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Hydrocarbon Formation over the Zeolite Catalyst ZSM-5 Using Model Reagents: Comments on the Primary Reaction Products

In the conversion of methanol to hydrocarbons over zeolite H-ZSM-5 (*1*) and other catalysts (*2*) neither the exact nature of the primary products nor the mechanism by which they are formed have been fully elucidated, though subsequent conversion of them to gasoline range hydrocarbons has been explained using carbocationic intermediates (*3*). A number of workers have considered the possibility that both ethene and propene might be primary alkene products (*4, 5*), while Haag *et al.* (*6*) have demonstrated, using very high methanol space velocities, that as the conversion to hydrocarbons decreases so does the propene/ethene ratio. Extrapolation of their data to zero conversion indicates that ethene may well be the primary alkene product and that diffusion desorption disguise may have masked the true primary products in the previous experimental work (*4, 5*). Subsequent studies by Chu and Chang (*7*) and Wu and Kaeding (*8*) have supported the proposition that ethene is the primary alkene product. However, Espinoza and Mandersloot (*9*) have recently demonstrated that the evidence of Haag *et al.* (*6*) is inconclusive since the propene/ethene ratio only depends on the dimethyl ether/methanol ratio present in the reactants and not on methanol conversion. Hence the findings of Espinoza and Mandersloot tend to support the proposal that both ethene and propene are the primary alkene products. The major problem in identification of the primary product(s) from methanol is that even at very low methanol conversion, significant quantities of ethene, propene, as well as higher hydrocarbons are observed (*8*) and extrapolation of the results in order to determine the primary products is inconclusive. A striking and important feature of H-ZSM-5 is the wide range of alcohols, ethers, esters, and carboxylic acids which it converts to hydrocarbons (*1*). Recently we have shown (*10*) that the zeolite converts a range of methylating agents to hydrocarbons, and in this paper we use these slightly less reactive methylating agents of the type Me–X (X = OSO_3Me; I) as model compounds for methanol in order to provide evidence on the nature of the primary hydrocarbon products.

The sodium form of the conjugate base of the zeolite ZSM-5 ($SiO_2/Al_2O_3 = 35$) was prepared according to the method of Howden (*11*) and then converted into the acidic H-ZSM-5 form by the following procedure. Na-ZSM-5 (100 g) was stirred in an aqueous solution of ammonium sulfate (1 liter, 1 *M*) for 30 min at 25°C, then filtered, washed with distilled water, and the procedure repeated twice. The zeolite was thoroughly washed with water to ensure removal of all the sulfate ions, then dried, calcined at 550°C for 3 h, and stored in a desiccator when cool.

Catalytic reactions were carried out using a continuous flow fixed-bed Pyrex glass reactor with a temperature control of 1°C. Zeolite catalyst (1 g) was dried *in situ* in the reactor using a stream of dry N_2 at 350°C for several hours prior to use. MeOH, Me_2SO_4, and MeI were individually reacted over the zeolite by vaporizing them at a regulated temperature using a dry N_2 carrier gas at a constant flow rate of 1 ml/s. The weight hourly space velocity of the reactants could be varied by control of the va-

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TABLE 1

Reactions of Methylating Agents over Zeolite H-ZSM-5 at 250°C

Methylating agent	WHSV (h^{-1})	Time on line (min)	Total conversion (mole%)	Product selectivity (mole%)				
				CH_4	C_2H_4	C_3H_6	C_4H_8	C_{5+}
MeOH	0.15	15	7.1	4.0	3.9	4.1	36.1	52.0
		60	16.7	1.1	14.1	5.6	28.8	51.3
		100	22.6	0.9	24.3	6.3	29.3	39.2
MeOH	2.0	30	0.18	1.5	19.4	41.8	37.3	0
		100	1.49	3.2	32.2	18.1	20.1	26.3
MeI	0.6	15	0.01	58.8	41.2	0	0	0
		30	0.02	51.7	48.3	0	0	0
		45	0.03	51.0	49.0	0	0	0
		60	0.10	1.9	7.3	38.8	40.0	12.0
		75	0.11	0.5	3.5	78.9	13.1	4.0
MeI	0.8	60	0.02	66.1	33.9	0	0	0
		100	0.13	7.0	44.1	32.5	13.6	2.8
Me_2SO_4	0.054	15	0.007	24	76	0	0	0
		30	0.010	21.3	78.7	0	0	0
		45	0.024	17.6	82.4	0	0	0
		60	0.90	2.4	14.8	29.6	38.4	14.8
		75	1.0	1.6	28.0	28.2	30.2	12.0
Me_2SO_4	0.075	15	0.12	81.5	18.5	0	0	0
		60	3.3	20.5	44.9	28.2	6.4	0
		100	12.9	2.5	28.9	11.2	18.6	38.8
		190	16.6	1.6	36.6	12.2	10.5	39.1
		230	21.2	1.5	45.2	15.1	10.8	27.4

