

***In situ* Fourier Transform I.R. Observation of Methylating Species in ZSM-5**

Timothy R. Forester, She-Tin Wong, and Russell F. Howe*

Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand

In situ Fourier transform i.r. spectra show that MeOH in ZSM-5 forms an AlOMe species above 473 K which correlates with the onset of hydrocarbon formation and which methylates benzene, ethene, propene, and cyclopentene; MeOMe is protonated by internal acid sites at low temperatures but forms the same methylating species at 473 K and above.

The mechanism of the methanol to gasoline conversion reaction over ZSM-5 and other acid zeolite catalysts continues to attract widespread attention. In particular, the route by which the first carbon-carbon bonds are formed from methanol or dimethyl ether has been the subject of consider-

able speculation.¹ Previous i.r. spectroscopic studies of the interaction of methanol with ZSM-5 have shown that methoxy groups are formed at low temperatures through reaction of methanol with zeolite hydroxy groups, and have detected a complex mixture of adsorbed hydrocarbon products after

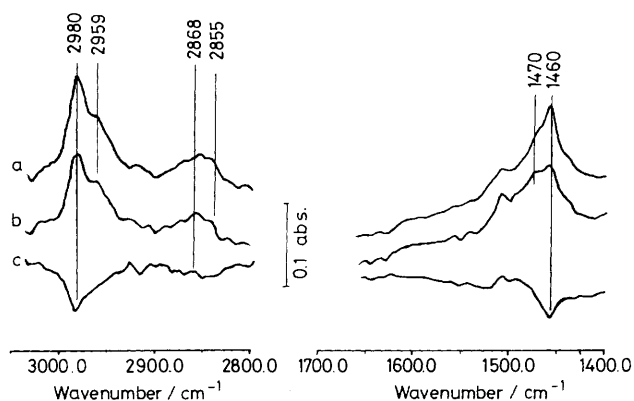


Figure 1. I.r. spectra (absorbance) in the $\nu(\text{CH})$ and $\delta(\text{CH})$ regions of: (a), ZSM-5 (5.8 Al per unit cell) 30 minutes after exposure to MeOH at 523 K; (b), same sample immediately following addition of C_6H_6 ; (c), difference spectrum (b) - (a).

heating ZSM-5 in methanol to higher temperatures.² In all of these previous studies however, spectra were recorded after cooling the catalyst samples to room temperature. We now show that *in situ* measurements at the reaction temperature, using an i.r. cell functioning as a pulse microreactor, allow for the first time the observation of an adsorbed intermediate which appears to be directly implicated in the formation of carbon-carbon bonds.

Samples of ZSM-5 containing 3.4[†] or 5.8[‡] Al per unit cell were mounted as pressed wafers (7–10 mg cm⁻²) in an *in situ* i.r. cell³ which permitted heating in an N_2 stream to reaction temperatures while spectra were measured with a Nicolet 5DX spectrophotometer.[§] Pulses of methanol or dimethyl ether were injected into the gas stream and reaction products either sampled on-line by gas chromatography or trapped downstream for off-line analysis.

Injection of a single pulse of methanol (*ca.* 5 MeOH per Al) onto freshly activated catalysts at temperatures of 473 K or below produced the i.r. bands characteristic of SiOMe groups at 2959, 2855, and 1470 cm⁻¹.⁴ This species is formed largely from external hydroxy groups (3720 cm⁻¹) although some decrease in the concentration of internal hydroxy groups (3610 cm⁻¹) was also observed. No hydrocarbon products were detected.

Injection of methanol onto fresh catalyst at 523 K produced the SiOMe groups plus a second species with frequencies 2980, 2868, and *ca.* 1460 cm⁻¹. The second species was formed from internal hydroxy groups, as revealed by a marked increase in the number of internal hydroxy groups lost on addition of methanol. The relative concentration of the second species increased with increasing aluminium content of the zeolite.

