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Selective conversion of allyl alcohol to oxygenates and hydrocarbons using ion exchanged zeolite Y

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The reaction of allyl alcohol using zeolite Y as catalyst has been investigated and it is shown that it can be converted into a range of products, including hydrocarbons, acrolein and diallyl ether. Control of product selectivity can be achieved by careful selection and manipulation of the charge balancing cation, a series of catalysts can be prepared which, for the conversion of allyl alcohol, lead almost exclusively to the initial 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). The effects of addition of H_2 and H_2O to the reactant are described and discussed with respect to the reaction mechanism and the reaction of potential intermediates (2-propanol and propene oxide) is also described. Mechanisms of formation of the major products are proposed that involve the concerted action of Brønsted acid and basic sites within the zeolite. In particular, since the addition of H_2O does not affect the product distribution, it is considered that the mechanism of hydrocarbon formation does not involve the allyl cation as an intermediate.

Keywords: zeolite Y; allyl alcohol conversion; acrolein; acetone; propene oxide

1. Introduction

The conversion of alcohols to hydrocarbons has been extensively studied for many years, particularly using zeolite catalysts [1,2]. The observation that methanol could be converted to high octane gasoline [3] led to this process being commercialised in New Zealand [4,5]. The conversion of a large range of alcohols and other oxygenates over zeolites has been investigated [3,6] but, in general, a very broad product range is typically observed. For example, over 150 hydrocarbons can readily be obtained from methanol using zeolite H-ZSM-5 [7] and although this product mixture has excellent properties for use as gasoline, this process has little to recommend it for the selective manufacture of a specific hydrocarbon. For the initial applications this lack of chemoselectivity was not a disadvantage but there is at present great interest in designing catalysts that exhibit high product selectivity since this eradicates the need for the costly processing of non-desirable by-products. In addition, alcohol conversion using zeolite catalysts typically only resulted in hydrocarbon products and oxygenates are observed in low selectivities [3]. This is particularly unfortunate in the case of methanol conversion since the oxygen is found almost exclusively in the water product which accounts for 56% of the product mass. The net result of three process steps is therefore to convert natural gas and water to C_{2+} hydrocarbons and water:

$$CH_4 + H_2O \longrightarrow CO + H_2 \longrightarrow CH_3OH \longrightarrow -[CH_2]_x- + H_2O$$

At present, there is considerable interest in the study of catalysts that can be used for the synthesis of fine chemicals and for such applications it is necessary that with alcohol conversion the oxygen is retained in the product molecules. In addition, the requirement for clean technologies has made it necessary 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 there are extensively used as catalysts for a range of organic transformations [8]. Recently, Dassau [9] demonstrated that selectivity control could be achieved for the conversion of acetylacetone over the zeolite ZSM-5 by use of either the Brønsted acidic proton form (H-ZSM-5), which gave dimethylfuran almost exclusively, or the basic form (Na-ZSM-5), which gave methylcyclopentenone almost exclusively. In this paper we extend this approach to the conversion of allyl alcohol, a reaction that has attracted recent attention [10–12], 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.

2. Experimental

2.1. CATALYST PREPARATION AND CHARACTERISATION

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 (7.0% 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^+), NaY (100% Na^+), K-NaY (17.3% Na^+) and Cs-NaY (21.1% Na^+). The degree of ion exchange was determined using X-ray fluorescence and energy dispersive X-ray analysis. The ion-exchanged zeolites were characterised using powder X-ray diffraction before and after ion exchange and calcination. The degree of crystallinity was determined using a standard procedure [13] with NaY as a standard assigned 100% crystallinity. The calcined ion-exchanged zeolites retained high crystallinity: HNaY (>95%), LiHY (>95%), KHY (>90%), CsHY (85%), LiNaY (100%), NaY (100%), KNaY (100%), CsNaY (100%).

2.2. CATALYST TESTING

Allyl alcohol, vaporised in a nitrogen carrier gas (feed rate: 0.5 g allyl alcohol/ g catalyst h), was reacted over the zeolite (0.5 g) in a conventional microreactor at 250°C. Product analysis was achieved by on-line gas chromatography. For all data reported satisfactory mass balances were obtained and no reaction was observed in the absence of catalyst. Following reaction for various reaction times 1–3 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 coke deposited on the catalyst.

