A combined MAS nuclear magnetic resonance spectroscopy, in situ FT infrared spectroscopy and catalytic study of the conversion of allyl alcohol over zeolite catalysts

Michael W. Anderson[a], John Dwyer[a], Graham J. Hutchings[b], Darren F. Lee[b], Marina Makarova[a] and Bodo Zibrowius[a]

[a] *Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, UK*
[b] *Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK*

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A combined study of allyl alcohol conversion over zeolite catalysts using catalytic measurements in a flow microreactor, in situ FTIR and MAS NMR spectroscopy is reported. Rate constants for the conversion in the flow reactor and the static in situ reactor used in the FTIR studies are in broad agreement, emphasising the viability of the experimental approach. In the flow microreactor allyl alcohol conversion over the zeolite catalyst is shown to form diallyl ether, hydrocarbons and acrolein. The in situ study successfully models the formation of diallyl ether and hydrocarbon as initial reaction products, but unfortunately acrolein is found to be rapidly converted to hydrocarbons under the condition used in the in situ cells. The studies are combined to provide a model for the reaction which involves two parallel pathways for the formation of the hydrocarbons and acrolein.

Keywords: zeolites: ZSM-5, HY, Cs-H-Y; allyl alcohol conversion; in situ MAS NMR; in situ FTIR

1. Introduction

The conversion of alcohols to hydrocarbons using zeolite catalysts has been extensively studied. In part this interest lies in the technological importance of the methanol to gasoline process [1,2], but it is also because of the mechanistic significance of these alcohol transformation reactions. For the most part the conversion of aliphatic alcohols leads to the formation of either the corresponding ether as the only oxygenated product or a diverse range of hydrocarbons. For example, over 200 hydrocarbon products are obtained from the methanol conversion reaction over zeolite H-ZSM-5. Recently, we have shown that for the conversion of allyl alcohol over zeolites Y and ZSM-5 [3] a much narrower product distribution is observed and, in particular, oxygenates (acrolein, diallyl ether and acetone) can be obtained as the major products. In a recent study, Munsen et al. [4] have studied allyl alcohol conversion over zeolites H-ZSM-5 and CsHX using MAS NMR spectroscopy. From their studies they concluded that there was evidence to support the existence of an allyl cation intermediate that had previously been proposed in our earlier study [3]. In this paper we present the results of a combined MAS NMR, in situ FTIR and catalytic study of this reaction in an attempt to elucidate aspects of this complex reaction.

2. Experimental

2.1. CATALYST PREPARATION

The zeolites used in this study were H-ZSM-5 and Na-ZSM-5 (Si/Al = 12 and 25) prepared according to a standard procedure [5], and Na-Y obtained commercially (Unilever, Si/Al ratio 3.3). H-Y was prepared by ion exchange of NaY with ammonium nitrate (0.1 mol/ℓ, 100°C) followed by drying and calcination. Cs-H-Y was prepared by ion exchange of H-Y with aqueous caesium nitrate (0.1 mol/ℓ, 100°C) to give 59% Cs exchange.

2.2. CATALYST TESTING

The catalytic reactions were carried out using a fixed bed microreactor. Allyl alcohol was fed to the reactor using a calibrated syringe pump so as to achieve a feedrate of 0.5 g/g catalyst h and vaporised in a stream of dry nitrogen (30 ml/min). The allyl alcohol vapour was then reacted over the zeolite catalyst (0.5 g) in a thermostatically controlled microreactor (i.d. = 10 mm). The products were analysed using on-line gas chromatography; in addition, products were collected in a low temperature trap and analysed using GC mass spectroscopy (VG 707E with DEC PDP 11-24 data system). Blank thermal reactions in the absence of catalysts were found to be negligible and satisfactory mass balances were obtained for all data presented.

2.3. FTIR STUDIES

FTIR spectra were recorded using a Cygnus-100 Mattson FTIR spectrometer in the spectral region 4000–1300 cm^{-1} with 2 cm^{-1} resolution and typically 10 scans. A detailed description of the in situ infrared cell is given elsewhere [6]. The cell was on-line to the vacuum rig and had a liquid-injecting system (silicon septum/microsyringe). It had a thermostatic zone which facilitates recording spectra at high temperatures during the course of reaction.

A self-supported disk of zeolite (10 mg, $\rho \approx 5$ mg/cm^{-2}) was placed into the cell and calcined under vacuum at 350°C overnight. A separate experiment using pyridine adsorption demonstrated that such a pretreatment does not create any Lewis acidity in the sample, and ammonia titration showed that every aluminium atom is compensated by an acidic proton. The sample was then cooled to 100°C and a spectrum of the initial sample was collected for reference purposes. The portion of allyl alcohol ($[C_3H_5OH] : [Z{-}OH] = 1 : 1$) was injected into the cell and this was considered as a starting point of the reaction. Subsequently spectra were recorded from time to time to monitor the kinetics of reaction.

2.4. MAS NMR STUDIES

Sample preparation. The zeolite powder (ca. 100 mg) was heated (50°C/h) under vacuum to the activation temperature of 400°C where it was kept under a pressure below 10^{-1} Pa for 24 h. Then the zeolite was cooled to room temperature and loaded with about 1 molecule allyl alcohol per 24 T atoms corresponding to about 0.07 mmol. In order to mimic the effect of the time-on-stream on the performance of the ZSM-5 catalysts, the samples were kept for 1 h at 100°C and all volatile products were subsequently pumped off. This loading-reaction-pumping (lrp) cycle was performed 1–3 times for H-ZSM-5 and Na-ZSM-5 which are denoted H-*n* and Na-*n* ($n = 1$–3). Finally, all samples were loaded with 1 molecule allyl alcohol per 24 T atoms and sealed. For the Cs-HY zeolite loaded with allyl alcohol and ZSM-5 loaded with acrolein, no lrp cycles were used but all the other conditions were identical.

NMR measurements. All ^{13}C MAS NMR measurements were performed on a Bruker MSL 400 spectrometer at a resonance frequency of 100.6 MHz. To increase the sensitivity, some spectra were recorded using the cross-polarisation (CP) technique. In all cases high-power proton decoupling was applied. Spinning speeds between 1.5 and 2.5 kHz were achieved for the sealed capsules in 7mm rotors (ZrO_2) with the standard double-bearing MAS probe. To remove spinning side bands from the spectrum, some measurements were performed using a TOSS pulse sequence. Since no ^{13}C enriched allyl alcohol was used, between 2000 and 40000 scans with repetition times between 2 and 5 s (CP) and 4 and 10 s (SPE, single pulse excitation), respectively, were necessary to achieve a reasonable signal-to-noise ratio.

