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Methanol Conversion to Hydrocarbons over Zeolite H–ZSM-5: Investigation of the Role of CO and Ketene in the Formation of the Initial C–C Bond

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Mechanistic studies concerning the formation of the initial carbon–carbon bond in the methanol conversion reaction over zeolite H–ZSM-5 are described and discussed. In particular, the possible roles of CO as a reaction intermediate or as a catalyst, via the formation of ketene, are evaluated. Experiments using $^{13}CH_3OH/^{12}CO$ reactant mixtures demonstrate that no CO is incorporated into ethene, the primary product of this reaction. In addition, CO is found to have no significant effect on the induction period for this reaction. Model experiments for the methylation of ketene by reaction with Me_2SO_4 and $Me_3O^+SbCl_6^-$ did not provide evidence for methylation of ketene on either of the C atoms, and from the products observed it is apparent that ketene acts only as an acylating agent in the normal way. Experiments using aluminium silica compounds as models for the active site in the zeolite are described and discussed. Hydrogen/deuterium exchange experiments indicate that a common intermediate exists that can lead to the eventual formation of CH_3OCH_3, CH_4, and C_2H_4. Coreaction of CD_3OCD_3 and CH_3OCH_3 indicates that at least two intermediates are required for the formation of the ethene primary product. The results of this study indicate that CO and CH_2CO play no significant mechanistic role in the formation of the primary products of methanol conversion. A mechanism consistent with the experimental evidence available involving a surface bonded methoxy group is proposed and discussed.

INTRODUCTION

The mechanism by which the primary hydrocarbon products are formed in the methanol conversion reaction has remained a controversial topic since the publication of the initial studies by Chang and Silvestri (*1*). A number of mechanisms have been proposed and these, together with the experimental data available until 1989, have been extensively reviewed and discussed (*2*, *3*). However, to date a general consensus on the reaction mechanism has yet to be reached. More recently, a number of NMR studies have addressed this problem and have suggested that CO could play a role, either as an intermediate (*4*, *5*), or as a catalyst (*6*) in the formation of the initial carbon–carbon bond. An nmr study by Munson *et al.* (*7*) has indicated that CO is not incorporated into the hydrocarbon products, but these experiments were conducted at a relatively high methanol conversion and are not conclusive with respect to the formation of the primary reaction products. Moreover, this study confirmed our previous initial experimental work in this area (*8*). More recently Munson and Haw (*9*) have observed the formation of trimethyloxonium ion from dimethyl ether on H–ZSM-5 at room temperature giving some support to the mechanistic proposals of van den Berg *et al.* (*10*). It is therefore clear that considerable uncertainty remains concerning this reaction mechanism and the aim of this paper is to evaluate the role of CO and ketene in the

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methanol conversion reaction. Furthermore, the H/D exchange experiments initially carried out by Mole and Whiteside (*11*, *12*) and the D labelling studies of Down (*13*) have been reevaluated at low temperature and low conversion to determine if a common intermediate links all the primary products from methanol, i.e. CH_3OCH_3, CH_4, and C_2H_4. In addition, some experiments using model compounds for the zeolite active site are discussed in order to provide further experimental evidence concerning the reaction mechanism for the formation of the primary reaction products.

EXPERIMENTAL

Zeolite Catalyst Evaluation

Zeolite H–ZSM-5 (Si/Al:60) was predried *in situ* in the reactor at 330°C in dry N_2 prior to use. All reactions were performed in a pyrex microreactor (5-mm i.d.) at atmospheric pressure. Product analysis was performed by gas chromatography (30-m DB1 megabore column, flame ionisation detector), as well as GCMS to determine isotopic distribution (using 30-m OV101 capillary column coupled to a 2-m Porapak QS column leading into a high resolution VG 7070E mass spectrometer, run at 6000 resolution and 60 eV ionising voltage. A DEC PDP 11-24 data system was used for data analysis).

Investigation of the Possible Incorporation of CO

A controlled feedrate (0.6 g h^{-1}, achieved by vaporisation at constant temperature) of $^{13}CH_3OH$ (Amersham, 92% ^{13}C) in either N_2 or CO/H_2 (1 : 1 by volume, BOC Ltd, 99% ^{12}C) was passed over H–ZSM-5 (0.2 g). Experiments were carried out with catalyst temperatures of 240, 260, and 290°C, respectively, at a constant GHSV = 3000 h^{-1} (P_{MeOH} 0.7 atm). Product analysis was performed using both GC and GCMS analysis.

H–D Incorporation from CH_3OD

A controlled feedrate (0.6 g h^{-1}) of CH_3OD (Aldrich) achieved by vaporisation at constant temperature, in flowing N_2 was passed over H–ZSM-5 (0.2 g) at temperatures of 240, 250, 260, 270 and 290°C, respectively, at a GHSV = 3000 h^{-1} in separate experiments. Gas samples were collected for product analysis by both GC and GCMS after 30 min reaction time, i.e., after 300 ml feed gas.

CD_3OCD_3 and CH_3OCH_3 over H–ZSM-5

CD_3OD (Aldrich) was vaporised at a controlled rate (0.6 g h^{-1}) in flowing N_2 and passed over two predeuterated-alumina catalyst beds held at 305 ± 5°C to produce CD_3OCD_3. The water produced and unreacted CD_3OD were removed from the gas stream in a trap maintained at −18°C after the first alumina bed. The second alumina bed served merely to drive the equilibrium-limited reaction further towards complete DME production. After the second alumina bed the gaseous products were passed through a room temperature trap and allowed to react over predeuterated H-ZSM-5 at 220°C for 2 h. A steady-state low conversion to fully deuterated hydrocarbons products, as determined by GC and GCMS analysis, was maintained. Complete predeuteration of all the catalyst beds was achieved by passing 2 ml D_2O (99.99%, Koch-Light) over each bed, in turn at 330°C, followed by drying in flowing N_2 for 3 h. Thereupon a controlled preset flow of CH_3OCH_3 (Aldrich) was fed into the CD_3OCD_3/N_2 stream to give the desired ratio. After 100 ml mixed feed gas was passed over the zeolite, a sample of the gaseous products was collected and analysed by GC and GCMS.

