

The Production of Alkane Chains from Methanol on HY Zeolite studied by ^{13}C N.M.R. Techniques

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^{13}C N.m.r. and Fourier transform i.r. techniques have been employed to identify surface intermediates in the reaction of methanol over HY zeolite.

Studies of the dehydration of methanol over HY zeolite¹ and ZSM-5² have been concerned mainly with the formation of a C-C bond from methanol to form hydrocarbons. We examine here the formation of this bond from direct observation of the surface species on HY zeolite by ^{13}C n.m.r. spectroscopy of solid samples.

The HY zeolite used was prepared by the replacement of NaY with HY using NH_4Cl , followed by calcination at 500 °C for 3 h in an electric oven. The percentage of HY was found to be 86% by atomic absorption spectrometry. Approximately 750 mg of HY zeolite (*ca.* 0.1 mm in size) was put into a sample tube, connected to a conventional recycle system under vacuum and after evacuation at 500 °C for 2 h, 35 Torr of methanol (26.62 atom % of $^{13}\text{CH}_3\text{OH}$) was intro-

duced at various temperatures: room temperature, 220, 380 and 480 °C. After reaction for 1 h, the gaseous phase was analysed by g.c. (Porapak-PS and active carbon). The HY zeolite samples were evaluated using ^{13}C n.m.r. and i.r. spectroscopy. The ^{13}C n.m.r. spectra of the samples were determined using high power proton decoupling, cross-polarization, and magic angle spinning over a range of 10 kHz with 8192 data points at 15 kHz. The rotor angle was adjusted to the magic angle (54.7°) using a test sample of hexamethylbenzene. Chemical shift values were calibrated against external adamantane, but all the values given here are relative to tetramethylsilane (TMS). The samples were pressed into a rotor with an external diameter of 10 mm. The spinning rate of the rotor was approximately 2.1 kHz and accumulation of between

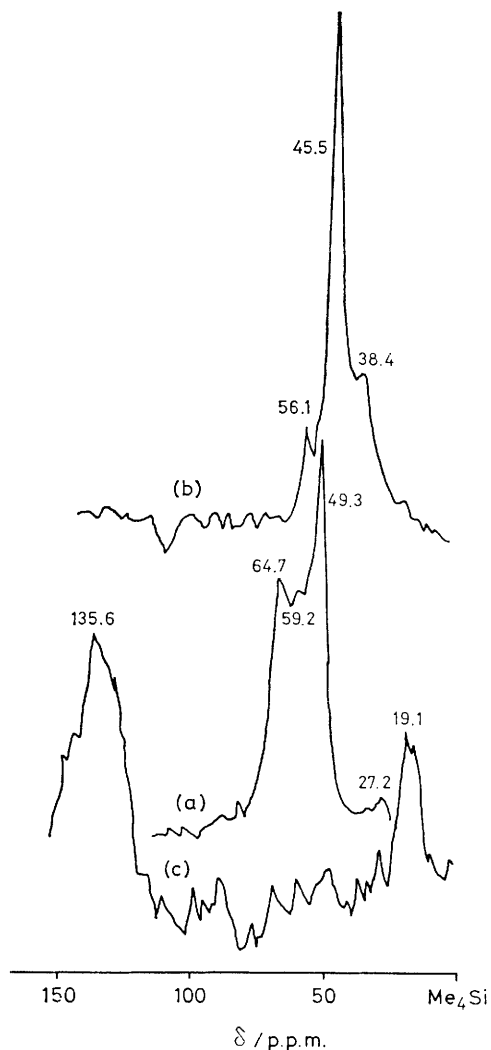


Figure 1. ^{13}C N.m.r. spectra of methanol on HY zeolite evacuated at (a) 220 °C, (b) 380 °C, and (c) 480 °C.

800 and 23000 pulses was made to obtain high signal to noise ratios.

The ^{13}C n.m.r. spectra (Figure 1) show the presence of different species on the surface at various evacuation temperatures. At room temperature a simple peak at 48.9 p.p.m. was obtained and this was assigned to molecular methanol.³ However, the surface species varied in a complex manner with a rise in evacuation temperature. At 220 °C, four peaks were observed at 49.3, 59.2, 27.2, and 64.7 p.p.m. The peak at 49.3 p.p.m. clearly corresponds to the peak at room temperature and the peak at 59.2 p.p.m. was assigned to the carbon of the methoxy-group.³ The other two peaks were identified by reference to the i.r. spectra and the reaction products in the vapour phase. The i.r. spectrum given in Figure 2(a) shows very small bands at 2930 and 2885 cm^{-1} ; liquid ethylene glycol has bands at 2940 and 2880 cm^{-1} for asymmetric and symmetric vibrations of $-\text{CH}_2-$, respectively. On the other hand, small amounts of propene were found in the vapour phase. In general, a ^{13}C n.m.r. resonance near 27 p.p.m. is due to an alkane $-\text{CH}_2-$ group, but in the present work, no i.r. data or reaction products related to alkanes were observed. The peak at 27.2 p.p.m. may therefore be due to the methyl carbon of propan-2-ol and the peak at 64.7 p.p.m. contributed by the two kinds of carbons adjacent to oxygen *i.e.* the hydroxy-methyl and the tertiary carbons of propan-2-ol.

