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Reaction of Acetylene over Fluorinated Alumina Catalysts

V. M. ALLENGER,* C. FAIRBRIDGE,* D. D. MCLEAN,† AND M. TERNAN*

**Energy Research Laboratories, CANMET, Energy, Mines & Resources Canada, Ottawa, Ontario, Canada K1A 0G1; and †Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4*

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A series of five amorphous fluorinated alumina catalysts (F/Al ratios between 0–3) was investigated with respect to their potential to convert acetylene to high-octane fuel components. Tests were performed in a tubular flow reactor at 1 atm. The effects of temperature (573–673 K), space velocity (1200–3600 h^{-1}), and initial concentration of acetylene (5–15%) on catalyst activity were examined. Catalyst performance was also correlated with the acidity of the five catalysts.

INTRODUCTION

Two technologies exist for converting methane, the principal component of natural gas, into transportation fuels: the Fischer–Tropsch and the Mobil Oil processes. Since acetylene is the primary product from the thermal pyrolysis of natural gas, alternative routes involving acetylene are being pursued by several groups (*1–3*). Although acetylene has been used as a major building block in the chemical industry, a commercial catalyst suitable for the transformation of acetylene to useful fuel-range products is not available. One of the research programs at our laboratories involves the development of suitable catalysts for the conversion of acetylene into high-octane fuel components.

Polymerization reactions of unsaturated hydrocarbons, e.g., butylene, are believed to be acid-catalyzed (*4*). The polymerization of olefins to hydrocarbons boiling in the gasoline range has been carried out commercially using both sulfuric and supported phosphoric acid. Reactions catalyzed by solid acids exhibit features similar to reactions catalyzed by mineral or supported mineral acids. Alumina has been used extensively as a catalyst and catalyst support for acid-catalyzed reactions such as isomerization, alkylation, and polymerization. Fluorination of alumina has been shown to alter the acid properties of the alumina (*5*) and to enhance some reactions, e.g., the polymerization of olefins and of conjugated dienes (*6*). The catalytic reactions of alkynes and specifically acetylene have not been reported with fluorinated alumina. This work was undertaken to study the reaction of acetylene over a series of amorphous-fluorinated alumina catalysts containing between 0–68 wt% F.

A comparison of catalyst activities requires examination of conversions under a variety of reaction conditions, i.e., temperature, weight-time, and initial concentration of reactant. Clearly, a complete investigation of each catalyst with respect to processing conditions would require a large number of experiments. To carry out the experimentation efficiently the effects of temperature, weight-time, initial concentration of acetylene, and degree of fluorination on conversion were examined using a central composite experimental design (*7*). This design allowed the testing of five catalysts at five levels of the operating variables. The response surface was modeled empirically and the resulting equation was used to suggest optimal operating conditions for catalyst evaluations. The model

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was also used to gain insight into the role of fluorination in altering the activity of the catalyst in this reaction.

EXPERIMENTAL METHODS

Catalyst Preparation

The materials used in this study were α-alumina monohydrate (Catapal SB, Conoco, Peterboro, NJ), ammonium fluoride (Aldrich Chem. Co.), and aluminum fluoride trihydrate (Aldrich Chem. Co.). The fluorinated alumina catalysts were prepared by impregnating the α-alumina support with an aqueous solution of NH_4F of the appropriate concentration at room temperature. Additional distilled water was added to obtain an alumina gel suitable for extrusion. The alumina and fluorinated alumina extrudates were dried in air at 378 K for 8 h and calcined in air at 723 K for 8 h. Following calcination, these extrudates were crushed and separated into appropriate fractions. A catalyst particle size 0.25–1 mm was used. The aluminum fluoride trihydrate was dried overnight at 383 K prior to use. Each catalyst was subsequently analyzed for fluoride content by selective ion electrode methods and by X-ray photoelectron spectroscopy (XPS). XPS observations were made using a Physical Electronics Model 548E X-ray photoelectron spectrometer with a dual Al/Mg anode X-ray gun operating at 300 W in the Mg$K\alpha$ mode (1253.6 eV). The samples were prepared by pressing the powdered catalysts into KBr type disks (14 × 2 mm) using an infrared die and hydraulic press. The surface areas of the catalysts were determined by N_2 adsorption (BET) on a Carlo Erba Sorptomatic Model 1800 instrument.