Methylation of Ketene

Ketene was prepared by the pyrolysis of distilled diketene (TCI Ltd) at 480°C in a quartz pyrolysis tube packed with silica wool. The diketene was fed into a stream of flowing N_2 (10 ml/min) via a syringe pump (3 ml/h). The resultant ketene/N_2 vapour was passed directly into the reaction flask without further purification. The reaction conditions required to achieve optimal ketene production were determined by studying the reaction of ketene with aniline (3 ml in 3 ml benzene). Under the conditions employed, essentially complete conversion of the aniline to acetanilide was achieved as determined by NMR spectroscopy, GC, and GCMS analysis (30 m OV351 capillary column).

The methylation of ketene was examined using trimethyloxonium hexachloroantimonate and dimethyl sulphate as methylating agents. Prior to reaction dimethyl sulphate was treated with K_2CO_3 and distilled immediately prior to use. The following methods were employed.

Method 1. Purified dimethyl sulphate (BDH Ltd.) was fed via a syringe pump (3 ml/h) into a stream of ketene/N_2, prepared as described above, at 200°C over a glass woolbed. The total reaction products were either (a) trapped at 0°C and quenched with methanol (5 ml) or (b) passed through a benzene/aniline trap solution (3 ml in 3 ml) and through a second trap to isolate volatile products.

Method 2. Ketene in N_2, prepared from 1.5 ml diketene, was bubbled through dimethyl sulphate (6 ml) held at 60°C. Upon completion, the solution was divided into two fractions, to one of which methanol (5 ml) was added. The clear dimethyl sulphate solution darkened steadily during ketene addition and lightened to a deep orange colour upon methanol addition.

Method 3. Ketene in N_2, prepared from 0.5 ml diketene, was passed through a partially dissolved solution of trimethyloxonium hexachloroantimonate (2.5 g) suspended in 12 ml benzene held at 65°C. Thereafter excess methanol was added to this solution which became homogeneous. The solution was analysed by NMR spectroscopy.

Synthesis and Reaction of Model Compounds

Hydrogen aluminium bis ethylene glycolate (A). This compound was synthesized according to the method outlined by Mehrotra and Mehrotra (*14*). Aluminium isopropoxide (5.3 g, 26 mmol) was dissolved in 60 ml of benzene. Ethylene glycol (8.6 ml, 154 mmol) was added and the mixture shaken and left to stand for 24 h. The isopropanol formed during the reaction was fractioned off and the remaining product filtered and washed with dioxane. The solid was dried *in vacuo* at 40°C for 3 h; 5.29 g of product was collected with melting point >300°C. Elemental analysis: experimental (theoretical) % C, 32.48 (32.46); % H, 6.58 (6.08); and % Al, 12.0 (18.2). Although the C and H analyses agree well with the expected values, the aluminium content is much lower than expected; this was considered to be due to the presence of polymeric aluminium oxygen species being formed.

Lithium aluminium bis 2,2-dimethyl-1,3-propanediolate (B). 2,2-Dimethyl-1,3-propanediol (27.4 g, 266 mmol) dissolved in THF (150 ml) was added dropwise to a stirred solution of $LiAlH_4$ (5.1 g, 133.6 mmol) in THF (200 ml) under N_2. This mixture was stirred for 48 h and the fine light grey product was collected by filtration and washed with pentane followed by THF. This was then dried *in vacuo* to give 29.6 g of product. The melting point was found to be >300°C.

Lithium aluminium bis catecholate (C). $LiAlH_4$ (5 g, 133 mmol) was added to dry THF (250 ml). Catechol (29.2 g, 266 mmol) dissolved in THF (70 ml) was added dropwise to the stirred $LiAlH_4$ solution dropwise. An exothermic reaction resulted with the evolution of H_2 and a further 150 ml THF was added. The reaction mixture was stirred for 48 h and subsequently refluxed for 28 h. The dark grey solid product was filtered off *in vacuo* and washed with THF. The product was then dried under reduced pressure to afford 43.26 g of product, with melting point 225–230°C. Elemental analysis: experimental (theoretical) % C, 59.06 (57.65); % H, 5.53 (3.20); and % Al, 5.6 (10.8).

Lithium aluminium oxide (D). An excess of water (10 ml) was carefully added to $LiAlH_4$ (4 g, 101 mmol) suspended in

THF (150 ml). After stirring the solution for 1 h, the THF was removed and the pale cream solid product dried *in vacuo* at 200°C for 2 h to yield 8.95 g of product. ^{27}Al MAS nmr of the product indicated that both tetrahedral and octahedral aluminium environments were present in approximately similar proportions. The tetrahedral environment is that expected from the product and the octahedral environment could be assigned to Al_2O_3 which was formed as a hydrolysis byproduct.

Catalytic Testing of Model Compounds

In a typical experiment the model compound (0.5 g) was reacted with dimethyl sulphate in a dry nitrogen gas stream in a fixed bed glass microreactor at atmospheric pressure. The reaction products were analysed by gas chromatography. Dimethyl sulphate was fed to the reaction at a controlled rate using a syringe pump and was vapourised in a stream of dry nitrogen. Prior to use the dimethyl sulphate was distilled from CaH_2 and sieved over 4A molecular sieve to ensure that no methanol, water or sulphuric acid were present.

TABLE I

Methanol Conversion in the Presence of Carbon Monoxide[a]

Temperature (°C):	240		260		290	
Feed[b]:	A	B	A	B	A	B
MeOH conv. (%)	84	82	78	79	99	99
Selectivity (%)						
C_1	tr[c]	tr	0.2	0.2	0.4	0.4
C_2	0.4	0.5	6.6	6.0	5.6	6.7
C_3	0.1	0.1	4.0	3.2	14	15
C_4	0.1	0.2	5.4	3.8	34	35
C_5	0.3	0.4	5.9	4.9	24	20
C_6	0.2	0.3	4.3	3.4	12	12
C_7	0.1	0.1	1.3	0.9	4.8	5.2
C_8	0.2	0.5	0.3	0.4	3.3	4.1
DME	99	98	72	77	1.3	1.6

[a] WHSV 3 h^{-1}, 0.2 g catalyst.
[b] A $MeOH/N_2$; B $MeOH/CO/N_2$
[c] tr = traces.

