak intensity of the acidic OH band in the time course. The reaction of methoxy species with both benzene and cyclohexane followed first order kinetics with respect to gas phase pressure of the reactants and the amount of methoxy species on H-ZSM-5. The activation energies were estimated from 473 to 523 K to be 54 ± 4 and $115 \pm 3\text{ kJ}\cdot\text{mol}^{-1}$ for benzene and cyclohexane, respectively (Figure 6). It should



be noted that the activation energy of methylation of cyclohexane with methoxy species is similar to that of ethene ($111 \pm 4\text{ kJ}\cdot\text{mol}^{-1}$). While ethene, propene and cyclohexane form C-C bond with methoxy species through the same mechanism (carbene-like intermediate), the reactivity of propene was much higher than those of the others, with the activation energy of $41 \pm 1\text{ kJ}\cdot\text{mol}^{-1}$ (unpublished data). This indicates that the rate determining step for the C-C bond formation of hydrocarbons with methoxy species through carbene-like mechanism cannot be simply attributed to the C-H bond cleavage of methoxy species. Therefore, it is further implied that the role of the reactant hydrocarbon for the C-H bond activation of methoxy species is significant in the activated complex.

Conclusions

Different mechanisms operate for reactions of methoxy species to form C-C bonds with various hydrocarbons: in methyl cation-like (Figure 5 Scheme A) and carbene-like (Figure 5 Scheme B) mechanisms, most probably both in concerted manner. While the hydrocarbon pool intermediates and their reactions inside the cage-type pores of zeolites should be the major processes of MTO reaction, the details of elementary pathways of MTO reaction would be also of importance. The mechanism of activation and the reactivity of methoxy species, one of the elementary intermediates, are markedly affected by the interaction with reactant molecules.

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