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Aromatic Co-Catalysis of Methanol Conversion over Zeolite Catalysts

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The rate of conversion of methanol and aqueous methanol to hydrocarbons over H-ZSM-5 zeolite is enhanced by the addition of aromatic hydrocarbons to the feed. The effect has been demonstrated by means of both continuous-feed and pulse-feed experiments, using H-ZSM-5 zeolite prepared by various methods and using zinc-exchanged dealuminized Y zeolite.

INTRODUCTION

Pentasil zeolites such as ZSM-5 convert methanol into hydrocarbons of the petroleum boiling range. The mechanism whereby carbon–carbon bonds are formed from methanol is not understood (*1–3*), but it is known unambiguously that autocatalysis is a most important feature of the conversion (*4–6*). All discussion of the autocatalysis has centered upon the role of olefins. Ono and Mori (*6*) have demonstrated that ethylene and *cis*-2-butene enhance the rate of conversion and have interpreted this as consistent with dominance of electrophilic addition of methyl carbenium ion to olefin in conversion (cf. the earlier suggestion (*7*, *8*) that most carbon–carbon bond formation in methanol conversion occurs by a sequence of Brönsted-acid catalyzed homologation and cracking reactions).

It does not seem to have been realized that the aromatic products of methanol conversion may also have a role in the autocatalysis. We now reveal that aromatic hydrocarbons can provide co-catalysts for conversion of aqueous methanol and methanol over the proton form of ZSM-5 catalyst (H-ZSM-5). From this we may infer that the aromatic hydrocarbon products of methanol conversion play a role in the autocatalysis.

EXPERIMENTAL

H-ZSM-5 (Sample A)

The ZSM-5 zeolite used in the continuous-feed experiments was prepared by a proprietary method of I.C.I. Ltd. (*9*), and was used in the proton form (H-ZSM-5), which contained 1.02 wt% Al and <100 ppm by weight Na. The X-ray powder pattern confirmed that the zeolite was ZSM-5 of good crystallinity. Scanning electron microscopy showed the crystals to be laths of ca. 2.4 × 0.9-μ size with two "picket" ends. Electron diffraction showed the ZSM-5 crystals to be fault-free. The zeolite absorbed 1.27 mmole of *n*-hexane per gram of H-ZSM-5 at 20 Torr.

Sample B of H-ZSM-5 zeolite was that described by Mole and Whiteside (*10*), and contained 1.28 wt% aluminum and 0.04 wt% sodium. Sample C of H-ZSM-5 was crystallized (2 days at 175°C) from a gel pre-

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pared using commercial sodium silicate solution and tetrapropylammonium bromide. The proton form, obtained by calcination and acid washing, contained 0.71 wt% aluminum and 0.02 wt% sodium and consisted of 1–5 μ clusters of noneuhedral crystals.

Dealuminized Y zeolite was prepared from ordinary Na–Y zeolite by the silicon tetrachloride method (*11*) at 360–520°C, and was acid washed (0.3M HCl) to an aluminum content of 1.5 wt% (sodium 0.2 wt%). This zeolite was used in the zinc form, obtained via the ammonium form by ion exchange with zinc nitrate solution.

Continuous Conversion of Aqueous Methanol

The reactor and gas chromatograph were as described by Mole and Whiteside (*10*). The quartz reactor tube contained 0.1 g of H-ZSM-5 (Sample A) of 60–100 mesh size, and this was fed with aqueous methanol (2.75 : 1 w/w H_2O/MeOH) at a rate of 0.66 ml/hr (*i.e.*, *ca.* 1.7 g methanol/g catalyst/hr) in a stream of nitrogen vector gas (6 ml/min). The nitrogen vector gas could be diverted through a small bubbler containing aromatic hydrocarbon, or any other potential co-catalyst, before mixing with the aqueous methanol vapour in the reactor tube.

The product gases were diluted with further nitrogen at the exit end of the reactor tube, and then passed via a small trap at room temperature (to condense most of the water product) and via heated lines to the gas chromatograph. The experimental variables were the reactor temperature and the bubbler contents.

