

## Evidence for the Allyl and Secondary Cation Intermediate on Adsorption of Allyl Alcohol on H-ZSM-5 Zeolite

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<sup>13</sup>C NMR spectroscopy is used to show that for surface coverages corresponding to less than one allyl alcohol molecule per Brønsted site in H-ZSM-5, there is evidence for the formation of an allyl carbocation.

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In a recent communication, Munson, Xu and Haw<sup>1</sup> provided evidence for the formation of the allyl cation from allyl alcohol on a C<sub>5</sub>HX zeolite, thus lending support to the mechanism proposed by Hutchings *et al.*,<sup>2</sup> but the former workers did not directly observe this cation on the catalytically active

H-ZSM-5 employed by the latter. From studies at low surface coverage, we now provide the necessary verification of the mechanism of Hutchings *et al.*<sup>2</sup> by providing direct evidence for the formation of the allyl cation and a secondary cation, which account for the observed chemistry.<sup>3</sup> At surface

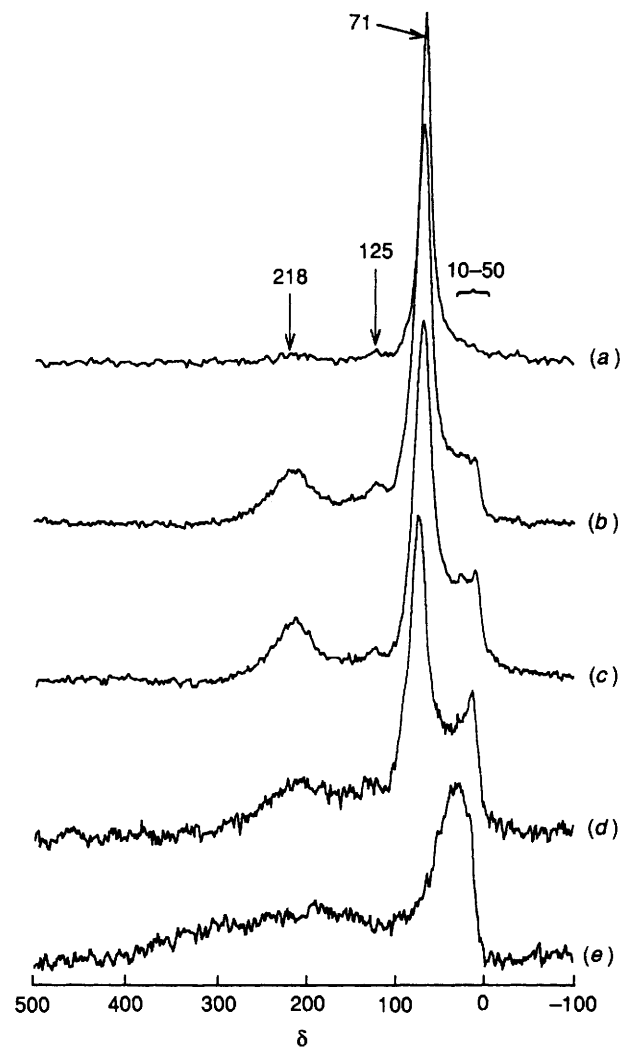
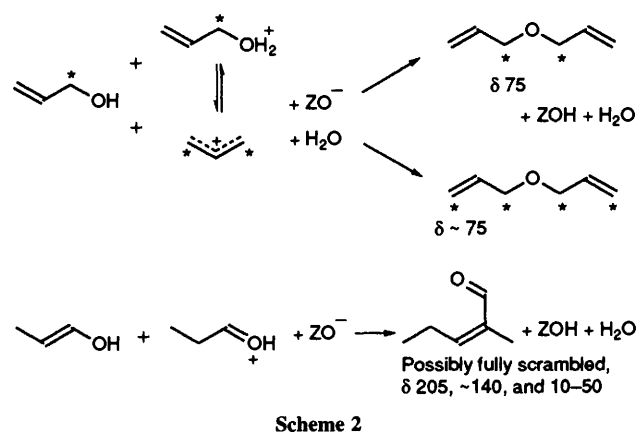
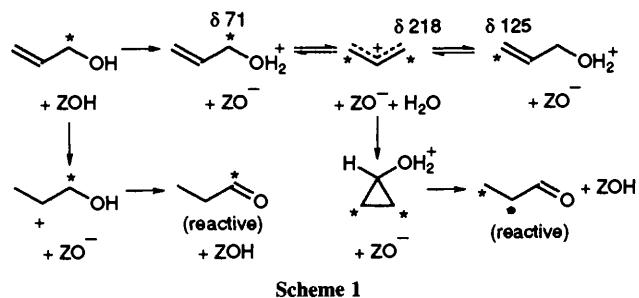


