Reaction of Acetylene over ZSM-5-Type Catalysts

P. TSAI AND J. R. ANDERSON

Catalysis and Surface Science Laboratory, CSIRO Division of Materials Science, University of Melbourne, Parkville, Victoria 3052, Australia

INTRODUCTION

A possible shortage of petroleum-based liquid fuels has revived interest in the Fischer–Tropsch process, and more recently has led to considerable interest in the Mobil process for converting methanol to gasoline using ZSM-5 zeolite catalysts (*1*). For this Mobil process the methanol may be prepared from, for instance, natural gas or from coal via synthesis gas.

A possible alternative strategy is available. Processes are available for the conversion of methane (*3, 4*) or coal (*5, 6*) to acetylene, and it has recently been disclosed that acetylene may be converted to a gasoline-useful range of hydrocarbon products over ZSM-5 zeolite catalysts (*2*). The aim of this paper is to provide details of the catalytic conversion of acetylene over a range of ZSM-5 zeolites.

It was recognized that trisubstituted carbenium ion intermediates are important in the conversion of methanol or olefins to aromatics over ZSM-5 (*16, 17*), and it was therefore of interest to compare the behavior of acetylene, which could yield a vinyl cation intermediate at a Brønsted acid site (*14*).

EXPERIMENTAL

The ZSM-5 zeolite was prepared by mixing 56.0 g of sodium silicate solution (29.1 wt% SiO_2, 9.1 wt% Na_2O, and 0.03 wt% Al_2O_3) with 100.0 g of distilled water. To this solution 1.04 g of sodium hydroxide (BDH, AR grade) was added, followed by the addition of 7.04 g of tetra-*n*-propyl ammonium bromide (Ajax, Unilab). To this mixture 4.9 g of 98 wt% sulfuric acid (BDH, AR grade) and 93.6 g of distilled water were added. After vigorous mixing, the material was placed in a Pyrex vessel inside a stainless-steel pressure vessel which was stirred continuously and held at 448K for 48 hr. After reaction the product was filtered, thoroughly washed with distilled water, dried at 383K overnight, and calcined at 773K for 16 hr. The product was cooled and then digested with 0.3 *M* hydrochloric acid (BHD, AR grade) at 373K for 16 hr. The resultant protonated form of ZSM-5 (H-ZSM-5) was filtered, washed with distilled water, and air-dried at 383K. X-Ray analysis showed that the diffraction pattern of the material was typical of ZSM-5. This catalyst, which is designated H-ZSM-5(2), gave on analysis a Si/Al ratio of 60.

A number of H-ZSM-5 zeolites with varying Si/Al ratios were prepared by following the experimental procedures above. The Si/Al ratio was varied by adding the appropriate amount of $Al_2(SO_4)_3 \cdot 28H_2O$ (Merck) to the reaction mixture. The zeolite designated H-ZSM-5(1) gave on analysis a Si/Al ratio of 25. The zeolites H-ZSM-5(3), H-ZSM-5(4), and H-ZSM-5(5) (Si/Al ratios of 103, 243, and 436, respectively) were prepared following the procedures above, except in this instance the sodium silicate solution contained 28.77 wt% SiO_2, 8.91 wt% Na_2O, and <0.001 wt% Al_2O_3. Again, the amount of Al in the zeolite was adjusted accordingly using aluminum sulfate. The chemical composition of the samples is given in Table 1.

Na⁺ back-exchanged ZSM-5. A Na⁺-exchanged zeolite was prepared from H-

TABLE 1

Chemical Composition of Zeolite Samples

Zeolite	Si/Al ratio	Chemical analysis wt%		
		Na	Al	Loss on ignition
H-ZSM-5(1)	25	0.016	1.72	1.81
H-ZSM-5(2)	60	0.02	0.72	1.40
H-ZSM-5(3)	103	0.007	0.42	1.38
H-ZSM-5(4)	243	0.007	0.18	0.95
H-ZSM-5(5)	436	0.009	0.10	1.37

ZSM-5(2) by using conventional ion-exchange techniques (7). Analysis showed that the product, designated Na-ZSM-5, contained 0.34 wt% Na, which corresponds to the replacement of 54% of exchangeable H^+ by Na^+.