Catalyst Acidity

The total acidity (sum of Brønsted and Lewis sites) of the catalysts prepared above was determined by high-temperature adsorption of ammonia. The adsorption capacity of the catalysts for ammonia was measured using a pulse-chromatographic technique (*8*) at conditions similar to those in the reactor. The catalyst samples were dried in air at 383 K for 1 h. Subsequently, 40 mg of catalyst was loaded into a 4-mm-i.d. Pyrex tube and this was installed in a gas chromatograph oven (Varian Vista 6000). The column oven temperature was raised from 303 to 623 K at 10°/min and maintained at that temperature for 1 h prior to adsorption studies at 623 K. Moisture- and oxygen-free argon flowed through the sample throughout this period. The exit stream was continuously monitored by means of a thermal-conductivity detector. Pulses of anhydrous ammonia (normally 15 pulses of 10 μmol) were injected into the argon stream via a temperature-controlled, automatic gas-sampling valve. Automation of the chromatograph, injection of the sample, and integration of the signal were accomplished with a Varian Vista 402 data station. The adsorption capacity of the catalyst for ammonia, C_{NH_3}, was calculated as

$$C_{NH_3} = \left(\sum_{i=0}^{n} (C_{in} - C_{out})\right) \Big/ m \qquad (1)$$

where n = number of pulses,

C_{in} = ammonia injected in each pulse (mmol g^{-1}),

C_{out} = ammonia remaining in each pulse after adsorption (mmol g^{-1}),

m = mass of catalyst [g].

Catalyst Testing

The reactions were carried out at 101 kPa total pressure in a 55-ml quartz tubular-flow reactor. The reactor was heated with a three-zone electric furnace designed with resistance wire elements. Each of the furnace zones was controlled separately. Atomic absorption grade acetylene supplied by Canadian Liquid Air, 99.6% stated purity, was stripped of acetone by passing the gas through a cold trap kept at dry-ice temperature, a concentrated sulfuric acid bath (98%), and an activated charcoal trap.

TABLE 1

Design and Coding of Operating Variables

Run no.	x_1[a]	x_2	x_3	x_4	Conversion[b]
1	1	1	1	1	51.5, 57.8
2	1	1	−1	−1	41.0, 48.1
3	1	−1	1	−1	99.5, 99.3
4	1	−1	−1	1	98.9, 96.3
5	−1	1	1	−1	48.0
6	−1	1	−1	1	0
7	−1	−1	1	1	97.6, 99.3
8	−1	−1	−1	−1	59.0, 50.0
9	2	0	0	0	98.1
10	−2	0	0	0	28.8
11[c]	0	2	0	0	85.9
12	0	−2	0	0	99.3
13	0	0	2	0	87.2
14	0	0	−2	0	29.2
15	0	0	0	2	99.6
16	0	0	0	−2	90.3
17	0	0	0	0	71.9, 64.5

[a] x_1 = (temperature (K) − 623)/25, x_2 = catalyst type (refer to Table 2), x_3 = (weight-time (g · s · ml^{-1}) − 2)/0.5; x_4 = (acetylene conc% − 10)/2.5.

[b] $\left[\frac{\text{(moles of } C_2H_2 \text{ in feed} - \text{moles } C_2H_2 \text{ in product at 15 min time-on-stream)}}{\text{moles of } C_2H_2 \text{ in feed}}\right]$.

[c] Experiment subsequently deleted from analysis.

The purified acetylene and nitrogen gases were metered separately and were well mixed prior to admission to the reactor. The reactor bed consisted of a 20-ml preheat zone containing crushed quartz (0.25–1 mm), a catalyst zone containing 5 g (≃10 ml) of catalyst, and a postreactor zone containing 20 ml of crushed quartz was employed in all studies. Temperatures in the catalyst zone were monitored using thermocouples located at regular intervals inside a thermowell centered in the reactor. A maximum temperature variation of ±5 K was observed. Reaction products exited the reactor via heated lines and were sampled at regular intervals of time using a gas-sampling valve maintained at 625 K. The techniques used to analyze the reaction products included GC/MS, GC/FID, and GC/TCD and have been described elsewhere (*9*).

Design and Modeling

To study the effects of temperature, weight-time, initial concentration of acetylene, and catalyst type on the acetylene reaction a central composite design consisting of a 2^{4-1} fractional factorial design, star points, and replicates was used (*7*). Not all replicated experiments were carried out at the center point of the design. The weight-time is defined as the ratio of the weight of catalyst (g) and the total volumetric feed rate (ml/s) at reaction conditions. The experimental design and coding for these variables are given in Table 1. The operating region for this work is defined by the following limits: temperature (573–673 K), weight-time (1–3 g · s · ml^{-1}), and initial concentration of acetylene (5–15%). The order of execution of the experiments was randomized.