3. Results

3.1. CATALYTIC STUDIES

3.1.1. Conversion of allyl alcohol over ZSM-5

The results for the conversion of allyl alcohol (WHSV = 0.5 h^{-1}) over H-ZSM-5 at 100°C are shown in fig. 1. At this temperature the products comprise, almost

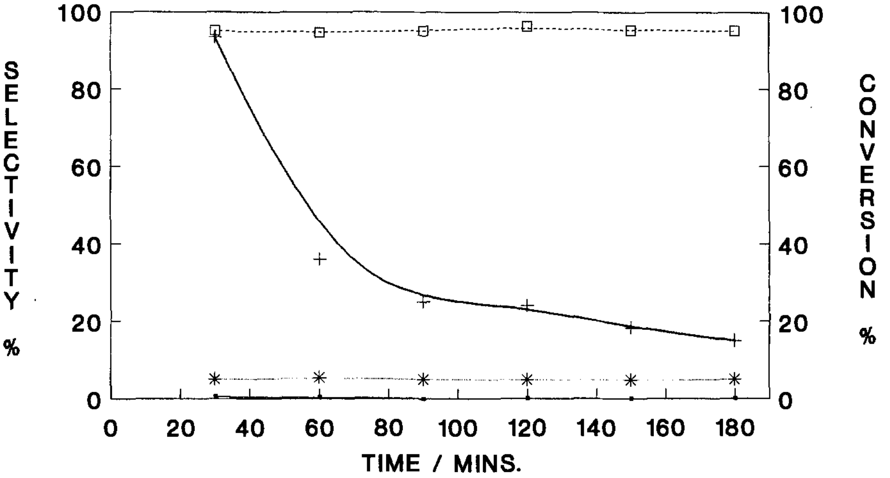


Fig. 1. Allyl alcohol conversion over H-ZSM-5 at 100°C. (+) Conversion; product selectivity: (□) diallyl ether, (■) propene, (∗) acrolein.

exclusively, of diallyl ether (ca. 95%) and a low selectivity (ca. 5%) to acrolein. Initially, there are very low amounts of propene formed, but after 60 min time-on-line, propene is no longer formed. At 100°C the rate constant for allyl alcohol conversion is calculated as 1.2×10^{-4} s^{-1}. At 100°C no conversion of allyl alcohol was observed over Na-ZSM-5.

Allyl alcohol conversion over H-ZSM-5 at 250°C (fig. 2) initially gives mainly hydrocarbon products. However, as the catalyst deactivates due to coke deposition, selectivity to hydrocarbons decreases and the selectivity to acrolein becomes significant. For Na-ZSM-5 at 250°C, the results for the conversion of allyl alcohol (fig. 3) show that the products are mainly acrolein and diallyl ether. Initially there is a low selectivity to hydrocarbon products, but this rapidly declines.

3.1.2. Conversion of allyl alcohol over zeolite Y

The results for the conversion of allyl alcohol over H-Y and Cs-HY at 250°C are shown in fig. 4. For zeolite H-Y the products at 30 min time-on-line are exclusively hydrocarbons, but as the catalyst deactivates, significant selectivities to acrolein are observed. For Cs-HY at 250°C the selectivity to acrolein is initially high (ca. 80%) and there is very little effect of time-on-line on the catalytic performance.

3.2. IN SITU FTIR STUDIES

The difference spectrum 1 min after the injection of allyl alcohol into the IR cell (i.e. the spectrum of the sample after adsorption minus the spectrum of the initial zeolite) shows the changes in IR absorbency caused by alcohol adsorption at 100°C (fig. 5). The hydroxyl band of H-ZSM-5 at 3610 cm^{-1} disappears giving rise to three broad components from hydrogen-bonded hydroxyls, at ~ 2900,