3. Results

3.1. ALLYL ALCOHOL CONVERSION OVER ION-EXCHANGED ZEOLITE Y

Allyl alcohol was reacted over zeolite NaHY at 250°C and the effect of time on line is shown in fig. 1. Initially allyl alcohol conversion was 100% and hydrocarbons were the dominant products (99.5% selectivity) and only a trace (0.5%) of acrolein was observed. At longer time on line the catalyst deactivated rapidly and the conversion and hydrocarbon selectivity decreased and the selectivity to acrolein became more significant, in addition diallyl ether and trace levels of acetone and

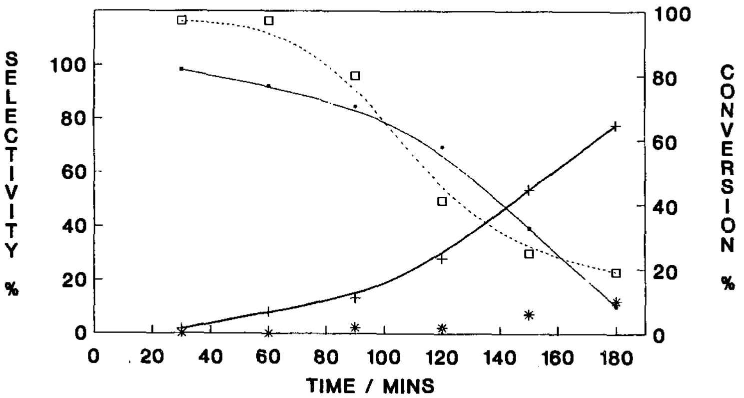


Fig. 1. Reaction of allyl alcohol over H-NaY at 250°C. (□) Conversion; product selectivity: (▪) C_2–C_6; (+) acrolein; (*) diallyl ether.

propene oxide were observed as products. The distribution of hydrocarbons also was a function of the reaction time and in particular the selectivity to propene was enhanced at the expense of C_{4+} hydrocarbons.

Allyl alcohol was then reacted individually at 250°C over the ion-exchanged zeolites and the results are shown in tables 1 and 2 and figs. 2–4. 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 Brønsted acid sites present. The infrared spectrum of the hydroxyl region of these zeolites was studied at 250°C in flowing nitrogen in an in situ diffuse reflectance cell. The results (fig. 5) confirmed the presence of Brønsted acid sites with the concentration decreasing in the order H-NaY > H-LiY > H-KY > H-CsY for the first set. For this series H-NaY was the most active catalyst and initially gave high selectivities to C_2–C_6 hydrocarbons and, 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 Brønsted 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

Table 1
Conversion of allyl alcohol over zeolite H-MY

Catalyst	Time (h)	Conv. (%)	Products (mol%)					
			C_2H_4	C_3H_6	C_4H_8	C_{4+}	acrolein	DAE[a]
H-NaY	0.5	100	5.7	41.3	25.8	26.7	0.5	0
	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	0.5	100	3.8	64.2	15.8	14.0	2.0	0
	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	0.5	98.9	2.3	82.6	3.8	4.8	6.5	0
	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	0.5	57.7	0.8	15.4	0	0	78.5	5.3
	1	29.9	0.6	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

[a] Diallyl ether.

Table 2
Conversion of allyl alcohol over zeolite M-Y

Catalyst	Time (h)	Conv. (%)	Products[a] (mol%)					
			C_2H_4	C_3H_6	C_4H_8	C_{4+}	acrolein	DAE[b]
Li-NaY	0.5	30.5	0	82.0	0	0	8.2	9.8
	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	0.5	26.1	0	57.4	0	0	11.5	31.1
	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	0.5	30.2	0	26.5	0	0	13.2	60.3
	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	0.5	33.5	0	11.0	0	0	22.7	66.3
	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] Products excluding acetone and propene oxide.
[b] Diallyl ether.

acrolein is the major product (fig. 2). The second set of catalysts comprise Li-NaY, Na-Y, K-NaY, Cs-NaY and these contain a lower number of weaker Brønsted acid sites as evidenced by the infrared spectrum of the hydroxyl region