Apparatus and analysis. Reactions were carried out in a quartz flow microreactor containing 0.1 g of catalyst at a total pressure of 1 atm. Prior to reaction, all samples were heated in a flow of oxygen at 773K for 12 hr. Acetylene (CIG, stated purity 99.1%) was purified by allowing the gas to bubble through concentrated sulfuric acid and then passed over a dehydrated Linde 5A molecular sieve.

The reactor effluent was introduced into a gas chromatograph (Varian 3700) through a gas sampling valve for analysis. In the normal analysis, a 4 m × 3 mm silicone OV-101 column was used in a temperature program mode. A Hewlett–Packard integrator (Model 3380A) was used to measure peak areas and retention times.

The higher-molecular-weight aromatic products were also studied with a Hewlett–Packard 5995A GC/MS system.

RESULTS

Preliminary experiments using undiluted acetylene as the reactant feed showed that acetylene was highly reactive over H-ZSM-5 at temperatures >573K, but the catalyst was subject to rapid deactivation in a pe-

riod of ≤60 min with the generation of coke and C_{11+} aromatics. For this reason it was necessary to work with a feed stream consisting of acetylene diluted with an inert gas such as helium, and the reactions were generally run under mild temperature conditions which resulted in <100% conversion. Even so, with the present catalysts appreciable deactivation was always observed.

Two important conclusions emerge from the nature of the reaction products. In the absence of hydrogen in the reactant, acetylene was converted with very high selectivity to aromatics (in most cases better than 99%) although the aromatics were themselves distributed over the range C_6–C_{13}. Second, hydrogen in the reactant drastically altered the product distribution in that it resulted in the conversion of a substantial fraction of acetylene into ethylene.

The main classes of reaction products are specified in Tables 2–5 and 7 for the various catalysts and reaction conditions. The aromatic products in the range C_9–C_{13} were always a mixture, but GC/MS study identified the following main components in each class: C_9, methylethylbenzene and trimethylbenzene; C_{10}, naphthalene and lesser amounts of tetralin and minor amounts of alkylbenzenes; C_{11}, 2-methylnaphthalene; C_{12}, dimethylnaphthalene and 2-ethylnaphthalene; C_{13}, alkylnaphthalenes.

Reactions over H-ZSM-5(1)–H-ZSM-5(5) Catalysts

The main classes of reaction products obtained at about 623K with an acetylene/helium feed mixture over H-ZSM-5 catalysts with varying aluminum contents are summarized in Table 2. The data refer to products after 15 min on stream and are thus representative of catalysts without substantial deactivation. All the catalysts gave aromatic hydrocarbons as the dominant product, with only trace amounts of nonaromatic products. There was a decrease in the extent of acetylene conversion with increasing Si/Al ratio, with the conver-

TABLE 2

Reaction of Acetylene over H-ZSM-5 Zeolites[a]

Catalyst[b]	H-ZSM-5(1)	H-ZSM-5(2)	H-ZSM-5(3)	H-ZSM-5(4)	H-ZSM-5(5)
Feed rate (cm^3 min^{-1}) (C_2H_2)	0.5	0.5	0.5	0.7	0.5
(He)	3.9	3.9	3.9	3.6	3.9
Volumetric space velocity[c] (hr^{-1})	3.9×10^3	3.9×10^3	3.9×10^3	3.8×10^3	3.9×10^3
Reaction temperature (K)	623	622	623	623	621
Conversion of acetylene (%)	29.9	25.5	22.5	9.1	6.8
Reaction products (wt%)					
Nonaromatics	Trace	0.1	Trace	Trace	Trace
Benzene	1.1	2.9	2.3	1.8	3.1
Toluene	2.9	7.4	5.2	3.3	7.8
Xylenes[d]	7.6	13.9	10.9	7.1	11.8
C_9 aromatics	11.7	11.2	13.6	8.3	10.4
C_{10} aromatics	31.2	32.4	31.8	34.3	50.9
C_{11} aromatics	33.1	21.3	19.9	32.8	16.0
C_{12} aromatics	12.4	9.5	16.3	12.4	Trace
C_{13} aromatics	Trace	1.3	Trace	Trace	—

[a] Time on-stream, 15 min.
[b] 0.1 g catalyst.
[c] Volume of *total gaseous* feed at reactor temperature per packed volume of reactor per hour.
[d] Some styrene and ethylbenzene.

sion changing most rapidly between Si/Al ratios of 103 and 243.