RESULTS

$^{13}CH_3OH/^{12}CO$ Reaction over H-ZSM-5

$^{13}CH_3OH/N_2$ and $^{13}CH_3OH/^{12}CO/N_2$ mixtures were individually reacted over H-ZSM-5 (Si/Al = 60) at temperatures from 240 to 290°C to enable the full range of methanol conversion to be investigated. Off-line gas chromatographic analysis of the reactor effluent gas is shown in Table 1. Within experimental error there are no differences in the conversion and selectivity for methanol conversion in the presence or absence of CO. The reaction products were analysed by GCMS. No increase in $^{13}C^{12}CH_4$, $^{13}C^{12}CH_3$, and $^{13}C^{12}CH_2$ (29.0347, 28.0268, 27.0190 amu, respectively) was observed in the presence of ^{12}CO at any of the temperatures studied. Representative mass spectra are shown in Fig. 1. The resolution of the GCMS utilised in this experiment was such that $^{13}C^{12}CH_4$ (29.0347 amu) and $^{13}C_2H_3$

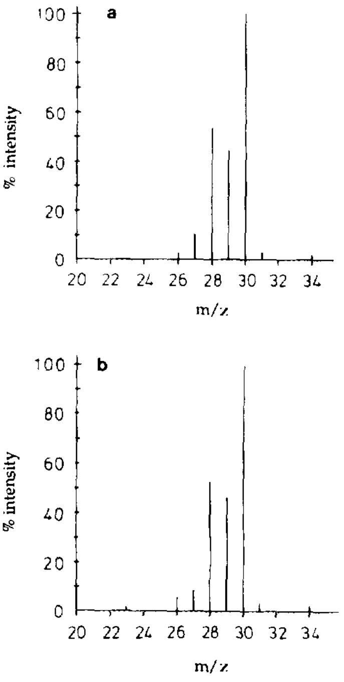


FIG. 1. Ethene mass spectra for reaction of (a) $^{13}CH_3OH/N_2$ and (b) $^{13}CH_3OH/^{12}CO/N_2$ over H-ZSM-5 at 240°C.

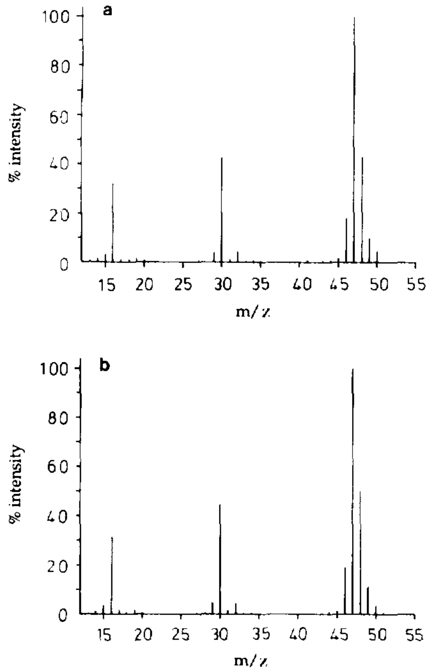


FIG. 2. Dimethyl ether mass spectra for reaction of (a) $^{13}CH_3OH/N_2$ and (b) $^{13}CH_3OH/^{12}CO/N_2$ over H-ZSM-5 at 240°C.

(29.0302 amu) could be easily differentiated. In addition, no increase in $^{13}C^{12}CH_5O$ (46.0374 amu) was observed in the dimethyl ether products and representative mass spectra are shown in Fig. 2. These results indicate that CO is not incorporated into the ethene or dimethyl ether products over a wide range of methanol conversions investigated.

Effect of CO on Initial Reaction Period

Previous studies have indicated that under certain conditions the methanol conversion over zeolite catalysts is subject to an induction period (*15*). During this period the methanol conversion is observed to increase rapidly, although the reaction conditions remain unchanged. The effect of adding CO to the reactants during the initial stages of the reaction was investigated using zeolite Y that had previously been calcined at 660°C to decrease the concentration of Brønsted acid sites. The results are shown in Fig. 3 and it is apparent that CO does not exhibit a positive effect on methanol conversion. In effect it appears to cause a slight decrease in the initial conversion, which may be due to a competitive adsorption process.

Investigation of the Methylation of Ketene

Ketene was reacted with methylating agents under a variety of conditions (Methods 1–3, Experimental section). GCMS analysis of the reaction products upon passing ketene through dimethyl sulphate at 60°C both prior to and after quenching with methanol indicated that the only reaction products were dimethyl ether, methyl acetate, ethanedioic acid, water and carbonic acid dimethyl ester. NMR analysis of the corresponding solution provided no indication for the presence of C_3 "propyl" units either before or after quenching.

Even after allowing ketene and dimethyl sulphate to react at 200°C and trapping the reaction products in a solution of aniline in benzene, no products consistent with methylation at either C atom of ketene were observed. In this reaction the total contents of the traps were analysed and identified as complex solutions of methyl acetate (8%), acetic acid (2%), acetamide (12%), N-

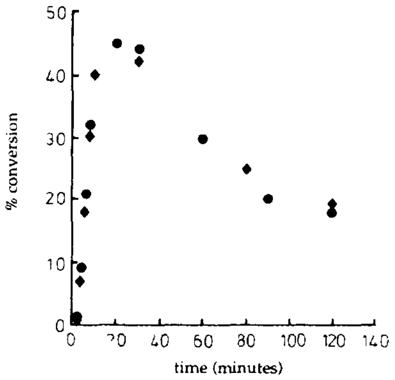


FIG. 3. Effect of CO on the initial reaction period for the conversion of methanol over zeolite HY (precalcined at 660°C) at 250°C: (◆) $CH_3OH/CO/N_2$; (●) CH_3OH/N_2.

methyl-N-phenyl acetamide (23%), N-acetyl or phenyl acetamide (22%), carbonic acid dimethyl ester (4%), unreacted dimethyl sulphate (4%), ketene (2%), and benzene (23%).