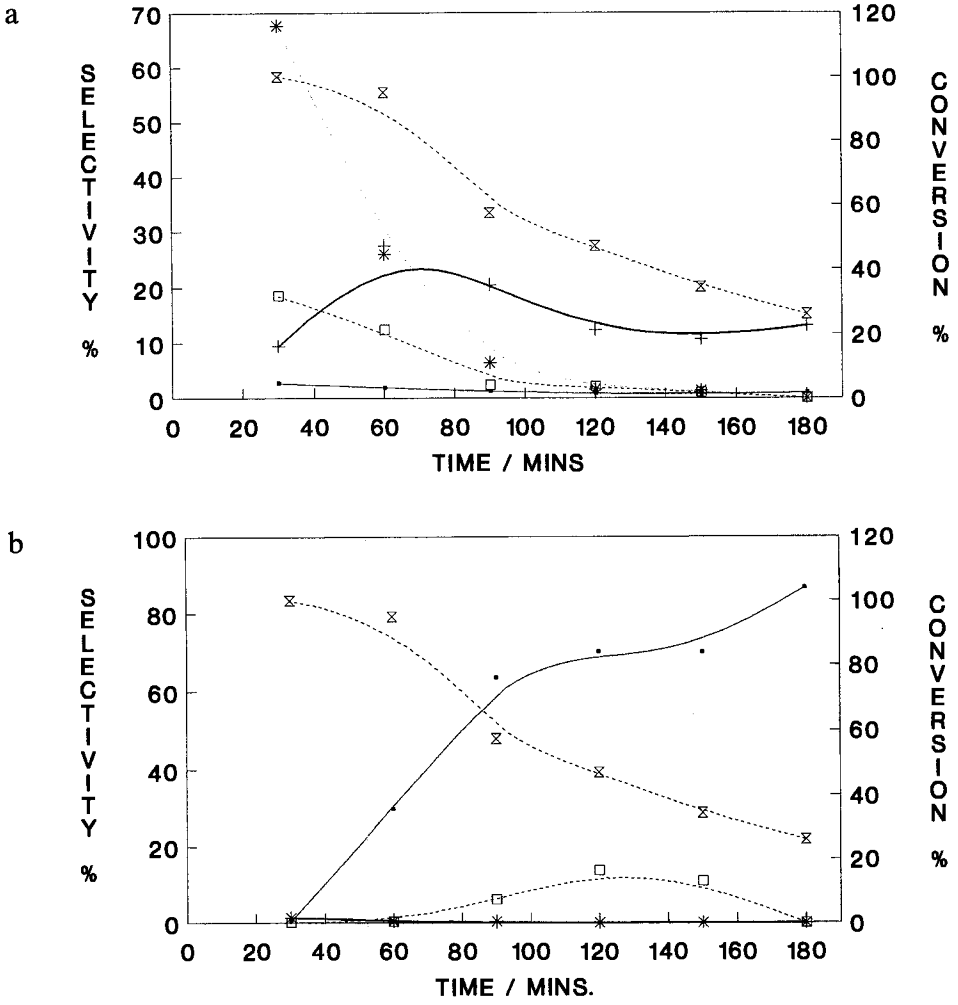


Fig. 2. Allyl alcohol conversion over H-ZSM-5 at 250°C. (⧖) Conversion; (a) hydrocarbon product selectivity: (■) ethene, (+) propene, (*) C_4, (□) C_5, (b) oxygenated product selectivity: (■) acrolein, (□) diallyl ether, (*) acetone.

~ 2380, ~ 1660 cm^{-1}. Also, peaks from adsorbed alcohol molecules are observed: a number of modes at 2890–2990 cm^{-1} from C–H stretching vibrations in the aliphatic groups, at 3092 cm^{-1} from C–H stretching vibrations near C=C double bond and at 1424 cm^{-1} from C–H deformation vibration. A broad peak at 3536 cm^{-1} corresponds to the OH groups in alcohol.

With increased time of reaction, the following bands reduce their intensities (fig. 5):

(1) ν_{OH} (alcohol) at 3536 cm^{-1};
(2) ν_{C-H} (C=C) at 3092 cm^{-1};
(3) ν_{C-H}(–CH_2–) at 1424 cm^{-1}.

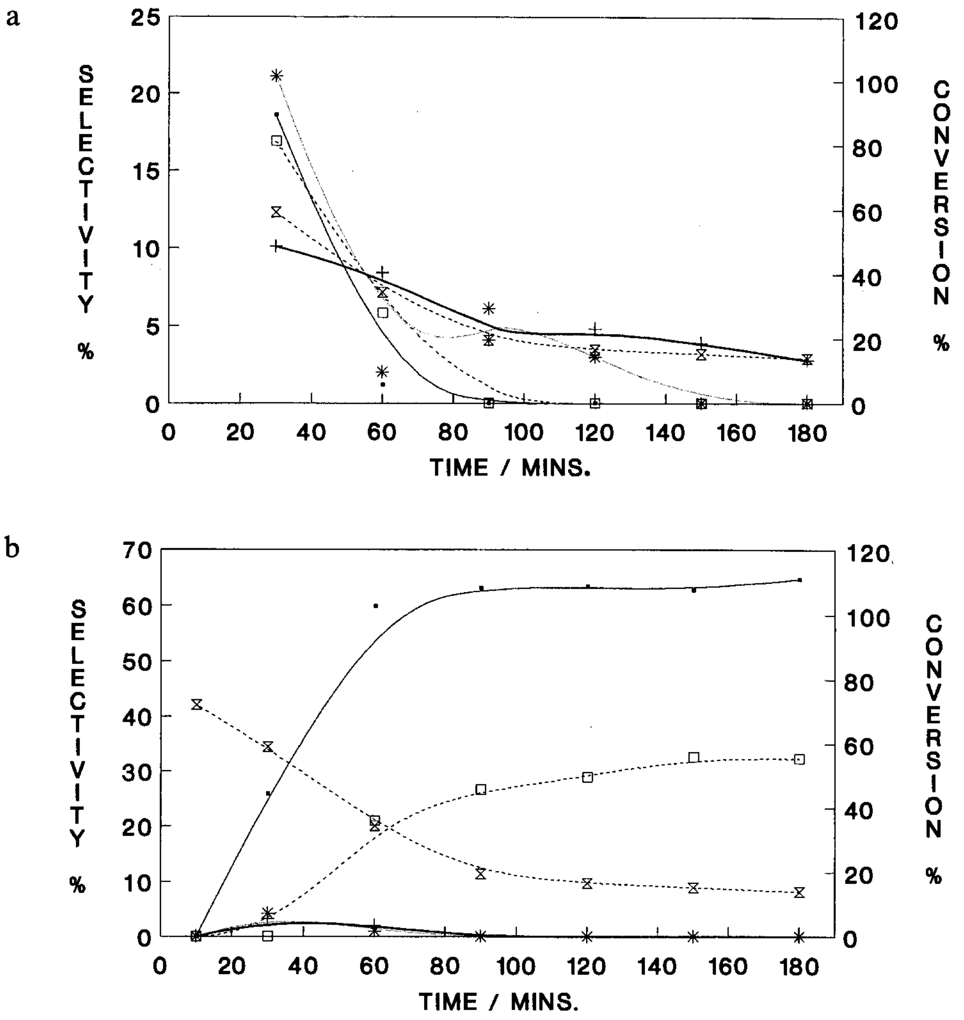


Fig. 3. Allyl alcohol conversion over Na-ZSM-5 at 250°C. (⧖) Conversion; (a) hydrocarbon product selectivity: (■) ethene, (+) propene, (*) C_4, (□) C_5, (b) oxygenated product selectivity: (■) acrolein, (*) acetone, (+) propene oxide, (□) diallyl ether.

Moreover, new bands at 1610, 1543, 1520 and 1466 cm^{-1} appear and increase in intensity, reflecting, most probably the formation of aromatics [7]. Also some rearrangements in the region at 2890–2990 cm^{-1} are observed. No bands from adsorbed water (at 1640 cm^{-1}) have been detected. However, the absence of water does not provide any information concerning the occurrence of the dehydration reaction, since it is possible that water is not detected in the spectra because it is desorbed into the gas phase under these conditions.