To interpret the experimental results, an empirical modeling procedure was employed (*7, 13*). The following second-degree polynomial was used to describe the conversion of acetylene:

$$\begin{aligned} E(C) = {} & l_0 + l_1x_1 + l_2x_2 + l_3x_3 + l_4x_4 \\ & + l_5(x_1x_2 + x_3x_4) + l_6(x_1x_3 + x_2x_4) \\ & + l_7(x_1x_4 + x_2x_3) + l_8x_1^2 + l_9x_2^2 \\ & + l_{10}x_3^2 + l_{11}x_4^2 \end{aligned} \tag{2}$$

$E(C)$ is the expected value of the acetylene conversion and x_1, x_2, x_3, and x_4 are the coded variables corresponding to temperature, type of catalyst, weight-time, and initial concentration of acetylene, respectively. The values of the parameters (l_i's in Eq. (2)) were estimated by least squares fitting of the model to the data using the statistical package SPSS (*10*). Since the central composite experimental design was based on a 2^{4-1} fractional factorial design some confounding of the interaction effects occurred. The defining relation for the design was $I = x_1x_2x_3x_4$ which led to the following aliases:

TABLE 2

Properties of Fluorinated Alumina Catalysts

Catalyst designation	Composition (wt% F)			Atomic ratio [F/Al]		Surface area[d] [m^2 g^{-1}]
	Nominal[a]	Bulk[b]	Surface[c]	Bulk	Surface	
[−2]	0	0	0	0	0	189
[−1]	1.8	1.45	3.6	0.04	0.10	222
[0]	3.6	2.57	3.24	0.07	0.09	199
[1]	6.9	4.35	8.28	0.13	0.24	156
[2]	67.9	17.98	68	1.3	3	—

[a] Fluoride content of catalyst based on preparation procedure.

[b] Analysis accuracy ±2% of quoted value.

[c] Analyses were performed at 10^{-9} Torr. The spectrometer's energy scale was calibrated using Au (Au $4f_{7/2}$ = 83.8 eV) and Cu^0 (Cu $2p_{3/2}$ = 933 eV). Photolines were referenced to the hydrocarbon (C 1*s*) line at 284.6 eV. A charge neutralizer system (electron flood gun) was used to control specimen charging. The elemental composition of each catalyst's surface was determined using XPS elemental sensitivity factors and the measured photoline intensity. These were calculated according to theoretical photoelectron cross sections, the kinetic energy dependence of the cylindrical minor analyzer (CMA), and an average value for the dependence of the electron escape depth on kinetic energy.

[d] Surface area quoted ±20 m^2 g^{-1}.

l_5 estimates the combined effects of the interactions x_1x_2 and x_3x_4,

l_6 estimates the combined effects of the interactions x_1x_3 and x_2x_4,

l_7 estimates the combined effects of the interactions x_1x_4 and x_2x_3.

Depending on the values of the estimates of l_1 through l_{11}, ambiguities in these effects can arise. Throughout the analysis the effects of the third- and higher-order interactions were assumed to be negligible.

RESULTS AND DISCUSSION

A summary of the properties of the five catalysts is given in Table 2. Generally, good agreement was found between the amount of fluoride in the catalyst calculated from the preparation procedure (nominal composition) and that found in the bulk, indicating that little fluoride was lost during calcination. A notable exception was the $AlF_3 \cdot 3H_2O$, for which the bulk fluoride content was considerably lower than expected. This was attributed to a nonlinearity in electrode calibration at high concentrations of fluoride. A comparison of the bulk F/Al atomic ratio and the XPS-determined surface atomic ratio showed some evidence of surface enrichment of fluoride as a result of the impregnation technique. Small changes in surface area were observed in catalysts containing between 0–5 wt% F. The surface area of the aluminum fluoride trihydrate was less than 20 m^2/g and could not be determined accurately with our apparatus.

The influence of fluoride on total acidity (Lewis and Brønsted) of the catalysts was determined by measuring their adsorption capacity for ammonia at conditions similar to those in the reactor. Ammonia may react with Brønsted and Lewis sites and therefore the acidity is the sum of both. Results for the chemisorption of ammonia at 623 K are given in Fig. 1. Pure and fluoride-promoted alumina show significant differences in adsorptive capacity for ammonia. The catalyst fluoride content has a complex influence on surface acidity. A maximum in ammonia chemisorption was observed be-

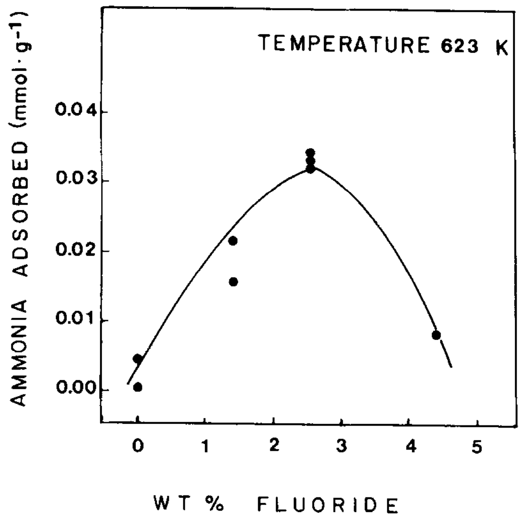

FIG. 1. Chemisorption of ammonia on fluorinated alumina as a function of fluoride content, adsorption temperature 623 K.

tween 1.5–3 wt% fluoride. This result is in good agreement with Gerberich *et al.* (*11*) who studied ammonia adsorption at 770 K and found a maximum between 1.2–2.7 wt% fluoride.