Fig. 1 Proton decoupled  $^{13}\text{C}$  CP spectrum of allyl alcohol adsorbed on H-ZSM-5 at a coverage of 0.85 molecules per Brønsted acid site. Unless otherwise noted, the contact time was 1.2 ms, the number of scans 524 288, and the repeat rate 100 ms. Arbitrary scaling of intensities. (a) Unheated alcohol 63 536 scans, repeat rate of 50 ms. (b) Heated to 325 K for 35 h. (c) Heated to 325 K for 70 h. (d) Heated to 355 K for 50 h. (e) Heated to 470 K for 10 min.

coverages below one allyl alcohol molecule per Brønsted site, product formation by bimolecular processes is greatly reduced<sup>3</sup> and there is either evidence for the stabilization of the carbocations, or a  $^{13}\text{C}$  label exchange consistent with the transients.

The H-ZSM-5 zeolite, Si/Al ratio of 35, was synthesized according to the method of Rollman and Valyocsik<sup>4</sup> using tetra-*n*-propylammonium bromide as a template. The concentration of Brønsted sites was determined using temperature programmed desorption-thermogravimetric analysis of isopropylamine<sup>5</sup> and was found to be 370  $\mu\text{mol}$  per g of zeolite, which corresponds to 2.1 sites per orthorhombic unit cell. 200–220 mg samples were prepared and sealed under vacuum after loading with  $1\text{-}^{13}\text{C}$  (99% enriched) allyl alcohol corresponding to approximately 0.85 molecules per Brønsted site.

The broadline (due to chemical shift anisotropy) proton decoupled  $^{13}\text{C}$  CP NMR spectrum of adsorbed allyl alcohol prior to any heating, obtained in a static probe at a field of 3.5 T,<sup>6</sup> is shown in Fig. 1(a). At low surface coverage the allyl alcohol-zeolite complex is formed at the acid site (low probability for physisorption), and the  $1\text{-}^{13}\text{C}$  frequency ( $\delta$  71) is shifted 8 ppm downfield from the pure liquid, characteristic of partial proton transfer. The spectra obtained after heating the sealed samples for 35 and 70 h at 325 K, Fig. 1(b) and Fig. 1(c), respectively, show the progressive development of two features; one in the vicinity of  $\delta$  220 and the other in the aliphatic region ( $\delta$  10–50). Further heating at a higher temperature, 355 K for 50 h, shown in Fig. 1(d), increases the rate of secondary reactions with the resultant decrease of the  $\delta$  220 feature. Only on heating to 460 K for approximately 10 min, Fig. 1(e), does one obtain a result similar to that reported by Munson *et al.*<sup>1</sup>

The present results, together with those reported previously<sup>1</sup> can be understood by separating the processes associated with a single molecule at the Brønsted site from bimolecular reactions, resulting from enhanced mobility, which have been shown to be dominant for allyl alcohol at high temperatures and high surface coverage.<sup>3</sup> At 325 K the localized chemistry associated with a single molecule is most apparent and includes the reactions shown in Scheme 1.

Each of the reactions in Scheme 1 can be observed in solution phase. While some of the intermediates are so reactive that they cannot be isolated at the Brønsted sites, other products of the reaction at a single acid site, prior to any bimolecular processes, are identifiable. The 1–3 label exchange of the allyl alcohol ( $\delta$  71 and 125) and the labelling of the aliphatic carbons ( $\delta$  10–50) in propanal are evidence for an allyl carbocation ( $\delta$  219).

The assignment of the peak at  $\delta$  218, Fig. 2(a), to the carbocation,<sup>7</sup> rather than the carbonyl of acetone<sup>2</sup> is based on the static spectra. At low surface coverages we have shown that the proton decoupled static CP spectrum of acetone exhibits a well-defined chemical-shift tensor,<sup>8</sup> which is similar, but not identical, to that of the neat solid.<sup>9</sup> The maximum occurs at  $\delta$  273 ( $\sim\sigma_{22}$ ) and the trace of the tensor  $\bar{\sigma} = \sigma_{\text{isotropic}}$  is  $\delta$  226.<sup>8</sup> An assignment of  $\delta$  218 to  $1\text{-}^{13}\text{C}$  of propanal is another possibility. However, this would require a mechanism involving the secondary rather than an allyl carbocation (see Scheme 1), as well as a non-rigid complex at the Brønsted site.