All these features show that a process of alcohol transformation takes place. The kinetics of this process were followed using I_{3536}, I_{1424} and I_{1610}. As seen from fig. 6a, the decrease in the intensity of the ν_{OH} and ν_{C-H} takes place simultaneously

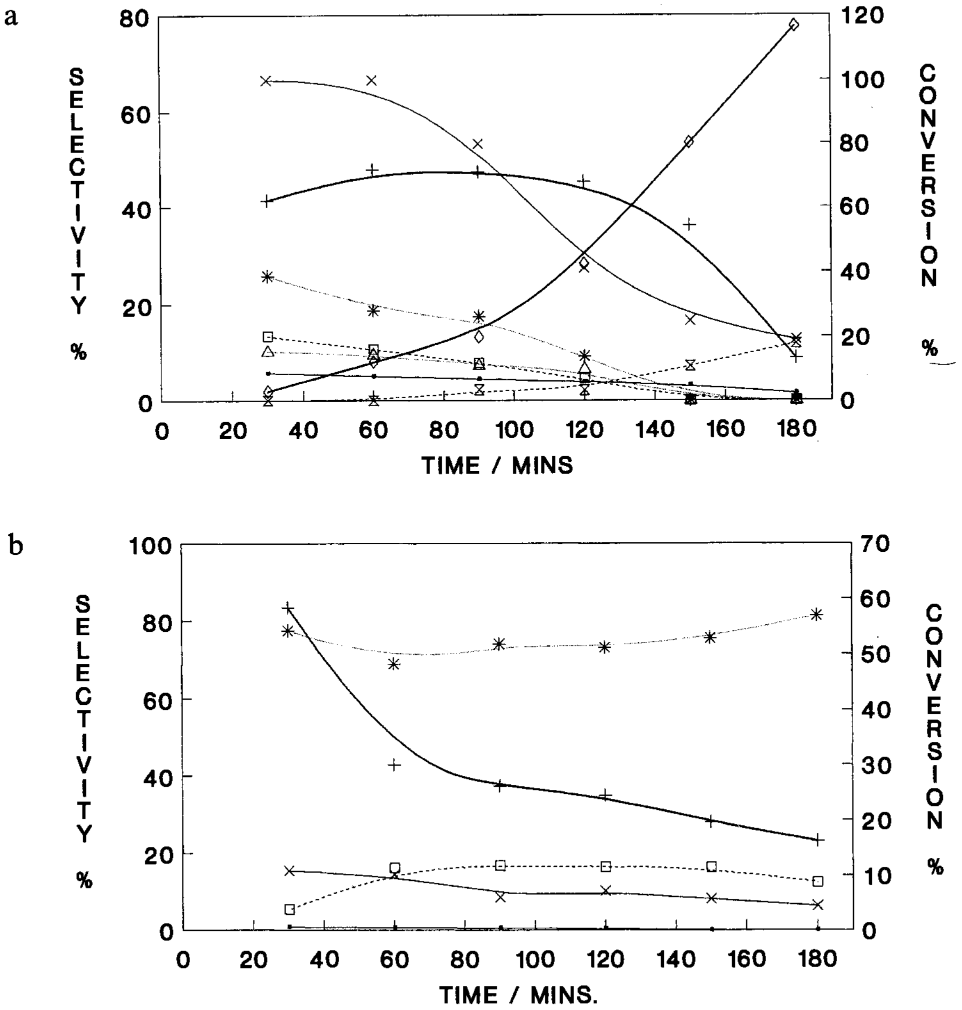
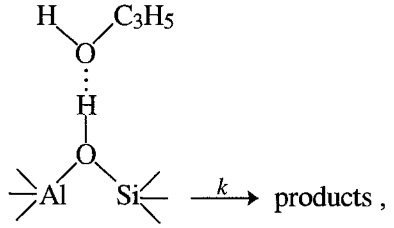


Fig. 4. Allyl alcohol conversion over zeolite Y at 250°C, (a) HY, (b) CsHY. (×) Conversion; product selectivity: (■) ethene, (+) propene, (∗) C_4, (□) C_5, (△) C_{6+}, (◇) acrolein, (⧗) diallyl ether.

demonstrating 65–68% conversion in the first hour of reaction. A rate constant estimated from these exponentials for pseudo-first order reaction,



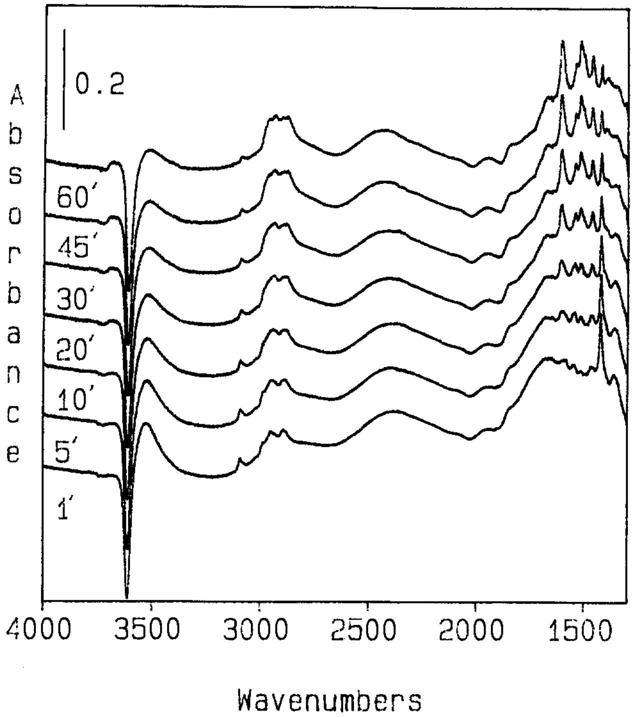


Fig. 5. FTIR difference spectra illustrating the transformation of allyl alcohol adsorbed on H-ZSM-5 at 100°C. Numbers on the spectra correspond to the time intervals after adsorption (min).

is 3.4×10^{-4} s^{-1} at 100°C (determined from a logarithmic regression in fig. 6b), and this is marginally higher than the rate constant determined under flow conditions.

Pumping the sample after 1 h of reaction removes the alcohol which remained unreacted and restores ~ 25% of the initial zeolitic hydroxyl groups. This corresponds roughly to the estimated amount of unreacted alcohol (32–35%). The difference spectrum of the products which remain adsorbed on the sample (fig. 7) shows that these products are not volatile and are linked to the surface via Z–O–P bonds (P = product), rather than being hydrogen bonded. It is possible to state that the adsorbed compounds is not diallyl ether, since the $\nu_{C=C}$ has disappeared, or aldehydes [8] or ketones [9,10]. These products most closely resemble adsorbed cyclopentene, cyclohexane and cyclopentadiene [7] which might be expected to be the cause of catalyst deactivation observed during the flow experiments.