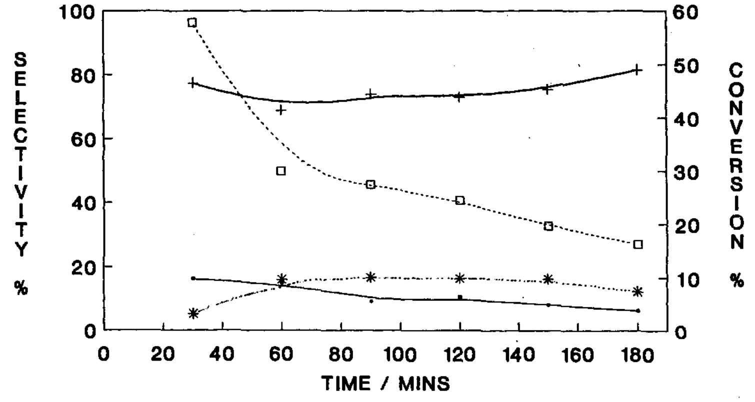


Fig. 2. Reaction of allyl alcohol over H-CsY at 250°C. (□) Conversion; product selectivity: (▪) C_2–C_3; (+) acrolein; (∗) diallyl ether.

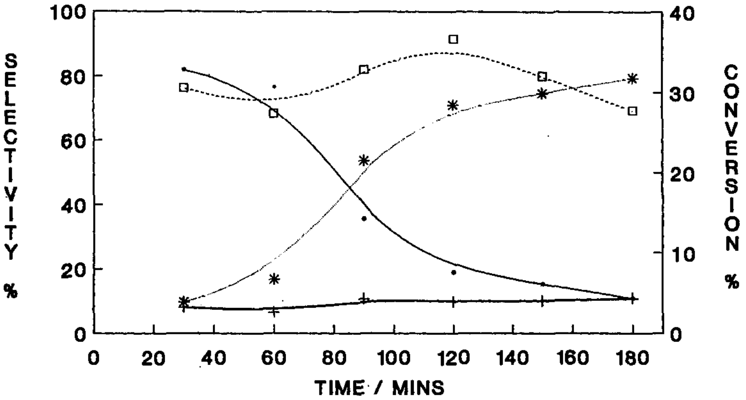


Fig. 3. Reaction of allyl alcohol over Li-NaY at 250°C. (□) Conversion; product selectivity: (▪) C_2–C_4; (+) acrolein; (∗) diallyl ether.

(fig. 5). For Li-NaY the major product is propene which in the absence of strong Brønsted acid sites is not reacted further (fig. 3). Replacing Li^+ by Na^+, K^+ and Cs^+ results in catalysts with increasing selectivity for diallyl ether which becomes the dominant product with Cs-NaY (fig. 4).

It is apparent that catalysts containing Brønsted acid sites deactivate during use. To investigate this the zeolites were reacted separately for 1, 2 and 3 h following which time 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 coke deposited on the catalyst and the results are given in table 3. The coke is considered to result from the polymerisation of the primary hydrocarbon and oxygenated products on the strong Brønsted acid sites.

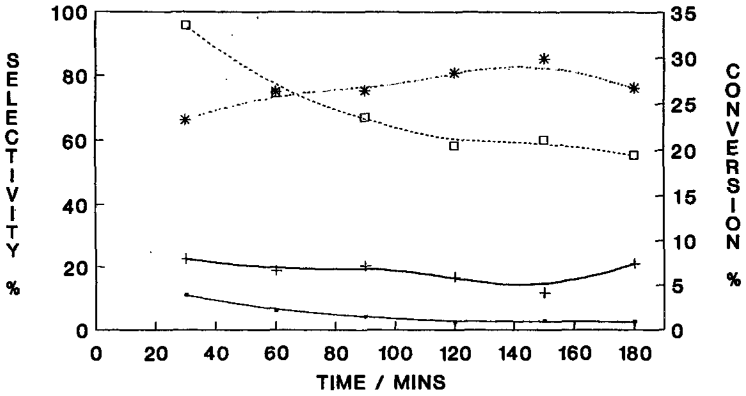


Fig. 4. Reaction of allyl alcohol over Cs-NaY at 250°C. (□) Conversion; product selectivity: (▪) propene; (+) acrolein; (∗) diallyl ether.

