

Investigation of Methanol Reaction Chemistry on H-ZSM-5 and-11

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ABSTRACT: *In order to gain a better understanding of the chemistry of methanol-to-hydrocarbon conversion, it is necessary to determine the nature of the primary reaction products. Experiments carried out in this work on H-ZSM-11, using a continuous flow reactor linked to an on-line gas chromatograph demonstrated that ethylene and methane are the primary reaction products. The results obtained using solid state MAS NMR for the same reaction further support the findings of this work. The results from H-ZSM-5 catalyst do not confirm that the CO of the reaction acts as a catalyst.*

KEY WORDS: *Methanol conversion, Pentasil zeolites, Reaction chemistry*

INTRODUCTION

The reaction of methanol to hydrocarbon has been extensively investigated since it was first reported by Chang and Silvestri [1]. A great deal of research effort has been devoted to unraveling the chemistry of this conversion [2-16]. However, the mechanism of this conversion is still in debate. The complexity of the reaction coupled with the limitation of techniques has always prevented chemists from gaining a complete understanding of the conversion mechanism. Jackson and Bertsch have reported a mechanism for the first C-C bond formation in methanol to hydrocarbon conversion. They proposed that CO activates methyl groups, originally from methanol, to function as carbon nucleophiles in the form of ketenes.

The object of this study is to get some information on the nature of the primary reaction products, which is

necessary in the mechanistic study of the first C-C bond formation. The reaction pathway in which carbon monoxide is supposed to play a catalyst role is discussed in this work.

The conversion reaction was carried out in an open flow-reactor system linked to a gas chromatograph to investigate the very early stages of the conversion process. Solid-state magic angle spinning (MAS) NMR was used to monitor the reaction within the zeolite pores.

EXPERIMENTAL

Enriched ¹³C (99.9%) and normal methanol (Aldrich, Milwaukee, WI, U.S.A) were used as the reactant. 50 mg of catalyst (powder) was placed in a specially designed glass tube connected to a highly evacuated gas handling line.

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The sample was dehydrated at 673 K overnight. A certain amount of methanol (mole per acid site), purified by the freeze-pump-thaw method, was adsorbed onto the catalyst. The glass microreactor was sealed at 77 K. The sealed samples were treated in the temperature range of 298-573 K for various lengths of time. ^{13}C MAS NMR spectra of the samples were measured on a Bruker MSL400 spectrometer using a chemagnetics APEX400 pencil probe under certain conditions. ^1H MAS NMR spectra of the bare zeolites were acquired by a Bruker double bearing 4mm probe at the spin rate of 10 kHz using the Hahn echo pulse sequence.

The conversion reaction was also performed in a continuous flow reactor system, containing 100 mg of the catalyst. Products were analyzed by an on-line gas chromatograph (Varian 3600) after the reaction had reached a steady-state condition, using a DB-1 fused silica capillary column (60 m l. \times 0.32 mm i.d.). Argon was used as a carrier gas to convey reactant/ products into a gas sample valve setup for on-line injection.

Catalyst preparation

An industrial zeolite Na-ZSM-5 was used in this work. Template used during its synthesis was removed by heating the sample at 823 K in a stream of dried air. To transform the Na-ZSM-5 to H-ZSM-5, the sample was cation-exchanged by three ammonium sulfate (1.8 M) exchanges at 333 K (3h for each step), followed by calcination in a stream of dried air at 723 K to remove the ammonia. Zeolite Na-ZSM-11 was synthesized by the author, using a method reported in literature[17]. It was transformed to H-ZSM-11 following similar procedure applied to ZSM-5. Both zeolites were fully characterized by techniques such as X-ray powder diffraction, scanning electron microscopy, adsorption/ desorption isotherm and solid-state MAS NMR. Results corresponding to ^{27}Al , ^{29}Si and ^1H MAS NMR are shown.

