

Synergism in Acetic Acid/Methanol Reactions  
Over ZSM-5 Zeolites

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INTRODUCTION

Carboxylic acids are readily converted to aromatic hydrocarbons over ZSM-5 zeolites (1). The initial step of the reaction sequence involves oxygen elimination by decarboxylation, decarbonylation and/or dehydration. The residual hydrocarbon moiety is then aromatized, we believe, via classical carbenium ion pathways (2).

The reaction causes rapid catalyst deactivation, which can be alleviated by adding methanol to the feed (3). The synergistic effect of methanol on acetic acid aromatization is the subject of this study.

EXPERIMENTAL DATA

A. FIXED BED RESULTS

Acetic Acid

Acetic acid was reacted over HZSM-5 at 316°C and 370°C, 1 atm., 1 LHSV. Results are shown in Table 1. At 316°C, activity is low (8% conversion). Decarboxylation is the principal mode of oxygen elimination, resulting in acetone and hydrocarbons, mainly isobutylenes and aromatics. At 370°C, both decarboxylation and dehydration are important, however, catalyst deactivation is rapid, with conversions dropping from 100% to 71.4% in 1.3 hr.

Again the main products are acetone, isobutylene and aromatics. Decarbonylation is a relatively minor reaction.

Acetic Acid/Methanol Mixture

A 4/1 molar mixture of methanol/acetic acid was reacted over HZSM-5 at 370°C, 1 atm., 1 As seen in Table 1, the conversion remains quantitative after 3 hr. No evidence of catalyst deactivation was seen during this period. The addition of methanol suppresses CO<sub>2</sub> formation, and dehydration becomes the main oxygen-elimination reaction. The hydrocarbons are mostly aromatic (79%).

## B. FLUID-BED RESULTS

Experimental data are presented in Table 2. Two conversions are presented for each run. "Total conversion" represents the conversion to all products, while "conversion to non-oxygenates" represents conversion to all hydrocarbon, COx and H<sub>2</sub>O products. The overall yields from the methanol experiment are in reasonable agreement with data obtained in the fluid bed MTG process (5). The hydrocarbon gas products, however, are higher in propene and lower in isobutane probably due to the lower reaction pressure used in this study.

### Acetic Acid and Methylacetate

The data obtained for acetic acid illustrate several interesting points which can be contrasted with the earlier continuous operation in a fixed bed. First, total conversions >90% may be maintained indefinitely provided periodic catalyst regeneration is employed. The experimental data show that decarboxylation takes place to a large extent.

On a weight basis, acetic acid yields less than 40% as much hydrocarbon as methanol. The lower yield is primarily due to carbon loss by decarboxylation, and to a small extent, to coke and CO production.

Methyl acetate has a higher carbon content (48.6% C) than acetic acid and methanol and despite decarboxylation and coke, the observed hydrocarbon yield remains comparable to that of methanol. Moreover, selectivity for direct conversion to C<sub>5</sub><sup>+</sup> hydrocarbons is higher than that of acetic acid or methanol (79.5%). Thus, the direct yield of C<sub>5</sub><sup>+</sup> liquid hydrocarbons is 32.1% on charge vs 23.3% for methanol.

### Acetic Acid/Methanol Mixtures

Processing a 1.9/1 or a 3.8/1 molar mixture of CH<sub>3</sub>OH and acetic acid provided observations similar to fixed-bed results, i.e. an enhancement in C<sub>5</sub><sup>+</sup> liquid yield at the expense of C<sub>4</sub><sup>-</sup> vs what might be expected if the mixture behaved as the average of its two components, the calculated values for which are shown in parentheses in Table 2. The selectivities of the hydrocarbon products amplify the observed synergism with respect to C<sub>5</sub><sup>+</sup> liquids. Furthermore, there is an enhancement in total hydrocarbon yield vs linear combination expectations.

This is illustrated in Figure 1 which shows the effect of increasing mole percent methanol in the MeOH/acetic acid charge and attendant decrease in oxygen rejection as CO<sub>2</sub> and increase in oxygen removal as H<sub>2</sub>O. Thus, more carbon remains available to form hydrocarbon products, much of it becoming C<sub>5</sub><sup>+</sup> liquids.