3.3. IN SITU MAS NMR STUDIES

The ^{13}C MAS NMR spectra of the as-prepared allyl alcohol/H-ZSM-5 samples are given in fig. 8. For the sample prepared after 3 lrp cycles (sample H-3) a spectrum similar to that of liquid allyl alcohol with lines at 137.8, 113.7 and 63.2 ppm is

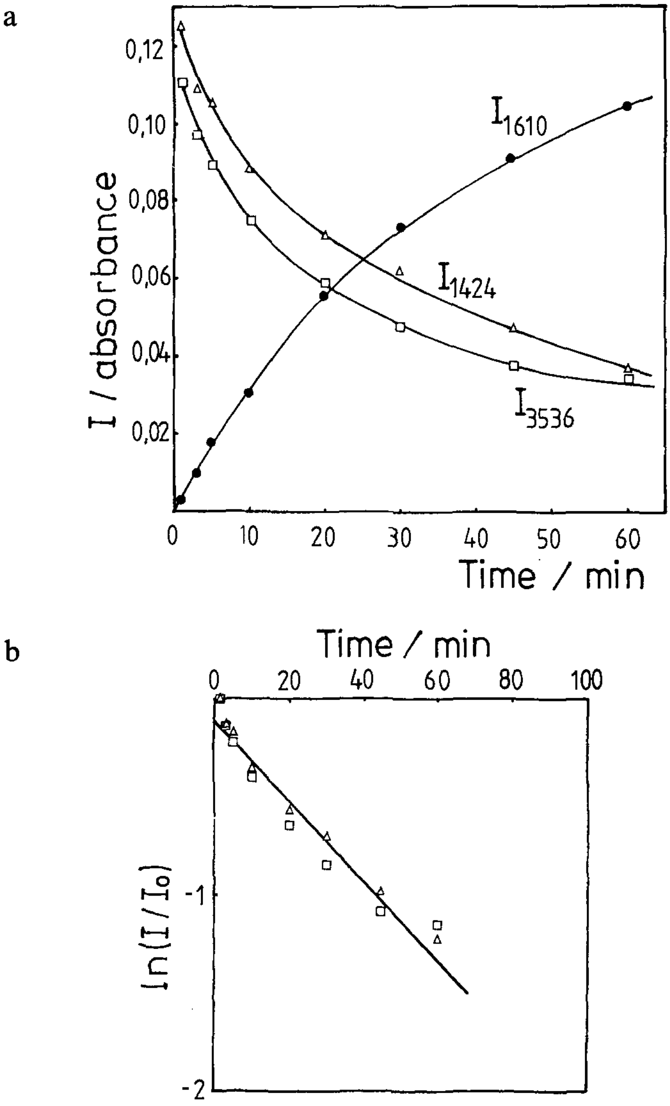


Fig. 6. Kinetics of the allyl alcohol transformation on H-ZSM-5 at 100°C (a) according to the intensities of the infrared characteristic bands and (b) the logarithmic regression.

obtained (see table 1 for characteristic chemical shifts). The smaller lines at ca. 135, 117 and 71 ppm can be assigned to diallyl ether. For the samples prepared after only 1 or 2 lrp cycles (H-1 and H-2), broad lines at about the line positions of allyl alcohol are observed. This finding indicates a strong interaction between the allyl alcohol and the zeolite. An additional broad signal between 40 and 10 ppm should be assigned to saturated hydrocarbons (CH_2 and CH_3 groups). It can be seen best in the CP spectrum of sample H-2.

As can be seen from fig. 9, there is still some adsorbed allyl alcohol remaining

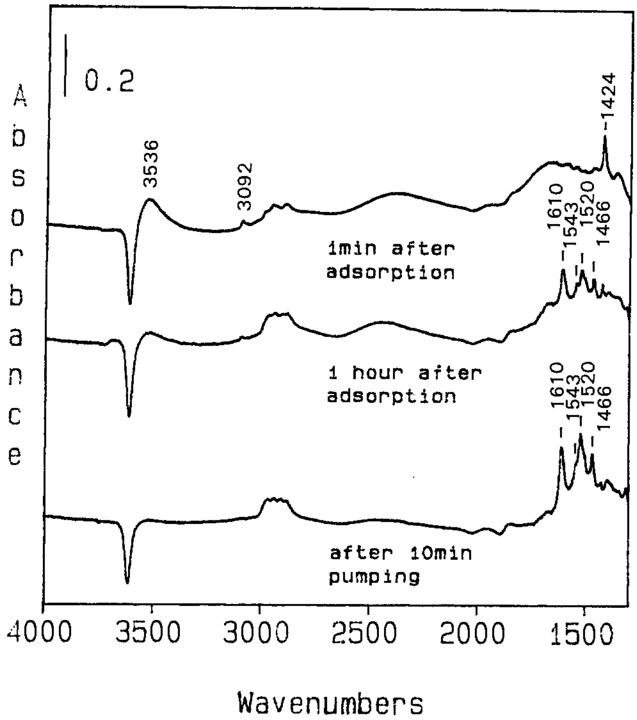


Fig. 7. FTIR difference spectra of allyl alcohol adsorbed on H-ZSM-5 at 100°C after different time intervals and after pumping.

in sample H-3 after a thermal treatment at 100°C for 1 h. The amount of diallyl ether has increased. The CP spectrum of sample H-3 demonstrates that more allyl alcohol has been converted, apparently via diallyl ether, to saturated hydrocarbons. Application of a TOSS pulse sequence eases spectral assignment considerably and results in a splitting of the CH_2 (28 ppm) and CH_3 (9 ppm) signals. The flat baseline between 220 and 160 ppm shows that under these experimental conditions no acrolein is present. As shown in fig. 9, a higher reaction temperature results in a complete conversion of allyl alcohol into saturated hydrocarbons.