RESULTS AND DISCUSSION

Fig. 1A shows ^1H , ^{27}Al and ^{29}Si MAS NMR spectra of H-ZSM-5 (Si/Al=40) used in this work. The proton spectrum shows three main signals at 1.8, 2.7 and 4.2 ppm with an underlying shoulder. These are assigned to

-SiOH, -AlOH (or AlOOH) and Bronsted acid sites, respectively[13,16]. The ^{27}Al spectrum shows a main signal at 54 ppm and a small peak around 0 ppm; these are respectively indicative of framework and extra framework aluminium[13,16,18] as demonstrated in proton spectrum. ^{29}Si spectrum shows a signal at 113 ppm with a small broad shoulder centered at ca. -105 ppm; these correspond to -Si(0Al) and -Si(1Al) groupings, respectively.

Fig. 1B illustrates ^1H , ^{27}Al and ^{29}Si MAS NMR spectra of H-ZSM-11 (Si/Al=30) sample used in this work. The proton spectrum shows the presence of silanol groups (1.8 ppm) and Bronsted sites (4.1 ppm); while extra framework aluminium is present in this zeolite. This is further evidenced by the aluminium spectrum. The silicon spectrum shows similar results to H-ZSM-5. Based on these findings, the two zeolite samples were good catalysts.

Methanol conversion was performed on H-ZSM-11. The product selectivities were then compared to those reported for H-ZSM-5 [9]. As shown in Table 1 (columns 5 and 6), there is a marked difference in the contents of aromatic, C_2 and C_3 hydrocarbons from the two zeolites. Although the reaction conditions were not identical (temperature difference 20°C , which seems not significant), the difference in product selectivity could be due to the structural architectures of the zeolites.

Table 1: Methanol to hydrocarbon conversion at different temperatures on H-ZSM-11 (WHSV=4h⁻¹).

T/K	523	573	623	653	673
Conv.	0.057	37.682	69.691	88.690	99.9
	Product distribution /wt%				
C ₁	—	0.51	0.37	0.44	1 ^a
C ₂	33.33	21.06	20.32	17.51	3.2
C ₃	52.63	28.18	27.46	32.84	12.1
C ₄ ^b	—	9.38	11.22	13.93	29
C ₅ ⁺	14.04	35.00	32.87	26.38	34.9
A	—	5.87	7.76	8.91	19.7

a: It consists of CO, CO₂ and CH₄

b: It is not involved i-C₄ hydrocarbon (except column 6). Column 6 corresponds to H-ZSM-5 (Si/Al= 35) from ref. 9. A= aromatics hydrocarbons. Conv. = conversion

Effect of reaction temperature on conversion and products

By carefully controlling the reaction temperature (523- 653 K), methanol was reacted on H-ZSM-11 at weight hourly space velocity (WHSV) 4h^{-1} . On-line gas chromatographic analysis of the reactor effluent gas from each experiment is shown in Table 1. At 523 K, methanol conversion was about 0.06%. Product selec-

tivities were as follow: 33.33% C_2 , 52.63% C_3 and 14.04% C_5^+ hydrocarbons. As the reaction temperature was increased to 653 K, a sharp increase in methanol conversion was observed. This indicates the autocatalytic nature of the reaction as reported by Ono *et al.* [10]. Concurrently, selectivities to C_2 and C_3 hydrocarbon products decreased and formation of larger hydrocarbons increased. It should however be noted that hydrocar-