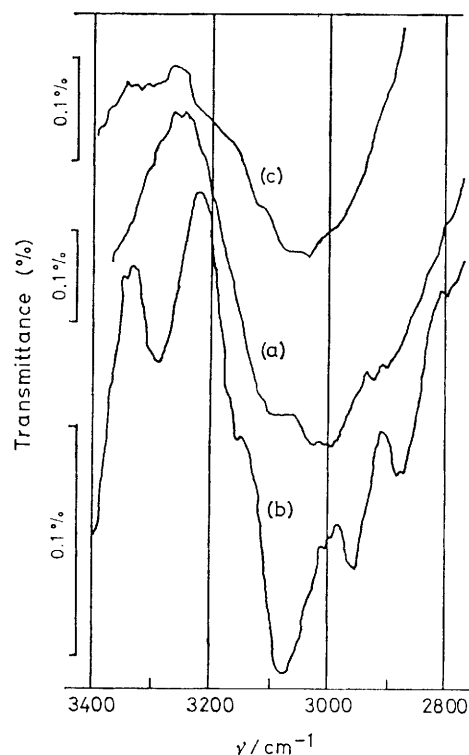
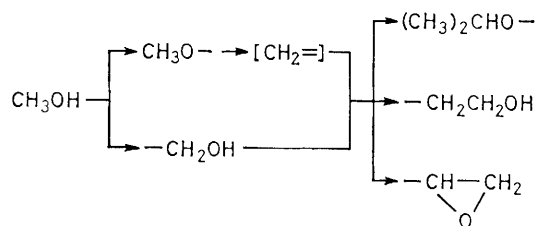


Figure 2. I.r. spectra of surface species on HY zeolite evacuated at (a) 220 °C, (b) 380 °C, and (c) 480 °C.



Scheme 1. Mechanism for the production of a C-C bond from methanol on HY zeolite.

At 380 °C, three peaks were observed at 38.4, 56.1, and 45.5 p.p.m. in the ^{13}C n.m.r. spectrum and the i.r. spectrum showed four bands at 3290, 3070, 2953, and 2870 cm^{-1} . The two bands at 2953 and 2870 cm^{-1} indicate the stretching vibration of the $-\text{CH}_2-$ or CH_2O -groups and the appearance of the band at 3290 cm^{-1} , which is due to an intermolecular hydrogen bond,⁴ suggests the presence of alcoholic species on the surface. This is supported by the formation of ethanol and propan-1-ol in the vapour phase. Based on these results, the peaks at 38.4 and 56.1 p.p.m. were assigned to the β - and α -carbons, respectively, of alcohols on the surface. A large peak appeared at 45.5 p.p.m. in the ^{13}C n.m.r. spectrum; from ^{13}C n.m.r. studies of oxiran compounds, the carbon of the methylene group in ethylene oxide was found to give a resonance at 39.7 p.p.m.⁵ and the carbons of the methine and methylene groups in propylene oxide to give resonances at 48.0 and 47.8 p.p.m.,⁵ respectively. In the i.r. spectrum at 380 °C a band was observed at 3070 cm^{-1} . Henbest and co-workers have reported that the C-H stretching band of the methylene in an alkylated oxiran ring appears near 3050 cm^{-1} .⁶ Consequently, we assigned the peak at 45.5 p.p.m. to the carbons of an epoxy group on the surface.

At 480 °C, the spectra became less complicated. Two peaks were observed at 19.1 and 135.6 p.p.m. in the ^{13}C n.m.r.

Table 1. Variation of ^{13}C n.m.r. chemical shifts in the reaction of methanol on HY zeolite.

Reaction temperature / °C	$\delta/\text{p.p.m.}^a$	Intensity ^b (%)	Identification
room temp.	48.9	100	MeOH
	49.3	46.3	MeOH
	59.2	19.5	MeO-
	27.2	13.4	$(^{13}\text{CH}_3)_2\text{CHOH}$
	64.7	20.7	$-\text{CH}_2\text{OH}$, $>\text{CHOH}$
380	38.4	26.3	$^{-13}\text{CH}_2\text{CH}_2\text{OH}$
	56.1	7.0	$-\text{CH}_2^{13}\text{CH}_2\text{OH}$
	45.5	66.7	$-\text{CHOCH}_2$
480	19.1	25.0	Me-
	135.6	75.0	=CH-

^a From Me_4Si . ^b Calculated by peak areas.

spectrum. Nagy *et al.* have identified surface species of but-1-ene on HY zeolite; the carbon of =CH- at 138.8 p.p.m. and the methyl carbon at 13.6 p.p.m. In the i.r. spectrum, the bands at 3290 and 3070 cm^{-1} , observed at 380 °C, disappeared. This suggests that the C-O bond of the hydroxymethyl group was cleaved at 480 °C to form an olefinic species. In Table 1, the results of identification of the surface species on HY zeolite are summarized. These results enable us to propose a

mechanism for the production of a C-C bond from methanol on HY zeolite. This mechanism is summarized in Scheme 1.

The carbenium ion theory proposed by Ono *et al.* was introduced to explain the present results.⁷ The observation of the hydroxymethyl group on the surface was significant, leading to the suggestion that there is a reaction between the surface methoxy-group and the hydroxymethyl group to form the C-C bond. The surface methoxy-group would be formed by the presence of protonic acid on the surface and converted into the carbene before the surface reaction.

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