Allyl alcohol reaction on Na-ZSM-5 gives very similar results, except that a higher reaction temperature is necessary to initiate the conversion of the alcohol. A thermal treatment at 100°C for 1 h has almost no effect on the ^{13}C MAS NMR spectra observed and only highly mobile allyl alcohol is observed. The spectra in fig. 10 obtained after a treatment at 200°C for 1 h are basically identical to those obtained for allyl alcohol on H-ZSM-5 after a treatment at 100°C. Besides the resonance lines of unreacted allyl alcohol, diallyl ether can clearly be identified via the line at ca. 72 ppm. The bulk of the carbon has been converted into saturated hydrocarbons as the broad line between 40 and 10 ppm shows. Again, no oxygenated product is observed. Typical spectra obtained for allyl alcohol loaded on Cs-HY are shown in fig. 11. The spectrum of the as-prepared sample shows the assigned

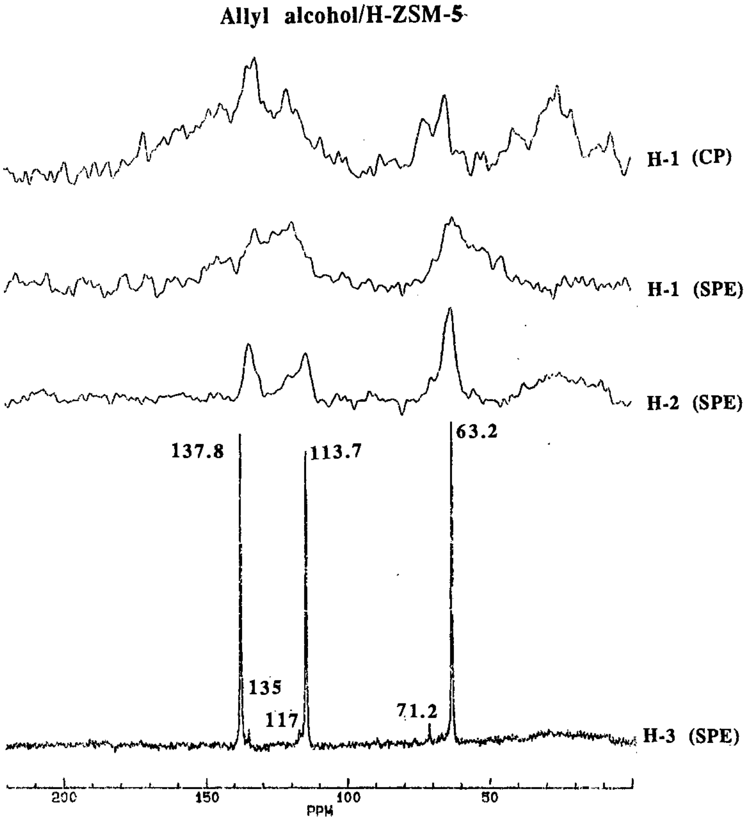


Fig. 8. ^{13}C MAS NMR spectra for allyl alcohol adsorbed on H-ZSM-5 after various loading cycles but no subsequent heating.

lines of allyl alcohol with shoulders indicating the presence of diallyl ether. The diallyl ether appears to be converted into saturated hydrocarbons after thermal treatment at 100°C. A rise in the reaction temperature to 200°C results in complete

Table 1
Chemical shift data for compounds relevant to this study

Compound	Chemical shift (ppm)		
	C1	C2	C3
allyl alcohol	62.5	136.7	114.0
diallyl ether	71.1	135.3	116.4
propan-1-ol	64.9	26.9	11.8
propan-2-ol	64.7	26.5	
propanol	202.7	36.7	5.2
acrolein	193.3	136.0	136.4
acetone	206.7	30.7	

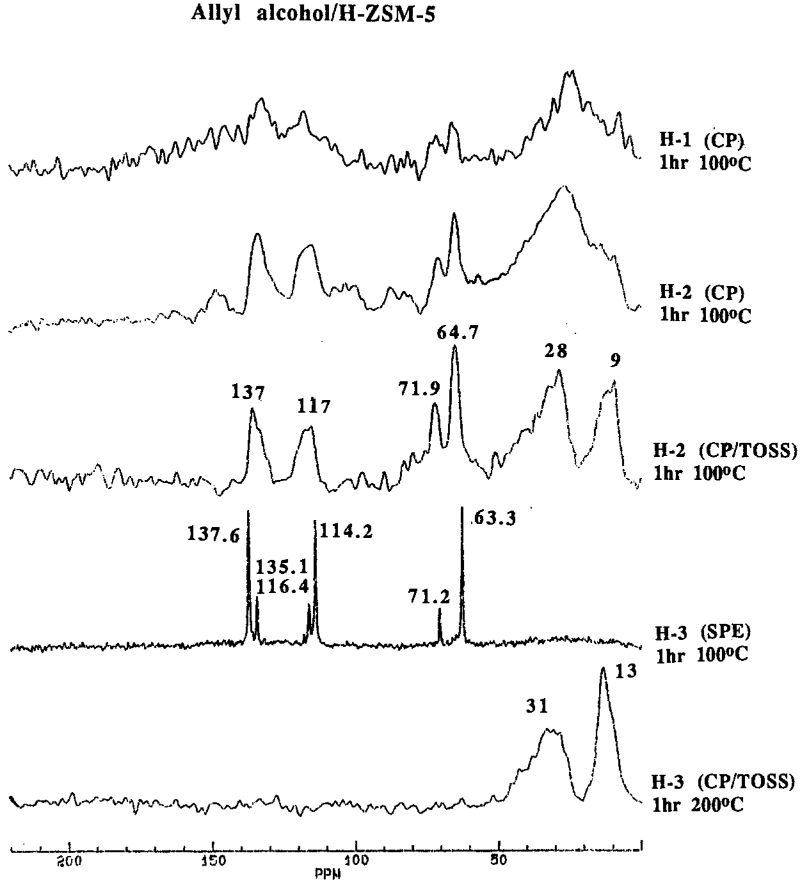


Fig. 9. ^{13}C MAS NMR spectra for allyl alcohol adsorbed on H-ZSM-5 after various loading cycles and subsequent heating.

conversion of allyl alcohol into aliphatic and partly aromatic (line at about 130 ppm) hydrocarbons. A reaction time of only a few minutes is sufficient to accomplish this complete conversion. As in the case of the ZSM-5 catalysts, no oxygenated product (i.e. acrolein) was observed.