Preliminary experiments using a feed gas consisting of 10% acetylene and 90% nitrogen by volume showed that the thermal reaction of acetylene was negligible below 673 K. However, acetylene was highly reactive over fluorinated alumina catalysts at temperatures as low as 473 K. The reaction products consisted mainly of aromatic hydrocarbons although small amounts of hydrogen, methane, ethylene, and higher olefinic hydrocarbons were also produced. A typical product distribution at a time-on-stream of 15 min was 59% liquid, 3% gas, and 38% polymeric deposits. The nature of the reaction products changed with increasing time-on-stream (a more detailed study of the reaction products is described elsewhere (*12*)). For example, the generation of high boiling aromatics (b.p. > 475 K) increased considerably over the first hour of operation. Therefore, the experimental runs were limited to 1 h to avoid condensation of the reaction products in the heated lines and sampling valve. Appreciable deactivation was observed at certain operating conditions. For this reason the acetylene conversions refer to the earliest reliable samples taken at a time-on-stream of 15 min. The results of 24 runs are listed in Table 1.

Using the modeling techniques described earlier, a model was determined for the conversion of acetylene over these catalysts at a time-on-stream of 15 min. Examination of the residuals revealed that the activity of AlF_3 (experiment 11) was inconsistent with that found for the fluorinated aluminas. This may have been due partly to the incomplete dehydration of the catalyst in the drying process (10% of the H_2O remained). Consequently, this experiment was deleted from the analysis. The estimates for the parameters in Eq. (2) which had a significant effect on the predictive ability of the model together with their marginal 95% confidence intervals are listed in Table 3. The model is summarized as

$$E(C) = 60.63 + 13.82x_1 - 26.26x_2 + 13.36x_3 - 4.97x_2^2 + 7.83x_4^2 - 9.81x_2x_4 \tag{3}$$

The significance of the global regression (Eq. (3)) is expressed by the ratio of the mean regression sum of squares to the mean residual sum of squares and, in this case, was calculated to have the value 70. When this value is compared with the ap-

TABLE 3

Parameter estimates for Eq. (2)

Parameter	Parameter estimates
l_0	60.63 ± 5.58[a]
l_1	13.82 ± 3.24
l_2	−26.26 ± 4.16
l_3	13.36 ± 3.17
l_6	−9.81 ± 4.05
l_9	−4.97 ± 4.18
l_{11}	7.83 ± 2.95

[a] 95% Confidence interval.

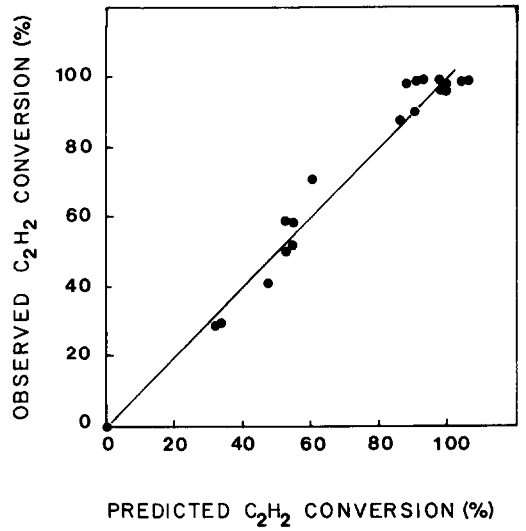

FIG. 2. Observed acetylene conversion (%) versus the predicted acetylene conversion (%).

propriate value of the F-distribution, $F(6, 14, 0.05) = 2.85$, the conclusion is that the model is a useful predictive tool (*13*).

The experimental and predicted conversions for all reaction conditions are compared in Fig. 2. An excellent fit is indicated, with a correlation coefficient, $R^2 = 0.96$. Neither lack of fit test ratios (*13*) nor analysis of residual plots revealed any significant lack of fit of the model. Since the model has been shown to fit all the data on the conversion of acetylene, it can now be used to describe and predict the effects of the operating variables and the role of the fluoride on the catalyst activity throughout the operating region.