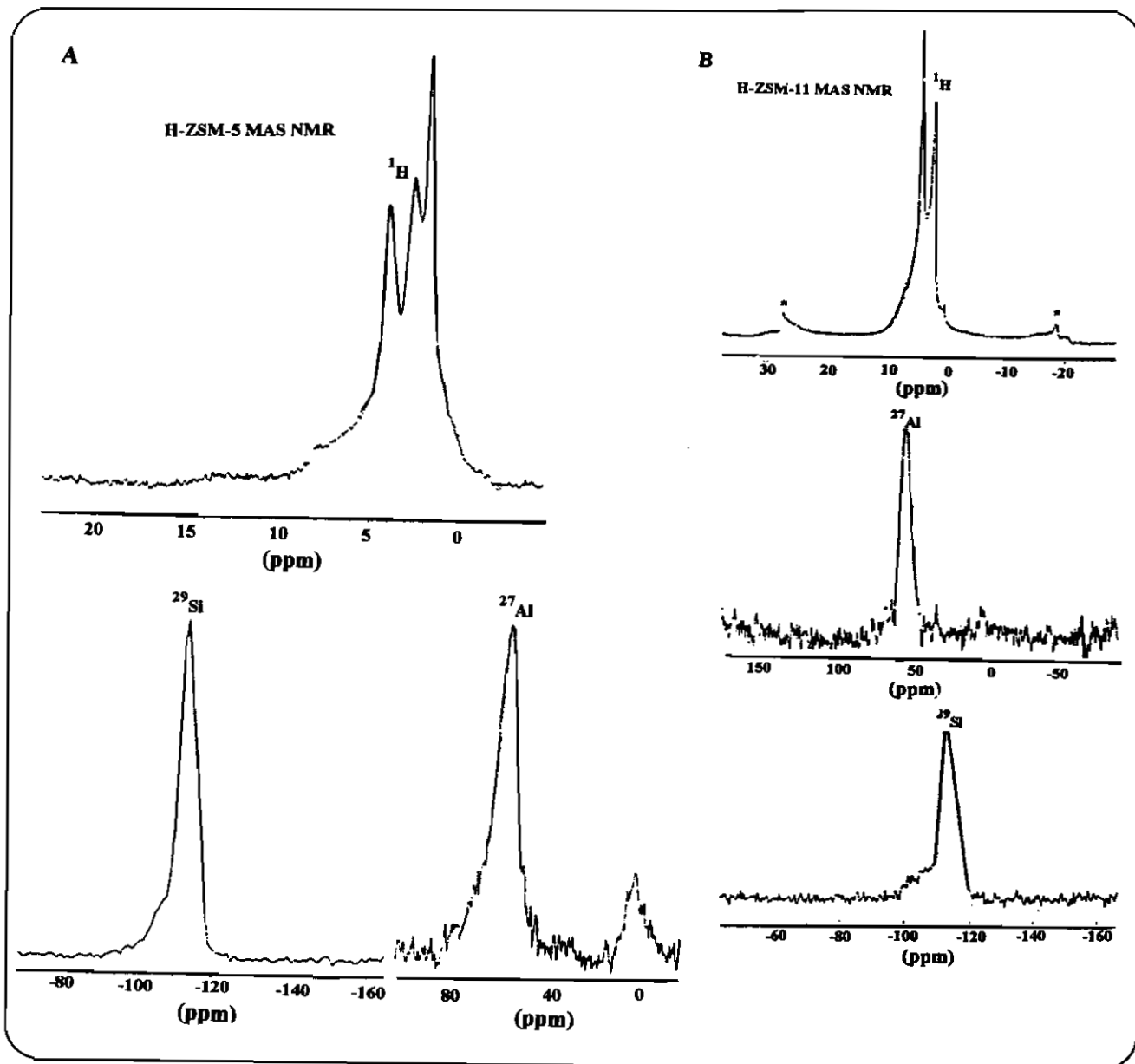


Fig. 1: ^1H , ^{29}Si and ^{27}Al MAS NMR of (a) H-ZSM-5 (Si/Al=40) and (b) H-ZSM-11 (Si/Al=30). Asterisk denotes spinning sideband.

bons increased. It should however be noted that the temperature increase and ease of cracking of large hydrocarbons result in a decrease in C_5^+ and increase in C_2 , C_3 and C_4 hydrocarbons, Table (1). The high selectivity to C_2 hydrocarbon at low conversion demonstrates that ethylene is a primary product. The formation of C_5^+ hydrocarbons under such conditions shows that the secondary reactions are more rapid than the primary reaction. Having accepted that, propylene is less likely to be a primary product. The nearly constant percentage of methane in the products of individual experiments may be due to an independent primary reaction.