Similarly, passing ketene through a partially dissolved slurry of trimethyl oxonium hexachloroantimonate in benzene at 60°C afforded no C methylation products either before or after quenching with methanol. The products formed were equivalent to that of the analogous dimethyl sulphate experiment previously described.

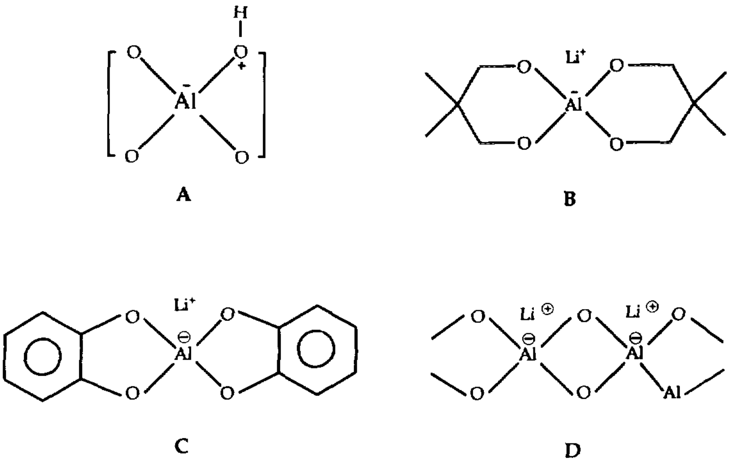
The observed product range indicates that ketene is only acting as an acylating agent and there is no evidence for methylation of ketene at either carbon atom.

Reaction of Model Compounds for Zeolite Brønsted Conjugate Basic Site with Methylating Agent

In our previous studies we demonstrated (*16*) that lithium aluminium tetraisopropoxide ($LiAl(OPr^i)_4$) was a useful and simple model for the investigation of the nucleophilicity of the Al–Ö bond in zeolitic systems. A limitation of this simple model was that on reaction with methylating agents $LiAl(OPr^i)_4$ was consumed. The purpose of this aspect of the study was to synthesise cyclic aluminium alkoxide model compounds of the conjugate base such that the alkoxide ligand could not easily be detached from the aluminium. The greater structural stability of these model compounds would enable their reaction with dimethyl sulphate to be investigated at temperatures significant for the formation of hydrocarbon products. The model compounds investigated were coded A–D, as shown in Fig. 4, and their preparation is described in the Experimental section. The model compounds were reacted with dimethyl sulphate in a stream of dry N_2 at temperatures in the range 200–300°C. In the absence of dimethyl sulphate it was found that the model compounds were thermally stable in this temperature range and that the blank thermal reaction of dimethyl sulphate was negligible. The results are given in Table 2.

Hydrogen–Deuterium Labelling Studies

Reaction of CH_3OD/H–ZSM-5. Previous studies by Mole and Whiteside (*11*, *12*) using CH_3OD/D_2O mixtures over H–ZSM-5 demonstrated that D was rapidly exchanged into the ethene and dimethyl ether products, indicating a common intermediate for these products. These studies, however, were conducted at a high temperature of 290–300°C and may not be totally representative of primary reaction chemistry. In this study, CH_3OD was reacted over H–ZSM-5 (Si/Al = 70) over the temperature range



A B

C D

FIG. 4. Model compounds for the zeolite active site.

TABLE 2

Reaction of Dimethyl Sulphate over Model Compounds

Model compound	Me_2SO_4 WHSV (h^{-1})	T (°C)	Time on line (min)	Me_2SO_4 conversion (%)	Product selectivity (% by mass)					
					CH_3OH	CH_3OCH_3	CH_4	C_2H_4	C_3	C_{4+}
A	0.21	250	30	0.1	82.9	15.8	0.2	1.1	—	—
B	0.21	200	45	0.1	63.2	36.6	tr	0.2	—	—
		250	10	0.2	61.0	38.2	0.1	0.4	0.3	tr
C	0.19	250	45	0.03	100	—	—	tr	—	—
D	0.10	250	60	0.1	37.3	62.3	tr	0.1	0.3	—

240–290°C to enable lower temperatures and conversions to be studied. Off-line gas chromatographic analysis gave product selectivity and conversions identical to that in Table 1 when CH_3OD was reacting at the same conditions. The products were analysed by GCMS and the total incorporation of D into the products was determined by computer simulation of the mass spectral parent ion envelope. The experimental data are given in Table 3. It is apparent that as the temperature increases so does the methanol conversion to hydrocarbons at the expense of conversion to dimethyl ether. At the very low conversion obtained at 240°C it is important to note that no incorporation of D was observed in the dimethyl ether, the major product at this condition. As the conversion increases it is apparent that the level of deuterium incorporation increases in all three primary reaction products, i.e., dimethyl ether, ethene, and methane. This work therefore confirms that the previous results obtained by Mole and Whiteside (*11*, *12*) at 290–300°C are also applicable at much lower temperatures. In addition, this investigation has extended the previous study to include methane which is known to be a significant primary product under these conditions.

Reaction of CD_3OCD_3 and CH_3OCH_3 over D–ZSM-5. Previous studies by Perot (*17*) using $^{13}CH_3O^{13}CH_3$, $^{12}CH_3O^{13}CH_3$, and $^{12}CH_3O^{12}CH_3$ mixtures have been used as evidence that an intramolecular reaction of dimethyl ether does not occur as a route for the formation of the primary ethene product. However, the studies of Perot were carried out at a high conversion of dimethyl ether and under such conditions it was not surprising that the major pathway for the reaction of dimethyl ether was intermolecular. Against this background we have studied the possibility of an intramolecular reaction of dimethyl ether at low conversions and reaction temperatures. CH_3OCH_3 and CD_3OCD_3 were reacted in approximately equimolar proportions over predeuterated H–ZSM-5 (Si/Al = 60) at 220 and 240°C. The products were analysed by off-line gas chromatography and the data are shown in Table 4. The conversion obtained at 220°C is sufficiently low to be relevant to the study of the primary reaction products. The products at 220°C were analysed by GCMS and the results are shown in Table 5. It is appar-