Since acrolein, the main product observed in the flow reactor studies with Cs-HY was not observed in the ^{13}C MAS NMR spectra, the question arose whether we were able to detect this molecule under our experimental conditions. Therefore, acrolein was loaded on ZSM-5 and exposed to the same thermal treatments as the samples loaded with allyl alcohol. Typical spectra are given in fig. 12. The as-prepared samples show a line at about 25 and 69 ppm which may be due to propanol formation in addition to the two easily assigned lines of acrolein. After 30 min at 100°C the spectrum for acrolein on Na-ZSM-5 is almost unchanged. After the same time at 200°C, most of the acrolein has been converted to saturated hydrocarbons. For acrolein on H-ZSM-5 a reaction temperature of 80°C was sufficient to

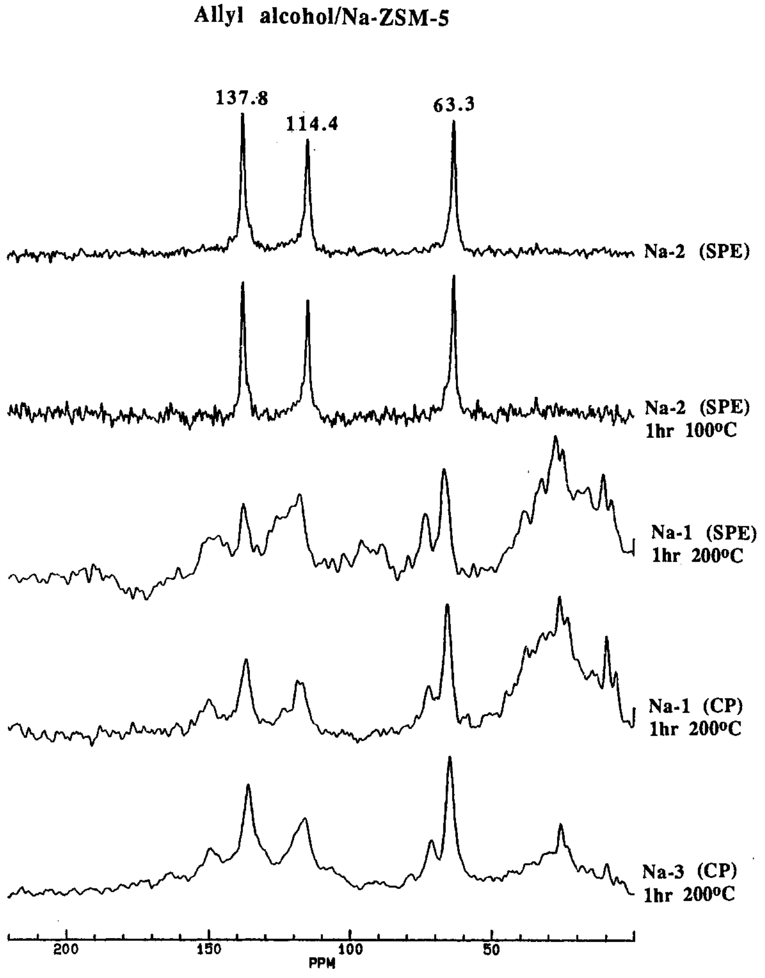


Fig. 10. ^{13}C MAS NMR spectra for allyl alcohol adsorbed on Na-ZSM-5 after various loading cycles and subsequent heating.

achieve an almost complete conversion to the same product. This finding explains why the MAS NMR results do not model the results obtained under flow reactor conditions. Under the static conditions used in the MAS NMR sample, any acrolein formed from allyl alcohol readily reacts to form saturated hydrocarbons and hence is not observed.

4. Discussion

The combined use of in situ spectroscopic methods and flow reactor studies can provide a powerful approach to the study of a complex catalytic reaction. In addition, the calculated rate constants for allyl alcohol conversion over H-ZSM-5 at

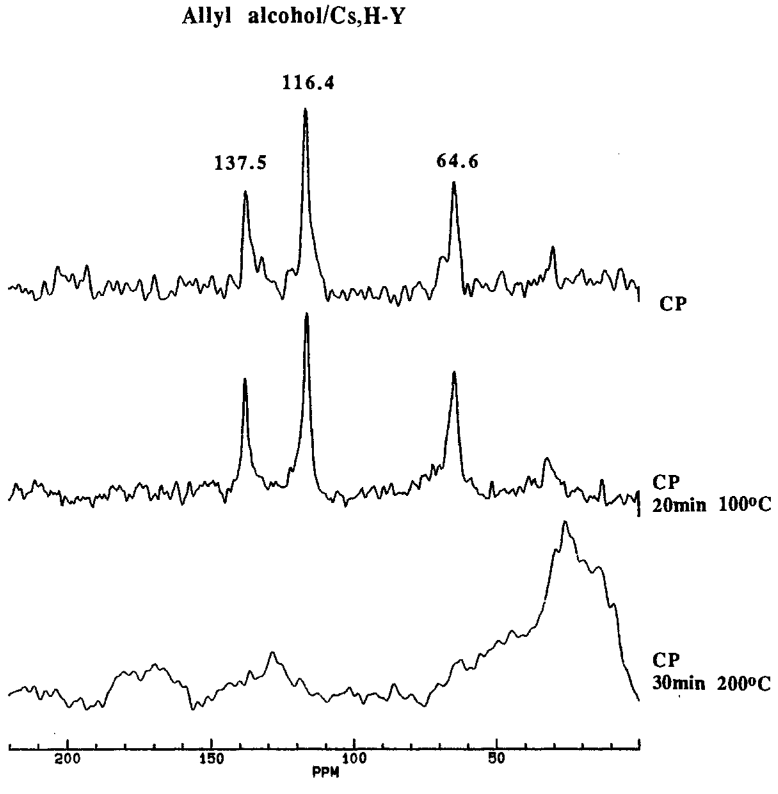


Fig. 11. ^{13}C MAS NMR spectra for allyl alcohol adsorbed on Cs-H-Y with subsequent heating.

100°C from the in situ FTIR studies and the catalytic studies are in reasonable agreement. This further confirms the usefulness of these combined studies. In the conversion of allyl alcohol over the Brønsted acid form of zeolite catalysts under most reaction conditions, the products are mainly hydrocarbons. Oxygenated products, e.g. acrolein, diallyl ether, are only formed after the catalyst has been deactivated by coke deposition. The initial formation of hydrocarbons can be easily understood in terms of protonation of allyl alcohol by the Brønsted acid site of the zeolite followed by elimination of water, with subsequent rearrangement, oligomerisation or cracking to give the broad range of products observed. This process is apparent in the in situ FTIR studies reported in this study. In these studies the loading of allyl alcohol was restricted to 1 molecule/acid site and hence, under these conditions, the formation of diallyl ether was not expected because of the absence of physisorbed allyl alcohol. However, the MAS NMR studies did indicate that when a higher loading of allyl ether is used, diallyl ether is the initial product at low temperatures.