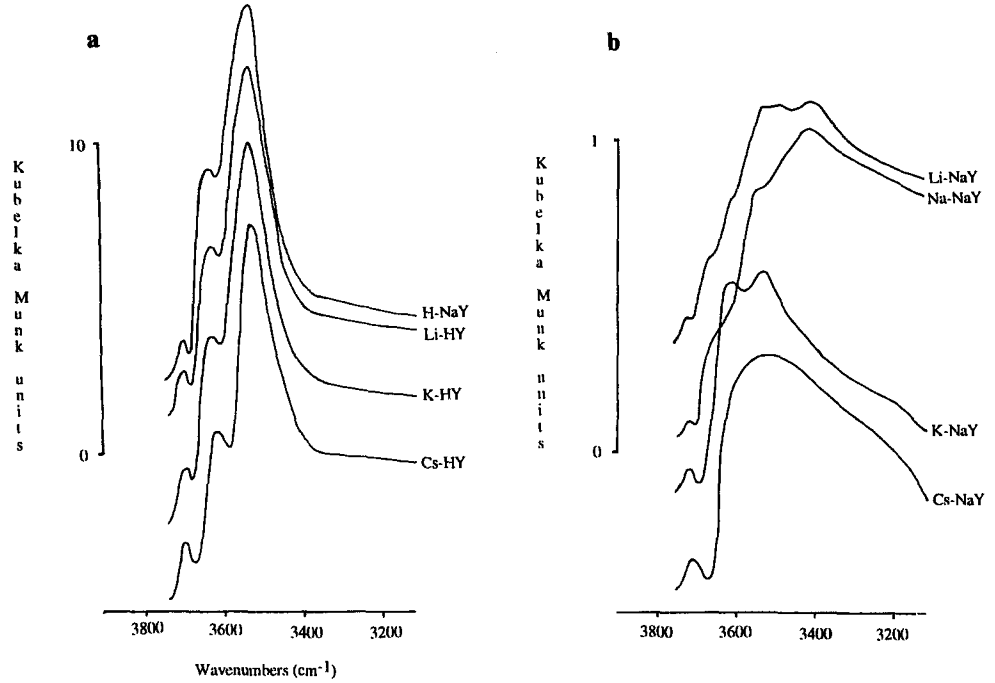


Fig. 5. Hydroxyl region of the infrared spectra of the ion-exchanged zeolites, (a) H-MY, (b) M-NaY.

3.2. ALLYL ALCOHOL CONVERSION OVER NaY WITH CO-FED H_2 AND H_2O

Allyl alcohol was reacted over NaY at various temperatures to study the formation of the minor oxygenated products (table 4). At temperatures <200°C the initial allyl alcohol conversion was <5%, at higher temperatures propene was the major product which decreased in selectivity as the catalyst deactivated. The selectivity to acrolein was enhanced at the higher temperatures, whereas diallyl ether was not observed at temperatures >250°C, and the selectivity to acrolein increased as the catalyst deactivated. Acetone and propene oxide decreased in selectivity at the higher temperature; in addition trace levels of propanal were observed at all reaction times. Co-feeding hydrogen (20% hydrogen in the nitrogen carrier at 250°C) significantly enhanced conversion and the formation of propene oxide and

Table 3
Conversion of allyl alcohol to coke over the different catalysts

Time (h)	Coke yield (g/100 g allyl alcohol)							
	H-NaY	H-LiY	H-KY	H-CsY	Li-NaY	NaY	K-NaY	Cs-NaY
1	6.3	5.9	5.0	3.1	1.8	1.5	0.7	0.2
2	6.9	6.4	6.1	4.0	2.3	2.1	1.3	0.6
3	7.4	6.4	6.2	5.0	3.8	3.3	2.0	0.8

Table 4
Effect of temperature on the conversion of allyl alcohol over NaY

Temp. (°C)	Time (h)	Conv. (%)	Products (mol%)							
			C_2H_4	C_3H_6	C_4H_8	C_{4+}	propene oxide	acrolein	acetone	DAE
250	0.5	26.3	2.3	57.8	1.9	14.8	2.3	9.5	0	11.4
	1.0	21.3	1.4	33.8	0.9	8.8	2.1	26.8	1.4	24.8
	2.0	17.3	1.1	27.8	1.6	7.7	2.4	19.4	2.2	38.9
	3.0	13.5	1.5	23.7	0.7	7.0	1.9	23.7	3.0	38.5
275	0.5	60.7	4.6	70.2	9.4	6.4	1.0	8.4	0	0
	1.0	40.9	4.4	62.1	6.4	6.2	2.3	14.2	4.4	0
	2.0	30.9	2.5	39.5	3.9	3.4	1.5	46.0	3.2	0
	3.0	22.0	0	31.8	5.5	2.4	2.1	54.5	3.7	0
350	0.5	74.1	3.4	44.5	5.6	6.4	2.0	36.8	0	0
	1.0	66.2	3.4	48.6	3.0	3.5	1.0	39.3	tr	0
	2.0	41.4	3.4	27.8	2.4	2.0	0.7	62.9	tr	0
	3.0	20.0	0	17.9	2.6	2.2	0.4	76.9	0	0