Pulse-Mode Methanol Conversion

The apparatus described above was also used in a pulse mode. In the first series of experiments, the reactor tube contained 63 mg of H-ZSM-5 (sample B), and was continually purged by nitrogen vector gas (6 ml/min) and maintained at 577 K. Successive 5 *μl* pulses of methanol, or methanol containing 2 wt% toluene, were fed into the nitrogen vector gas at 10-min intervals. A sample of effluent nitrogen was analyzed by a Porapak Q column to give an approximate composition of the products of up to four carbon atoms (including methanol and dimethyl ether).

When methanol alone was used on fresh catalyst, the percentage (*C%*) of methanol plus dimethyl ether in the product sample (up to C_4) decreased with pulse number. No pulse was fed for 40 min at 577 K, then pulsing was resumed. Again the *C%* of methanol plus dimethyl ether decreased with pulse number, but this time much more rapidly. When the methanol contained 2 wt% toluene, and the catalyst had been freshly regenerated, the *C%* of methanol plus dimethyl ether again decreased rapidly with pulse number. All the results are shown in Fig. 1.

In the second series of pulse-mode experiments, Sample C of H-ZSM-5 (40 mg) was treated with 5 *μl* pulses of methanol, or methanol containing 1 wt% of an aromatic hydrocarbon, at 562 K (the catalyst was regenerated between feeds). Conversion of

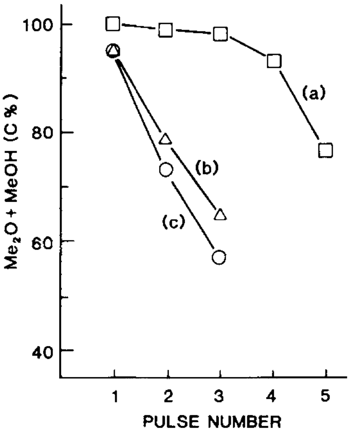

FIG. 1. Variation of amount of residual oxygenates (Me_2O plus MeOH) with pulse number over H-ZSM-5 catalyst (sample B) at 577 K. (a) Over fresh catalyst, (b) over used catalyst 40 min after concluding run (a), and (c) over fresh catalyst with 2 wt% toluene in the methanol. The amount of residual oxygenates is expressed as *C%* of the products of up to four carbon atoms.

the oxygenates (methanol plus dimethyl ether) was always less than 10 *C*%. The amount of ethylene as a *C* percentage of the amount of C_{1-3} hydrocarbons plus oxygenates, estimated for a sample of effluent nitrogen and taken as a measure of the extent of conversion, is plotted against pulse number in Fig. 2. As expected, the ethylene yield increases with pulse number. Toluene and *p*-xylene accelerate conversion markedly, whilst *o*-xylene and ψ-cumene (1,2,4-trimethylbenzene) have little or no effect.

The third series of pulse-mode experiments resembled the second except in that zinc-exchanged, dealuminized Y zeolite (60 mg) was used at 624 K. Five μl pulses of methanol and methanol containing 1 wt% of aromatic hydrocarbon were fed, without regeneration between feeds. In this case the ethylene yield was independent of pulse number, as shown in Fig. 3. Ethylene yields (*C*%) were 0.2% for pure methanol; 1.8% for 1% toluene in methanol; 2.2% for 1% *p*-xylene in methanol; 0.6% for 1% *o*-xylene in methanol; and 0.3% for 1% ψ-cumene in methanol.

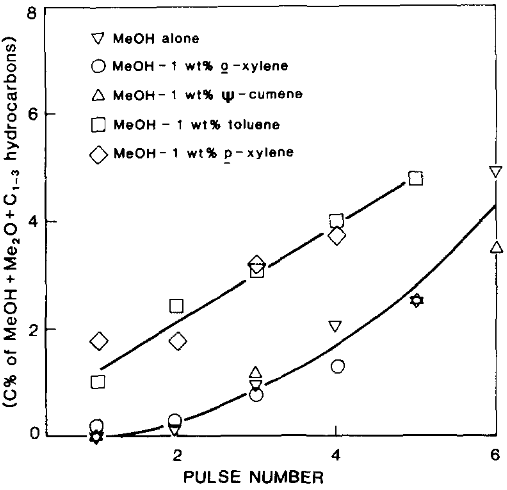

FIG. 2. Variation of ethylene yield with pulse number over H-ZSM-5 catalyst (sample C) at 562 K, for (a) pure methanol feed, and for methanol containing 1 wt% of (b) *o*-xylene, (c) ψ-cumene, (d) toluene, and (e) *p*-xylene. The plots for feeds (a)–(c) can be represented by one line, and (d)–(e) by another.