Based on the fitted model the three operating variables and the catalyst type were all found to have a significant effect on the conversion of acetylene either singly or jointly. However, as a result of the confounding discussed earlier and the large values of l_1, l_2, l_3, l_6, l_9 and l_{11}, some ambiguity in the interpretation of the results arises. As stated previously, l_6 estimates the combined effects of the interactions x_1x_3 and x_2x_4. This implies that either the temperature and weight-time interaction or the catalyst and acetylene concentration interaction or both are significant. An interaction between the reaction temperature and the weight-time means that the effect of temperature on conversion depends upon the value of the weight-time and vice versa. If the entire effect is attributed to the interaction x_1x_3, then the fitted model predicts a maximum conversion at 658 K, and a weight-time of 2.7 g · s · ml^{-1}, both of which are less than their maximal operating values. This situation is highly unlikely. On the other hand, if the l_6-effect is attributed to the interaction x_2x_4, the model predicts a maximum conversion of acetylene at a boundary of the operating region corresponding to maximal levels of both temperature and weight-time. This is a more probable situation and is the interpretation taken here.

The effects of the reaction temperature and the weight-time on the conversion of acetylene are shown in Figs. 3 and 4. The solid lines represent the predicted response for 1.5, 2.6, and 4.3 wt% F on alumina catalysts. It can be seen in Figs. 3 and 4 that the conversion of acetylene increases with tem-

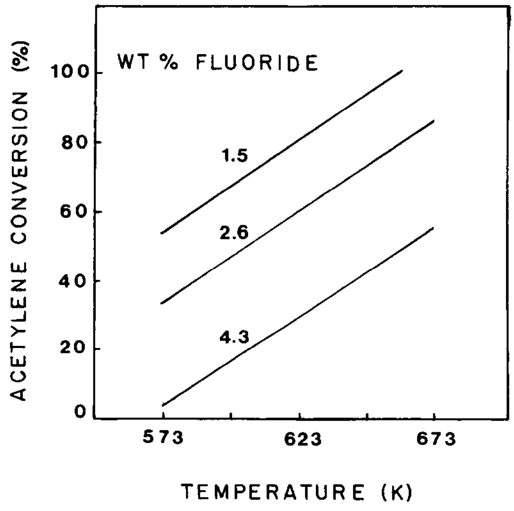

FIG. 3. The effect of temperature on acetylene conversion over fluorinated alumina for various fluoride loadings, weight-time = 2 g · s · ml^{-1}, C_2H_2 concentration = 10 vol%.

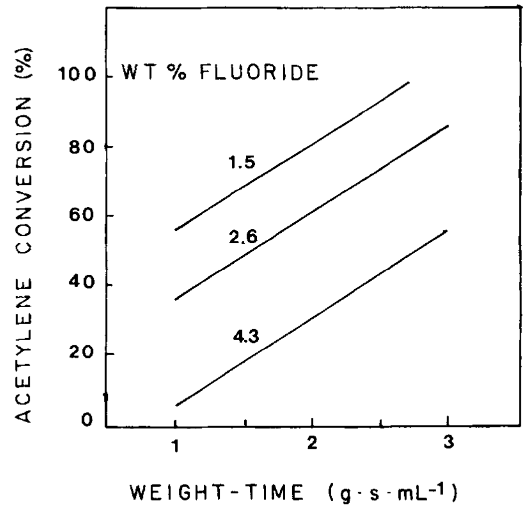

FIG. 4. The effect of weight-time on acetylene conversion over fluorinated alumina for various fluoride loadings, temperature 523 K, C_2H_2 concentration = 10 vol%.

perature and weight-time for any type of catalyst. This implies that the maximum conversion for any catalyst is obtained at an operating boundary defined by a temperature of 673 K and a weight-time of 3 g · s · ml^{-1}. Therefore, these would be appropriate conditions for comparing other catalysts.

