Reaction of Ethyl Diazoacetate with the Zeolite Catalyst H-ZSM-5: a Model Study of Carbon–Carbon Bond Formation

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Reaction of the substituted diazomethane with the acidic and conjugate base forms of the zeolite ZSM-5 is used to model carbon–carbon bond formation for methanol conversion into hydrocarbons, and the results re-inforce the involvement of a surface bonded C_1 intermediate rather than a non-bonded trimethyloxonium ion ylide.

In the conversion of methanol into hydrocarbons over the Mobil ZSM-5 zeolite and other catalysts, controversy[1,2] still continues over the mechanistic nature of the crucial $C_1 \rightarrow C_2$ conversion step. Two mechanistic proposals that have received considerable support, yet are in direct opposition, are those involving a non-bonded, electrostatically bound, trimethyloxonium ion[3] and a surface bonded carbene species[4] as key reaction intermediates. It has been reported recently that diazomethane acts as a suitable precursor to hydrocarbons[5] and this was suggested as strong evidence in favour of the carbene mechanism. More recently, however, Olah[1] has criticised these results, particularly the possibility of carbene insertion into the C–H bond of a surface methyloxonium species. Furthermore using diazomethane as a model compound a complication of carbene dimerisation to ethene and subsequent reaction to propene arises. However, substituted diazomethanes can overcome this problem but as yet no such model studies have been reported. In this communication we present results using the substituted diazomethane ethyl diazoacetate,[6] which we consider lend further support for C–C bond formation involving surface bonded intermediates in the methanol conversion reaction.

In a typical experiment, distilled ethyl diazoacetate was reacted over pre-dried acidic H-ZSM-5 or the conjugate base form Na-ZSM-5 (*ca.* 0.1 g), in a glass microreactor. The products were passed through two traps, each at −35 °C, to remove unreacted starting material which was found to interfere with subsequent gas chromatography. ^{1}H N.m.r. spectroscopy of each trap sample showed the bulk of the material collected (>99%) to be starting material. Gas samples were analysed using a suitably calibrated gas chromatograph. Results for both acidic and basic forms of the zeolite are given in Table 1 along with the results for reaction of dimethyl sulphate over the conjugate base which were reported previously.[7] Blank experiments were carried out using the diazo compound in the absence of catalyst, and both

Table 1. Reaction of ethyl diazoacetate with zeolite ZSM-5.

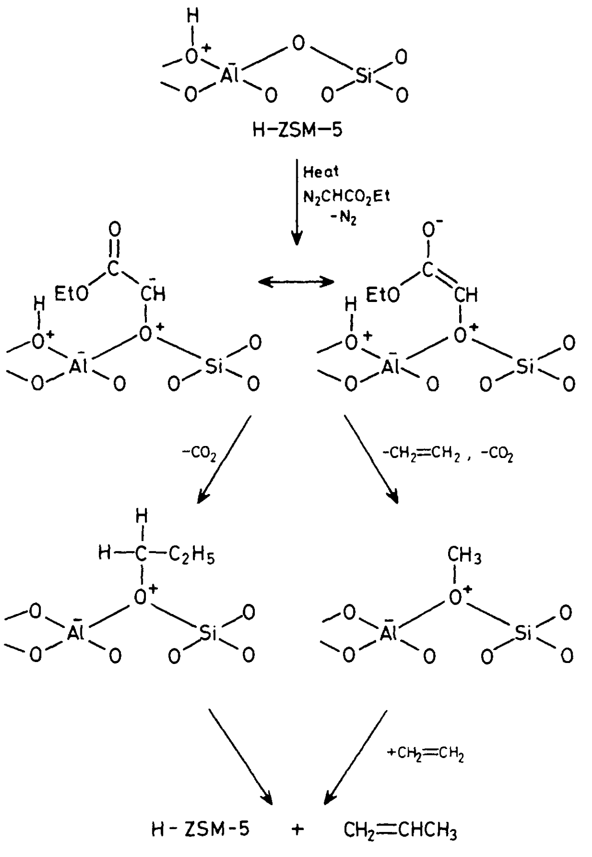
Catalyst	TOL[a]/ min	WHSV[b]/ h^{-1}	t/ °C	Conversion/ %	Product selectivity/mol % C_1	C_2=	C_3=	C_{4+}
H-ZSM-5	5	0.7	189	16	tr[c]	99.1	0.3	0.6
	15	0.7	189	20	tr	95.4	1.0	3.6
H-ZSM-5	5	1.0	210	45	tr	99.8	0.2	tr
	10	1.0	210	45	tr	97.4	0.4	2.2
H-ZSM-5	65	0.6	80	0.1	—	52	48	—
	130	0.6	125	2.0	—	97.2	2.8	—
Na-ZSM-5	5	0.5	125	2	tr	19	81	tr
	20	0.5	170	18	tr	48.8	50.9	0.3
	50	0.5	195	22	tr	56	43	1
Na-ZSM-5 + Me_2SO_4	130	0.075	300	2	48.1	51.9	tr	—