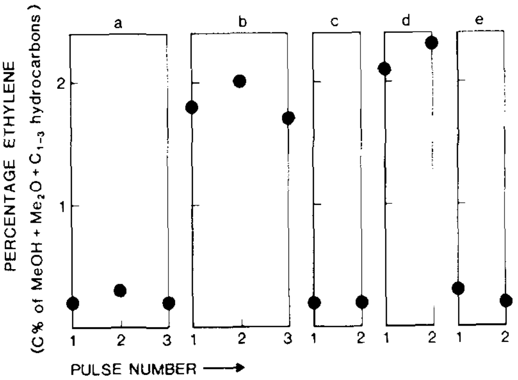

FIG. 3. Variation of ethylene yield with pulse number over Zn-dealuminized Y catalyst at 624 K for methanol feed containing (a) no additive, (b) 1 wt% toluene, (c) no additive, (d) 1 wt% *p*-xylene, and (e) 1 wt% ψ-cumene. The catalyst was not regenerated between feeds.

RESULTS AND DISCUSSION

On feeding 2.75/1 water/methanol w/w continuously to H-ZSM-5 catalyst (sample A) at a methanol w.h.s.v. of 1.7 hr^{-1}, conversion is >95% complete at temperatures ≥576 K. The product composition at 576 K is shown in Table 1, and is broadly consistent with that reported previously (*10*). As the temperature is lowered below 576 K, conversion of methanol to hydrocarbons falls rapidly to ≤10% at 563 K.

Conversion is thus dramatically dependent upon reaction temperature. Methanol conversion is strongly exothermic, and so temperature-runaway might occur in a large reactor, but is less likely using aqueous methanol in a microreactor. We attribute the strong temperature dependence to the autocatalytic nature of the reaction, which has been established (*4–6*) beyond all reasonable doubt.

Our interpretation is supported by pulse-mode experiments, carried out using methanol without water diluent. Ten min, with a flow of 60 ml of vector nitrogen, was allowed between pulses for the restoration of temperature equilibrium.

Plot (a) of Fig. 1 shows how, over H-

ZSM-5 (sample A), conversion increases with pulse number. Plot (b) shows how, when pulses are discontinued for 40 min and are then resumed, conversion again increases with pulse number but much more rapidly. This behavior is consistent with autocatalytic action being exerted by species which diffuse slowly (on a 10-min time scale) in ZSM-5 zeolite, but not with a temperature-runaway explanation. Plot (c) shows how conversion increases rapidly with pulse number when the methanol contains 2 wt% toluene. Since toluene would be expected to diffuse rapidly in ZSM-5 zeolite, this behavior suggests that toluene causes generation of autocatalytically active species instead of possessing autocatalytic activity in its own right.

The autocatalytic behavior was also demonstrated in pulse-mode experiments at low conversion. Figure 2 shows data obtained with H-ZSM-5 (sample C) of lower aluminum content at a lower temperature. Conversion to hydrocarbons is, in every case, <10%. The percentage of ethylene provides a measure of the conversion, and the increase in conversion with pulse number is again clear. One wt% toluene or *p*-xylene accelerates conversion markedly, particularly for the first two or three pulses. By contrast *o*-xylene and ψ-cumene which should be less readily sorbed into the ZSM-5 structure have little or no effect.

The third series of pulse experiments used zinc-exchanged[3] Y zeolite of low aluminium content (1.5 wt%), and gave results quite different to those observed with the two samples of ZSM-5 zeolite. Ethylene yield does not change markedly with pulse number. Thus the autocatalytically active species appear to diffuse rapidly in the Y lattice (but slowly in the ZSM-5 lattice). Toluene and *p*-xylene promote activity strongly (a tenfold increase in ethylene yield), but *o*-xylene shows much lower activity (a threefold increase) and ψ-cumene little or no activity, even though both *o*-xylene and ψ-cumene might be expected to diffuse into the Y lattice.

On the basis of all the above results we think it possible that *p*-xylene is the aromatic species which is responsible for the promotion of catalytic activity. It will, of course, be formed when benzene or toluene are added to the methanol feed. Furthermore, *p*-xylene is formed in substantial amounts as a product of methanol conversion, even in the absence of added aromatic compounds (see Table 1).