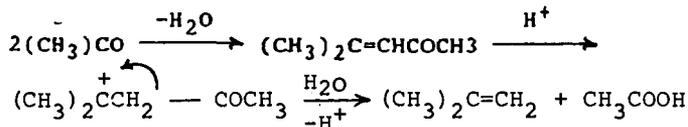
## DISCUSSION

### A. AROMATIZATION PATHWAY FOR ACETIC ACID

As shown previously, the major initial products of acetic acid reaction over HZSM-5 are acetone, isobutylene and CO<sub>2</sub>.

Acetone formation from acetic acid is a known reaction and is often referred to as "ketonization" (6,7). The reaction was originally observed on 3d-oxides, but has been reported for SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and mordenite (8,9) catalysts. The mechanism of ketonization via decarboxylation is discussed later.

Isobutylene formation from acetone decomposition over silica gel and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (8,9,10) and zeolites (1,12) has also been reported. The reaction mechanism over acid zeolites is believed to involve an aldol condensation followed by β-scission (12):



In the present case, the isobutylene is converted by HZSM-5 to aromatics and paraffins, while the acetic acid re-enters the catalytic cycle.

Neglecting catalyst deactivation for the moment, the main reactions of hydrocarbon formation from acetic acid over HZSM-5 are summarized in the following scheme:

Scheme A



[CH<sub>2</sub>]<sub>x</sub> = aromatics + paraffins

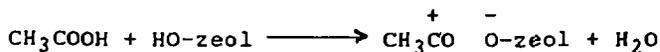
### B. MECHANISM OF CATALYST DEACTIVATION AND THE ROLE OF METHANOL

The ketonization of acetic acid over 3d-oxides such as chromia and TiO<sub>2</sub> at 350°-460°C has been shown to involve the bimolecular nucleophilic attack of an acylium ion by an acetate species with CO<sub>2</sub> elimination (7,13):

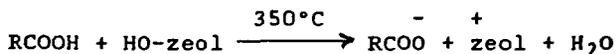


Over the  $\text{TiO}_2$ , the acylium ion precursor was ketene, detected by IR (7).

It seems reasonable to assume a similar mechanism for strongly acidic zeolites, except that in this case, the acylium ion may be directly generated:

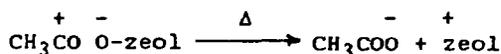


At sufficiently high temperature, an acetate species results, as has been reported for NaHY (14):

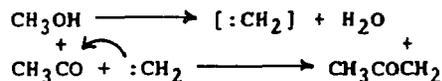


Note that this is a zeolite dehydroxylation. The crystallinity of Na mordenite is gradually destroyed in ketonization of AcOH and  $\text{EtCO}_2\text{H}$  at 200-450°C (8). ZSM-5, however, is regenerable, as shown in the fluid studies.

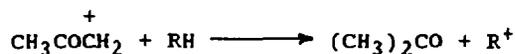
We assume that dehydroxylation is the primary mechanism of zeolite deactivation by carboxylic acids. We propose that the acylium ion is the precursor to acetate



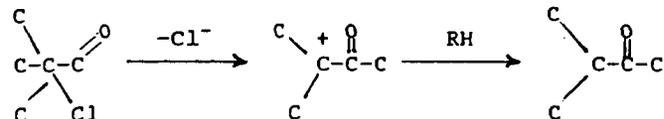
and that methanol "traps" the acylium ion



The resulting  $\alpha$ -ketocarbenium ion is converted to acetone by hydride abstraction from a suitable source, e.g. isoalkane.



As support for this step we cite the  $\text{AlCl}_3$ -catalyzed conversion of pivaloyl chloride to methylisopropyl ketone in the presence of isopentane as hydride source (15):

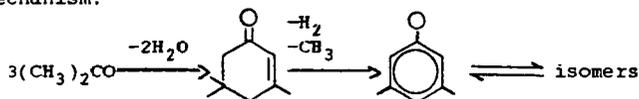


This intervention by methanol, therefore, competes with acetate formation,  $\text{CO}_2$  formation and attendant zeolite



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16. Dimethyl phenols are most likely formed according to the following mechanism:



Step A is well known (17,18). The dimethyl analogue of Step B has been described by Horning (19). Demethylation from a quaternary carbon upon dehydrogenation is a known reaction (20).