Because of the significant interaction, x_2x_4, the effects of catalyst type, x_2, and initial concentration of acetylene, x_4, must be considered jointly. To do this contours of acetylene conversion were plotted in the x_2x_4 plane for the mean values of x_1 and x_3 (temperature 623 K, weight-time 2 g · s · ml^{-1}) and are given in Fig. 5a. The operating region used in this study (the region where the experiments were performed and where the model is valid) is contained within the dashed lines shown in Fig. 5a. The contour surface shown in Fig. 5a has a saddlepoint, indicated by a plus sign, at a 0.5 wt% fluoride content ($x_2 = -1.632$) and a 7.5 vol% initial concentration of acetylene ($x_4 = -1.023$). This point represents a minimum in the conversion as the acetylene concentration is varied from 5 to 15% (at 0.5% F) and a maximum in the conversion as the fluoride content of the catalyst is varied from 0 to 5% (at 7.5 vol% acetylene). For any given type of catalyst (vertical line in Fig. 5a), the conversion of acetylene passes through a minimum with respect to the initial concentration of acetylene. This minimum is clearly evident in the family of curves shown in Fig. 5b. At any level of initial concentration (horizontal line in Fig. 5a), the conversion passes through an optimum with respect to the type of catalyst. At low initial concentrations of acetylene, this optimum lies within the operating region and is fairly broad, as depicted in Fig. 5c. As the initial concentration of acetylene is increased, however, this optimum shifts to lower fluoride contents, moves rapidly out of the experimental region, and narrows considerably. Only the declining portion of the curve can be represented within the operating region and need be discussed further. For example, at an initial concentration of 12.5 acetylene any degree of fluorination results in a loss of activity for polymerization of acetylene. The outer dashed lines in Fig. 5c define the upper and lower limits of the 95% confidence interval calculated for the expected value of conversion at an initial concentration of 7.5% acetylene. For this model it can be seen that the variance of the predicted conversion increases as the operating conditions at which the prediction is made move away from the centre of the design. Although the existence of a family of maxima is indicated, some caution must be exercised when interpreting this because of the large variances.

The minimum in the conversion of acetylene with respect to the initial concentration can be explained, at least qualitatively, as the result of two competing effects. First the initial rate of the reaction of acetylene will increase with increasing initial concentrations of acetylene. Second, the rate of deactivation of these catalysts was observed to be a function of the initial concentration of acetylene (therefore a function of