[†] Provided by Mobil in the ammonium exchanged form; crystallinity checked by X-ray powder diffraction and Al content determined by X-ray fluorescence (XRF) and atomic absorption (AA) analysis; activated by heating in flowing N_2 to 673 K.

[‡] Synthesized according to U.S. Patent 4 257 885 (1981) and converted into the acid form by aqueous ion exchange; crystallinity checked by X-ray powder diffraction and Al content determined by XRF and AA analysis, activated by heating in flowing N_2 to 673 K.

[§] Typically 200 scans were averaged (1 s per scan) at a resolution of 4 cm⁻¹. The spectra shown here were further smoothed with a 9-point quadratic function and the spectrum of the activated zeolite subtracted.

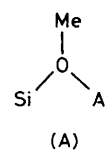


Figure 1(a) shows a spectrum obtained from methanol in H-ZSM-5 containing 5.8 Al per unit cell at 523 K; the bands due to SiOMe groups are present as shoulders on the side of those of the second species. Both species decayed slowly on standing in flowing N_2 at 523 K, and hydrocarbon products were detected downstream.[¶] At higher temperatures the i.r. bands decayed more rapidly and higher yields of hydrocarbons were detected. The spectra at 573 K and above also began to show additional features due to adsorbed reaction products which were enhanced on adding further pulses of methanol.

At temperatures below 473 K dimethyl ether reacted exclusively with internal hydroxy groups in fresh catalyst samples to form a protonated dimethyl ether species.⁴ At 473 K and above however dimethyl ether gave the same i.r. bands obtained with methanol, except that the intensities of the SiOMe bands were lower relative to those of the second species. Hydrocarbon products were detected from dimethyl ether at 473 K and above.^{||}

The first appearance of hydrocarbon products from both methanol and dimethyl ether correlates with the formation of the species responsible for i.r. bands at 2980, 2868, and 1460 cm⁻¹. The temperature range in which this species begins to desorb at an appreciable rate (>523 K) also corresponds to that in which deuterium exchange between CD_3OH and zeolite hydroxy groups begins to occur. This suggested that it may be involved in carbon-carbon bond formation, and we therefore investigated its ability to function as a methylating agent. Pulses of either methanol or dimethyl ether were injected into fresh catalyst samples at 523 K and spectra recorded after a delay of 30 minutes to allow desorption of products.^{**} A pulse of the substrate to be methylated was then injected, the spectrum recorded again, and reaction products trapped downstream and analysed.

The spectra in Figure 1 were obtained in such an experiment with methanol in ZSM-5 containing 5.8 Al per unit cell. Injection of benzene caused no change in the SiOMe bands, but an immediate reduction in intensity of the 2980, 2868, and 1460 cm⁻¹ bands of the second species [the difference spectrum in Figure 1(c) shows clearly the changes in the 2980 and 1460 cm⁻¹ bands]. At the same time the $\nu(\text{OH})$ band at 3610 cm⁻¹ due to internal hydroxy groups increased in intensity, and toluene and traces of xylenes were detected downstream as reaction products. Benzene injected onto a fresh catalyst which had not been pretreated with methanol did not react under these conditions. Likewise, no changes occurred in the spectrum and no reaction products were detected when benzene was injected onto a catalyst containing only SiOMe (pretreated with methanol below 523 K). The analogous experiments with dimethyl ether gave similar results.

Methylation of benzene over a ZSM-5 catalyst pretreated with methanol was previously reported by Ono and Mori.^{2a}

[¶] Typical hydrocarbon product distribution: CH_4 , 8%; C_2H_4 and C_2H_6 , 23%; C_3H_8 , 23%; C_3H_6 , 17%; *i*- C_4H_{10} , 12%; *n*- C_4H_{10} , 17%.

^{||} Typical hydrocarbon product distribution at 523 K: CH_4 , 2%; C_2H_4 and C_2H_6 , 12%; C_3H_8 , 14%; C_3H_6 , 55%; *i*- C_4H_{10} , 9%; *n*- C_4H_{10} , 8%.