In the MAS NMR experiments it was observed that had acrolein been formed, under the experimental conditions, it would have been rapidly reacted. Hence the

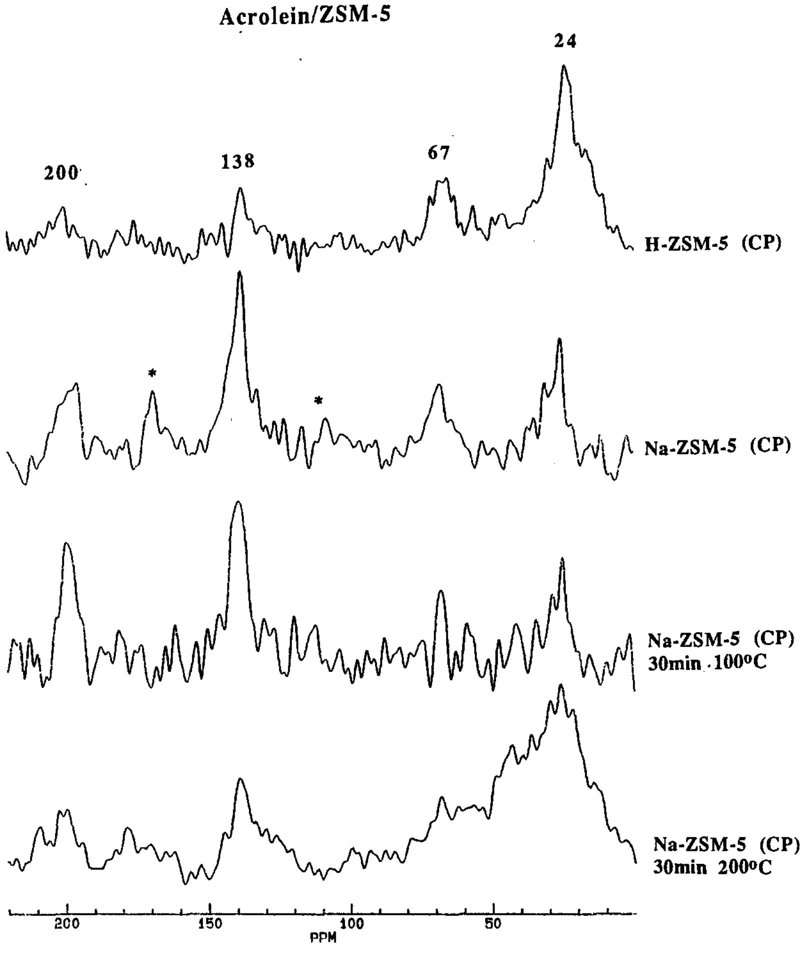


Fig. 12. ^{13}C MAS NMR spectra for acrolein adsorbed on H-ZSM-5 and Na-ZSM-5 with and without subsequent heating. Asterisks denote spinning side bands.

lack of acrolein formation in these studies cannot be taken as evidence that it is not formed initially under the conditions used. Indeed, the rapid reaction of acrolein to form coke could be an important step in creating the active surface of the zeolite. This surface is then more active and selective for the formation of acrolein and subsequently this product is observed. It is therefore necessary to consider whether two parallel pathways exist on the zeolite catalyst, i.e. dehydration to give hydrocarbons and acrolein formation via an alternative mechanism, or whether acrolein formation only occurs once catalyst deactivation occurs. If it is the latter case then the active sites for the formation of acrolein must be different from the Brønsted acid site that is responsible for the dehydration reaction. Both the in situ FTIR and MAS NMR experiments are useful in this respect. It is clear from both these studies that the initial products formed on the zeolite that can be considered as coke precursors are non-oxygenated species. The FTIR studies indicate that these initial products are hydrocarbons, probably cyclopentene, cyclohexene or cyclopentadiene. These studies model hydrocarbon formation at low allyl alcohol/ Brønsted acid site ratios. Under these conditions if acrolein were to be formed and react, probably via an acid catalyst aldol condensation, then the initial lower molecular mass products would all be oxygenated. This is not observed and hence it can be concluded that the formation of acrolein does not occur on unmodified Brønsted acid sites in the acid form of the zeolite. It is possible that coke formation leads to the creation of a modified acid site. The highest selectivity to acrolein was observed with Cs-HY and it is possible that the bulky Cs^+ cation also has a function of providing a sterically hindered active site.

Previously, Munsen et al. [4] have studied allyl alcohol conversion over H-ZSM-5 and CsHX using MAS NMR spectroscopy. In agreement with our findings they also observed no oxygenate formation in their NMR studies. However based on their studies with CsHX they concluded that there was evidence, based on hydroxyl exchange between the C_1 and C_2 atoms of 1-propanol, to support the existence of an allyl cation intermediate $CH_2{=}\underset{+}{C}H{=}CH_2$. This was in support of our previous proposal that this species was an intermediate [3]. Recently Biaglow et al. [11] have also studied the reaction of allyl alcohol with H-ZSM-5 using MAS NMR and have observed a signal at δ 218 ppm which they assigned to the formation of the allyl cation. Most recently, Farcasiu [12] has shown that the lifetime of the allyl cation would be too short to be observed and he assigned the in situ MAS NMR spectra to allyl alcohol, diallyl ether and surface silyl allyl ether, hydrocarbons and carbonyl compounds. In our studies no signals, that could be assigned to carbonyl compounds, in the region δ 160–220 ppm were observed due to the rapid reaction of acrolein under our conditions. Therefore we would agree that the timescale of the MAS NMR technique is such that it would not be possible to observe a reactive intermediate such as the allyl cation and that appropriate chemical trapping experiments need to be designed to elucidate the mechanism in more detail. The hydroxyl exchange noted by Munson et al. [4] is not conclusive evidence in favour of the formation of the allyl cation since, as noted by Farcasiu [12] a number of alternative pathways can account for the observations.

In conclusion, this study demonstrates that the combined use of in situ spectroscopic techniques, together with flow reactor studies, can be instructive in understanding the reaction sequences in the conversion of allyl alcohol over zeolite catalysts. In particular, this combined approach has demonstrated that the active sites for the formation of acrolein from allyl alcohol are different from those responsible for hydrocarbon formation.

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