Using H-ZSM-5(2) and H-ZSM-5(3) as typical catalysts the effects of varying space velocity and reaction temperature were studied, and the results are recorded in Tables 3 and 4, respectively.

With the reaction temperature increasing from 524 to 775K (cf. Table 4) the extent of acetylene conversion (measured at 15 min on-stream time, i.e., before substantial deactivation) increased from 4.3 to 38.2%, and at the same time the distribution of reaction products changed mainly by decreasing the proportion of C_9–C_{10} aromatics and increasing the proportion of other products. Increasing the space velocity (cf. Table 3) resulted in a decrease in the extent of acetylene conversion and a reduction in the relative rate of catalyst deactivation.

Catalyst deactivation increased with increasing on-stream time. A typical result is

shown in Table 5 for the catalyst H-ZSM-5(2), which demonstrates the fall in the extent of acetylene conversion and the change in the nature of the reaction product distribution toward higher-molecular-weight aromatic products as the on-stream time increased.

Since catalyst deactivation was an important feature of the reaction, the rate of deactivation was studied as a function of catalyst composition and feed gas composition. Table 6 shows that, as judged by the extent of acetylene conversion, the rate of deactivation decreased with increasing Si/Al ratio, although this improvement was achieved at lower overall conversion levels.

The data given in Table 7 show that, other things being approximately equal, the addition of hydrogen to the reactant gas stream increased the level of acetylene conversion and substantially altered the prod-

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TABLE 3

Effect of Varying Space Velocity[a,b,c]

Volumetric space velocity[d] (hr^{-1})	3.9×10^3		15.0×10^3	
Time on stream (min)	15	45	15	45
Conversion of acetylene (%)	10.7	7.5	3.9	2.3
Reaction products (wt%)				
Nonaromatics	Trace	Trace	Trace	Trace
Benzene	2.3	1.5	1.9	1.6
Toluene	4.3	3.7	3.7	2.9
Xylenes[e]	8.7	3.5	6.6	3.1
C_9 aromatics	10.0	6.2	6.6	3.9
C_{10} aromatics	36.6	22.1	36.8	32.3
C_{11} aromatics	38.1	40.5	40.6	32.9
C_{12} aromatics	Trace	21.0	3.8	20.2
C_{13} aromatics	Trace	1.5	Trace	3.1

[a] H-ZSM-5(2); Si/Al = 60. Catalyst mass, 0.1 g.
[b] Reaction temperature, 573K.
[c] Feed gas C_2H_2/He molar ratio, 1/7.5
[d] Volume of *total gaseous* feed at reactor temperature per packed volume of reactor per hour.
[e] Some styrene and ethylbenzene.

uct distribution in the sense that hydrogen greatly increased the proportion of nonaromatic products (mainly ethylene).

It was found that the Na-ZSM-5 catalyst still retained activity for acetylene conversion although under comparable reaction conditions (623K) this catalyst was considerably less active (conversion 13.9%) than the corresponding H-ZSM-5(2) (conversion 25.5%). Furthermore, the products obtained over Na-ZSM-5 contained a larger proportion of C_{10}–C_{13} aromatics (85.8 wt%) than did the products from H-ZSM-5(2) (64.5 wt%).

DISCUSSION

The conversion of acetylene to aromatic products over H-ZSM-5 proceeds relatively easily, and the effective temperature range ($\geq$530K) is approximately 100° below that for the conversion of olefins or methanol. It thus seems probable that the species responsible for chain growth from acetylene are of considerably greater intrinsic reactivity than those involved in olefin or methanol conversion.