Effect of space velocity on conversion and products

It was observed that different levels of conversion and product distributions could be obtained depending on the reaction conditions. The experimental findings of this work showed that the secondary conversion of the primary products is more rapid than the primary reaction and this therefore caused a range of C_n hydrocarbons to be present even at a very low conversion (0.06%). This necessitates extrapolation of the data based on C_2/C_3 hydrocarbon ratios to determine primary product function. This method was applied to the data obtained from experiments carried out at different space velocities and showed that ethylene and methane were the primary reaction products (Fig. 2). Haag *et al.* [2] has previously reported similar results in methanol conversion on a siliceous zeolite H-ZSM-5.

Nature of the primary hydrocarbons by ^{13}C MAS NMR

The adsorption of $^{13}CH_3OH$ on H-ZSM-11 led to a signal around 50 ppm. In situ heating of the sample to 423 K resulted in an additional signal at about 60 ppm with a small shoulder at a higher chemical shift, indicating the presence of dimethylether and surface methoxy groups [16]. These observations were common to all loadings of methanol on H-ZSM-11. The second stage of the reaction commenced at 553 K with the degree of conversion varying for the loadings in the order $0.5:1 > 1:1 > 3:1$ (Fig. 3). This implies that the reactant molecules them-

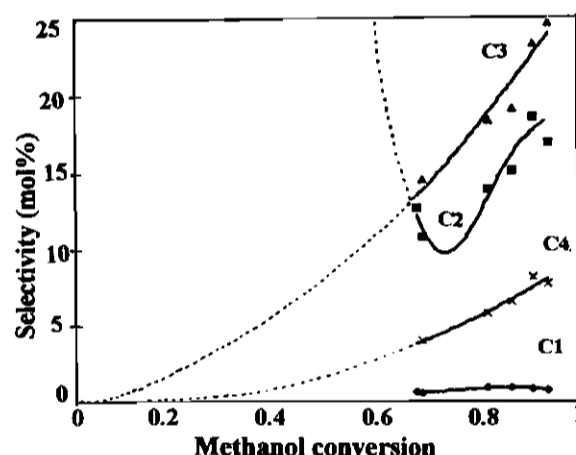


Fig. 2: Effect of conversion (or space velocity) on product selectivity over H-ZSM-11.

selves sterically hinder each other towards interaction with active center as the methanol coverage increases. Of great interest in the spectra of these loadings is the product distributions at low conversions ($\ll 1\%$) and relatively low temperatures. Isobutane ($i-C_4$) and isopentane ($i-C_5$) were the only products detected at 0.5:1 loading. This complies with our observation in a continuous flow system. It is noted that the contact time under a static condition compared to a continuous flow system is infinite. Upon increasing the methanol loading to 1:1, similar results accompanied by methane was observed at the same temperature (553 K, Fig. 3B-c.). To enhance the existence of primary reaction products, it was necessary to prevent the secondary conversion by decreasing the activity of the zeolite active centers. To do this, the coverage of methanol on zeolite was increased to 3:1, assuming that methanol due to its high polarity compared to hydrocarbons can occupy the zeolite active centers. The results obtained from such a system (see Fig. 3C-c.,) show an additional signal at 123 ppm, indicating the presence of ethylene. This result together with the findings from the other loadings is taken as a strong evidence for ethylene formation during a primary reaction. The presence of methane under such conditions suggests that methane is also a primary product.