acetone (table 5). Co-feeding 2 and 5% water at 250°C did not significantly affect the observed catalytic performance (table 5). For all these reactions over NaY the coke formation was determined as described previously and the results are shown in table 6.

Table 5
Effect of co-feeding hydrogen and water on the conversion of allyl alcohol over NaY at 250°C

Cofeed	Time (h)	Conv. (%)	Products (mol%)							
			C_2H_4	C_3H_6	C_4H_8	C_{4+}	propene oxide	acrolein	acetone	DAE
20% H_2	0.5	64.0	2.8	65.6	5.6	5.6	6.8	13.7	0	0
	1.0	30.6	2.3	48.7	4.6	5.5	7.8	16.3	4.3	10.5
	2.0	22.6	1.3	30.5	2.7	3.1	11.1	21.7	9.7	19.9
	3.0	13.8	1.4	20.3	2.1	2.9	2.9	32.2	2.9	35.3
2% H_2O	0.5	33.9	2.7	55.7	2.1	2.9	0.9	31.6	0	4.1
	1.0	22.1	2.7	47.5	1.8	3.6	1.4	28.5	0	14.5
	2.0	16.7	1.2	34.1	1.8	3.6	1.8	16.0	2.4	39.1
	3.0	16.4	1.8	33.5	1.8	3.0	1.8	15.2	3.0	39.9
5% H_2O	0.5	36.7	4.4	54.5	2.7	3.3	3.0	23.7	0.3	8.1
	1.0	24.0	2.0	41.3	2.0	2.2	1.6	26.0	0.9	24.0
	2.0	17.8	1.7	32.6	2.2	1.9	1.4	19.7	3.3	37.2
	3.0	11.8	1.7	22.9	0.8	1.0	2.2	21.0	4.0	46.4

Table 6
Conversion of allyl alcohol to coke

Time (h)	Allyl alcohol % converted to coke					
	NaY 250°C	NaY 275°C	NaY 350°C	NaY 20% H_2	NaY 2% H_2O	NaY 5% H_2O
1.0	7.7	8.7	16.5	13.1	7.1	7.2
2.0	7.0	7.8	14.2	10.7	6.7	6.8
3.0	5.6	6.2	8.5	7.8	5.2	5.3

3.3. REACTION OF ISOPROPANOL AND PROPENE OXIDE OVER NaY

Isopropanol was reacted over NaY using identical reaction conditions to allyl alcohol at 250°C and propene was observed to be the only product. It was found that the initial conversion was 5% at 30 min time on line, i.e. considerably lower than that observed for allyl alcohol at these conditions (26%).

Propene oxide was reacted over NaY using identical reaction conditions to allyl alcohol at 250°C and the results are shown in table 7. Propene, allyl alcohol, propanal and acetone were the observed products but propene was only observed at the initial time on line.

4. Discussion

It is apparent from the results of this study 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 initial 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). Hence, as has been previously demonstrated by Dessau [9], the nature of the charge balancing cation can control the product selectivity and this control is achieved by the creation of active sites with specific features.

It is of interest to consider the mechanism of formation of the products in this

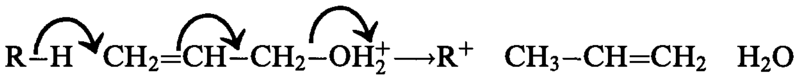
Table 7
Conversion of propene oxide over NaY at 250°C

Time (h)	Conv. (%)	Products (mol%)			
		C_3H_6	allyl alcohol	propanol	acetone
0.5	100	7.9	19.3	66.5	6.3
1.0	98.0	1.0	5.1	68.4	25.5
2.0	91.3	0.3	5.5	76.1	18.1
3.0	70.0	0	12.6	72.9	14.6

reaction system. It should be noted that the oxidation level of allyl alcohol is that of an alkyne and to form the dominant reaction products, i.e. acrolein and alkenes, requires either a formal oxidation or reduction. To form propene an oxygen atom must be removed as water and this requires the formal addition of H_2 to the allyl alcohol, whereas to form acrolein requires the formal removal of H_2 from allyl alcohol. In the presence of Brønsted acid and base sites the formal addition or removal of H_2 can be achieved via H^+ and H^- transfers.

