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IN ACETYLENE POLYMERIZATION

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DEACTIVATION OF FLUORINATED ALUMINA CATALYSTS IN ACETYLENE POLYMERIZATION

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ABSTRACT

There has been a significant amount of interest recently in the production of aromatics for use as fuels by polymerization of acetylene. However, this route generally suffers from severe catalyst deactivation. In this study a series of fluorinated alumina catalysts containing between 0-4.4 wt % F was tested in a tubular flow reactor at 101 kPa. The deactivation of these catalysts was examined as a function of both catalyst properties and processing conditions. The deactivation data were described adequately by an exponential-decay relationship with two parameters, initial activity, X_0 , and decay velocity, k_d . An empirical model was developed which describes the effects of the processing conditions on catalyst activity.

No differences were observed in the pore structure or in the fluoride contents of the fresh and used catalysts. Measurements of the catalyst coke content after 1 h and in some cases 4 h on stream revealed between 1 and 8 wt % carbon. Catalyst deactivation was attributed to coke formation. Coke deposition was shown to decrease with increasing fluoride content of the catalysts. Surface analysis by X-ray photoelectron spectroscopy revealed preferential siting of carbon at the exterior of the catalyst particle. The carbon profile in the reactor bed was indicative of a parallel deactivation mechanism.

INTRODUCTION

Transportation fuels are at present almost exclusively manufactured from petroleum crude oil. Natural gas might be an alternative feedstock in those geographical locations having abundant natural gas reserves. Two commercial-scale technologies exist, Fischer-Tropsch and Mobil MTG, but so does the potential for more efficient routes. Since acetylene is the primary product from the thermal pyrolysis of natural gas, alternatives involving acetylene are being pursued by several groups (1-3). Acetylene has been used as a major building block in the chemical industry, however, severe catalyst deactivation has prevented commercial transformation of acetylene to useful fuel-range products (3-5). In this article the deactivation of a series of fluorinated alumina catalysts was examined in the polymerization of acetylene.

The catalytic reaction of acetylene over fluorinated alumina was investigated and has been reported earlier (6). The deactivation over these catalysts was severe. The objectives of this work were to investigate the effect of acidity on the deactivation by comparing the performance of a series of amorphous fluorinated alumina catalysts containing 0 to 4.4 wt % F and to determine the operating conditions where the deactivation could be minimized for such a process.

To achieve efficiency of experimentation a central composite experimental design was used (7). This allowed both of our objectives to be met simultaneously. Five catalysts were examined at five levels of the operating variables (temperature, weight-time defined as the ratio of the catalyst weight

and the total gas flowrate at reaction conditions and initial concentration of acetylene). A two-parameter exponential model was developed to describe the deactivation curves. Models were then developed to describe the influence of temperature, weight-time, initial concentration of acetylene and degree of fluorination on the two parameters in the deactivation model. A model was also derived to describe the coke deposition within the operating region. These models suggested optimal operating conditions for this process and provided valuable insight into the roles of coke deposition and acidity in altering the activity of the alumina catalyst.

EXPERIMENTAL

A series of fluorinated alumina catalysts containing from 0 to 4.4 wt % F was used. The catalysts were prepared by impregnating α -alumina monohydrate (Catapal SB, Conoco, New Jersey) with an aqueous solution of NH_4F (Aldrich Chem. Co.) of the appropriate concentration at room temperature. Extruded alumina and fluorinated alumina pellets were dried (110°C , 8 h) and calcined (450°C , 8 h) in air. These pellets were subsequently ground and sieved to 0.25-1 mm.

X-ray photoelectron spectroscopic observations were made of both fresh and spent catalysts using a Physical Electronics Model 548 electron spectrometer with a dual Al/Mg anode equipped X-ray gun operating at 300 W in the $\text{MgK}\alpha$ mode. The bulk carbon content of the spent catalysts was determined by elemental analysis on a LECO CHN 600 elemental analyzer. The nature of the carbonaceous deposit was determined by cross polarization magic angle spinning ^{13}C NMR spectroscopy. The spectra were obtained with a Varian XL-300 spectrometer and recorded using a 10 MHz sweep width, and acquisition time of 0.128 s, a pulse width of 8 s and a contact time of 1 ms.

