Methanol Conversion to Hydrocarbons over the Zeolite Catalyst H-ZSM-5 in the Presence of Oxygen and Nitric Oxide: Further Evidence Against a Radical Reaction Mechanism

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A study of the reactions of dimethyl ether and methanol over H-ZSM-5 with added NO and O_2 provides strong evidence against the involvement of radical intermediates in these reactions, and also indicates a possible mechanism of catalyst deactivation.

The conversion of methanol into hydrocarbons has attracted considerable research interest in recent years, not only in determining the mode of action of the zeolite catalyst H-ZSM-5, but also as to the mechanism by which catalyst deactivation occurs. Most attention has focused on the elucidation of the mechanism of formation of the initial C–C bond, and a number of reaction intermediates have been proposed including carbenes,[1,2] trimethyloxonium ion,[3,4] and surface-bonded methylide.[5] A number of studies[6–8] have proposed that a free radical process based on the methoxymethyl radical is the dominant reaction pathway, but recently we have shown[9] that this particular radical is not a suitable ethene precursor under typical reaction conditions. However, in order to investigate the possibility of other radical pathways we have now studied the conversion reaction in the presence of known radical scavengers, the monoradical of nitric oxide and the diradical species triplet oxygen. The results of these studies not only provide clear evidence against the involvement of a radical reaction in methanol conversion but also give information concerning the mechanism of catalyst deactivation.

H-ZSM-5 (1 g) was treated in a fixed bed microreactor with dimethyl ether in the absence of carrier gas at 300 °C; the results are shown in Table 1 (experiment 1). The experiment was then repeated but with the addition of 1 mol % NO to the dimethyl ether (experiment 2); the results show that addition of NO has no effect either on catalyst activity or on product selectivity, and experiments with addition of 3 mol % NO only slightly enhanced catalyst deactivation. Conversely experiments involving the addition of oxygen at 1 mol % (experiment 3) and 3 mol % (experiment 4) to the dimethyl ether reactant show significantly different results. Oxygen at these concentrations causes an immediate and irreversible deactivation of the zeolite catalyst, the effect being more pronounced at the higher oxygen concentration. The effect is also observed for methanol conversion (MeOH was introduced to the H-ZSM-5 catalyst using dry Ar carrier gas); these results are also shown in the Table (experiments 5 and 6).

NO, a monoradical, is well known as a radical scavenger[10] even at temperatures of up to 600 °C.[11] The results of this study present strong evidence against the involvement of radical gas phase intermediates in the formation of the initial carbon–carbon bond, because oxygen would not have been expected to be much more effective as a radical scavenger than NO under these conditions (compare experiments 1—3). In addition, the production of methane relative to C_{2+} products was not affected; hence this study further confirms that methane is not generated *via* a radical mechanism distinctly

Table 1. Results of conversion experiments.

