Reaction of Carbenoid Species from Diazomethane Decomposition over Zeolite ZSM-5

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Decomposition of diazomethane over zeolite ZSM-5 gives ethene and propene as the major products; this supports the existence of carbenoid intermediates proposed in methanol conversion into ethene and higher hydrocarbons over this catalyst.

A three-step process has been described for the production of gasoline from natural gas or coal, *via* a methanol intermediate, using an acidic ZSM-5 zeolite catalyst.[1] The mechanism of methanol conversion and especially formation of the first carbon–carbon bond over ZSM-5 is still a subject of speculation and controversy.[2] A range of reactive intermediates has been proposed, including carbenoid species,[3a] carbenium ions,[3b] ylides,[3c] and free radicals.[3d] We have studied the reaction of dilute gaseous diazomethane, a source of methylene (CH_2:), at 200 °C over ZSM-5, silica, and alumina to probe the behaviour of carbene or carbenoid species over this catalyst.

Diazomethane (**1**), is widely used as a reagent in organic synthesis. It produces methylene (**2**) on heating or irradiation. In the presence of an acid, diazomethane becomes an electrophilic methylating agent (**3**) [equation (2)]. Carbene or carbenoid intermediates like (**2**), as well as electrophilic methylating agents like (**3**), may be present in methanol conversion into hydrocarbons over zeolite ZSM-5.

$$\underset{(\mathbf{1})}{CH_2N_2} \xrightarrow{\text{Heat or } h\nu} \underset{(\mathbf{2})}{:CH_2} + N_2 \qquad (1)$$

$$CH_2N_2 + HA \longrightarrow \underset{(\mathbf{3})}{{}^{+}CH_3\text{–}N_2} + A^{-} \qquad (2)$$

We have compared the reaction products from decomposition at 200 °C of dilute gaseous diazomethane† over three high-surface-area catalysts: ZSM-5 with $SiO_2/Al_2O_3 = 70$,[4a] low acidity ZSM-5 with $SiO_2/Al_2O_3 \geqslant 26\,000$,[4a] and γ-Al_2O_3.[4b] Diazomethane was also passed over low-surface-area quartz chips to determine the thermal background for decomposition. These results are shown in Table 1.

Decomposition of diazomethane over the high-surface-area catalysts resulted in a higher yield of hydrocarbons than did reaction over the quartz chips. Ethene was the major product with all catalysts. The yield of propene increased with the acidity of the catalyst, *i.e.* the highest yield of propene was observed for ZSM-5 with $SiO_2/Al_2O_3 = 70$. To determine whether propene may have resulted from ethene oligomerization followed by cracking, a dilute stream of ethene was tested under the same conditions. As seen in Table 2, ethene gave a significant amount of C_4 and higher hydrocarbons, but only

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† Diazomethane was generated by pumping a solution of *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in 2-(2-ethoxyethoxy)ethanol into aqueous KOH. The diazomethane was swept from the reaction mixture with a helium stream, through a KOH drying tube, and then through a quartz microreactor packed with 0.2 g calcined catalyst. Small samples, dilute diazomethane, and low temperatures were necessary to minimize the chance of explosion.

Table 1. Relative hydrocarbon product yields from diazomethane.[a]

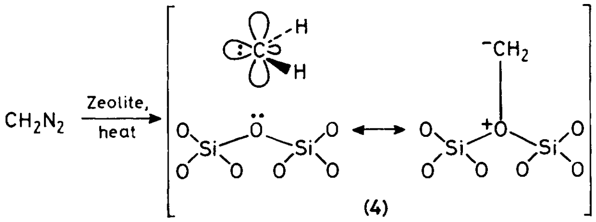
Catalyst	ZSM-5,[b] $SiO_2/Al_2O_3=70$	ZSM-5,[b] $SiO_2/Al_2O_3 \geqslant 26000$	γ-Al_2O_3[c]	Quartz chips
Relative hydrocarbon yield	8.9	6.3	4.9	1.0
Hydrocarbon product distribution (wt.%)				
CH_4	2.2	2.9	1.6	4.1
C_2H_4	83.3	91.0	92.9	85.4
C_3H_6	8.1	2.1	1.7	2.6
C_4H_8	2.9	1.0	0.8	
Others[d]	3.5	3.0	1.4	7.8

[a] Weight hourly space velocity: CH_2N_2, 1.8, He, 0.12; 200 °C. [b] Surface area = 300 $m^2\ g^{-1}$. [c] Surface area = 225 $m^2\ g^{-1}$. [d] Predominantly alkynes.

Table 2. Dilute ethene reaction over ZSM-5, SiO_2/Al_2O_3 = 70.

Relative hydrocarbon yield	14.5 (same scale as Table 1)
Hydrocarbon product distribution (wt.%)	
CH_4	0
C_2H_4	45.0
C_3H_6	0
C_4H_8	16.0
Others[a]	39.0

[a] Predominantly C_{5+}.



(4)
(3)

traces of propene. This shows that propene is not formed from ethene alone, but requires the presence of both a C_1 and a C_2 species.

