In situ Nuclear Magnetic Resonance Study of Allyl Alcohol Conversion on Zeolites: Evidence for an Allyl Cation Intermediate

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^{13}C Label exchange between the 1 and 3 positions of allyl alcohol at high temperatures on CsHX zeolite demonstrates the presence of an allyl cation as an intermediate in hydrocarbon synthesis.

The conversion of methanol and other alcohols to low molecular weight aliphatic and aromatic hydrocarbons over zeolite catalyst HZSM-5 is of great interest.[1,2] Hutchings and coworkers have previously shown that allyl alcohol can be converted to acetone and other oxygenates on HZSM-5.[3] They proposed that allyl alcohol passes through a symmetrical allyl cation on its way to hydrocarbons or acetone. In this communication, we report *in situ* ^{13}C MAS NMR[4,5] spectroscopic studies of allyl alcohol-1-^{13}C on zeolites HZSM-5 and CsHX, and show that 1,3-label exchange occurred on the latter. This result demonstrates the transient existence of the symmetric allyl cation.

Fig. 1 shows ^{13}C CPMAS NMR spectra of allyl alcohol-1-^{13}C on zeolite HZSM-5 as the sample was heated from 298 to 473 K in the NMR probe.† At 353 K, approximately 50% of the unconverted allyl alcohol (δ 66) had been converted to allyl ether (δ 73). Further heating of this sample to 473 K resulted in the conversion of allyl alcohol and ether to a mixture of aliphatic and aromatic compounds. Fig. 2 shows ^{13}C CPMAS NMR spectra of the reactions of acetone-1,3-^{13}C on HZSM-5 as the sample was heated to 473 K using the same protocol as described for Fig. 1. Careful comparison of the two figures shows that there was little or no acetone (δ 30) formed from allyl alcohol on HZSM-5. These results agree with

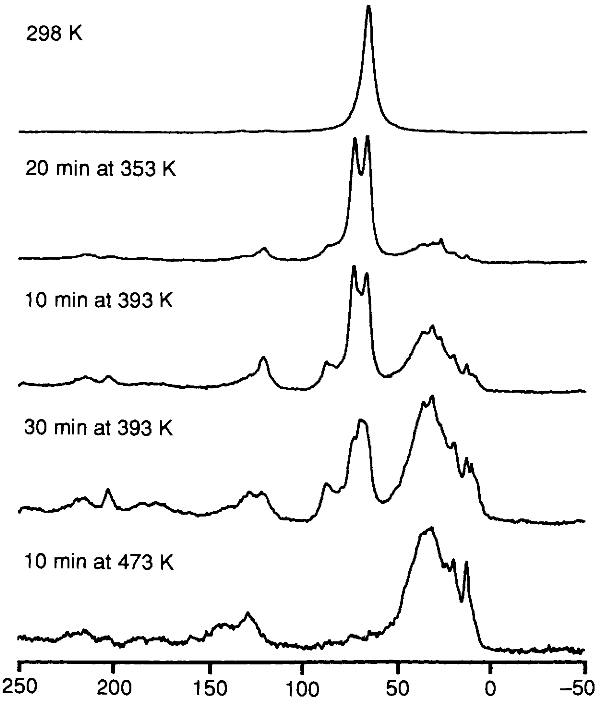

Fig. 1 ^{13}C CPMAS NMR spectra of the reactions of allyl alcohol-1-^{13}C on zeolite HZSM-5. Allyl alcohol (δ 66) was converted to allyl ether (δ 73) and eventually to hydrocarbons (δ 0–50) upon heating to 473 K.

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† Details of sample preparation and the NMR protocol for *in situ* experiments can be found in ref. 5. Typically, 0.4 mmol of reactant was adsorbed on 0.25–0.4 g of catalyst. All spectra shown were acquired using either cross polarization (400 transients, contact *t* 2 ms, repetition delay = 1 s) or single-pulse excitation (100 transients, repetition delay = 4–8 s) with high-power proton decoupling.