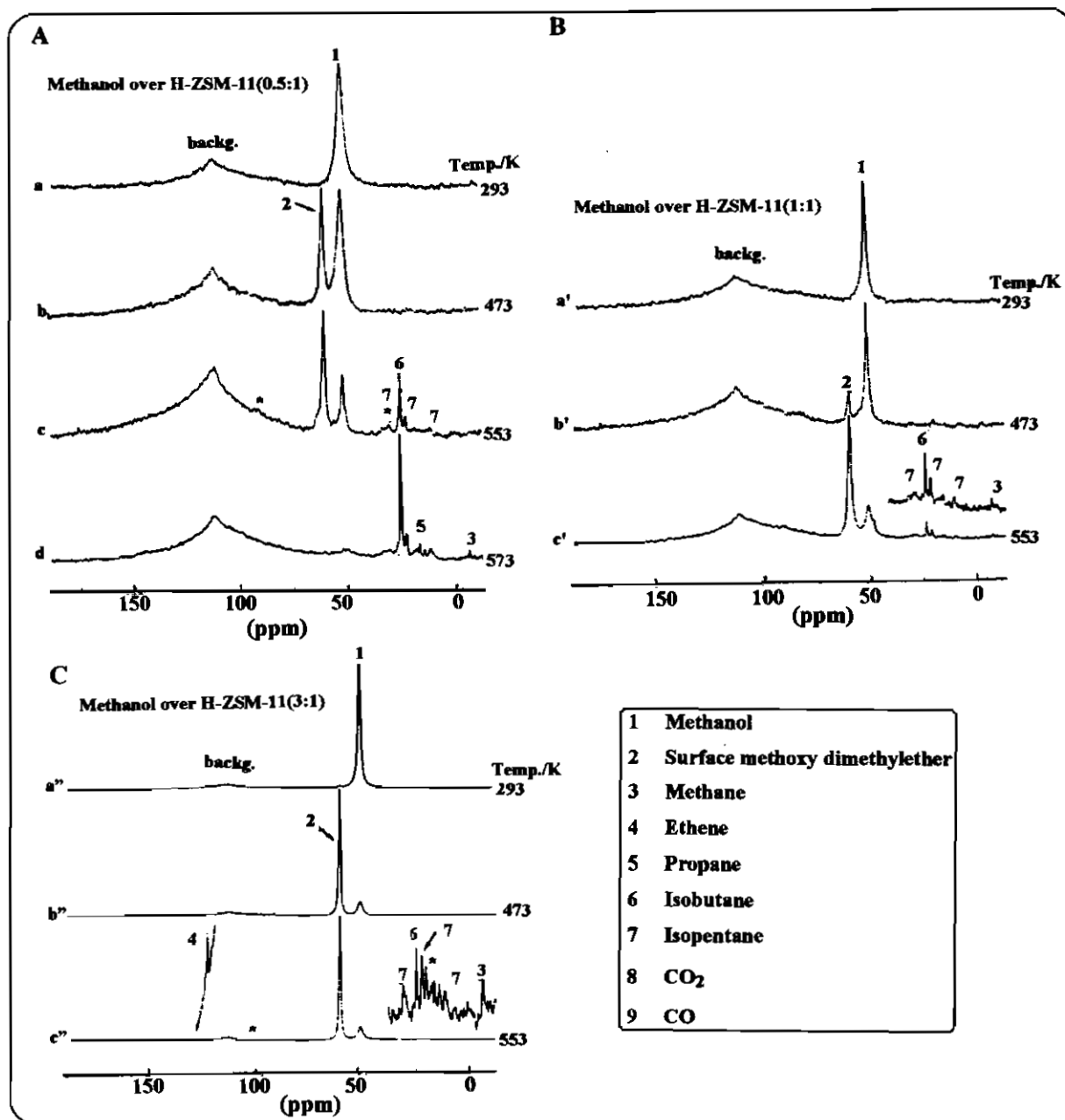


Fig. 3: $^{13}\text{C}\{\text{H}\}$ MAS NMR spectra of the sample with 0.5, 1 and 3:1 methanol to acid site after (a, a' and a'') no thermal treatment and (b, b', b'', c, c' and c'') heating for 2.5min. Hydrocarbon regions are expanded in c' and c''. Asterisk denotes spinning sideband. Backg.=background.