The experiments were carried out in a quartz, continuous-flow, tubular reactor (10 mm ID) at 101 kPa. The reactor was mounted in a tube furnace having three electrical heating zones. Prior to the reaction 5 g of catalyst was loaded into the centre of the reactor and a stream of dry nitrogen was passed through the bed until the desired temperature was achieved. The feed gas mixture was then introduced at the predetermined space velocity and composition. After 1 h (longer for some experiments) the reactor was purged with N_2 , cooled to room temperature and the catalyst removed for analysis.

RESULTS AND DISCUSSION

A summary of the physical properties of the catalysts and their relative total acidity as measured by adsorption of ammonia is given in Table 1. The activity of these fluorinated alumina catalysts at 15 min on stream for the polymerization of acetylene was reported earlier (6). In all the experiments, the catalyst activity decreased with time-on-stream. The deactivation is always accompanied by the accumulation of carbonaceous compounds on the catalyst surface. Since coke is one of the products formed during acetylene polymerization knowledge of the carbon content of the catalyst is essential. For this reason, separate experiments from 1 to 4 h were carried out in the tubular reactor and the carbon content of the catalysts determined. Two examples of the simultaneous decrease in conversion with the increase in carbon content of the catalyst are shown in Fig. 1. The open symbols represent the experimental activity data whereas the solid symbols represent the catalyst carbon content

data. The deactivation can be attributed at least partly to this coke buildup on the catalyst surface.

Having established qualitatively that the catalyst deactivation and the coke deposition are correlated for this reaction, it is of interest for any practical application of such a process to determine the operating region in which the coke deposition and thus deactivation could be minimized. For this reason, the response surfaces for the two parameters of a simple time-on-stream model used to describe all the conversion-time data [$X = X_0 \exp(-k_d t)$] were modelled empirically. Similarly the response surface for the catalyst carbon content at a fixed time-on-stream of 1 h was modelled. The resulting models showed that both the deactivation and the coke content at 1 h on stream could be minimized by using the following processing conditions: temperature 400°C, weight-time 3 g·s·ml⁻¹ and 5 vol % C₂H₂ in the feed.

Influence of Fluorination

The catalyst carbon content at the end of 1 h on stream was found to decrease linearly with the degree of fluorination. This decrease appears to parallel the decrease in initial activity of the catalyst. This would imply that fluorination succeeded in diminishing the total quantity of coke formed. The decrease in the catalyst carbon content with increased fluoride loadings would indicate that the degradation reaction leading to coke is catalyzed by the same ion-pair sites needed for acetylene adsorption (6).

Fluorination also altered the acidity of alumina catalysts used in this study as demonstrated in Table 1. Although the total amount of coke deposited appears to be correlated with the number of active sites, a parabolic relationship predicted by the model between the deactivation parameter k_d and the fluoride content suggests that not all of the coke constituents deactivate the catalyst. The relationship between k_d and the catalyst fluoride content would imply that the nature and distribution of the coke may have varied with the catalyst acidity. A maximum in the total acidity of the catalysts was obtained between 1.5 and 3 wt % F (Table 1). The minimum in the k_d curve is observed at a fluoride content of 2 wt %. The fact that this value is within the high acidity region would indicate that perhaps the deactivation decreased as the total surface acidity increased. One possible explanation for this is that the coke builds up on the strong acid sites generated in the fluorination process before distributing itself throughout the bulk. This would explain why the deactivation is a function of the catalyst acidity whereas the total catalyst carbon content is not.

Catalyst Physical Properties

Coke has sometimes been found to act by blocking the catalyst pores in addition to covering the active sites. A number of workers have shown that coking is accompanied by a significant decrease in catalyst surface area and pore volume. However, the loss in surface area as observed in this study is negligible for coke in the 0-10 wt % range. No measureable change in the pore distribution of three spent catalyst samples removed from various positions in the tubular reactor and of the fresh catalyst was detected. The corresponding surface areas of the used catalyst samples from the different bed layers were also similar (within the instrument error). Furthermore, the surface fluoride contents of the fresh and spent catalysts determined by X-ray photo-

electron spectroscopy showed no loss of fluoride. Therefore, the deactivation of these catalysts in the polymerization reaction cannot be attributed to blocking of the catalyst pores, changing of the catalyst surface area or loss of fluoride from the catalyst.