TABLE 3

D/H Labelling Studies for the Conversion of CH_3OD over H–ZSM-5

	Temperature (°C)				
	240	250	260	270	290
MeOH Conv (%)					
DME	80	79	55	1	1
Hydrocarbons	1	2	22	97	98
D incorporation (%)					
DME	0	2	5	7	—
Ethene	—	12	16	17	19
Methane	—	—	10	12	13

TABLE 4

Conversion of Dimethyl Ether (CD_3OCD_3 and CH_3OCH_3) over H-ZSM-5

	Temperature (°C)	
	220	240
DME conversion		
(a) MeOH	6.5	12.6
(b) hydrocarbons	2.5	14.4
Product selectivity		
CH_4	3.2	1.7
C_2H_4	21.9	27.5
C_2H_6	*tr*	0.4
C_3	39.8	39.1
C_4	15.8	16.3
C_5	7.2	7.7
C_6	4.7	4.3
C_7	3.9	2.1
C_{8+}	3.5	0.9

ent from these data that even at very low conversion there is no evidence for an exclusive intramolecular pathway for the formation of ethene from dimethyl ether.

It is clear that there is a very rapid exchange of CD_3OCD_3 and CH_3OCH_3 to form CD_3OCH_3 even at the low conversion level observed at 220°C, which is in agreement with the observations of Down (*13*) for studies at 278°C. However, the uptake of deuterium into ethene as C_2D_4 is much lower than that expected from the corresponding level of deuterium available. Similarly the methane formed at 220°C as CH_4 is considerably higher than the expected level.

DISCUSSION

Evaluation of the Role of CO

It is interesting to note that B. Nagy *et al.* [18] were the first to investigate the potential role of CO in the methanol conversion reaction using a ^{13}C NMR study and found that CO could be incorporated into the aromatic products at 350°C. This was considered to be due to the formation of an aromatic aldehyde via the Gatterman Koch reaction. However, as the methanol conversion was typically >30%, the results of this study are not relevant to the formation of the primary hydrocarbon products. The possibility that CO could be a reactive intermediate was first proposed by Anderson and Klinowski (*4*, *5*) on the basis of *in situ* NMR studies. Based on the known chemistry of carbon monoxide, there are four reaction pathways that lead to the incorporation of CO into the reaction products of methanol conversion (Figure 5). Three of these pathways (1, 2, and 4) lead directly to formation of a carbon–carbon bond and are therefore of relevance concerning the formation of the primary reaction products. The fourth, the formation of methyl formate, would lead to the formation of methanol on eventual hydrolysis of this ester, and hence this could lead to the indirect incorporation of CO into the reaction products. However, the results of the isotopic studies involving the reaction of $^{13}CH_3OH/^{12}CO/N_2$ mixtures show conclusively that CO is not incorporated into the primary hydrocarbon reaction products during the methanol to gasoline reaction over H–ZSM-5. Subsequently, Jackson and

TABLE 5

Reaction of CD_3OCD_3 and CH_3OCH_3 Mixtures over H–ZSM-5: D/H Isotopic Labelling Results at 220°C

DME conv.(%)	Feed[a] DME		Product[a]								
			DME			Ethene			Methane		
	CD_3OCD_3	CH_3OCH_3	CD_3OCD_3	CH_3OCH_3	$CD_xH_{6-x}O$	C_2D_4	C_2H_4	$C_2D_xH_{4-x}$	CD_4	CH_4	CD_xH_4
2.5	0.63	0.37	0.37	0.11	0.52	0.12	0.11	0.77	0.36	0.27	0.37

[a] Isotope distributions are expressed in terms of fractional selectivity.

$$1.\ CO + H_2 \longrightarrow CH_4 + C_2H_4 + \ldots\ldots\ldots$$

$$2.\ CH_3OH + CO + H_2 \longrightarrow C_2H_5OH \longrightarrow C_2H_4$$

$$3.\ CH_3OH + CO \longrightarrow CH_3O.CO.H \xrightarrow{H_2O} CH_3OH$$

$$4.\ CH_3OH + CO \longrightarrow CH_3\,COOH \longrightarrow C_2H_4$$

FIG. 5. Possible reaction pathways for carbon monoxide.

Bertsch (*6*) proposed a mechanism for the methanol conversion reaction based on their studies using the Pearson reaction (*19*) in which CO was involved in a catalytic role. In their mechanistic proposal carbon monoxide was considered to be methylated to form ketene which was subsequently methylated on the methylene carbon, which then decomposed to form ethene and carbon monoxide (Fig. 6). This mechanistic proposal requires that CO is not incorporated into the hydrocarbon products and is therfore consistent with the labelling studies presented in this paper. However, the mechanistic studies presented in this paper provide three conclusive sets of evidence that the mechanism presented by Jackson and Bertsch does not occur within the zeolite catalysts. The first experimental evidence concerns the role of CO during the induction period. The data presented in this paper show that addition of CO leads to a slight decrease in conversion which is in agreement with previous observations by B. Nagy *et al.* (*18*), and certainly no enhancement in initial rate was observed.If CO were acting catalytically, then the enhanced concentration of CO present in our experiments would have been expected to significantly enhance initial conversion. The second experimental evidence concerns the model experiments conducted with ketene. Ketene was reacted with potent methylating agents under a range of conditions and at no time was the methylation pathway suggested by Jackson and Bertsch confirmed experimentally. Indeed, the only methylation products observed were those for the expected methylation of the oxygen atom of ketene. The third experimental evidence concerns the observation in our studies of a rapid incorporation of deuterium from CH_3OD into the hydrocarbon product even at low conversion and at low reaction temperatures. Jackson and Bertsch indicate that with the Pearson reaction no hydrogen isotope exchange between the acidic $O\underline{H}$ and methoxyl $\underline{H}CH_2O$ groups is observed at 200°C. This is essential to their mechanistic proposal. They noted the previous D/H studies of Mole and Whiteside (*11*, *12*), but concluded that the exchange reaction was a consequence of the higher temperature (290–300°C). The present study shows that the D/H exchange reaction with CH_3OD or CH_3OH/D_2O as reactants is a central feature of the zeolite-catalysed reaction pathway, and hence any reaction mechanism proposed must be consistent with this observation. Based on the wide range of model and catalyst studies presented in this paper, we conclude that CO does not play any significant role, either via direct incorporation or via a catalytic pathway, in the formation of the primary reaction products.