^{**} After such a delay the spectrum was unchanged between successive scans.

These authors suggested that methoxy groups were the methylating species, but did not measure *in situ* i.r. spectra. Our results show that it is not the SiOMe groups formed at low temperature but the second species formed at high temperature which methylates benzene, and that this species is formed only at internal acid sites.

Similar methylation experiments were attempted with other substrates. Injection of ethene caused a slight decrease in the intensity of the 2980 cm^{-1} band (changes in the other bands were too small to measure) and gave traces of propene as a product. Larger intensity changes were observed with propene, but the spectra were complicated in this case by the appearance of new bands due to propene oligomerization products, and no unique methylation products could be distinguished by gas chromatography from those of oligomerization. Loss of the second species was also found when cyclopentene was injected, and traces of a new product tentatively identified as methylcyclopentene were detected downstream. No clear evidence was obtained for methylation of hex-1-ene: the spectrum of the methylating species was obscured by bands due to oligomerization products and no unique methylation products could be detected by gas chromatography.

Methylation of dimethyl ether to form a trimethyloxonium cation or related species has been proposed⁵ as a key step in the formation of the first carbon-carbon bonds from methanol or dimethyl ether. The trimethyloxonium cation is itself a methylating agent. The number of i.r. bands observed for the methylating species in ZSM-5 [2 $\nu(\text{CH})$ modes and 1 $\delta(\text{CH})$ mode] and their frequencies do not correspond at all however to the vibrational spectrum of the trimethyloxonium cation in $\text{Me}_3\text{OSbCl}_6$.⁶ The simplicity of the vibrational spectrum of the zeolite species suggests that it contains in fact only a single methyl group. Its formation on internal hydroxy groups only and the correlation with the aluminium content of the zeolite further suggests that it may be represented as (A), which is the

methyl equivalent of the Brønsted proton site in acid zeolites.

This species may thus be regarded as an incipient methyl cation which could methylate dimethyl ether to form a transient trimethyloxonium cation not detected spectroscopically, although other reaction schemes involving loss of a proton from this species can also be envisaged. What is clear at this point is that the *in situ* Fourier transform i.r. technique allows us to observe directly the methylating species that initiates carbon-carbon bond formation. This work also supports the suggestion of methylation of initially formed alkenes and aromatics as a major route to higher hydrocarbons during methanol conversion.⁷

We acknowledge helpful discussions with Dr. T. Mole of CSIRO Division of Materials Science on the subject of methylation, and thank Mobil for providing a sample of ZSM-5.

Received, 11th July 1986; Com. 957

References

- 1 See, for example, C. D. Chang, *Catal. Rev.-Sci. Eng.*, 1983, **25**, 1.
- 2 (a) Y. Ono and T. Mori, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2209; (b) J. Haber, J. Komorek-Hłodzik, and T. Romotowski, *Zeolites*, 1982, **2**, 179; (c) M. Sayed and R. P. Cooney, *Aust. J. Chem.*, 1982, **35**, 2483; (d) L. Kubelkova, J. Novakova, and P. Jiru, 'Structure and Reactivity of Modified Zeolites,' ed. P. A. Jacobs, Elsevier, Amsterdam, 1984, p. 127.
- 3 S. H. Moon, H. Windawi, and J. R. Kratzer, *Ind. Eng. Chem., Fundam.*, 1981, **20**, 396.
- 4 T. R. Forester and R. F. Howe, to be published.
- 5 G. A. Olah, *Pure Appl. Chem.*, 1981, **53**, 201; *J. Am. Chem. Soc.*, 1984, **106**, 2143; J. P. Van den Berg, J. P. Wolthuizen, and J. H. C. Van Hoof, 'Proceedings of the Fifth International Conference on Zeolites (Naples),' Heyden and Son, 1980, p. 649.
- 6 R. F. Howe and M. J. Taylor, *Spectrochim. Acta*, in the press.
- 7 R. M. Desau and R. B. LaPierre, *J. Catal.*, 1982, **78**, 136.