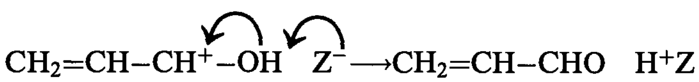
4.1. FORMATION OF HYDROCARBONS

The formation of C_2–C_6 hydrocarbons and coke is dominant for zeolite NaHY and decreases across the series NaHY > LiHY > KHY > CsHY, which is consistent with the Brønsted acidity of these ion-exchanged zeolites. It is therefore proposed that strong Brønsted acid sites are necessary for the formation of C_2–C_6 hydrocarbons and coke and hence the initial process involves the protonation of allyl alcohol. A number of recent studies have addressed this reaction and in particular have involved the use of in situ MAS NMR [10–12]. It has been proposed that the protonated allyl alcohol $CH_2CHCH_2OH_2^+$ eliminates water to form the allyl cation $CH_2^+CHCH_2$, as a reactive intermediate. The allyl cation is known to be highly reactive and has not been isolated to date, the MAS NMR evidence is not conclusive partly due to the timescale of this technique being much slower than the lifetime of the allyl cation. For example, Munson et al. [10] investigated the reaction of ^{13}C labelled allyl alcohol over CsX zeolite using in situ MAS NMR and showed that the ^{13}C label was scrambled from the C_1 to the C_3 positions. They considered that this was evidence in favour of the formation of an allyl cation intermediate. However, the formation of an allyl cation would be expected to lead to the formation of some hydrocarbons and this was not observed. Also the re-formation of allyl alcohol from the allyl cation would necessitate attack by the water formed in the initial dehydration which would be expected to form 2-propanol in preference to allyl alcohol. In our study the results of the water co-feeding experiments are considered to be significant since the addition of 2 and 5% water to the reactants does not affect the formation of hydrocarbons or coke to any extent. This in contrast to the effect of water on the related reaction of methanol conversion over zeolite catalysts [1]. In the methanol reaction the addition of water leads to a decrease in conversion and the average carbon number of the hydrocarbon product. This reaction is considered to involve the surface methyl cation as a central intermediate [2] and the observed effects of water are consistent with this. The allyl cation would be expected to be very reactive towards water and it would be expected to significantly change the product distribution, which is not observed. Hence we consider that the allyl cation is not an intermediate in the conversion of allyl alcohol. The formation of hydrocarbons clearly requires the involvement of protonation and dehydration and we propose that the protonated allyl alcohol scavenges a hydrogen atom as H^- to yield propene which would subsequently oligomerise and crack to form the observed products via known acid catalysed reactions:



$$R{-}H\ \ CH_2{=}CH{-}CH_2{-}OH_2^+ \longrightarrow R^+\quad CH_3{-}CH{=}CH_2\quad H_2O \tag{1}$$

This mechanism can also be used to explain the high selectivities to propene observed for allyl alcohol conversion over LiHY, since in the absence of strong Brønsted sites the propene would not be reacted in the secondary reactions. The most likely hydride source in the initial stages of the reaction is probably the hydrogen α to the allyl alcohol hydroxyl group. Abstraction of this hydrogen as hydride would result in the formation of the CHO cation, which could either oligomerise with other molecules of allyl alcohol which would eventually lead to coke formation or react with a basic site in the zeolite to form acrolein:

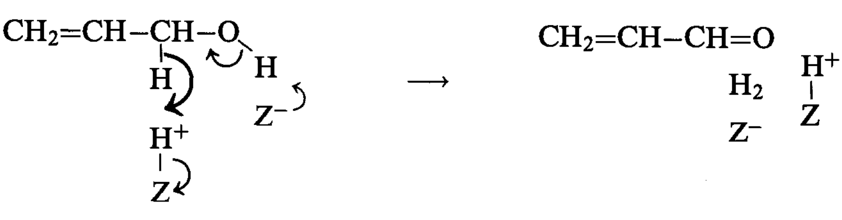


$$CH_2{=}CH{-}CH^+{-}OH\ \ Z^- \longrightarrow CH_2{=}CH{-}CHO\quad H^+Z \tag{2}$$

For the zeolite NaHY the dominant process would be expected to be coke formation due to the lack of a significant concentration of basic sites.