Reaction of Model Compounds for the Zeolite Active Site

A number of mechanistic proposals have suggested that the basicity of the conjugate base site in the zeolite ZSM-5 is important for the activation of the reactant molecules. For example, in the initial mechanistic proposal by Chang and Silvestri, the conjugate base site was considered to deprotonate a gas phase, i.e., non-surface-bonded, metha-

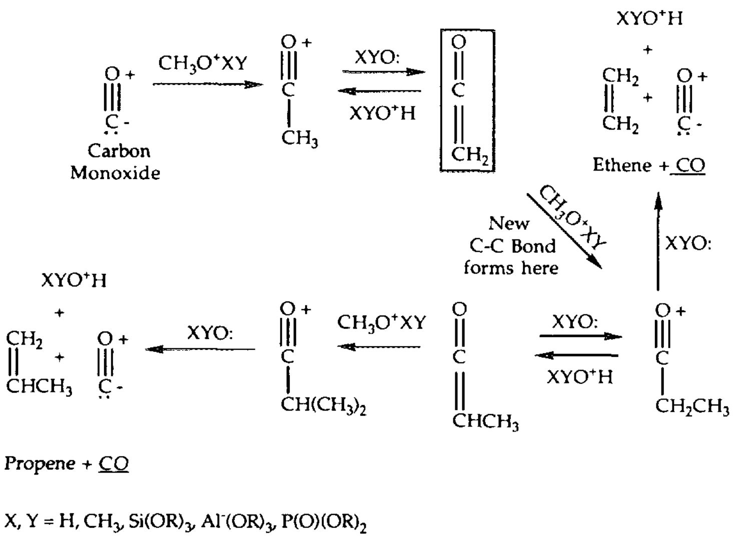


FIG. 6. Mechanistic proposal for the involvement of ketene as a central intermediate (taken from Ref. (6)).

nol molecule (1). In addition, the trimethyloxonium proposals of Olah (20) and van den Berg *et al.* (10) suggest as similar deprotonation of a nonbonded intermediate as a key step. In our initial studies of attempting to model the zeolite active site using simple compounds, we utilised lithium aluminium tetraisopropoxide (16). This model compound was used to demonstrate the nucleophilicity of the conjugate base site in preference to it acting as a true base. However, the inherent reactivity of this model compound has promoted the present more detailed study which utilises model compounds involving cyclic alkoxide structures. In these model compounds the aluminium atom is tetrahedrally coordinated and carries a formal negative charge. Hence, they can be considered to model aspects of the geometry and electronic structure of the conjugate base site.

For compounds A and B it is apparent that significant conversion to dimethyl ether and hydrocarbons is observed. In particular ethene is observed as a product. However, it is possible that some of the ethene observed from compound A may have been due to β-elimination of ethene following methylation of the model compound (Fig. 7). Such a pathway requires reductive conditions and it is unlikely that this could account for all of the ethene observed. To overcome this potential complication, compound B, derived from 2,2-dimethyl propanediol, was utilised since this compound has no β-hydrogens and hence the elimination pathway available for model compound A cannot occur. The observation that ethene could be observed on reaction of dimethyl sulphate with compound B is indicative that ethene is being formed as a primary reaction product.

Lithium aluminium bis catecholate, compound C, was found to be unreactive to dimethyl sulphate, presumably due to the reduced nucleophilicity of the phenoxide oxygens. It is apparent that the model compounds containing aromatic structures, although very stable, are not particularly useful for the study of the methanol conversion reaction.

The use of a polymeric model compound D also gave trace conversion to hydrocarbon products. It was noted that for all the model compounds, hydrocarbon formation was always accompanied by DME forma-

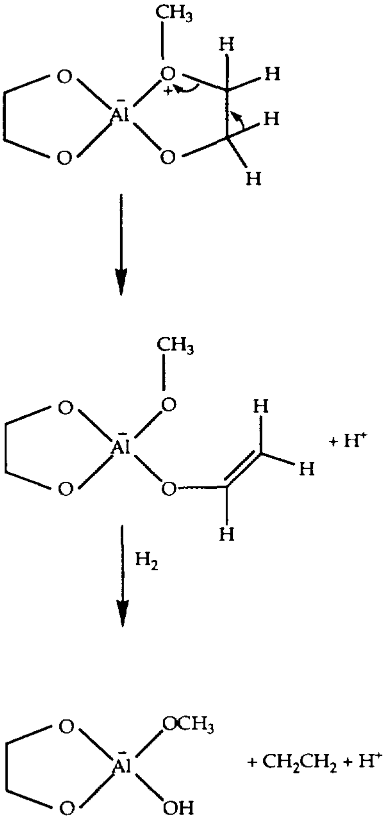


FIG. 7. β-elimination pathway for the formation of ethene from model compound A.

tion, which can be considered to occur via methylation of the nucleophilic Al–Ö oxygen in the model compound by dimethyl sulphate, which is a potent methylating agent, and subsequent reaction of the methoxy species with methanol, which is also observed as a product. These model experiments therefore provide possible evidence for the role of a surface methoxy species as an intermediate in the formation of the primary ethene product. The coformation of dimethyl ether and ethene is indicative that the surface methoxy species may be a common intermediate for both primary reaction products. It is clear that only very low, but significant, levels of hydrocarbons are observed with these model compounds. It should be noted that features present on the zeolite, e.g., proximity of adjacent Al–Ö sites and the cage structure, were not successfully modelled in this study. However, the use of simple model compounds can provide indirect evidence concerning the role of the surface methoxy intermediate in the methanol conversion reaction.