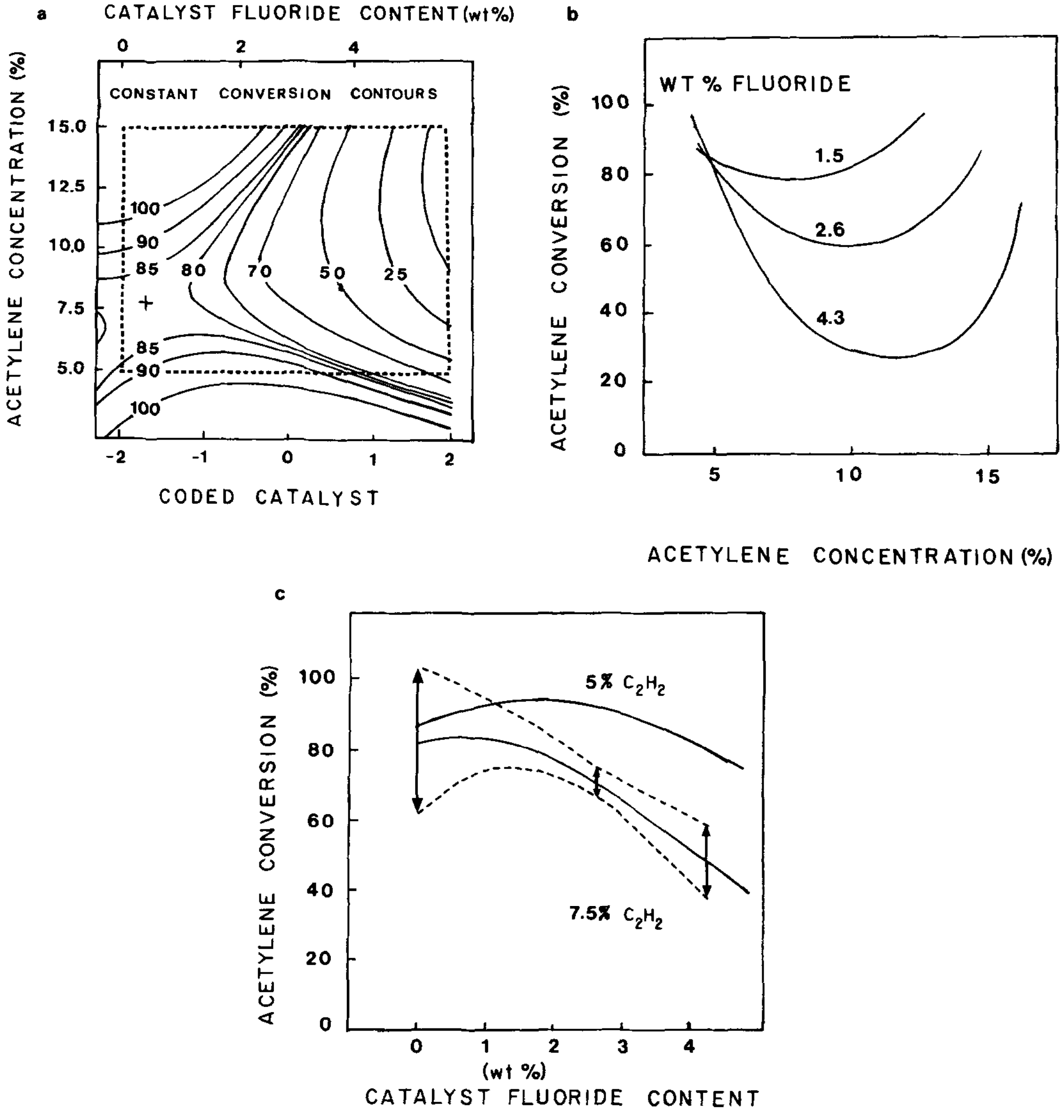

FIG. 5. (a) A contour plot of the concentration of acetylene and the catalyst fluoride content. (b) The effect of acetylene concentration on acetylene conversion over fluorinated alumina at various fluoride loadings, temperature 623 K, and weight-time 2 g · s · ml^{-1}. (c) The effect of fluorination on acetylene conversion at various concentrations of acetylene, temperature 623 K, and weight-time 2 g · s · ml^{-1}.

catalyst activity). For example, the activity of a 2.6 wt% F on alumina catalyst, as a function of the time-on-stream is shown in Fig. 6 at three levels of initial concentrations. At small times-on-stream, the conversion of acetylene is the greatest when the initial concentration of acetylene is the highest, but, at large times-on-stream, the conversion is the least at the highest initial concentration of acetylene. A larger decrease in activity is evident at the highest initial concentration of acetylene in the feed. The results at a time-on-stream of 15 min clearly show the existence of a minimum at an intermediate initial concentration of acetylene. It should be noted that the initial activity of the catalyst is very large in all cases and would not have given

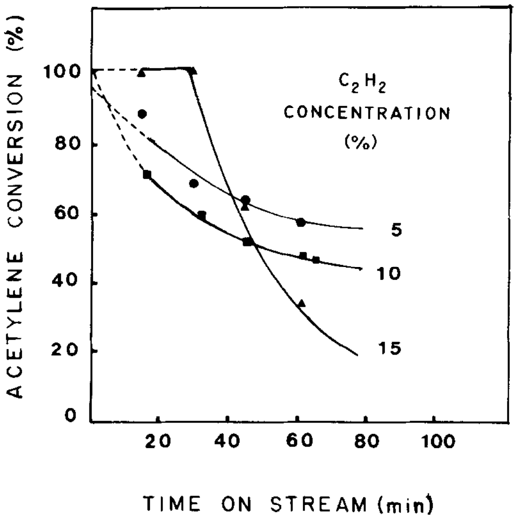

FIG. 6. Decrease in catalyst activity with time-on-stream for 2.6 wt% F on alumina catalyst at various initial concentrations of acetylene.

any information on the effect of initial concentration of the reactant.

The effect of the fluoride content of the catalyst on the conversion of acetylene, observed in Fig. 5c, can be understood in terms of the chemical interactions of fluoride with alumina. The modifications of the catalyst surface induced by the addition of fluoride include changes in the surface acidity (*5*) and in the number of sites available for adsorption of acetylene (*14*). Infrared and Raman studies of the adsorption of acetylene on alumina (*14–17*) have demonstrated that variations in the number of exposed Al ions and OH groups on the catalyst surface strongly influence the mode of adsorption of acetylene at room temperature. As a result, Bhasin *et al.* (*14*) have postulated that the chemisorption of acetylene on alumina occurs at ion-pair sites consisting of exposed aluminum ions (Lewis acid sites) and neighbouring oxide ions or OH groups (Brønsted sites). Other studies (*15, 19*) have shown that replacement of surface hydroxyl and oxide ions with fluoride serves to decrease the number of such ion pairs. The decrease in the catalyst activity with increased fluoride loadings is consistent with these findings.

It is generally accepted that polymerization reactions are acid catalyzed. More specifically, Tsai and Anderson (*2*) proposed that acetylene polymerized to form aromatic products via a vinyl cation intermediate when a ZSM-5 zeolite catalyst was used. The concept of the vinyl cation is consistent with the carbonium ion theory of acid-catalyzed reactions. It was shown in Fig. 1 that fluorination altered the acidity of alumina. In addition, Paukshtis *et al.* (*15*) have shown that the introduction of fluoride generates a different distribution of acid sites on the alumina surface. Fluoride-modified alumina possessed a greater portion of medium and strong acidic centers. It would appear, therefore, that the reaction may have been influenced by the acid-site distribution at low gas phase concentrations of acetylene. This would be consistent with the correspondence between the maximum in the acidity (Fig. 1) and the maximum in conversion (Fig. 5c). In contrast, the reaction may have been influenced by the number of reaction sites at large gas phase concentrations of acetylene. This would be consistent with the continuous decrease in conversion as the catalyst fluoride concentration increased. The influence of fluoride on conversion could be a result of a combination of these two factors, the strong acid sites which are generated and the adsorption sites which are lost in the fluorination process.

