Catalytic Conversion of Allyl Alcohol to Acetone over the Zeolite H-ZSM-5

Graham J. Hutchings,* Darren F. Lee and Craig D. Williams

Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

Allyl alcohol can be converted to oxygenated products in preference to hydrocarbons using the zeolite catalyst H-ZSM-5; in particular acetone can be produced in high selectivity.

The conversion of alcohols to hydrocarbons using zeolite catalysts is an important industrial reaction and in particular the conversion of methanol to gasoline using the pentasil zeolite H-ZSM-5[1] continues to be a reaction that attracts considerable research interest.[2,3] However, the products of

the conversion of alcohols over zeolite catalysts are almost exclusively hydrocarbons, and ethers are usually the only oxygen containing product. The exclusive loss of oxygen in the products is considered to be due to the reaction mechanism,[4,5] since the alcohol OH group is initially protonated by the
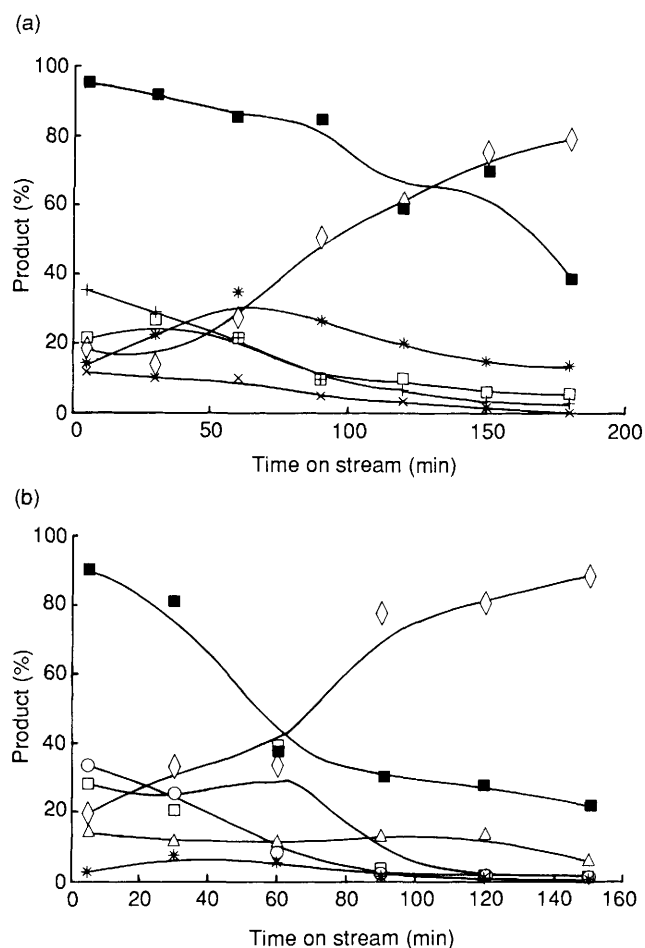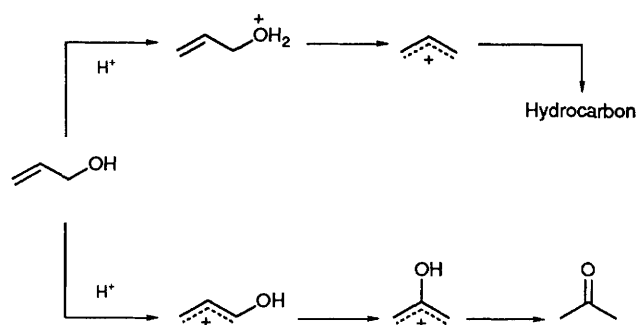
(a)

(b)

Time on stream (min)

Fig. 1 Conversion of allyl alcohol over H-ZSM-5 and product selectivities. (a) 250 °C and (b) 100 °C; + ethene, * propene, □ butenes, × pentenes, ◇ C₃ oxygenates (CH₃COCH₃ + CH₂CHCHO + CH₃CH₂CHO), △ propan-2-ol, ○ dimethyl ether, ■ conversion of allyl alcohol

Scheme 1 Reaction scheme for the conversion of allyl alcohol to acetone

Brønsted acid site of the zeolite and as a consequence water is eliminated from the molecule. In addition, the products of alcohol conversion tend to be non-specific in that a very broad range of C_1–C_{11} hydrocarbons are produced.[1] These features are unfortunate, since considerable advantage would be achieved if the oxygen could be retained in the product. However, to date this aspect of alcohol conversion has received scant attention. We have now successfully addressed this problem and in this communication we report our initial findings for the conversion of allyl alcohol over the zeolite H-ZSM-5 which demonstrate that oxygenated products can be formed in high selectivity.

In a typical experiment allyl alcohol vapour was passed over the proton form of the zeolite H-ZSM-5,[6] (0.5 g), using nitrogen as a carrier gas so that the weight hourly space velocity (WHSV) of allyl alcohol was 0.5 g alcohol.g catalyst⁻¹. h.⁻¹ The products were analysed by gas chromatography and satisfactory mass balance was obtained for all data presented. Blank thermal reaction of allyl alcohol in the absence of zeolite catalysts was found to be negligible. The results for reaction at 250 °C (Fig. 1a) indicate that initially the products consist mainly of hydrocarbons, but as the conver-

sion decreases with catalyst use, the selectivity to oxygenated products CH₃COCH₃, CH₂CHCHO and CH₃CH₂CHO becomes significant. Product identification was confirmed by GCMS and it was found that acetone represented >50% of this oxygenated product. At 100 °C the selectivity to acetone and the other C₃ oxygenates was higher at the expense of conversion (Fig. 1b).

Similar experiments using propan-1-ol in place of allyl alcohol did not yield any C₃ oxygenate products, confirming that the introduction of the carbon–carbon double bond into the reactant molecule significantly affects its reactivity. In particular, allyl alcohol has two functional groups that could be protonated by the Brønsted acid sites of the zeolite. Protonation of the OH group would lead to loss of water via an elimination mechanism resulting in the formation of hydrocarbons as the exclusive products, as demonstrated by propan-1-ol. However, protonation of the carbon–carbon double bond could lead to oxygen retention and this is observed for allyl alcohol at low conversions. Further experiments using allyl alcohol–water mixtures indicated that addition of water markedly decreased the formation of acetone. In addition, propan-2-ol conversion over H-ZSM-5 at low flow rates was found to produce significant yields of acetone indicating that it could be a possible intermediate in the formation of this product, and a possible reaction mechanism consistent with these observations is given in Scheme 1. Further work is now continuing to elucidate fully the reaction mechanism to enable improved yields to be obtained.

References

1 S. A. Tabak and S. Yurchak, Catal. Today, 1990, 6, 307.
2 C. D. Chang, S. D. Hellring and J. A. Pearson, J. Catal., 1989, 115, 282.
3 G. J. Hutchings, L. Jansen van Rensburg, R. G. Copperthwaite, R. Hunter, J. Dwyer and J. Dewing, Catal. Lett., 1990, 6, 7.
4 C. D. Chang, Stud. Surf. Sci. Catal., 1988, 36, 127.
5 G. J. Hutchings and R. Hunter, Catal. Today, 1990, 6, 279.
6 H-ZSM-5 (SiO₂/Al₂O₃ = 35) was prepared according to the method of Howden; M. G. Howden, CSIR Report C. Eng. 413 (CSIR, Pretoria, South Africa, 1982).