Nature of the Coke Deposit

The nature of the coke deposits was determined by CP MAS ^{13}C NMR spectrometry. These spectra revealed the presence of both aliphatic and aromatic structures in the coke. A summary of the total NMR signal, the ratio of aliphatic/aromatic carbon and the bulk carbon content is given in Table 2. There is excellent agreement between the bulk carbon measured via elemental analysis and the total carbon signal obtained with NMR.

A relationship between the deactivation parameter, k_d , and the ratio of the aliphatic/aromatic ^{13}C NMR signal is clearly visible in Fig. 2. This correlation implies that as the proportion of the aliphatic components of the coke increases, the deactivation becomes more severe ($k_d > 10^{-3} \text{ min}^{-1}$). Aliphatic molecules with $\text{H/C} > 1$ are probably formed by abstraction of hydrogen from highly condensed aromatic structures ($\text{H/C} < 1$) which are believed to be coke precursors.

CONCLUSIONS

Catalyst deactivation in acetylene polymerization over fluorinated alumina has been shown to be primarily due to coking. Empirical models, developed to describe the influence of the reaction temperature, the feed gas concentration and the weight-time on the initial activity parameter X_0 , the deactivation parameter k_d and the catalyst carbon content at 1 h on stream showed that both the deactivation and the coke content could be minimized by using the following processing conditions: temperature 400°C , weight-time $3 \text{ g}\cdot\text{s}\cdot\text{m}^{-1}$ and 5 vol % C_2H_2 in feed.

The degradation reactions leading to coke have been associated with ion-pair sites which are responsible for acetylene adsorption. A decrease in these sites by fluorination brings about a simultaneous decrease in the coke produced. The coking process appears to be complex. Small amounts of coke dispersed throughout the catalyst bulk deactivate the catalyst more readily than coke buildup on the external surface. Coking on the external surface appears to increase with increased catalyst acidity.

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Table 1 - Catalyst Properties

Catalyst designation	Fluoride content [wt %]	Surface area ^a [m ² ·g ⁻¹]	Pore volume ^b [cm ³ ·g ⁻¹]	Acidity [mmolNH ₃ ·g ⁻¹]
MB550	0	190	0.63	0.003
MB607	1.46	222	0.44	0.018
MB548	2.5	199	0.48	0.034
MB608	4.3	156	0.51	0.007
MB615	68	<20	-c	-c

a ± 20 m²·g⁻¹

b ± 2% of quoted value

c not determined

Table 2 - Characterization of some used catalysts

Experiment	Carbon content		¹³ C NMR		k _d [10 ³ min ⁻¹]
	[wt %]	[mg]	Total signal	Ratio ^a	
4b	7.8	12.9	0.5147	0.587	0.3 0.6 ^g
2c	2.5	4.3	0.2290	0.370	0.44 0.17
17d	3.1	5.5	0.2286	0.818	0.8 1.3
11e	5.2	8.4	0.4280	0.695	1.0
13f	2.7	4.6	0.2120	0.724	0.9

a ¹³C NMR ratio of signal corresponding to aliphatic and aromatic carbon.

b MB 607, 375°C, 1.5 g·s·ml⁻¹, 12.5 vol % C₂H₂.

c MB 608, 375°C, 1.5 g·s·ml⁻¹, 7.5 vol % C₂H₂.

d MB 548, 350°C, 2.0 g·s·ml⁻¹, 10 vol % C₂H₂.

e MB 550, 350°C, 2.0 g·s·ml⁻¹, 10 vol % C₂H₂.

f MB 548, 350°C, 3.0 g·s·ml⁻¹, 10 vol % C₂H₂.

g repeated experiment.