An enhanced rate of hydrocarbon formation was observed over all three high-surface-area catalysts relative to the thermal background. Since ZSM-5, $SiO_2/Al_2O_3 \geqslant 26000$ and γ-Al_2O_3 both have few strong-acid sites, we conclude that strong-acid sites are not required for hydrocarbon formation. We propose two means by which the catalyst surfaces may increase the yield of hydrocarbons. Firstly, the surface facilitates the decomposition of diazomethane by stabilizing the methylene formed, and secondly, the concentration of methylene is increased by adsorption on the surface. The singlet methylene‡ initially formed by decomposition of diazomethane can be stabilized by electron donation from the oxygen lone pairs of the catalyst surface into the vacant p-orbital of the lowest unoccupied molecular orbital to form the carbenoid or ylide species (**4**) [equation (3)]. The reaction of a silyl ether with diazomethane is directly analogous to the reaction of ethers with diazomethane, which is postulated to proceed with formation of an oxygen ylide.[5] The formation of this intermediate on the zeolite surface is supported by recent *ab initio* calculations which show that methylene is significantly stabilized (by *ca.* 72 kcal/mol; 301 kJ/mol) by interaction with a zeolite.[6] This surface stabilization would increase the lifetime of the singlet C_1 species and its surface concentration, leading to increased ethene formation by coupling of adjacent C_1 units, or by reaction with additional diazomethane. Reactions of diazomethane with metal surfaces[7a] and over an olefin disproportionation catalyst[7b] have also been suggested to form surface methylene groups which subsequently dimerize to form ethene.

Diazomethane reaction with a strong-acid site results in a surface methyl oxonium ion (**5**).[8] This species would be a reactive methylating agent to convert ethene into propene [equation (5)]. It could also react with additional diazomethane to form an ethyl oxonium ion, which can then eliminate ethene [equation (6)]. Thus, strong-acid sites provide an additional route for ethene formation and a route for propene formation. This is consistent with the observation of higher propene yields over acidic ZSM-5 (SiO_2/Al_2O_3 = 70). In addition, a smaller amount of propene must come from uncatalysed methylene insertion into an ethylenic C–H bond, since some propene was observed over quartz chips.

In conversion of methanol into hydrocarbons over ZSM-5, ethene and propene are the principal early products observed.[3a,9] However, agreement on a mechanism for the first carbon–carbon bond formation has not yet been reached. We have shown that methylene generated independently from diazomethane reacts over ZSM-5 at low temperature (200 °C) to give predominantly ethene, and that strong-acid sites are necessary for significant selectivity for propene formation. This leads us to believe that α-elimination of methylene from methanol or dimethyl ether and formation of a surface carbenoid may be involved in the conversion of methanol into ethene over ZSM-5, as proposed by Chang and Silvestri.[3a] Equation (7) shows a general scheme for zeolite-mediated interconversion of carbenoid and carbenium ion species over ZSM-5.[2b] Semi-empirical quantum mechanical calculations have shown that methanol dehydration to methylene (path 7a) would be possible within the electrostatic field of a zeolite cavity.[10] Furthermore, the formation of carbenes from carbenium ions, a model for path (7c), has previously been demonstrated.[11]

Methanol conversion into hydrocarbons over ZSM-5 requires a higher temperature than that used in this study. In this higher temperature region (≥280 °C), the light hydrocarbon products we observed from methylene reaction would be masked by secondary reactions involving the acid sites on ZSM-5.[12] Although a direct comparison of products from methanol reaction and diazomethane reaction over ZSM-5 is not possible, the formation of both ethene and propene from

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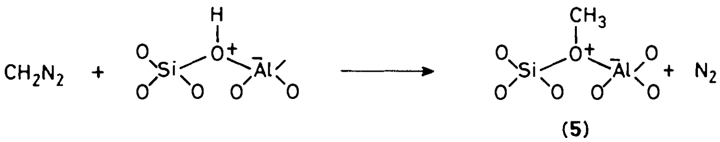
‡ Thermal decomposition of diazomethane generates singlet methylene which readily decays to the triplet species, resulting in polymerization to higher hydrocarbons (A. A. Shteinman, *Russ. J. Phys. Chem.*, 1970, **44**, 779). Gas-phase thermal decomposition of diazomethane in a closed system at 290 °C has been found to produce mainly CH_4, C_2H_6, C_2H_4, C_2H_2, and HCN in addition to some polymethylene (W. J. Dunning and C. C. McCain, *J. Chem. Soc. B*, 1966, 68).



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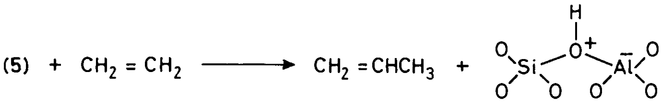

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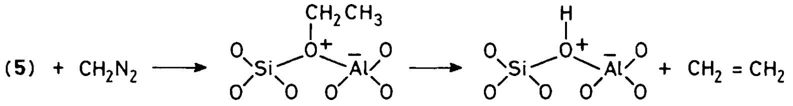

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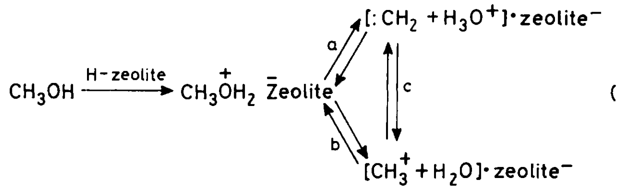

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an independently generated source of methylene over acidic ZSM-5 supports the proposed presence of carbenoid intermediates in the conversion of methanol over ZSM-5.

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