[a] Cumulative time-on-line to end of run. [b] WHSV = Weight hourly space velocity. [c] tr = Trace.

methanol and ethanol, since these were observed as trace products, over both catalysts. The results obtained indicated that the blank reactions were neglible (up to 210 °C); in particular no propene was formed under any conditions tested.

Reaction over the conjugate base (sodium form) gave some striking results. At 125 °C the amount of propene produced was far greater than that of ethene. This contrasts significantly with dimethyl sulphate conversion over the conjugate base, in which propene was observed in only trace amounts (<1%) at the much higher temperature of 300 °C. The high propene : ethene ratios observed, also contrast with the studies of Lee and Wu[5] in which diazomethane conversion over H-ZSM-5 was found to give ethene as by far the major product. This suggests that the majority of the propene formed at low temperature from the diazoacetate is not formed *via* methylation of ethene, nor *via* methylene insertion into an ethylenic C–H bond. Over the acid form of the zeolite, production of both ethene and propene occurred as low as 80 °C albeit at low conversion (0.1%). With both types of catalyst relative propene concentrations fell with elevation of temperature, with concomitant increase in ethene concentrations, the decrease being more rapid with H-ZSM-5 (see 125 °C). At higher temperatures over H-ZSM-5 (189, 210 °C), by far the major product initially is ethene (>99%) but with increase in time-on-line the relative concentration of ethene decreases with a corresponding increase in both relative propene and C_4 concentrations. Despite the low temperature traps, some C_4 hydrocarbons did not condense and so relative trends in C_4 formation could be satisfactorily monitored. Furthermore, the absence of C_4 hydrocarbons at low temperatures (80, 125 °C) over H-ZSM-5 compared with high temperatures suggests that decrease in relative propene concentration with increasing temperature is not as a result of oligomerisation reactions.

We consider these relative trends in ethene/propene production over both catalysts to be indicative of an interplay of two mechanisms in which propene can be generated in two different ways (Scheme 1). Loss of nitrogen from the diazo compound generates an electrophilic ethoxycarbonylcarbene which could bond to an oxygen of the zeolite[8] generating a surface stabilized carbene or ylide consistent with the type of species proposed by Lee and Wu[5] in their diazomethane work, and also consistent with the reaction of carbenes with oxygen atoms.[9] Such a species could well be formed on both silyloxy and aluminoxy type oxygens. At low temperatures the high relative propene concentrations could be accommodated by C–C bond formation between the ylide carbon and the ethyl side chain, with formation of CO_2, to generate a surface bonded propyl group which could cleave to propene. The presence of CO_2 in the products was confirmed by mass spectrometry.



Scheme 1

Some mechanistic pathways for C–C bond formation involve a formal [1,3] sigmatropic[10] rearrangement, intermolecular attack depending on surface concentrations, or reaction between a surface bonded methylene ylide and an adjacent surface bonded ethyl group generated by elimination of CO_2 from the oxonium ion ylide. Alternatively, cleavage of the ethyl side chain, favoured with H-ZSM-5 owing to the Brönsted acid sites, would generate ethene, CO_2, and a surface methyloxonium species (for H-ZSM-5). At the higher temperature range where relative propene concentrations begin to increase with time-on-line, it is likely that C–C bond formation to propene is predominantly *via* methylation of ethene[11] by the surface methyloxonium species[12] as suggested for methanol conversion.

These results are strongly indicative of reactions involving species bonded to the catalyst surface. Moreover, we consider that the behaviour of this particular substituted diazo compound suitably models C–C bond formation, albeit $C_1 \rightarrow C_3$ and not $C_1 \rightarrow C_2$, as well as ethene methylation, thus re-inforcing the idea of the involvement of a surface bonded C_1 species as the crucial intermediate for initial carbon–carbon bond formation in the formation of hydrocarbons from methanol.

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