porization temperature, which ranged from −60°C for MeI to 130°C for Me_2SO_4. Products were analyzed using gas chromatography (column: Porapak Q, 2 m, temperature programm 50°C for 3 min, heated to 70°C at 10°C/min and held for 7 min and then raised to 200°C at 20°C/min and held for 55 min). MeOH (A.R., BDH) and MeI (Carlo Erba, stored over 4A molecular sieve) were used without further purification. Me_2SO_4 (Hopkins and Williams) was distilled from CaH_2 and stored over 4A molecular sieve. Before use Me_2SO_4 was analyzed using NMR spectroscopy to ensure that no MeOH was present.

MeOH, MeI, and Me_2SO_4 were individually reacted over H-ZSM-5 for a range of weight hourly space velocities at 250°C and the results are shown in Table 1. All reagents showed increasing conversion with time on stream as has been previously shown for MeOH by Ono and Mori (*12*) and this is ascribed to the autocatalytic nature of this reaction. Even at low conversions with MeOH (0.18%), a range of C_1–C_4 hydrocarbons were observed confirming the findings of previous studies (*8*). The most reactive of the three reagents, as expected, was MeOH with a total conversion to hydrocarbons, at WHSV = 0.15 h^{-1}, of 22.6 mole% after 100 min. Me_2SO_4 proved to be a very good reactant, too, with a conversion of 12.9 mole% after 100 min at a WHSV = 0.075 h^{-1}. MeI proved to be much less reactive although owing to its boiling point much higher weight hourly space velocities were utilized. Moreover, when MeI and Me_2SO_4 were used as reagents the initial conversions were always low (<0.1%) and the initial hydrocarbon products were always methane and ethene. Higher hydrocarbons were only observed after a considerable time on stream when the conversion of the MeI or Me_2SO_4 had increased to 0.1–1.0% depending on the experimental conditions employed. At conversions >0.1% the product distributions observed are very similar and the C_{5+} products for all reactants are predominantly a range of alkanes and alkylated aromatic compounds as typically observed for methanol (*1*). We therefore conclude that the same mechanism of carbon–carbon bond formation is operating for all three reactants and the higher selectivities to methane observed at conversions of >0.1% for MeI and Me_2SO_4 are a result of their reduced reactivity toward H-ZSM-5.

The data clearly show that the initial products with the less reactive reactants at low conversion (i.e., Me_2SO_4 and MeI) over H-ZSM-5 are always methane and ethene under our conditions. Since similar products and product distributions are observed at higher conversions for these reactants and methanol we suggest that these results support the proposal that methane and ethane are the primary hydrocarbon products formed during methanol conversion. Our finding that methane is a significant primary product with Me_2SO_4 and MeI is in agreement with the previous results obtained for MeOH by Haag *et al.* (*6*), Wu and Kaeding (*8*), and Ono and Mori (*12*).

The results of this study are therefore in agreement with the results of the extrapolation experiments of Haag *et al.* (*6*) that the primary hydrocarbon products are methane and ethene. The findings of Espinoza and Mandersloot (*9*) that the propene/ethene ratio at low methanol conversions correlates well with the (dimethyl ether)/methanol reactant ratio are not inconsistent with our findings. We consider that the propene/ethene ratio observed in their experiments reflects the relative methylating ability of protonated dimethyl ether versus protonated methanol for the alkylation of ethene within the zeolite catalyst.

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