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TABLE 1  
Conversion of AcOH and AcOH/MeOH over HZSM-5  
Fixed Bed Data

Feed	AcOH	AcOH	AcOH (1 mol) + MeOH (4 mol)
T, °C	316	370	370
P, psig	0	0	0
HSV, hr <sup>-1</sup>	1	1	1
HSV, hr	1.5	1.3	3.0
Conversion, wt. %	8.0	71.4(a)	100
<u>Products, wt. %</u>			
H <sub>2</sub>	0.1	--	--
CO	1.7	1.6	1.3
CO <sub>2</sub>	32.9	15.7	22.8
H <sub>2</sub> O	tr	56.1	24.3
Acetone	33.4	6.0	32.8
Other n-cpds	2.7	0.7(b)	3.8(b)
Hydrocarbons	29.2	19.9	39.8
<u>Hydrocarbons, wt. %</u>			
C <sub>1</sub>	--	0.1	0.2
C <sub>2</sub>	--	--	0.5
C <sub>2</sub> =	0.6	1.7	1.3
C <sub>3</sub>	--	2.7	0.1
C <sub>3</sub> =	1.8	2.7	3.3
C <sub>4</sub>	--	0.4	0.2
C <sub>4</sub> =	17.1(c)	7.1(c)	26.2(c)
C <sub>5</sub>	--	0.1	--
C <sub>5</sub> =	--	0.3	0.3
C <sub>6</sub> aliphatic	--	0.3	4.0
Aromatics	80.5	84.6	68.1

(a) 100% conversion at 0.3 hr.  
 (b) >70% dimethylphenols (16).  
 (c) >5% isobutylene.  
 (d) 81% conversion at 1.5 hr.

TABLE 2  
Conversion of AcOH, MeOH, and AcOH/MeOH over HZSM-5  
Fluid Bed Data

410°C, 1 atm, 1.0-1.1 WHSV, 20 min Reaction Intervals		Fluid Bed Data			
Total Conversion	Methanol CH <sub>3</sub> OH	Acetic Acid CH <sub>3</sub> COOH	Methyl Acetate CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	1.9/1 (molar) MeOH/ Acetic Acid	3.8/1 (molar) MeOH/ Acetic Acid
98.6	98.6	91.2	89.4	>91 (94.9)	95
Conversion to Non-Oxygenates		79.8	86.1	90.4 (89.2)	--
<u>Products (Wt. % of Charge)</u>					
CO	0.0	3.7	6.2	2.1 (1.8)	1.1 (1.2)
CO <sub>2</sub>	0.2	31.4	17.6	9.4 (15.8)	5.2 (10.6)
H <sub>2</sub> O	55.8	28.4	21.5	45.3 (42.1)	48.8 (46.7)
Oxygenates	1.4	20.2	13.9	9.6 (10.8)	5.2 (7.7)
C <sub>1</sub> Hydrocarbon gas	19.0	3.8	6.0	7.9 (11.4)	9.9 (13.9)
C <sub>2</sub> Liquid Hydrocarbon	23.3	10.6	32.1	24.9 (17.0)	28.7 (19.1)
Total Hydrocarbons	42.3	14.4	38.1	32.8 (28.4)	38.6 (33.0)
Coke	0.3	1.9	2.7	0.8 (1.1)	1.1 (0.8)
<u>Wt. %'s of Hydrocarbon</u>					
C <sub>1</sub> + C <sub>2</sub>	5.4	1.5	5.6	7.2	7.6
C <sub>3</sub>	1.6	0.1	0.7	0.4	0.6
C <sub>3</sub> =	25.9	5.2	6.7	13.8	14.2
iC <sub>4</sub>	5.5	0.5	0.3	0.4	0.5
nC <sub>4</sub>	0.4	0.3	0.0	0.1	0.1
C <sub>4</sub>	5.8	15.7	1.4	1.6	1.9
Total C <sub>4</sub>	44.6	23.3	14.7	23.5 (34.0)	24.9 (37.5)
C <sub>5</sub> liquid	54.7	65.0	78.7	74.1 (59.8)	72.3 (58.1)
Coke	0.7	11.7	6.6	2.4 (6.2)	2.8 (4.4)