On the basis of the above discussion, the high reactivity of alumina and fluoride-modified alumina could result from the presence of a significant number of ion-pair sites available for adsorption and from the particular acid strength distribution of these sites. At comparable operating conditions, the fluorinated alumina catalysts used in this study were more active than the ZSM-5 zeolite used by Tsai and Anderson (*2*). The use of fluorinated alumina catalysts could be a distinct improvement over ZSM-5 catalysts. For the same conversion, fluorinated alumina catalysts could be used at less severe processing conditions, e.g., lower temperature. Lower operating temperatures were shown to give a more desirable product distribution (*2*).

CONCLUSION

The conversion of acetylene to aromatic products has been shown to proceed relatively easily over fluorinated alumina catalysts. This reactivity is believed to be the result of acid–base properties of the fluoride-modified alumina. The following empirical model has been obtained to describe the conversion (C) of acetylene over fluorinated alumina:

$$C[\%] = 60.63 + 13.82x_1 - 26.26x_2 + 13.36x_3 - 4.97x_2^2 + 7.83x_4^2 - 9.81x_2x_4 \quad (3)$$

where x_1 is the reaction temperature [573–673 K], x_2 is the catalyst [refer to Table 2], x_3 is the weight-time [1–3 g · s · ml^{-1}], and x_4 is the initial concentration of acetylene [5–15%]. Examination of the model revealed a stationary point at (2, −1.63, 2, −1.0) corresponding to the highest levels of temperature [673 K] and weight-time [3 g · s · ml^{-1}], an initial concentration of 7.5% and a catalyst with approximately 1 wt% F. Results indicate that the optimal location for catalyst testing is at the boundary of the operating region in both temperature and weight-time, increased conversion being favored by higher temperatures and weight-times. The complex interaction between the initial concentration of acetylene and the type of catalyst suggests that in testing other catalysts at least 3 levels of initial concentration may be warranted.

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REFERENCES

1. Seddon, D., *BHP Tech. Bull.* **27,** 1 (1983).
2. Tsai, P., and Anderson, J. R., *J. Catal.* **80,** 207 (1983).
3. Cooke, N., *et al.*, *in* "Proceedings, 34th Canadian Chemical Engineering Conference, Québec," Sept. 30–Oct. 3 (1984).
4. Satterfield, C. N., "Heterogeneous Catalysis in Practice." McGraw–Hill, New York, 1980.
5. Ghosh, A. K., and Kydd, R. A., *Catal. Rev.-Sci. Eng.* **27**(4), 539 (1985).
6. Choudhary, V. R., *Ind. Eng. Chem. Process Res. Dev.* **16**(1), 12 (1977).
7. Himmelblau, D. M., "Process Analysis by Statistical Methods." Wiley, New York, 1970.
8. Ghosh, A. K., and Curthoys, G., *J. Chem. Soc., Faraday Trans. 1* **79,** 2569 (1983).
9. Allenger, V. M., McLean, D. D., and Ternan, M., *J. Chromatogr. Sci.* **24**(3), 95 (1986).
10. Nie, N. H., Hull, C. H., Jenkins, J. G., Steinbrenner, K., and Brent, D. H., "SPSS, Statistical Package for the Social Sciences," 2nd ed. McGraw–Hill, New York, 1975.
11. Gerberich, H. R., Lutinski, F. E., and Hall, W. K., *J. Catal.* **6,** 209 (1966).
12. Allenger, V. N., McLean, D. D., and Ternan, M., in preparation.
13. Draper, N. R., and Smith, H., "Applied Regression Analysis," 2nd ed. Wiley, New York, 1981.
14. Bhasin, M. M., Curran, C., and John, G. S., *J. Phys. Chem.* **74,** 3973 (1970).
15. Paukshtis, E. A., Soltanov, P. I., Yurchenko, E. N., and Jiratova, K., *Collect. Czech. Chem. Commun.* **47,** 2044 (1982).
16. Sheppard, N., and Yates, D. J. C., *Proc. Roy. Soc. A* **238,** 69 (1956).
17. Yates, D. J. C., and Lucchesi, P. J., *J. Chem. Phys.* **35**(1), 243 (1961).
18. Heaviside, J., Hendra, J., Tsai, P., and Cooney, R. P., *J. Chem. Soc. Faraday Trans. I* **74,** 2542 (1978).
19. Peri, J. B., *J. Phys. Chem.* **69,** 211 (1965).