TABLE 4

Effect of Varying Reaction Temperature[a,b,c]

Reaction temperature (K)	524	572	621	673	728	775
Conversion of acetylene[d] (%)	4.3	11.5	13.2	17.0	27.7	38.2
Volumetric space velocity[b] (hr^{-1})	6.5×10^3	7.0×10^3	7.6×10^3	8.3×10^3	9.0×10^3	9.5×10^3
Reaction products (wt%)						
Nonaromatics	Trace	Trace	Trace	Trace	Trace	Trace
Benzene	Trace	0.8	2.1	3.2	7.1	7.7
Toluene	4.5	5.0	6.0	7.3	9.4	8.2
Xylenes[e]	9.7	9.3	11.6	13.3	15.4	9.2
C_9 aromatics	12.8	11.4	14.0	14.4	12.5	4.3
C_{10} aromatics	47.4	48.0	38.2	34.2	36.2	30.8
C_{11} aromatics	16.5	19.0	19.6	18.1	14.0	31.0
C_{12} aromatics	9.1	6.5	8.5	8.5	5.0	7.7
C_{13} aromatics	Trace	Trace	Trace	1.0	0.4	1.1

[a] H-ZSM-5(3); Si/Al = 103. Catalyst mass, 0.1 g.
[b] Volume of *total gaseous* feed at reactor temperature per packed volume of reactor per hour.
[c] Feed gas C_2H_2/He molar ratio 1/4.3.
[d] At 15 min on-stream time.
[e] Some styrene and ethylbenzene.

TABLE 5

Catalyst Deactivation with Increased On-Stream Time[a,b,c]

Time on-stream (min)	15	45	95	190
Conversion of acetylene (%)	10.7	7.5	5.9	3.3

Reaction products (wt%)

Nonaromatics	Trace	Trace	Trace	Trace
Benzene	2.3	1.5	0.8	0.6
Toluene	4.3	3.7	4.7	1.1
Xylenes[d]	8.7	3.5	2.0	1.1
C_9 aromatics	10.0	6.2	3.0	1.0
C_{10} aromatics	36.6	22.1	17.3	14.2
C_{11} aromatics	38.1	40.5	32.1	30.0
C_{12} aromatics	Trace	21.0	33.2	34.5
C_{13} aromatics	Trace	1.5	6.9	11.0

[a] H-ZSM-5(2); Si/Al = 60. Catalyst mass, 0.1 g.

[b] Reaction temperature, 573K.

[c] Feed gas C_2H_2/He molar ratio 1/7.5. Volumetric space velocity (volume of *total* gaseous feed at reactor temperature per packed volume of reactor per hour), 3.9×10^3 hr^{-1}.

[d] Some styrene and ethylbenzene.

Since (in the absence of added hydrogen) aromatics are virtually the exclusive product type from acetylene, and since the conversion of acetylene to a polyene is well known with certain types of acidic cata-

TABLE 6

Catalyst Deactivation at Different Si/Al Ratios[a,b,c]

Si/Al	Conversion of acetylene (%)		Ratio conv. at 95 min
	15 min on-stream	95 min on-stream	Conv. at 15 min
25 (H-ZSM-5(1))	34.3	5.0	0.146
60 (H-ZSM-5(2))	10.7	5.9	0.551

[a] Reaction temperature, 573K.

[b] Volumetric space velocity (volume of *total* gaseous feed at reactor temperature per packed volume of reactor per hour), 3.9×10^3 hr^{-1}.

[c] Feed gas C_2H_2/He molar ratio 1/7.5.

[d] 0.1 g catalyst.

TABLE 7

Effect of Hydrogen on Extent of Acetylene Conversion and on Product Distribution[a,b]

	Feed rate (cm^3 min^{-1})					
	C_2H_2	He	H_2	C_2H_2	He	H_2
	0.5	3.9	0	0.3	1.9	1.6
Volumetric space velocity[c] (hr^{-1})	3.9×10^3			3.4×10^3		
Conversion of	22.5			32.5		

Reaction products[d] (wt%)

Nonaromatic	Trace	30.1[f]
Benzene	2.3	2.5
Toluene	5.2	6.6
Xylenes[e]	10.9	15.1
C_9 aromatics	13.6	9.1
C_{10} aromatics	31.8	20.5
C_{11} aromatics	19.9	16.1
C_{12} aromatics	16.3	Trace
C_{13} aromatics	Trace	—

[a] H-ZSM-5(3); Si/Al = 103. Catalyst mass, 0.1 g.

