

## Mechanistic Studies on Initial C–C Bond Formation in the Zeolite ZSM-5 Catalysed Methanol Conversion Reaction: Evidence against a Radical Pathway

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The behaviour of the methoxymethyl radical in the gas phase has been studied and the results provide strong evidence against a radical mechanism for the title reaction.

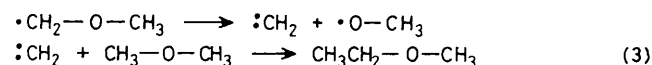
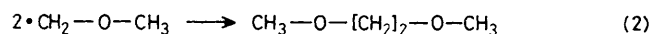
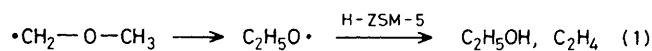
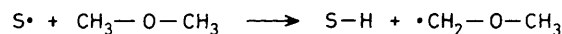
Recently, a number of studies on the methanol conversion reaction using the catalyst H-ZSM-5<sup>1–3</sup> have suggested that a radical pathway is the dominant mechanism for initial carbon–carbon bond formation. Only one<sup>2</sup> of these communications has put forward a plausible mechanism under realistic reaction conditions, involving the homolytic fission of a C–H bond in dimethyl ether by a surface radical (S•) as the initial step in the radical process. Three subsequent reactions of the methoxymethyl radical thus generated were suggested as possibilities for initial carbon–carbon bond formation (Scheme 1). We have shown recently that the third of these possibilities (equation 3), namely the insertion of a free methylene carbene into the C–H bond of dimethyl ether to form methyl ethyl ether which can subsequently form ethene, is not a plausible possibility.<sup>4</sup> Here we present results obtained from reaction of dimethyl ether under radical conditions which we consider provide strong evidence against the other two radical pathways which have been suggested for initial carbon–carbon bond formation.

Dimethyl ether (1.25 ml s<sup>-1</sup>) was passed over a radical initiator, pre-dried dibenzoyl peroxide supported on Celite, at various reaction temperatures, in a glass microreactor. The products were analysed by off-line gas chromatography, and the results are shown in Table 1. Although the dibenzoyl peroxide was short-lived under these conditions, as evidenced by the conversion data, enough was active in the time period studied, with typical experiments being of 5 minutes' duration. Under all conditions only dimethoxyethane was observed as a dimerisation product, showing that the methoxymethyl radical was generated under these conditions. Furthermore, the absence of other products, particularly ethanol, discounts the methoxymethyl radical fragmentation–recombination pathway (equation 1, Scheme 1) as a viable one for initial C–C bond formation.

To ascertain whether such a radical fragmentation–recombination pathway might be influenced in some way by the

zeolitic pore structure, dimethyl ether was passed over dibenzoyl peroxide supported in Celite mixed with Na-ZSM-5. Na-ZSM-5 was chosen as it is essentially inactive towards dimethyl ether under these conditions. Again, dimethoxyethane was observed as the only product, and no hydrocarbons were found even at 250 °C, a temperature at which zeolite H-ZSM-5 produces significant quantities of hydrocarbon products.

In order to investigate whether equation (2), (see Scheme 1) in which dimethoxyethane is suggested as the crucial hydrocarbon precursor, is a viable one, dimethoxyethane was passed over H-ZSM-5 (1 g) at 250 and 300 °C. The products, analysed by off-line gas chromatography, consisted of methanol, dimethyl ether, and trace amounts of hydrocarbons at total conversions of 12 and 20% at 250 and 300 °C, respectively. Under these conditions dimethyl ether reacted over H-ZSM-5 to give 20 and 90% conversion into hydrocarbons at 250 and 300 °C, respectively. These results confirm that dimethoxyethane is not an ethene precursor with H-ZSM-5, which is reasonable from consideration of its oxidation state, and hence equation (2) can also be discounted.



Scheme 1

Table 1. Reaction of dimethyl ether with dibenzoyl peroxide.

Dibenzoyl peroxide (% by mass)	Temp./°C	MeOMe conversion /%	Product selectivity		
			MeO[CH <sub>2</sub> ] <sub>2</sub> OMe	EtOH	C <sub>2</sub> H <sub>4</sub>
10 <sup>a</sup>	25	0.2	100	0	0
	50	0.5	100	0	0
	80	5.3	100	0	0
	140	3.9	100	0	0
	200	2.3	100	0	0
20 <sup>a</sup>	25	0.3	100	0	0
	50	0.3	100	0	0
	80	1.6	100	0	0
	140	7.1	100	0	0
	170	2.0	100	0	0
10 <sup>b</sup>	100	2.1	100	0	0
	250	2.3	100	0	0

<sup>a</sup> Dibenzoyl peroxide supported on Celite. <sup>b</sup> Dibenzoyl peroxide supported on Celite/Na-ZSM-5.

These results provide strong evidence against the gas-phase radical possibilities put forward to date. We still consider that the surface plays a much more active role and that the active site essentially traps out an electrophilic methyl group,<sup>5</sup> generated under the super-acid conditions, which can then give rise to initial carbon-carbon bond formation *via* a surface bonded methylide.<sup>6</sup>

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