4.2. FORMATION OF ACROLEIN

The formation of acrolein is most pronounced for the ion-exchanged zeolites containing Brønsted acid sites and in particular with CsHY when it is the dominant product. Reaction schemes (1) and (2) can be used to explain the combined formation of hydrocarbons and acrolein in at most equal molar quantities but such processes cannot be used to explain the almost exclusive formation of acrolein over CsHY. It is therefore apparent that a different process must be occurring for this zeolite. It is interesting to note that for the series of ion-exchanged zeolites NaHY, LiHY, KHY the selectivity to acrolein increases as the catalyst deactivates due to coke formation. It is clear that the formation of acrolein requires Brønsted acid sites on the catalyst to initiate the dehydrogenation reaction. In addition it is apparent that strong basicity is also required. We propose that these sites act in concert to form acrolein in the following manner:



$$\begin{array}{l} CH_2{=}CH{-}\underset{\displaystyle H}{CH}{-}O{-}H \\ \qquad\quad H^+ \qquad Z^- \\ \qquad\quad \,| \\ \qquad\quad Z \end{array} \longrightarrow \begin{array}{l} CH_2{=}CH{-}CH{=}O \\ \qquad\quad H_2 \quad H^+ \\ \qquad\quad Z^- \quad\ \ \,| \\ \qquad\qquad\quad\ \ Z \end{array} \tag{3}$$

Such a proposal is consistent with the experimental observation that the Cs-exchanged zeolite Y that contains Brønsted acid sites gives the highest yields of acrolein.

4.3. FORMATION OF DIALLYL ETHER

Diallyl ether is the dominant product with zeolite CsNaY and decreases across the series CsNaY > KNaY > NaY > LiNaY. The formation of diallyl ether could occur via an intermediate resulting from the protonation of allyl alcohol at a weak Brønsted acid site, however Cs-NaY demonstrates the highest diallyl ether selectivity and this catalyst contains the lowest concentration of Brønsted 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 hydroxyl group is polarised by adsorption on a basic site.

4.4. FORMATION OF ACETONE AND PROPENE OXIDE

Acetone and propene oxide are observed as minor products from the conversion of allyl alcohol over ion-exchanged zeolite Y. The addition of hydrogen to the reactants significantly enhanced the formation of acetone and propene oxide as well as increasing the allyl alcohol conversion. This finding again emphasises the difference between the zeolite catalysed reaction of allyl alcohol and methanol, since addition of hydrogen to the methanol conversion reaction leads to no marked effects being observed [13]. Recently Ebitani et al. [14] indicated that treatment of a zeolite with molecular hydrogen followed by heat treatment led to an increase in Brønsted acid sites relative to Lewis acid sites and Sano et al. [15] demonstrated that ethene could be hydrogenated by H-ZSM-5 in the presence of molecular hydrogen. Both these studies indicate that hydrogen can interact with the zeolite framework and this may be one of the effects responsible for the increased conversion. It is also possible that the presence of hydrogen decreases the rate of coke formation thereby increasing conversion.

The formation of acetone is of mechanistic interest since it is possible that it could be formed either by addition of an oxygen containing species to a deoxygenated intermediate (e.g. via the formation of 2-propanol formed by the reaction of water with the allyl cation) or via an internal oxygen transfer. When water was added to the reactants no increase was observed in the formation of acetone. In addition reaction of 2-propanol over NaY at 250°C resulted only in the formation of propene and no acetone was observed. These observations indicate that acetone is most likely to be formed via an internal oxygen transfer reaction. In addition the reaction of propene oxide over NaY at 250°C indicated that both allyl alcohol and acetone were readily formed in addition to propanol, which is also observed as a minor product from allyl alcohol conversion. It is therefore possible that the formation of propanal, acetone and propene oxide are mechanistically related. The formation of a ketone from the corresponding aldehyde can occur under acidic condition and can involve the formation of a protonated oxirane [16]. The observation that propene oxide and acetone are enhanced by the presence of hydrogen is also consistent with such a scheme since the formation of hydrogenated oxygenates would be favoured under these conditions.

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