[b] Reaction temperature, 623K.

[c] Volume of *total gaseous* feed at reactor temperature per packed volume of reactor per hour.

[d] At 15 min on-stream time.

[e] Some styrene and ethylbenzene.

[f] >90% ethylene.

lysts, including solids such as γ-Al_2O_3 (8), zeolite KX (8), and TiO_2 (9), as well as soluble catalysts of the Natta–Ziegler type (10, 11), it seems probable that the reaction can be described by the general scheme

$$\text{acetylene} \rightarrow [n\text{-polyene}] \rightarrow \text{aromatic,} \quad (1)$$
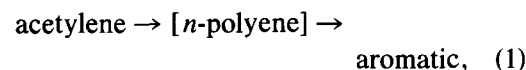
where the molecular size is limited for steric reasons within the zeolite channels. This scheme is not intended to imply that n-polyene exists as a stable neutral molecule species as an intermediate product. Further mechanistic comments will be given later in the discussion.

Table 4 shows that, as expected, the extent of conversion increases with increasing temperature. Increasing temperature resulted in no dramatic changes to the product distribution: there was only a modest increase in the fraction of benzene and toluene and a decrease in C_{10} aromatic (mainly naphthalene), while toward the upper end

of the experimental temperature range there was a significant increase in C_{11} aromatic (mainly 2-methylnaphthalene).

Table 3 shows that increasing the space velocity resulted, as expected, in lower conversion, but it also resulted in an increased fraction of C_{12} and C_{13} aromatic products. We ascribe this latter effect to an increased efficiency for the desorption of high-molecular-weight products at higher space velocities. As is also apparent from Table 3, the effect of space velocity on catalyst deactivation was relatively small.

Deactivation of the catalyst increased with onstream time (cf. Table 5), and this correlates with an increase in the fraction of higher aromatic products (C_{12} and C_{13}): the latter can presumably act as precursors to coke formation.

The use of the sodium-exchanged Na-ZSM-5 catalyst showed that acetylene conversion still occurred, although to a reduced extent compared with the corresponding H-ZSM-5(2), while Na-ZSM-5 also gave an increased proportion of aromatic products in the C_{10}–C_{13} range. Na-ZSM-5 contained Na^+ corresponding to the replacement of 54% of exchangeable H^+ by Na^+. If no other factors intervened, one would expect the strongest Brønsted acid sites to be preferentially exchanged: if this is so, it implies that even the weaker Brønsted acid sites are capable of effecting the conversion of acetylene. The fact that Na-ZSM-5 gave an enhanced proportion of C_{10}–C_{13} aromatics implies that in generating Na-ZSM-5 it is the acidic sites within the channels which have been preferentially exchanged, with the weaker unexchanged sites on the external surface. This conclusion would be in agreement with the acid site distribution previously proposed (15), but this agreement must be regarded as quite tentative because of the uncertainty with which this acid site distribution can be assigned.

Finally, we turn to the question of the details of the chemical reactions from acetylene.

