Activation of hydrocarbons on acidic zeolites: superior selectivity of methylation of ethene with methanol to propene on weakly acidic catalysts†

Qingjun Zhu,[a] Junko N. Kondo,[a] Tooru Setoyama,[b] Masashi Yamaguchi,[b]
Kazunari Domen[c] and Takashi Tatsumi*[a]

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The study of methylation of ethene with methanol to propene over MFI zeolites with different heteroatoms has found that an efficient catalyst with weak acidities prevented the side reactions related with the formation of ethene oligomers from occurring, as evidenced by *in situ* IR spectroscopy, leading to superior propene selectivity in the product distribution.

Methanol is of considerable interest as a potential material for the chemical and energy industry; most importantly, use of methanol as chemical feedstock stems from the methanol to olefins (MTO) process.[1] A major challenge in understanding the catalytic activity in MTO lies in complexity of the reaction mechanisms while a variety of reaction pathways have been documented in the literature.[2] The MTO studies on the cmolecular sieve SAPO-34, one of the most efficient catalysts, pointed to the hydrocarbon-pool mechanism in which the methylation of arene and the subsequent splitting to alkenes (ethene and propene) play vital roles.[3–5] However, Kolboe *et al.* studied the methylation of alkenes with methanol on H-ZSM-5 zeolites, another important catalyst for MTO, by the isotope experiments, and concluded that methylation of methanol on MMA, methyl methacrylate;hydrocarbons, in particular on the produced alkenes, constitute a significant part in the reaction process. Propene is formed not only from the hydrocarbon-pool mechanism but also from methylation of alkenes (*e.g.*, ethene) with methanol and the subsequent interconversions.[6] In other words, the MTO reaction mechanisms upon H-SAPO-34 and H-ZSM-5 are significantly different, particularly in the propene formation. It is well known that the MTO catalysis over zeolites are determined by the zeolite topologies and their acidities, which are induced by the nature of trivalent heteroatoms and their locations in the zeolite frameworks. Here we present our MMA, methyl methacrylate;*in situ* IR spectroscopic studies on methylation of ethene with methanol to propene over aluminium- or boron-containing MFI zeolites to elucidate the function of acidities in the activation of reactants.

The zeolite materials, provided by the Mitsubishi Chemical Company, were prepared by the hydrothermal synthesis method. Two kinds of zeolitic materials in proton forms, H-ZSM-5 with the Si to Al ratio of 25 and H-[B]-MFI borosilicate with the Si to B ratio of 41, were employed (Fig. S1–S3 in the ESI†). The discrepancy between the ratios of Si to heteroatoms (Al and B) was mainly attributed to the difficulty in incorporating desired boron contents into zeolites.[7] It is noteworthy that a trace amount of Al was present (0.06 wt%) in H-[B]-MFI borosilicate.

Reaction data were collected by using a plug flow reactor and three well-calibrated on-line gas chromatographs (Shimadzu) were used as the analyzing equipment, with TCD as detectors. Methanol was fed by a syringe pump (Harvard) to an evaporator and the tubing of the reaction system was heated to avoid condensation of heavy product molecules to guarantee their detection. Typically, 0.1 g catalyst was centered at a quartz reactor in a furnace, and the overall flow rates of all the studied reactions were fixed at 625 ml h^{-1}. Four types of reactions were carried out: (1) co-reaction of 6% methanol and 6% ethene over H-ZSM-5 and H-[B]-MFI, respectively; (2) reaction of 6% ethene diluted with N_2 over H-ZSM-5 and H-[B]-MFI, respectively. Catalysts were calcined at 823 K prior to the reaction. The temperature of the catalyst bed was cooled down to 573 K and the reactant was introduced into the reactor. The reaction temperature was raised from 573 to 773 K by several steps during the reaction. Reaction products were analyzed 30 min after the start of the reaction under steady state conditions. We estimate that carbon mass balance was close to 95%.

The zeolite was pressed into a self-supporting wafer and placed in an *in situ* IR cell which was connected to a flow line of ethene and a methanol evaporator.[8] All the infrared spectra were recorded on an FT/IR 7300 spectrometer (JASCO) with an MCT detector at a resolution of 4 cm^{-1} and 64 scans. Prior to the measurements, the sample was heated to 773 K in simulated air atmosphere for 1 hour. After the sample was cooled down to 573 K, the catalyst was exposed to the flow of ethene or methanol vapor diluted with N_2 for 10 minutes. Finally, the sample was flushed with N_2 until no gas phase of the reactant (ethene or methanol) was observed by IR spectroscopy. Difference spectra were obtained by subtracting the spectra taken at 573 K before adsorption.