Other products as well as the disappearance of the allyl carbocation can be accounted for by bimolecular processes known to occur in acid media,<sup>10</sup> (Scheme 2). This is better illustrated in the higher resolution MAS spectra shown in

Fig. 2. Heating at 325 K, Fig. 2(a) shows some evidence of such products. These features are considerably enhanced by heating to a higher temperature, Fig. 2(b). The peaks at  $\delta$  75 and in the vicinity of  $\delta$  125 can be identified with the ether;

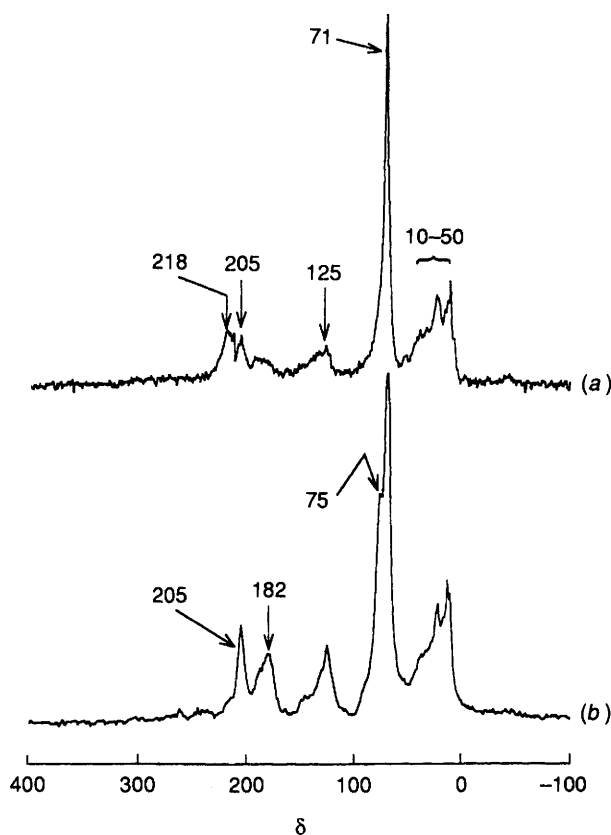


Fig. 2 Proton decoupled  $^{13}\text{C}$  CP MAS (cross polarisation magic angle spinning) (2.1 kHz) spectrum of allyl alcohol at a coverage of 0.85 molecules per Brønsted site. Arbitrary scaling of intensities. (a) Same as Fig. 1(c), 32 768 scans, repeat rate of 100 ms. (b) Same as Fig. 1(d), 32 768 scans, repeat rate of 200 ms.

features at  $\delta$  205,  $\sim$ 140 and 10–50 with the aldol addition of propanal under acidic conditions. Other features that also grow at higher temperatures are probably associated with larger unsaturated carbocations, acetal species and possibly aldehydes and esters. (Unsaturated species are observed in the IR spectra of allyl alcohol adsorbed on H-ZSM-5 above the desorption temperature of water.<sup>2</sup>)

Finally, we note that the results of Munson *et al.*<sup>1</sup> are completely dominated by bimolecular processes involving physisorbed species. The initial step is the formation of the ether from allyl alcohol, but this is followed by other more complex chemistry. The details of that chemistry both at high and low surface coverages will be presented in detail at a later date.<sup>11</sup>

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### References

- 1 E. J. Munson, T. Xu and J. F. Haw, *J. Chem. Soc., Chem. Commun.*, 1993, 75.
- 2 G. I. Hutchings, D. F. Lee and C. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1990, 1475.
- 3 C. Pereira, G. T. Kokotailo, R. J. Gorte and W. E. Farneth, *J. Phys. Chem.*, 1990, **90**, 2063.
- 4 L. S. Rollman and E. W. Valyocsik, *Inorg. Synth.*, 1983, **61**, 22.
- 5 T. J. Kofke, R. J. Gorte and W. E. Farneth, *J. Catal.*, 1988, **34**, 114.
- 6 K. R. Carduner, M. Villa and D. White, *Rev. Sci. Instrum.*, 1984, **55**, 68.
- 7 G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, 1975, **97**, 1539.
- 8 A. I. Biaglow, R. J. Gorte and D. White, *J. Phys. Chem.* in the press.
- 9 A. Pines, M. G. Gibby and J. S. Waugh, *Chem. Phys. Lett.*, 1972, **15**, 373.
- 10 See, for example, A. Streitwieser and C. H. Heathcock, *Introduction to Organic Chemistry*, Macmillan, New York, 1985, pp. 215 and 536.
- 11 A. I. Biaglow, PhD Dissertation, University of Pennsylvania, 1993.