The polymerization of acetylene to polyenes is well known using soluble Natta–Ziegler catalysts such as a mixed solution of aluminum triethyl and tetraalkyl titanate (10, 11). The reaction is highly sensitive to traces of moisture or oxygen, and most certainly involve reaction at Lewis acid sites. Furthermore, the reaction typically occurs very readily in the range 300–350K.
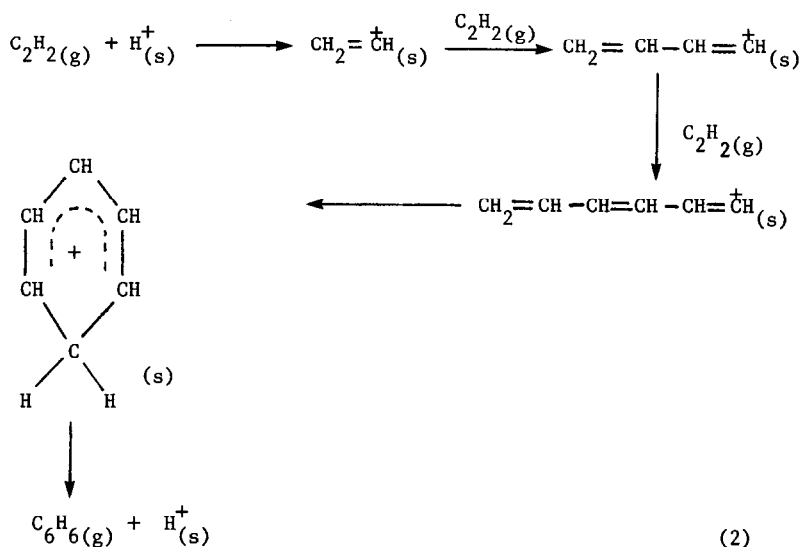
The characteristics of the conversion of acetylene over ZSM-5 are quite different. The activity of the catalyst is maintained in the presence of even relatively large amounts of water in the feed (2), and the required temperature range is typically $\geq 530K$. Since it is very improbable that Lewis acid sites could survive in worthwhile concentrations in ZSM-5 in the presence of excess water, we conclude that the acetylene conversion is a Brønsted acid-catalyzed reaction. We propose that the reaction proceeds via vinyl cation intermediates ($CH_2\!\!=\!\!\overset{+}{C}H$ and its homologs (18)), involving the basic reaction as shown in (2), exemplified for the formation of benzene. The subscript (s) indicates an entity at a site in the zeolite.

The concept of vinyl cations is not novel (12, 13, 14).

The polymerization of acetylene to polyene has been observed by Raman spectroscopy at the surfaces of γ-Al_2O_3 (8), zeolite KX (8), and TiO_2 (9) at room temperature and below. Although the extent of polymer formation was relatively small, its presence was beyond question. In these cases the polymerization mechanism is obscure, although it was reported for γ-Al_2O_3 (8) that the expected increase in polymerization with increased activation temperatures (which would result in an increased number of Lewis acid sites) could not be confirmed experimentally so it is possible that Brønsted acidity might have played a role in this case too.

The formation of higher-molecular-weight products can be readily elaborated from reaction (2), while the formation of

$$C_2H_{2(g)} + H^+_{(s)} \longrightarrow CH_2 = \overset{+}{C}H_{(s)} \xrightarrow{C_2H_{2(g)}} CH_2 = CH - CH = \overset{+}{C}H_{(s)}$$

$$\Big\downarrow C_2H_{2(g)}$$

$$\longleftarrow CH_2 = CH - CH = CH - CH = \overset{+}{C}H_{(s)}$$

(2)

$$C_6H_{6(g)} + H^+_{(s)}$$

methyl aromatics such as toluene or the xylenes from a two-carbon-atom precursor no doubt involves cracking and isomerization reactions similar to those already discussed (*16*).

In the conversion of acetylene over ZSM-5, the effect of added hydrogen is markedly different from the behavior with reactants such as methanol or olefin. With the latter, hydrogen is essentially an inert diluent, but in the case of acetylene the addition of hydrogen results in a major increase in the proportion of lower-molecular-weight products, particularly ethylene (cf. Table 7). We conclude that the vinyl cations of the type represented in reaction (2) can react with molecular hydrogen, e.g.,

$$CH_2 = \overset{+}{C}H_{(s)} + H_{2(g)} \rightarrow$$
$$CH_2 = CH_{2(g)} + H^+_{(s)}, \quad (3)$$
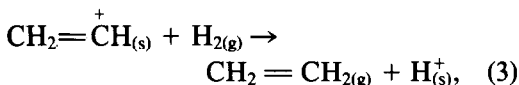
whereas an analogous reaction is not possible from a trisubstituted carbenium ion.

ACKNOWLEDGMENTS

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18. We do not suggest that vinyl cations exist as *long-lived* species, rather we suggest that they act as short-lived reaction intermediates. It is known that protonation of alkynes under strongly acid conditions has so far failed to give *stable* vinyl cation solutions (cf. Siehl, H.-U., and Mayr, H., *J. Amer. Chem. Soc.* **104,** 909 (1982)).