# Selectivity Control in the Reaction of Allyl Alcohol Over Zeolite Y

## Graham J. Hutchings and Darren F. Lee

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

Allyl alcohol can be converted into hydrocarbons, acrolein and diallyl ether and control of product selectivity can be achieved by selection of the cation exchanged form of zeolite Y used as catalyst.

In recent years considerable emphasis has been placed on the identification of 'clean technologies' for the chemical industry.[1] At the centre of this research has been the desire to control the product selectivity for reactions since this eradicates the need for the costly processing of non desirable by-products. It is therefore of interest to design research strategies that enable the control of product selectivity, particularly for microporous materials, *e.g.* zeolites, since these are extensively used as catalysts for a range of organic transformations.[2] Recently Dessau[3] demonstrated that selectivity control could be achieved for the conversion of acetylacetone over the zeolite ZSM-5 by use of either the Brönsted acidic proton form (H-ZSM-5) which gave dimethylfuran almost exclusively or the basic form (Na-ZSM-5) which gave methylcyclopentenone almost exclusively. Here we extend this approach to a reaction that has attracted recent attention[4-6] and demonstrate that product selectivity can be readily achieved for the conversion of allyl alcohol over zeolite Y by careful selection of the charge balancing cations associated with the zeolite anionic framework.

Zeolite NaY [Crosfield Chemicals, Si/Al = 2.5 (molar)] was ion-exchanged three times with aqueous ammonium nitrate (0.1 mol l$^{-1}$, 100 °C) recovered by filtration, washed with

distilled water and dried (100 °C, 5 h). The resultant NH$_4$-NaY was calcined (550 °C, 5 h) to form H-NaY with *ca.* 65% Na$^+$ present in the original NaY exchanged for protons. H-NaY was subsequently ion-exchanged using the same method with a solution of the appropriate metal nitrate to obtain Li-HY (0.7% Na$^+$), K-HY (7% Na$^+$, 81.8% K$^+$, 11.2% H$^+$), Cs-HY (19.6% Na$^+$, 59.2% Cs$^+$, 21.2% H$^+$). In addition the NaY was ion-exchanged using the same procedure with the appropriate metal nitrate solutions to form Li-NaY (65.4% Na$^+$), Na-NaY (100% Na$^+$), K-NaY (17.2% Na$^+$) and Cs-NaY (21.1% Na$^+$).

Allyl alcohol, vaporised in a nitrogen carrier gas (feedrate: 0.5 g allyl alcohol g$^{-1}$ catalyst h$^{-1}$), was reacted over the zeolite (0.5 g) in a conventional microreactor at 250 °C. Product analysis was achieved by on-line gas chromatography. No reaction was observed in the absence of a catalyst. The results for each of the zeolite catalysts showing the effect of increasing time on line are shown in Table 1. Following reaction for 3 h the allyl alcohol feed was stopped and the zeolites were treated in a stream of dry nitrogen (20 ml min$^{-1}$, 1 h) to remove any residual volatile hydrocarbon products adsorbed on the catalyst. The zeolites were then cooled in dry nitrogen and analysed for carbon to determine the amount of

**Table 1** Conversion of allyl alcohol over zeolite Y

| Catalyst | *t*/h | Conversion (%) | Products/mol% | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | C$_2$H$_4$ | C$_3$H$_6$ | C$_4$H$_8$ | C$_{4+}$ | acrolein | DAE$^a$ |
| H-NaY | 1 | 100 | 5.1 | 47.8 | 18.7 | 20.3 | 8.1 | 0 |
| | 2 | 41.1 | 3.9 | 45.2 | 9.2 | 11.2 | 28.4 | 2.1 |
| | 3 | 19.2 | 1.5 | 14.8 | 0 | 0 | 77.6 | 6.1 |
| H-LiY | 1 | 98.1 | 2.5 | 51.2 | 8.7 | 11.0 | 26.6 | 0 |
| | 2 | 56.2 | 0.9 | 20.6 | 1.8 | 2.8 | 70.0 | 3.9 |
| | 3 | 45.6 | 0 | 7.6 | tr | 1.4 | 85.7 | 5.3 |
| H-KY | 1 | 86.1 | 1.6 | 42.3 | 2.6 | 5.1 | 48.4 | 0 |
| | 2 | 45.2 | 0.7 | 14.5 | 0.8 | 5.6 | 72.8 | 5.6 |
| | 3 | 30.0 | 0.6 | 6.0 | 1.7 | 1.6 | 83.3 | 6.8 |
| H-CsY | 1 | 29.9 | 0.8 | 14.4 | 0 | 0 | 68.9 | 16.1 |
| | 2 | 24.4 | 0.4 | 10.2 | 0 | 0 | 73.0 | 16.4 |
| | 3 | 17.2 | 0 | 6.0 | 0 | 0 | 81.6 | 12.4 |
| Li-NaY | 1 | 29.3 | 0 | 78.2 | 0 | 0 | 6.1 | 15.7 |
| | 2 | 31.6 | 0 | 25.3 | 0 | 0 | 11.4 | 63.3 |
| | 3 | 27.7 | 0 | 10.8 | 0 | 0 | 9.8 | 79.4 |
| NaY | 1 | 25.7 | 0 | 47.4 | 0 | 0 | 12.1 | 40.5 |
| | 2 | 27.8 | 0 | 11.2 | 0 | 0 | 8.9 | 79.9 |
| | 3 | 23.1 | 0 | 6.5 | 0 | 0 | 10.4 | 83.1 |
| K-NaY | 1 | 24.2 | 0 | 20.7 | 0 | 0 | 16.8 | 62.8 |
| | 2 | 22.8 | 0 | 8.8 | 0 | 0 | 9.2 | 82.1 |
| | 3 | 19.1 | 0 | 5.8 | 0 | 0 | 13.6 | 80.6 |
| Cs-NaY | 1 | 26.1 | 0 | 6.1 | 0 | 0 | 18.8 | 75.1 |
| | 2 | 20.4 | 0 | 2.4 | 0 | 0 | 16.7 | 80.9 |
| | 3 | 19.4 | 0 | 2.5 | 0 | 0 | 11.1 | 86.3 |