Fig. 1 presents the reactant (methanol and ethene) conversions of different reactions on H-ZSM-5 and H-[B]-MFI at various temperatures.‡ The conversions of methanol increased with temperatures, and the methanol conversions on H-ZSM-5 were

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[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan. E-mail: ttatsumi@cat.res.titech.ac.jp; Fax: +81-45-9245282*
[b] *Mitsubishi Chemical Group, Science and Technology Research Center, 1000 Kamoshida-cho, Aoba-ku, Yokohama, 227-8502, Japan*
[c] *Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku Tokyo, 113-8656, Japan*

† Electronic supplementary information (ESI) available: Experimental details; XRD, SEM and IR spectra of studied catalysts; reaction stability over H-[B]-MFI catalyst at 773 K. See DOI: 10.1039/b809718f

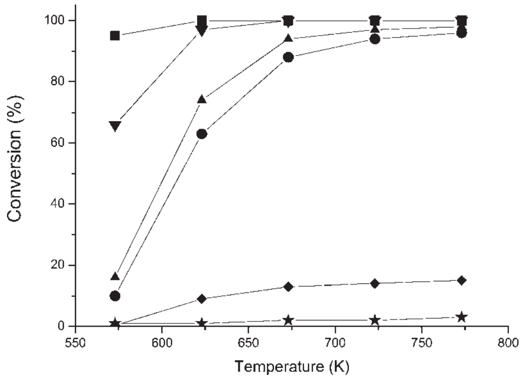

Fig. 1 Reactant conversions in different feed compositions: (■) CH_3OH conversion in CH_3OH + C_2H_4 over H-ZSM-5, (▼) CH_3OH conversion in CH_3OH + C_2H_4 over H-[B]-MFI, (●) C_2H_4 conversion in CH_3OH + C_2H_4 over H-ZSM-5, (▲) C_2H_4 conversion in pure C_2H_4 over H-ZSM-5, (◆) C_2H_4 conversion in CH_3OH + C_2H_4 over H-[B]-MFI, (★) C_2H_4 conversion in pure C_2H_4 over H-[B]-MFI.

higher than those on H-[B]-MFI. This was attributed to the relatively strong acidity of H-ZSM-5. The methanol conversions over both catalysts were close to 100% above 623 K. When only ethene was employed as the reactant on H-ZSM-5, a small consumption of ethene was observed at 573 K, and ethene conversion remarkably increased with temperature. Nevertheless, co-feed of ethene and methanol over H-ZSM-5 led to a slight decrease in the apparent ethene conversion, possibly resulting from extra ethene produced by the methanol transformation. This also indicated the difficulty in studying the methylation of ethene with methanol since ethene is a product of the MTO process. In contrast, co-feed of ethene and methanol over H-[B]-MFI resulted in a significant increase in the ethene conversion, whereas the transformation of ethene as the only reactant over H-[B]-MFI led to a very low conversion. Clearly, the presence of methanol facilitated ethene conversion over H-[B]-MFI. In addition, the catalytic activity of H-[B]-MFI was found to be fairly stable at 773 K (Fig. S4 in the ESI†). Inspired by the isotope experiments that proved the methylation of ethene with methanol readily occurring on H-ZSM-5(MFI topology),[6c] we would suggest that the enhancement of ethene conversion over H-[B]-MFI was caused by the methylation of ethene with methanol, leading to propene formation.

Fig. 2 exhibits the productivity in various reactions over H-ZSM-5 and H-[B]-MFI at 773 K. The productivity in the reaction of only ethene over H-[B]-MFI is not shown because the conversion of ethene was very low, leading to a negligible propene formation rate (0.08 mmol g^{-1} h^{-1}). In contrast, the reaction of ethene over H-ZSM-5 (reaction A) resulted in a considerable production of propene despite the fact that the major products were aliphatic C_4–C_6. The co-reaction of ethene and methanol over H-ZSM-5 (reaction B) increased the propene formation. The most interesting aspect of the reactions on H-ZSM-5 was that propane and aromatics (benzene, toluene and xylene, denoted by BTX) constituted significant portions in the product distribution. However, the application of H-[B]-MFI to the methylation of ethene with methanol dramatically increased the propene productivity (reaction C) and, more importantly, the by-products of propane and BTX became nearly negligible (selectivity less than 1%). We thus propose that the aromatic products and propane were mainly produced by the strongly acidic sites of H-ZSM-5, whereas the weakly acidic sites of H-[B]-MFI efficiently avoided various hydrogen-transfer reactions producing propane and BTX simultaneously. Moreover, the overall converted carbon atoms (particularly ethene) in the co-reaction of ethene and methanol over H-[B]-MFI was remarkably lower than those in the co-reaction of ethene and methanol over H-ZSM-5, indicating higher propene selectivity when H-[B]-MFI was employed as a catalyst. In other words, the introduction of methanol as a reactant resulted in more efficient transformation of ethene to propene over H-[B]-MFI.

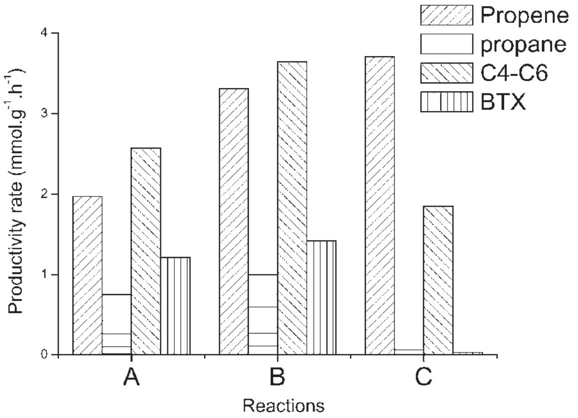

Fig. 2 Productivity rate of various reactions: (a) pure C_2H_4 over H-ZSM-5, (b) CH_3OH + C_2H_4 over H-ZSM-5, (C) CH_3OH + C_2H_4 over H-[B]-MFI.