Mechanism of Formation of the Primary Reaction Products

As noted recently by Chang (*2*) there are a large number of mechanistic proposals concerning the formation of the primary hydrocarbon product, ethene. Previous mechanistic studies have largely ignored the formation of the other significant primary hydrocarbon product, i.e., methane, probably because its formation does not require the formation of a carbon–carbon bond. However, it is important that any mechanistic proposal should be able to account for the formation of all three primary reaction products, i.e., dimethyl ether, methane and ethene (*21*). Most effort has centred on the nature of the intermediate involved in the formation of these products. The present study has confirmed that at low conversion and low temperature intramolecular reaction of dimethyl ether does not occur and therefore this is not a central intermediate in this process. In addition, we have confirmed that CO does not play any direct or catalytic role in the formation of the initial reaction products.

Very recently model *in situ* NMR experiments conducted by Munson and Haw (*9*) have indicated that the trimethyloxonium (TMO) ion can be slowly formed from dimethyl ether on the zeolite ZSM-5. This study has provided the first experimental observation that the intermediate proposed previously by Olah (*20*) and van den Berg *et al.* (*10*) can be formed on the zeolite from dimethyl ether. This study does not show the formation of any hydrocarbon products from the trimethyloxonium ion and therefore does not provide any evidence concerning the role of this bulky species as a reaction intermediate. Previously, Chang has provided evidence, also using NMR spectroscopy, that TMO–ZSM-5 is unstable and ion decomposition results in the formation of a methylated zeolite surface (*22*). Our previous studies (*21, 23*) concerning the reactivity of methylating agents that cannot form the corresponding intermediate, analogous to the trimethyloxonium ion, and the relative reactivity of oxygen versus sulphur containing reactants have provided conclusive evidence that the trimethyloxonium ion is not a central intermediate in the methanol conversion reaction mechanism. If it is present within the porous structure of the zeolite, then it is most likely to act as a potent methylating agent for the zeolite Al–Ö centres, rather than a ylide source.

As noted previously (*2, 3*), there is apparent consensus that the initial step in the reaction sequence involves the formation of a surface methoxy group (Fig. 8a) via methylation of the zeolitic Al–Ö centre by protonated methanol, dimethyl ether or the trimethyloxonium ion. Evidence in support of this proposal is evident from the FTIR studies of Forrester and co-workers (*24, 25*), as well as the reactivity of a range of methylating agents (*23*). In this study the use of model compounds for the zeolite active site has provided further evidence for this methylation pathway. This methoxy species is considered to be a common intermediate for the formation of the three primary reaction products, CH_4, C_2H_4, and CH_3OCH_3 (Fig. 8a). Evidence to support this proposal is obtained from the D/H isotopic experiments described in this paper, which showed that the incorporation of D from CH_3OD into dimethyl ether, methane, and ethene increases for all three compounds with increasing conversion. The question that remains is by what route ethene is formed from the methoxy intermediate. Previous studies (*15*) have also proposed the involvement of a surface methoxy group in the formation of ethene. However, these proposals consider that the methoxy is the sole intermediate en route to ethene. Consideration of the relative ratios of CH_4/alkene during the induction period of the reaction (*23*) has indicated that it is unlikely that a single intermediate can account for the observed trends. This led to the proposal of the involvement of a surface bound oxonium methylide as the key intermediate, a species that is iso-electronic with a gas phase carbene (*23*). In this respect the difference in distribution of the deuterium label between dimethyl ether and ethene in the experiments conducted with mixed CD_3OCD_3 and CH_3OCH_3 reactants at 220°C is considered to be of mechanistic significance. It indicates that the crucial C_1 intermediate leading to the formation of ethene is more readily derived from a C_1 species containing hydrogen than that containing deuterium, indicating that a primary isotope effect is apparent. Furthermore, this observation indicates that this C_1 intermediate is different from that for the formation of dimethyl ether, since if only one C_1 intermediate was involved then the distribution of the deuterium label between dimethyl ether and ethene would be similar. Since the evidence obtained from the reaction of CH_3OD indicates that there is a common C_1 intermediate, this result indicates that a further C_1 intermediate is required to be formed prior to the formation of ethene. The observation of a primary isotope effect with respect to this C_1 intermediate is consistent with the slow formation of a surface methylide species from the surface methoxyl species by loss of H^+. The formation of the oxonium methylide has been the subject of much debate and it has been proposed that it may involve a radical pathway (*22*). In addition, we consider that recent theoretical calculations of the surface bound methoxy species may be instructive (*26*). These indicate that one of the C–H bonds of the methoxy group is asymmetric with respect to the other two, in that it is lengthened. This in effect causes a polarity in this C–H bond which would give rise to a small net positive charge to be on the hydrogen and a small net negative charge on the carbon atom. In this sense, as noted previously by Chuvylkin *et al.* (*26*) and by Chang (*2*),