$^a$ Diallyl ether

**Table 2** Conversion of allyl alcohol to coke after 3 h reaction

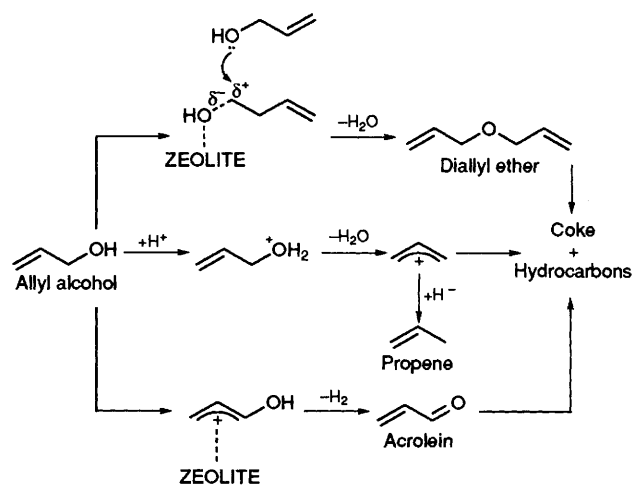| Catalyst | H-NaY | H-LiY | H-KY | H-CsY | Li-NaY | NaY | K-NaY | Cs-NaY |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Carbon (%) | 11.8 | 10.2 | 10.0 | 8.1 | 6.0 | 5.3 | 3.2 | 1.3 |

**Fig. 1** Reaction scheme

coke deposited on the catalyst and the results are given in Table 2.

It is clear from the results that the nature of the charge balancing cation markedly affects the product selectivity for the conversion of allyl alcohol. The catalysts can be considered as two sets. The first set comprises H–NaY, H–LiY, H–KY, H–CsY and these are derived from H–NaY as the parent zeolite which has strong Brönsted acid sites present. IR spectroscopy of the hydroxy region of these zeolites confirmed the presence Brönsted acid sites with the concentration decreasing in the order H–NaY> H–LiY> H–KY>H–CsY. H–NaY was the most active catalyst and initially gave high selectivities to $C_2$–$C_6$ hydrocarbons and coke, which results from the polymerisation of the primary hydrocarbon products on the strong Brönsted acid sites. As the catalyst became deactivated high selectivities to acrolein were observed but this was only after 3 h time on line. Replacing Na$^+$ partially by Li$^+$, K$^+$ and Cs$^+$ decreased the number of strong Brönsted acid sites present and these catalysts demonstrated enhanced initial selectivity to acrolein. In particular H–CsY demonstrates high acrolein selectivity from the start of the reaction and acrolein is the major product. The second set of catalysts comprise Li–NaY, Na–Y, K–NaY, Cs–NaY and these contain weaker Brönsted acid sites. For Li–NaY the major product is

propene, *i.e.* a product resulting from initial dehydration, which in the absence of strong Brönsted acid sites is not reacted further. Replacing Li$^+$ by Na$^+$, K$^+$ and Cs$^+$ results in catalysts with increasing selectivity for diallyl ether which becomes the dominant product with Cs–NaY.

It is therefore apparent that by careful selection and manipulation of the charge balancing cation in zeolite Y, a series of catalysts can be prepared which, for the conversion of allyl alcohol, lead almost exclusively to the formation of either (a) $C_2$–$C_6$ hydrocarbons and coke (H–NaY), (b) acrolein (H–CsY), (c) propene (Li–NaY) or (d) diallyl ether (Cs–NaY). A reaction scheme indicating the possible origin of these products in shown in Fig. 1. Hydrocarbon and coke formation is considered to occur *via* the formation of the allyl cation which has been proposed in a number of recent studies.[4–6] Acrolein formation is *via* a dehydrogenation reaction and hydrogen is observed as a reaction product. The formation of diallyl ether could occur *via* an intermediate resulting from the protonation of allyl alcohol at a weak Brönsted acid site, however Cs–NaY demonstrates the highest diallyl ether selectivity and this catalyst contains the lowest concentration of Brönsted acid sites of all the zeolites examined. We therefore consider that diallyl ether could result from the nucleophilic attack of allyl alcohol on an allyl alcohol for which the hydroxy group is polarised by adsorption on a basic site.

No attempt has been made to optimise these initial results but it is clear that selection of the charge balancing cation of zeolite catalysts can provide a useful parameter enabling the control of reaction selectivity.

## References

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