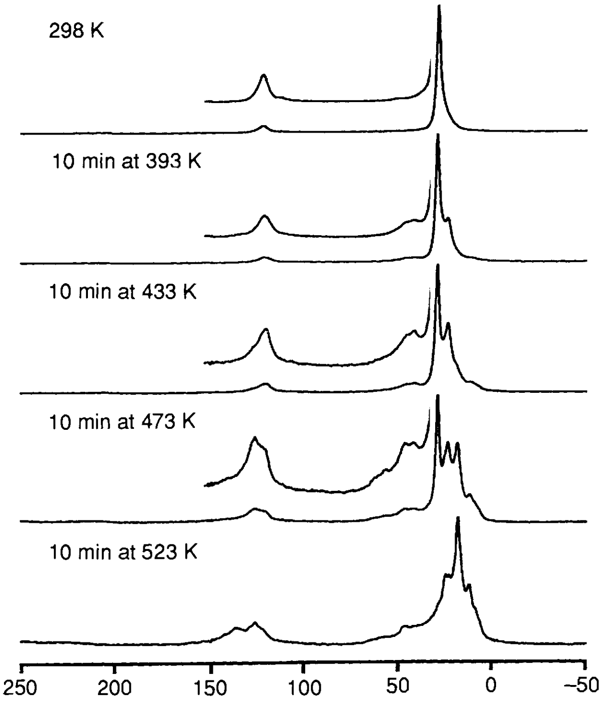


Fig. 2 ^{13}C CPMAS NMR spectra of the reactions of acetone-1,3-^{13}C on zeolite HZSM-5. Acetone (δ 30) oligomerized and ultimately formed hydrocarbons upon heating.

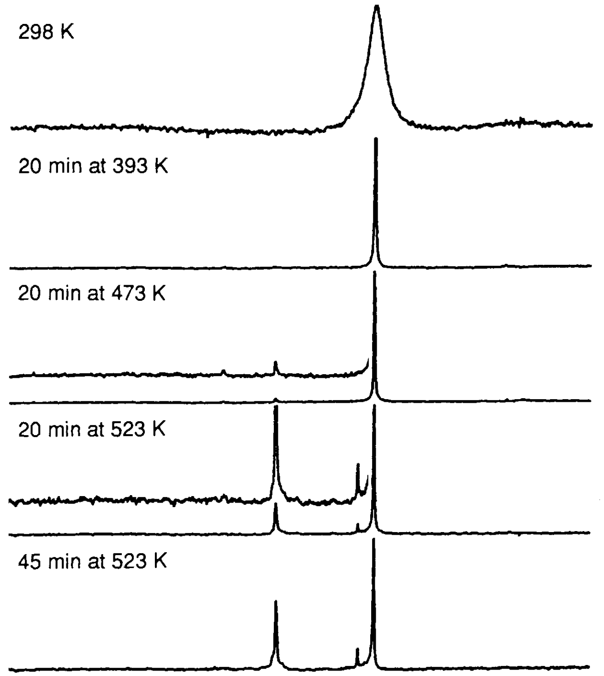
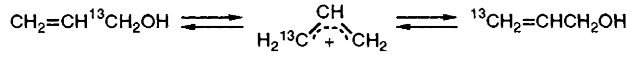


Fig. 3 ^{13}C MAS NMR spectra of the reactions of allyl alcohol-1-^{13}C on zeolite CsHX. Label exchange between the 1 (δ 64) and 3 (δ 115) positions was observed as well as the formation of allyl ether (δ 72).

Hutchings findings[3] that allyl alcohol initially forms hydrocarbons on HZSM-5 and that only after several hours on stream is the catalyst selective for the production of C_3 oxygenates. However, no 1,3 label exchange was observed in Fig. 1.



Scheme 1

I

II

An alternative to the above protocol is to study the reaction under conditions that favour the rehydration of the allyl cation to regenerate the alcohol. We chose to study the reaction on zeolite CsHX,‡ because the weaker acid sites of this zeolite limit the rate of the oligomerization reaction. Fig. 3 shows ^{13}C MAS NMR spectra of allyl alcohol-1-^{13}C on zeolite CsHX. When the sample was heated to 523 K, a peak at δ 115 appeared due to allyl alcohol-3-^{13}C. This observation implies 1,3-label scrambling (Scheme 1). Allyl alcohol was protonated and dehydrated to form the allyl cation. The reverse reaction scrambled the label. On HZSM-5, oligomerization occurred rapidly, and no scrambling was observed.

Fig. 3 clearly implies that there is an allyl cation intermediate, but why was that cation not directly observed in this study? The expected C-1 and C-3 chemical shift for the equilibrating ion should be *ca.* of δ 220,[6] although an attempt to generate sufficient quantities of this ion in solution for ^{13}C characterization was unsuccessful owing to its low stability.[7] All of the resonances downfield of δ 150 in our study are accounted for by propionaldehyde-1-^{13}C, another product in Hutching's study.[3] The more stable allylic ions **I** and **II** have been observed during *in situ* NMR studies of propene oligomerization[4] and hydrocarbon cracking,[8] respectively, but the simple allyl cation is too unstable for direct observation, either in the zeolite or in solution. The observation of 1,3-label scrambling is, however, unambiguous evidence for its transient existence. In a previous *in situ* NMR study, a similar argument was made to account for label scrambling in isobutylene through the symmetrical trimethylcarbenium ion.[9]

The *in situ* NMR studies reported here thus establish a major feature of the mechanism proposed by Hutchings and coworkers.[3] We are currently studying the reactions of acetone on a variety of zeolites in an attempt to better understand the reactions of C-3 oxygenates on acidic catalysts.

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‡ Elemental analysis showed the cations were 80% Cs^+ and 20% H^+.