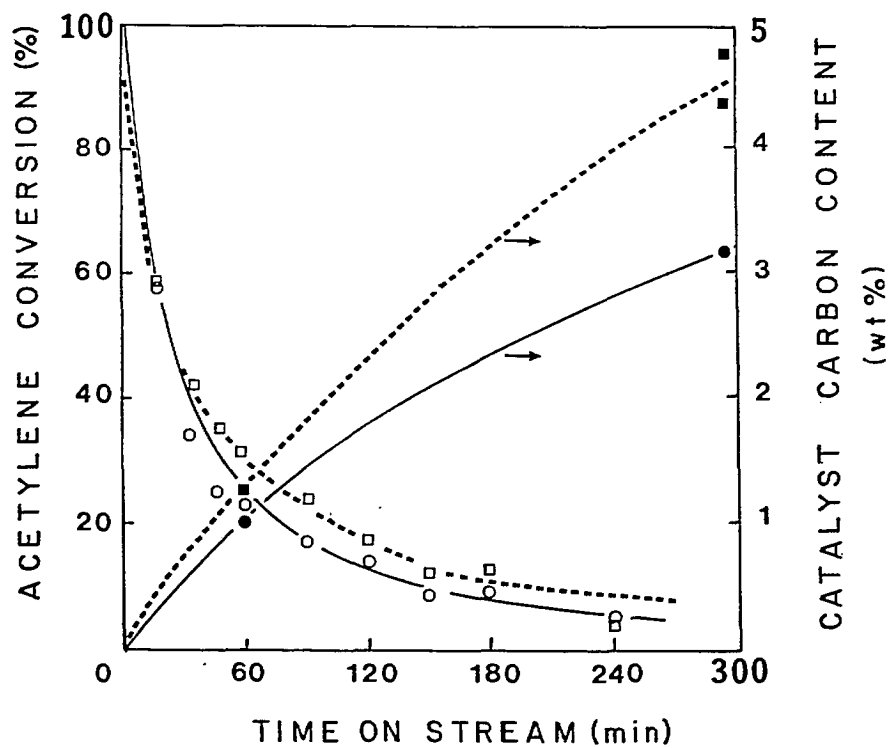


Fig. 1 - Acetylene conversion (open symbols) and catalyst carbon content (solid symbols) as a function of time-on-stream.

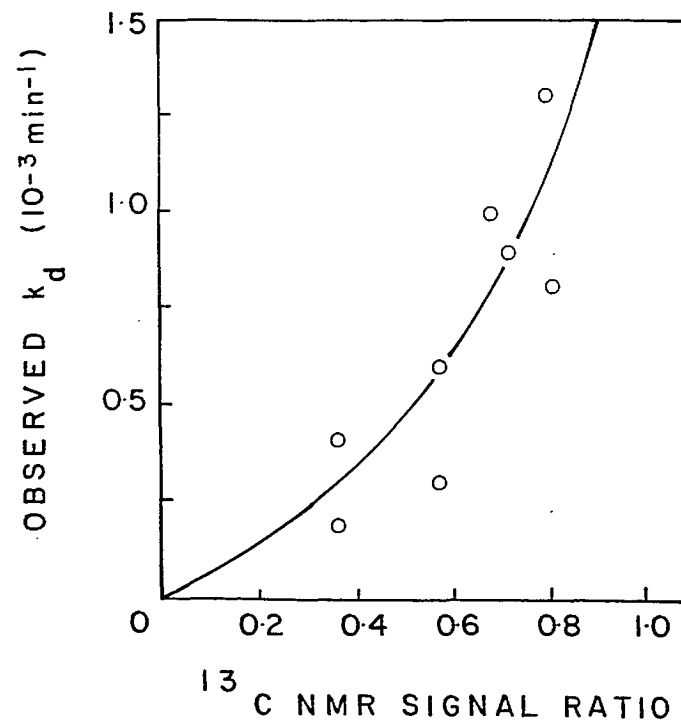


Fig. 2 - Relationship between the observed deactivation parameter (k_d) and the ratio of the ^{13}C NMR signal associated with aliphatics and aromatics in the coke on the used catalysts.