Expt. no.	Reactant	W.H.S.V.[a] /h^{-1}	Additive (mol %)		Reaction[b] time (min)	Reactant conversion (mol %)	Product selectivity (mass %)					
			O_2	NO			CH_4	C_2H_4	C_2H_6	C_3	C_4	C_{5+}
1	Me_2O	50	0	0	30	28.8	0.8	12.4	0.1	24.7	21.5	40.5
			0	0	60	7.7	0.3	9.2	0.1	16.4	34.5	42.5
			0	0	120	6.8	0.5	10.7	0.1	19.8	38.9	30.0
			0	0	180	5.5	0.5	10.2	0.1	20.0	45.4	23.8
2	Me_2O	50	0	1.0	30	27.4	0.9	12.9	0.3	23.6	26.2	36.1
			0	1.0	60	11.3	0.5	14.1	0.1	20.1	27.8	37.4
			0	1.0	120	6.9	0.5	13.5	0.1	20.8	34.3	30.8
			0	1.0	180	6.6	0.5	13.1	0.1	20.8	37.1	28.4
			0	0	200	5.5	0.4	8.4	0.1	18.9	40.6	31.6
3	Me_2O	50	0	0	10	75.1	1.6	13.7	0.7	31.0	31.6	21.4
			1.0[c]	0	20	6.0	0.4	11.4	0.3	21.5	21.3	45.1
			0	0	30	5.9	0.5	15.1	0.3	24.6	39.3	20.2
4	Me_2O	14.8	0	0	10	95.7	1.3	11.7	0.5	28.2	34.5	23.8
			3.0[c]	0	37	4.3	2.2	26.1	0.7	34.0	14.1	22.9
			3.0	0	66	2.0	0.9	2.2	0.7	4.5	14.9	76.8
5	MeOH	2.0	0	0	6	99.8	0.4	11.6	0.1	14.7	28.5	55.5
			0	0	60	99.5	0.3	12.4	0.2	15.3	21.1	50.7
			0	0	120	98.0	0.3	14.9	0.1	14.8	21.2	48.7
			0	0	180	98.5	0.3	15.1	0.2	15.3	20.7	48.4
6a	MeOH	2.0	1.0	0	6	99.6	0.7	12.5	0.1	14.1	32.9	39.7
			1.0	0	36	99.0	0.4	13.8	0.2	19.1	27.2	39.3
			1.0	0	72	98.3	0.4	18.4	0.2	19.9	24.3	36.8
			1.0	0	120	92.0	0.4	19.3	0.2	12.2	20.7	47.2
			1.0	0	180	86.9	0.5	21.2	0.1	16.9	19.5	41.8
6b	MeOH	2.5	3.0	0	6	98.4	0.5	9.5	0.0	4.3	34.9	50.8
			3.0	0	120	59.7	0.4	20.7	0.1	21.1	27.7	30.0
7	$Me_2O/CH_2O/H_2$	14.8[d]	0	0	6	97.7	1.4	10.6	0.9	25.3	31.7	30.1
			0	0	60	80.4	1.2	15.2	0.3	23.2	26.6	33.5
			0	0	120	8.7	0.3	7.5	0.1	12.3	28.5	51.3
8	Me_2O/H_2O	14.8[e]	0	0	6	88.8	1.2	11.8	0.7	24.5	35.2	26.6
			0	0	60	85.8	1.1	14.5	0.3	23.1	28.5	32.5
			0	0	120	19.8	0.6	18.4	0.1	25.1	21.7	34.1

[a] Weight hourly space velocity: g reactant (g catalyst)$^{-1}$ h^{-1}. [b] Cumulative reaction time. [c] O_2 added after 10 min. reaction time. [d] Me_2O bubbled through formalin; CH_2O W.H.S.V. 0.015 h^{-1}. [e] Me_2O bubbled through water to give same water vapour pressure as in experiment 7.

separate from the main carbon–carbon bond formation reaction. We must therefore conclude that the radicals observed in the experimental work of Clarke *et al.*[7] play no role in the mechanism of methanol conversion.

The most likely explanation for this effect is that the crucial reaction intermediate in the C–C bond formation reaction is oxidised by the molecular oxygen rather than by NO. It has been suggested that methanol oxidation over an oxide catalyst[12] proceeds *via* a surface methylide species, similar to that proposed by us[5] for the methanol conversion reaction, and precedent for oxygen attack at carbon on other ylides is well documented.[13] The product of such an oxidation could be formic acid or formaldehyde, the latter of which under the strongly acidic conditions of the zeolite would undergo polymerisation, eventually resulting in coke formation and hence deactivation of the catalyst. To determine the validity of this explanation a model experiment was conducted in which formaldehyde was added to the dimethyl ether reactant (experiments 7 and 8); this was shown to deactivate the zeolite catalyst even at low formaldehyde levels (*ca.* 0.1% by mass of dimethyl ether feed). Separate experiments with addition of formic acid did not demonstrate such a severe deactivation even at feed levels of up to 10% (by mass of formic acid relative to dimethyl ether). These results indicate that the rapid deactivation observed with O_2 co-feeding is due to formaldehyde formation rather than formic acid formation. The deactivation of the catalyst cannot therefore be due to the reaction of gas phase methylene with oxygen since this reaction would yield formic acid *via* a Criegee intermediate;[14] hence this argues against the gas phase methylene being an intermediate in the carbon–carbon bond formation reaction, in agreement with our previous studies.[15]

The results of these studies provide clear evidence that the mechanisms of carbon–carbon bond formation and methane production do not involve a gas-phase free radical reaction pathway. The studies using oxygen may be of technological value with respect to catalyst deactivation and reactivation. Zeolite catalysts are usually reactivated using oxygen[16] and the results of this study clearly show that if reactants are reintroduced prior to complete removal of the oxygen then severe deactivation could be encountered. Further studies are now in progress in our laboratories to determine the lower limits of oxygen concentration that can be tolerated in this reaction.

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