Formation of the first C-C bond

The role of CO in conversion of methanol on zeolite H-ZSM-5 has been previously reported [5]. The existence of CO prior to hydrocarbon formation and its

decrease afterwards has stimulated some authors to conclude that CO can act as intermediate or as a catalyst in the conversion of methanol on H-ZSM-5[5,6]. Jackson and Bertsch [6], based on their studies and other authors'

results [5] for methanol conversion, proposed that CO exerts a catalytic role on H-ZSM-5 (Scheme 1). In order to test this hypothesis two series of experiments with enriched (^{13}C) methanol were performed over zeolite H-ZSM-5 (Si/Al= 40). In the experiments with a 0.5:1 loading CO was not observed during the course of the conversion (Fig. 4A). However, the experiments with a loading 1:1 showed that carbon monoxide formed before the formation of hydrocarbon products (Fig. 4B). The presence of CO at this stage of the experiment (523 K) make the system similar to an experiment when CO is added. Further heating the sample to 563 K demonstrated that the presence of CO in the reaction phase did not enhance the formation of hydrocarbon as compared with the lower loading experiment. On heating the sample for a longer period at the same temperature, methane

signal appeared in the corresponding spectrum. Concurrently, the signal assigned to CO_2 (125ppm) was growing, indicating that CO was partially being converted to CO_2 via the water-gas shift reaction. The next spectrum resulting from the sample at 573 K showed propane and isobutane, which may have been formed via further methylation of ethylene.

The findings of this work do not support the Jackson's mechanism to be operative in the methanol conversion over zeolites. If CO catalyzes the reaction, the CO signal should be detected in the experiments with a 0.5:1 loading (see Fig. 4A). The results of experiments corresponding to a 1:1 loading cannot confirm the intermediate role of CO in the methanol reaction due to lack of enhancement in the conversion rate.