The pulse-mode experiments described above detect changes in conversion and yields, but do not measure them quantitatively. The effect of aromatic additives was also observed in experiments using a continuous feed of aqueous methanol. When, in these experiments, the vector nitrogen was bubbled through toluene, conversion was still complete at 576 K (required for >95% conversion in the absence of toluene). The product composition differed slightly; in particular the ethylene yield was lowered. The notable feature of conversion

TABLE 1

Yields of Hydrocarbon Products from Aqueous Methanol over H-ZSM-5 (sample A)

	(a) At 576 K without co-catalyst[a]	(b) At 556 K with toluene co-catalyst[b]
Ethylene	14	22
C_3H_6/C_3H_8 (mainly C_3H_6)	13	15
C_4 hydrocarbons	17	13
C_{5+} aliphatic hydrocarbons	21	14
Toluene	4	11
Xylenes	12	14
C_{9+} aromatics	16	9

[a] Percentage of the carbon of methanol appearing as the product. Total methanol conversion, 95–100%.

[b] Percentage of the carbon of methanol plus toluene appearing as the product. The ratio carbon of toluene/carbon of methanol is 0.1 (i.e., mole ratio of toluene/methanol ~1/70). Total methanol conversion, 95–100%.

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[3] Zinc-exchange has little effect on methanol conversion over ZSM- zeolite; Zn-ZSM-5 and H-ZSM-5 show much the same behavior.

in the presence of the toluene was that complete conversion was sustained down to 556 K. The product composition was then comparable with that in the absence of toluene at 576 K. The yields are shown in Table 1; they include the added toluene and products derived from it. It can be seen that only a small part of the toluene has undergone methylation to xylenes or like reactions, and that the ethylene yield is enhanced.

It can again be concluded that toluene promotes the catalytic activity of the catalyst for conversion of methanol to hydrocarbons. Various other aromatic hydrocarbons likewise increase the activity: namely benzene, ethylbenzene, and *p*-xylene. All these are readily sorbed into the channels of ZSM-5 zeolite. *o*-Xylene shows no effect, consistent with its being less easily sorbed than the *p*-isomer (*12*). *n*-Hexane also shows no co-catalytic effect, even though it is readily sorbed (*7*).

Aromatics have also been observed (*13*) to promote methanol conversion over H-ZSM-11 zeolite, prepared according to U.S. Patent 4,108,881 (*14*), and over mordenite (Norton Co., H-Zeolon) dealuminized to 0.95% residual Al by refluxing with 6*N* nitric acid. Thus the effect of aromatics may be a ubiquitous feature of conversion of methanol over highly siliceous zeolites.

Methanol conversion over zeolite catalysts, in particular H-ZSM-5 zeolite, is now seen to be of autocatalytic character and to be promoted by the presence of olefins (and olefin precursors such as alcohols) or aromatic hydrocarbons in the feed. Olefins and aromatic hydrocarbons may appropriately be described as co-catalysts for methanol conversion over zeolite catalysts. Both classes of hydrocarbon are products of methanol conversion, and so both may be implicated in the autocatalytic character of conversion. We suspect (but cannot prove) that the olefins are more important.

The co-catalytic and autocatalytic role of olefins can readily be understood if the homologation mechanism (*6–8*) is operative in methanol conversion. It has also been suggested that olefins may play a co-catalytic role in the conversion of methanol to ethylene and other hydrocarbons by an oxonium–ylide mechanism (*10*). On the other hand olefins are converted to aromatic hydrocarbons under conditions of methanol conversion (*15*), and this may account for some of their co-catalytic and autocatalytic activity.

The chemical basis of aromatic co-catalysis is quite uncertain. It may relate to the basicity (proton-acceptor capacity) of the aromatics. Thus reversible protonation of the aromatic may facilitate the proton-transfer reactions involved in methanol conversion (see, for example, Ref. (*10*)). Alternatively, a mechanism whereby methanol can extend the alkyl side chain of an aromatic (e.g., Aryl–CH_3 to Aryl–C_2H_5 to Aryl–C_3H_7) may provide a route from methanol to C_2 and higher aliphatic chains, and thus an explanation of the observed co-catalysis. The latter possibility is being investigated.

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