Fig. 3 displays IR spectra taken after exposure of catalysts to methanol or ethene followed by a sweep with nitrogen at 573 K. Methanol reacted with the hydroxyl group on H-ZSM-5, leading to the negative bands at 3740, 3660 and 3606 cm^{-1}. These bands are assigned to the O–H stretching vibration of silanol on the external surface, the O–H stretching vibrations of the hydroxyl group associated with extra-framework aluminium and framework aluminium, respectively. Simultaneously, the methoxy group

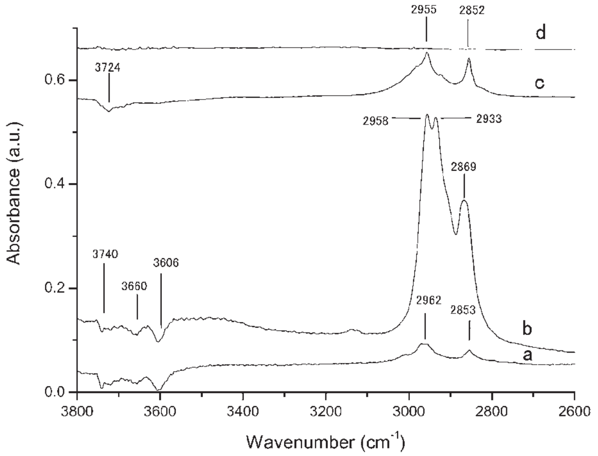

Fig. 3 IR difference spectra of catalysts exposed to reactants followed by purge of N_2: (a) CH_3OH on H-ZSM-5, (b) C_2H_4 on H-ZSM-5, (c) CH_3OH on H-[B]-MFI, (d) C_2H_4 on H-[B]-MFI.

with characteristic asymmetric and symmetric vibrations of methyl groups at 2962 and 2853 cm^{-1} was observed (Fig. 3a).[9] In contrast, methanol reacted with H-[B]-MFI to show a broad negative band centered at 3724 cm^{-1}, methoxy species on H-[B]-MFI being also clearly distinguished (Fig. 3c). When H-ZSM-5 was exposed to ethene, we observed the ethene oligomer species with asymmetric vibrations at 2958, 2933 cm^{-1} and the symmetric stretching mode at 2869 cm^{-1} accompanied by the consumption of the acid sites (Fig. 3b).[10] However, when H-[B]-MFI was exposed to ethene, ethene was weakly adsorbed, and was nearly completely removed with a N_2 sweep (Fig. 3d). It is concluded that the formation of ethene oligomers was effectively prevented on H-[B]-MFI owing to its weak acidity, leading to higher propene selectivity and negligible formation of propane and aromatics. The adsorption of the reactant is a prerequisite for the catalysis; however, the correlation between the ethene oligomers and the production of BTX and propane remains elusive. We propose that (1) BTX and propane are produced by the cracking of ethene oligomers, and (2) that the strong acidity is responsible for the formation of the ethene oligomers and the hydrogen-transfer reactions. Thus the ethene oligomer formation can be taken as an indicator of the production of BTX and propane.

We conclude that, in the reaction of methylation of ethene with methanol to propene, there are several interwoven reactions such as transformation of methanol to hydrocarbons, methylation of alkenes with methanol, and possible cracking of ethene oligomers to the by-products such as BTX and propane. In the MTO process, methanol is transformed to hydrocarbons (*e.g.*, propene) by different reaction pathways after ethene is produced. We note that a trace amount of Al present in H-[B]-MFI might play important roles as reported in literature.[7] However, the adsorption of ethene is dependent on the acidity. It is well established in the literature that H-[B]-MFI showed weaker acidity than H-ZSM-5.[11] Weakly acidic sites of H-[B]-MFI prevent the formation of ethene oligomers, resulting in more efficient use of ethene and higher propene selectivity. The weakly acidic sites we refer to here include: (1) weak Brønsted acid sites induced by the incorporation of boron into the zeolite framework compared with framework Al;, (2) a trace amount of Al-induced Brønsted acidity if the impurity Al is taken into consideration; and (3) the weakly acidic sites associated with crystallographically-different tetrahedral sites in MFI topology.[12] Hence, we suggest that the Al impurity in H-[B]-MFI, if it were to participate in the reaction, would be categorized as weakly acidic sites based on the observation that it did not activate ethene to form ethene oligomers as shown in Fig. 3d.

Notes and references

‡ Thermon3000 on Chromosorb, Gaskuropack 54 were used to detect the aliphatic products of C_2–C_6 and aromatic products of C_6–C_{10}, respectively. Gases were analyzed by a silica gel column. Methanol conversion was defined as the methanol consumed divided by methanol fed to the reactor, and dimethyl ether was not considered to be a product. The product selectivities were based on carbon mass balance.

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