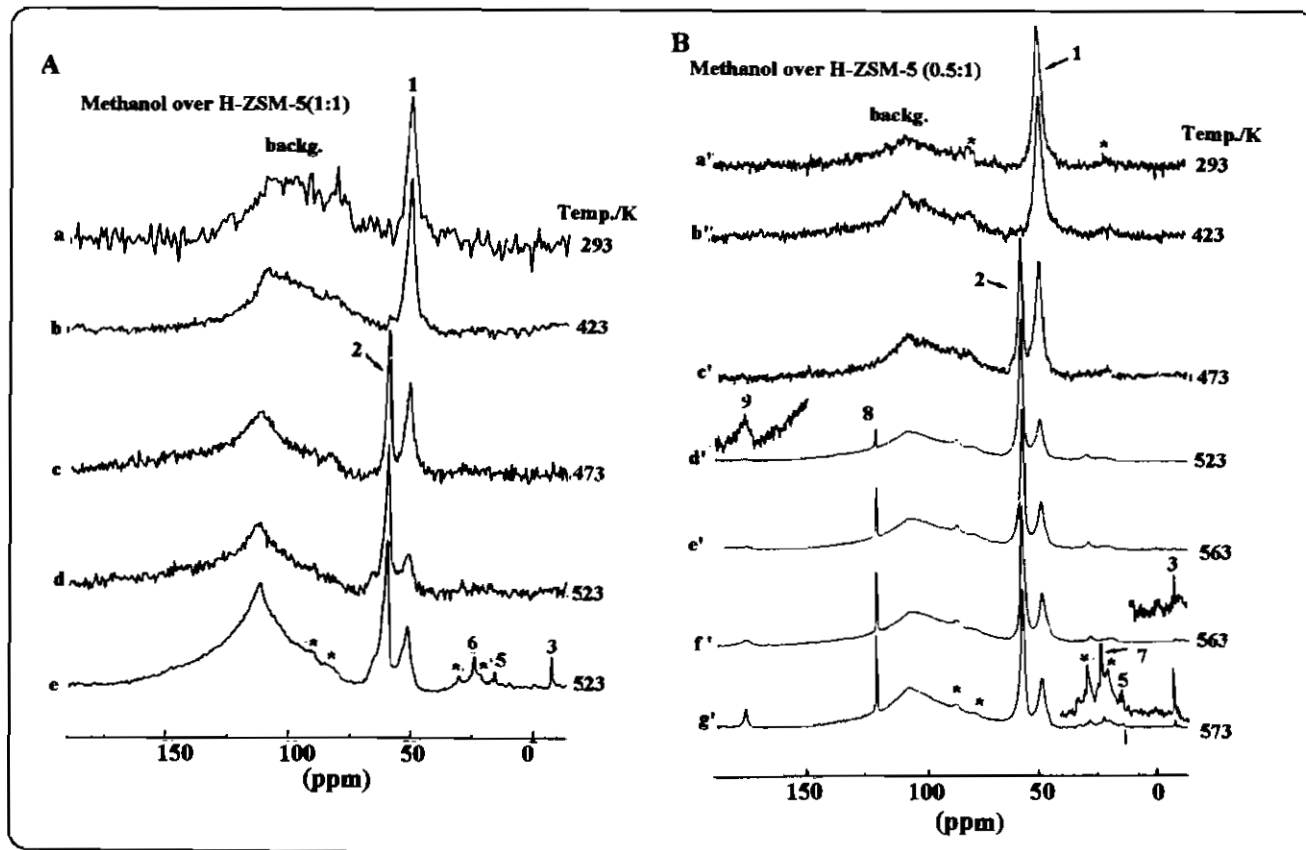
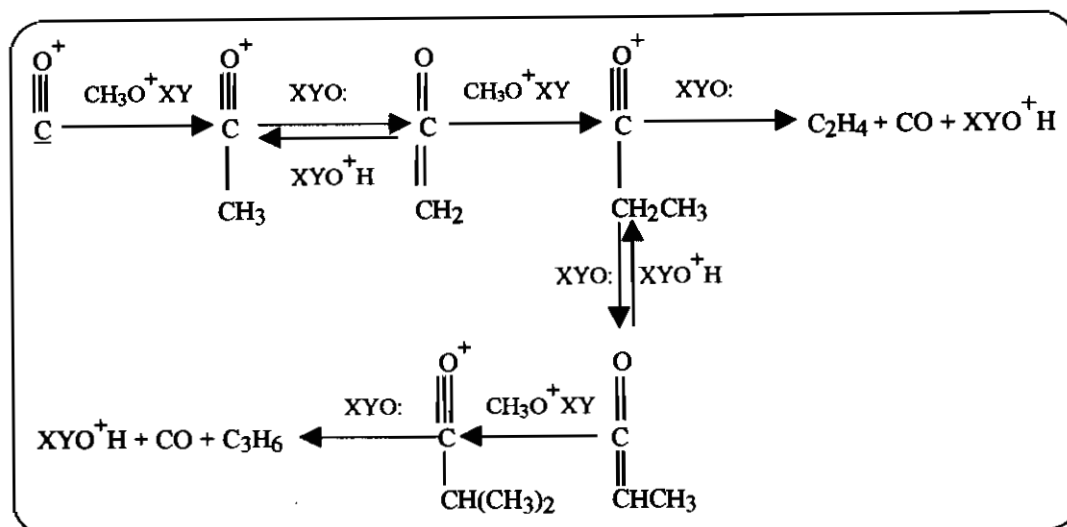


Fig. 4: $^{13}\text{C}\{\text{H}\}$ MAS NMR spectra of the sample with 0.5 and 1:1 methanol to acid site coverages after (a and a') no thermal treatment and (b, c, d, b', c' and e') heating for 25min, (e and d') heating for 25min, (f') heating for 10min and (g') heating for 3.5min. Hydrocarbon regions are expanded in d', f' and g'. Asterisk denotes spinning sideband. Backg.=background.



CONCLUSIONS

Methanol conversion over H-ZSM-11 proceeded in a similar fashion to that on H-ZSM-5. The results obtained from a continuous flow system showed that ethylene and methane were the primary reaction products. This was confirmed by further experiments carried out over the same zeolite, using solid-state MAS NMR technique. The chemistry of the conversion reaction was investigated by experiments performed on zeolite H-ZSM-5. The findings of these experiments showed that CO was neither an intermediate nor a catalyst in the chemistry of methanol-to-hydrocarbon reaction on the zeolite.

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