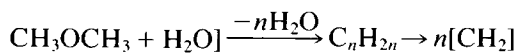
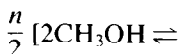


## On the Existence and Role of Free Radicals in Methanol Conversion to Hydrocarbons over HZSM-5

### I. Inhibition by NO

The past 15 years have seen the development of zeolite-catalyzed methanol conversion to gasoline (MTG) from laboratory observation (1) to commercial realization (2, 3). The general reaction path has been elucidated (4) and is represented by



where  $[\text{CH}_2]$  is the average formula of a paraffin-aromatic mixture.

However, the nature of the critical initial step of hydrocarbon formation from methanol remains obscure. The constitution and fate of the reactive  $\text{C}_1$  species involved in the formation of the initial C-C bond have been the subject of wide speculation. Proposed reactive intermediates include (5) carbenes, methyl cations, trimethyloxonium ions, and a variety of surface-bonded species. Since alkenes are intermediates, it is clear that C-H bond scission (from methyl or methoxyl) must occur at some early stage of the reaction. How and when this occurs is the heart of the problem.

An intriguing result reported by Clarke *et al.* (6) in the recent literature (6) is the ESR detection of free radicals during decomposition of dimethyl ether (DME), over zeolite HZSM-5 (7, 8) at 240°C, using the spin trapping reagent  $\alpha$ -phenyl-*N-t*-butyl-nitrone. Mechanisms were proposed (6) for formation of the initial C-C bond involving either direct coupling of (methoxymethyl) radical species or C-H bond insertion by

methylene, generated by methoxy radical scission. These mechanisms were disputed by Hunter *et al.* (9, 10), who found, in model experiments, no participation of methoxymethyl radicals in C-C bond formation in the presence of HZSM-5. In a subsequent study Hunter *et al.* (10) observed no effect of adding 1-3% NO, a known radical scavenger, during methanol/DME conversion over HZSM-5, and took this as further evidence against a radical pathway.

We have examined the effect of NO on methanol conversion to hydrocarbons over HZSM-5 and arrive at conclusions somewhat different from those of Hunter *et al.* Our findings are reported here.

Methanol cofed with nitrogen (1000 VHSV) over HZSM-5 (1800  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) at 450°C, 1 atm, in a packed-bed microreactor (11) converted quantitatively to hydrocarbons and water (Table 1, column A). Addition of 450 ppm NO to the feedstream completely inhibited hydrocarbon, but not DME formation (Table 1, column B). Removal of NO from the feed resulted in complete recovery of hydrocarbon production.

The effect of NO on conversion of propene, a major MTG intermediate (4) was examined under conditions essentially identical to those above. No effect was observed (Table 1, columns C and D). It may be argued that since propene oligomerization, as well as DME formation from methanol, is known to proceed by ionic mechanisms (5, 12), NO should exert no inhibitory effect.

At this point it would have been tempting

TABLE 1  
Effect of NO on Methanol and Propylene  
Conversion over HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$   
= 1800, 450°C, 1 atm)

| Experiment:                                 | A    | B    | C    | D    |
|---|------|------|------|------|
| Feed (mol/g × hr)                           |      |      |      |      |
| Methanol                                    | 0.05 | 0.05 | —    | —    |
| Propylene                                   | —    | —    | 0.05 | 0.05 |
| N <sub>2</sub>                              | 0.05 | 0.05 | 0.05 | 0.05 |
| NO (ppm)                                    | 0    | 450  | 0    | 450  |
| Time on stream (hr)                         | 6.8  | 4.0  | 2.4  | 2.6  |
| Reactor effluent (wt% (ex N <sub>2</sub> )) |      |      |      |      |
| H <sub>2</sub> , CO, CO <sub>2</sub>        | 0.2  | 0    | —    | <0.1 |
| MeOH  | 0    | 39.6 | —    | —    |
| DME   | 0.1  | 42.9 | —    | —    |
| H <sub>2</sub> O                            | 55.9 | 17.4 | —    | —    |
| CH <sub>4</sub>                             | 0.2  | 0    | 0.3  | 0.7  |
| C <sub>2</sub> <sup>0</sup>                 | 0.1  | 0    | 0.2  | 0.2  |
| C <sub>2</sub> <sup>1-</sup>                | 2.2  | tr   | 6.8  | 8.3  |
| C <sub>3</sub> <sup>0</sup>                 | 0.6  | 0    | 2.0  | 2.8  |
| C <sub>3</sub> <sup>1-</sup>                | 12.2 | tr   | 33.5 | 32.0 |
| iC <sub>4</sub> <sup>0</sup>                | 1.4  | 0    | 1.5  | 2.4  |
| nC <sub>4</sub> <sup>0</sup>                | 0.3  | 0    | 0.6  | 1.0  |
| C <sub>4</sub> <sup>1-</sup>                | 13.4 | 0    | 36.3 | 34.9 |
| C <sub>5</sub> <sup>1-</sup> aliphatic      | 12.2 | 0    | 18.8 | 17.0 |
| Aromatics                                   | 1.2  | 0    | 0    | 0.7  |

to conclude that the free radical nature of initial C–C bond formation had been established. However, additional methanol conversion experiments with varying NO and zeolite acid site concentration ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) revealed a somewhat more complex situation.