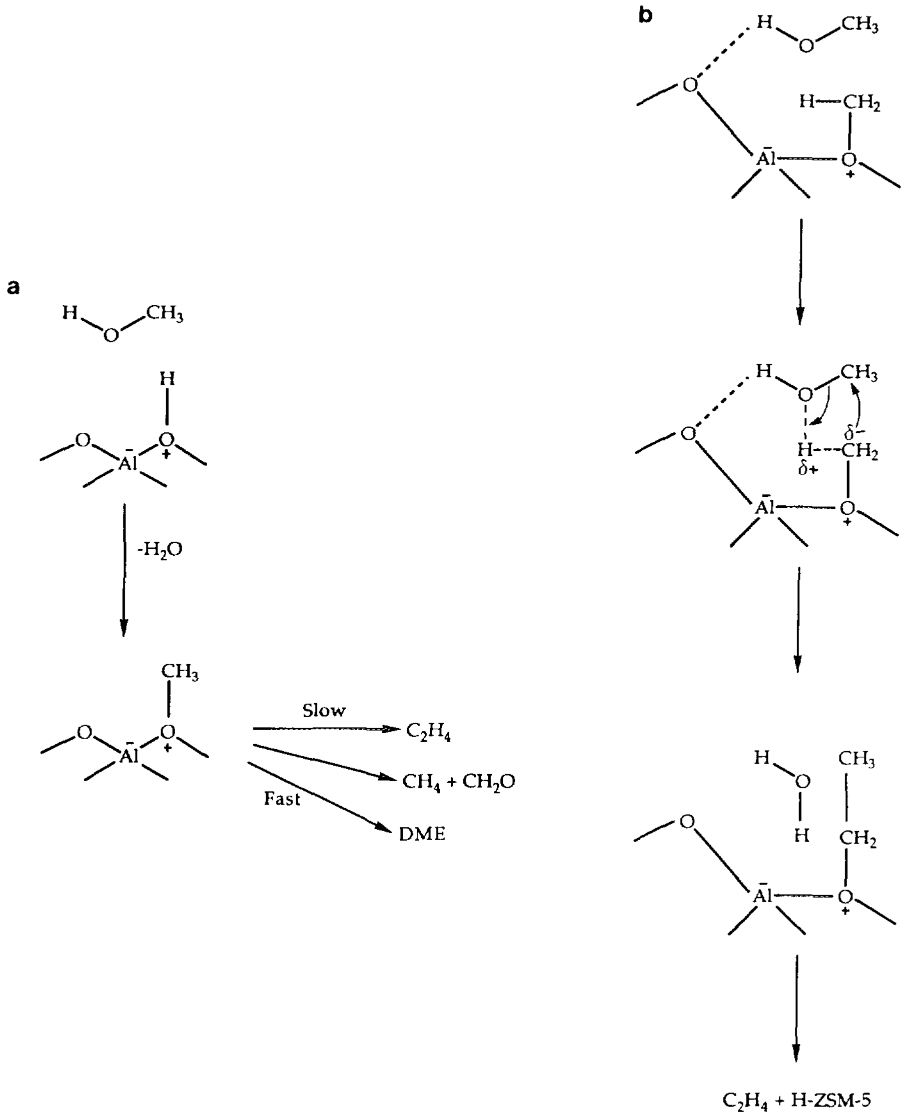


FIG. 8. Proposed reaction mechanism for the formation of the primary ethene product for the conversion of methanol over zeolite catalysts: (a) formation of surface methoxyl species and (b) formation of initial C–C bond.

the formation of the oxonium methylide intermediate may not formally occur in the formation of the primary ethene product, since this net polarity may be sufficient for the carbon to interact with a gas phase methanol molecule within the cage structure of the zeolite via a concerted process. Since the transition state for this process involves transfer of a hydrogen, it would be expected that an isotope effect would be observed (Fig. 8b). Additional evidence to support this mechanism is provided by semiempirical cluster calculations (CNDO/BW) made by Gale *et al.* (*27*) on the interaction between methanol and a Brønsted acid site in H–ZSM-5 which show that, via hydrogen bond formation, such a methanol molecule is activated with respect to nucleophilic attack at the carbon atom. Hence, reaction of the surface methoxy via a concerted pathway could therefore result in the formation of a surface ethyl group, which on β-elimination would re-establish the zeolite Brønsted acid site and give the ethene primary product. Alternatively, reaction of the oxygen of a gas-phase methanol with a surface methoxy group would result in dimethyl ether formation, whereas hydride transfer from methanol to the surface methoxy would result in methane formation.

This mechanistic proposal is outlined in Figs. 8a and 8b and is considered to be consistent with the experimental data currently available for the methanol conversion reaction over zeolite catalysts with respect to the formation of ethene, methane and dimethyl ether.

Previously there has been some debate as to whether ethene alone is the primary hydrocarbon product containing a C–C bond or that propene and possibly butene should also be considered as possible primary products. The formation of C_3 and higher hydrocarbons can be considered to occur by two possible routes. First, ethene formed via β-elimination from the surface ethoxy species could be methylated by reaction with a surface methoxy group. The propene so formed could also be methylated to form butenes and hence chain propagation could be via a methylation process (*23, 28*). Second, the surface ethoxy could interact with a gas phase methanol/dimethyl ether to form a surface iso-propoxy by an analogous process to that described for the formation of the surface ethoxy species (Fig. 8b). Propene would then be formed by β-elimination from the surface isopropoxy species, alternatively the surface isopropoxy species could interact with a further gas phase methanol/dimethyl ether to form a surface C_4 species which on subsequent β-elimination would yield butene. If this second pathway is operative, then propene and butene would be considered to be primary reaction products. This type of propagation pathway is an essential feature of the mechanistic proposal of van den Berg *et al.* (*10*).

At the present time there are very few experimental data which enable differentiation of these two pathways to be made. Some studies have been indicative that propane and butene are primary products (*29–31*). For example, Kolboe (*30*), using DSC with associated gas chromatography, showed that dimethyl ether pre-adsorbed on H-ZSM-5 was rapidly transformed on heating to hydrocarbons, mainly propene and isobutane, with very small quantities of methane and ethene. The high propene/ethene was in agreement with similar infrared spectroscopy studies of Forrester and Howe (*25*). However, as noted by Espinoza and Mandersloot (*31*) the propene/ethene ratio is a function of the reactant dimethyl ether/methanol ratio and is not a function of conversion. In the experiments of Kolboe (*30*) and Forrester and Howe (*25*) high levels of propene were observed solely as a result of using dimethyl ether as a reactant, which is a more effective methylating agent. Hence, these studies do not provide information concerning the initial mechanism of propene formation. However, if the formation of propene was the result of a second concerted interaction of a surface ethoxy species and gas-phase methanol, then the rate of isopropoxy formation would be expected to be similar to the rate of initial ethoxy formation, i.e., slow. Consequently in the initial stages of the reaction the zeolite surface would have a high concentration of surface methoxy groups, a very low concentration of surface ethoxy groups and a lower concentration of iso-propoxy groups. The subsequent β-elimination steps would then result in the formation of more ethene than propene and this would not be expected to be affected significantly by changing the methanol/dimethyl ether reactant ratio. However, this is not observed experimentally and this may indicate that propene is formed via methylation of the initial ethene product. Although the rate of ethene methylation is known to be slow compared to higher alkenes (*12, 32*), the zeolite surface would be highly methylated at the low conversion conditions and this could represent a potent methylating agent towards ethene. In addition, due to the microporous nature of the zeolite catalyst it is expected that ethene could be readily readsorbed and reacted prior to desorption from the intracrystalline space. This effect, known as adsorption–desorption disguise (*33*), is known to complicate the identification of primary products.

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