The effect of NO concentration (0, 450, 5000 ppm) was examined at two different zeolite  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (1800 and 70). Results are summarized in Figs. 1a and 1b, which show methanol breakthrough, i.e., percentage unreacted methanol in the reactor effluent (an indicator of reaction inhibition), against stream time. With the lower acidity (higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) HZSM-5 (Fig. 1a), addition of 5000 ppm NO completely suppressed hydrocarbon formation within  $\frac{1}{2}$  hr. At 450 ppm NO inhibition required nearly 2 hr after an induction period. At higher catalyst acidity (Fig. 1b), similar behavior was observed; however, time to methanol breakthrough was longer. Clearly a cumulative catalyst poison was being produced. We assert that NO added during methanol/DME decomposition over

HZSM-5 generates poisons, by a process involving radicals, for zeolite Brønsted acid sites.

DME is known to be a good source of methyl radicals, via gas-phase pyrolysis at 400–600°C (13–18). The NO inhibition of DME pyrolysis has been investigated by many workers (19–23) since the pioneering study of Staveley and Hinshelwood (19). The most extensive investigation was that of McKenney *et al.* (20), who showed that NO consumption during maximal inhibition of DME pyrolysis is due in part to formation of  $\text{CH}_3\text{NO}/\text{CH}_2=\text{NOH}$  (25, 26), Beckmann rearrangement of the oxime, and decomposition of the product  $\text{HCONH}_2$  to  $\text{NH}_3$  and CO (27, 30). Zeolites are known to catalyze the Beckmann rearrangement (28, 29).  $\text{NH}_3$  formed from  $\text{HCONH}_2$  will (reversibly) poison HZSM-5 acid sites or undergo methylation to methylamines (31, 35), which are stronger poisons. In support of this interpretation, the above set of experiments was duplicated using  $\text{NH}_3$  in place of NO, and identical effects were observed.  $\text{NH}_3$  had little effect on propylene conversion, yet sharply inhibited methanol reactions. This indicates that methylamines are among the acting poisons.

We therefore conclude, in agreement with Clarke *et al.* (6), that free radicals are present during the early stages of methanol/

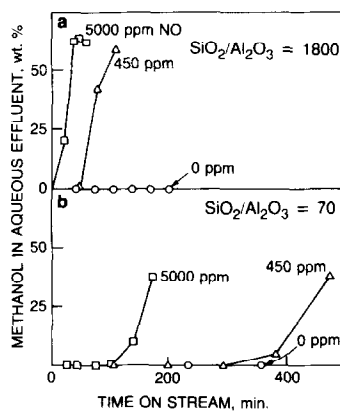
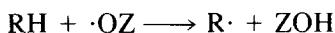
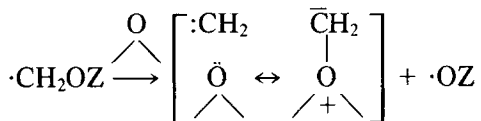
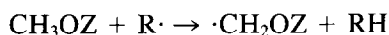
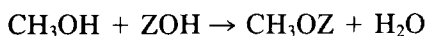


FIG. 1. NO inhibition of olefin formation from methanol over HZSM-5 (450°C, 1 atm,  $\text{N}_2/\text{MeOH} = 1$ ).

DME conversion over HZSM-5. In contrast to Hunter *et al.* (10), we find that NO inhibits the reaction. NO may be a radical initiator above certain levels (19–21) (protonated DME may be more susceptible to NO oxidation (37)), which may account in part for the contrasting results of Hunter *et al.* However, the role of free radicals in MTG initiation remains unsettled at this writing since the NO-consuming inhibition process generates catalyst poisons simultaneously.

The notion of radical initiation of the MTG reaction is, nevertheless, an appealing one. The profusion of (nonradical) mechanisms thus far encountered suffer the weakness of invoking either strongly basic zeolite sites for proton abstraction from C–H or the formation of hypervalent carbon entities. Hellring *et al.* (32) have shown that the zeolite conjugate base (in HZSM-5) is nucleophilic rather than basic toward methylium. Hypervalent carbon intermediates are unlikely where competitive formation of oxonium species is possible (33). Radical coupling, as proposed by Clarke *et al.* (6), is unlikely in view of the high probability of radical interaction with the zeolite surface. We offer the following alternative scheme:



The radical R· may be alkyl, alkoxy, alkoxyalkyl, etc., and is generated either homogeneously via gas-phase pyrolysis or by homolytic scission of surface alkoxy. The surface-bound carbene (in brackets) is the reactive C<sub>1</sub> moiety (34, 35) engaged in C–C bond formation, most likely via alkylation by methyloxonium intermediates (33). The surface species ZO· may be identified with the paramagnetic center or surface defect

envisaged by Clarke *et al.* (6). Solid-state defects (positive holes on lattice oxygen) have been detected in calcined HZSM-5 (36). The species ·CH<sub>2</sub>OAl, analogous to ·CH<sub>2</sub>OZ above, has been observed on photolysis of methanol sorbed on alumina (37). Finally, since coke deposited on aluminosilicate catalysts, and in particular methanol-derived coke on HZSM-5, is paramagnetic (36, 38), its role in radical initiation cannot be discounted at this time.

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