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catalytic combustion of hydrocarbons

IV. EFFECT OF PREPARATION METHOD
ON CATALYTIC ACTIVITY

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CATALYTIC COMBUSTION OF HYDROCARBONS

IV. Effect of Preparation Method on Catalytic Activity

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FOREWORD

The research described in this report, *Catalytic Combustion of Hydrocarbons. IV. Effect of Preparation Method on Catalytic Activity*, by E. P. Koutsoukos and Ken Nobe, was carried out under the technical direction of Ken Nobe and is part of the continuing program in Air Pollution Research in the Department of Engineering.

ABSTRACT

Five types of CuO catalysts were prepared in this study by varying the amount of KOH used in the precipitation of $\text{Cu}(\text{OH})_2$ from aqueous $\text{Cu}(\text{NO}_3)_2$ solutions. The rate of the catalytic combustion of ethylene was used as a measure of the activity of these catalysts. Overall rate expressions of the form $r = k p_E^n$ were used to correlate the experimental data. An average reaction order of 0.60 provided the best correlation of all the kinetic data.

The experimental data indicated that the temperature required for a given conversion decreased with increasing amounts of KOH used in the preparation of the catalyst (up to 25 per cent greater than stoichiometric). The BET surface area and mechanical strength of the catalyst increased with increasing KOH used. Using the specific rate constant per unit surface area as a measure of activity it was found that the catalytic activity of CuO decreased with increasing pH (or amount of KOH used).

Comparison of the activity of the stoichiometric catalyst prepared in this investigation with the activity of cupric oxide-alumina (1:1) catalyst studied by Accomazzo for the same reaction proved greatly in favor of pure CuO.

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LIST OF SYMBOLS

A	Arrhenius equation frequency factor
cc	cubic centimeters
$^{\circ}\text{C}$	degrees centigrade
d_p	reduced pellet diameter
E	activation energy (cal. /gr. mole)
F	total molal flow rate of gas stream at any point in the reactor (moles/hour)
G	total superficial mass flow rate (gr. moles/hr. , cm^2)
k_p	reaction rate constant (gr. moles/hr. , gr. catalyst, atm. ^(n+m))
k	$k_p x_{\text{O}_2}^m$ (gr. moles/hr. , gr. catalyst, atm. ⁿ)
$^{\circ}\text{K}$	degrees Kelvin
m, n	reaction orders
P_t	total pressure (atm.)
P_E	partial pressure of Ethylene at any point in the reactor (atm.)
P_{O_2}	partial pressure of oxygen at any point in the reactor (atm.)
$p_{\text{O}}, p_E^{\circ}$	initial partial pressure of Ethylene
ppm	parts per million by volume
m	meters
Q	volume flow rate at 25°C , 1 atm. (liters/hour)
q	Ethylene flow rate (liters/hour)
R	Universal gas constant (calories/gr. mole, $^{\circ}\text{K}$)
R_{IN}	hydrocarbon analyzer reading at reactor inlet

R_{OUT}	hydrocarbon analyzer reading at reactor outlet
R_e	modified Reynold's number ($Gd_p / \mu (1 - \delta)$)
r	reaction rate (gr. moles Ethylene converted/hr. , gr. catalyst)
S_g	BET surface area of catalyst ($m^2/gr.$)
SV	space velocity (volume flow rate at 25°C, 1 atm. per reactor volume), $hr.^{-1}$
T	absolute temperature ($^{\circ}K$)
t	time (hours)
w	weight of catalyst (grams)
X	conversion of Ethylene
X_o	initial Ethylene concentration (ppm)
Δ	change in, uncertainty in
δ	bed void fraction
μ	viscosity (poise)
ρ	molal density at 25°C, 1 atm. (gr. moles/liter)

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INTRODUCTION

The activity of Catalysts depends on their chemical and physical surface properties. Properties such as surface area, pore size and pore distribution, crystal structure, grain size, pH, depend to a large extent upon the method of preparation of the catalyst. A survey of the literature indicates that there is a dearth of available data on the effect of preparation of the catalyst on its activity. There have been only a limited number of investigations on the factors that influence the surface area of a given catalyst and even fewer studies on the effect of the acidity or alkalinity of a given catalyst on its activity. This effect, in the case of acid catalysts such as silica-alumina, is considerable and studies made on this rather narrow group of catalysts have been extensive and quantitative.¹⁻⁵ Methods for determining quantitatively both Lewis acidity and protonic acidity have been developed.^{6, 7} In general, the catalytic activity increased with increasing acidity. Unfortunately, in most cases, either the specific rate constant or the temperature of a specific conversion was used as a measure of activity. Thus, it was not clear whether the surface area of the catalyst increased or the activation energy decreased or both.

Recently, studies of other types of acid or base catalysts have been reported.^{8, 9, 10} The main problem seems to be the lack of a method for quantitative measurement of the pH of a catalyst which is not strongly acidic, and the few investigations reported were either qualitative or semiquantitative. Usually, the activity was related to the amount of base or acid used in the preparation of the catalyst.^{8, 10}

The investigation reported here is a study of the activity of CuO in the catalytic combustion of ethylene — specifically the effect of the amount of KOH used in the precipitation of $\text{Cu}(\text{OH})_2$ from $\text{Cu}(\text{NO}_3)_2$ on the overall kinetics of the reaction, the activation energy of the reaction, the surface area of the catalyst.

Five different CuO catalysts were prepared by varying the amount of KOH added to the copper nitrate solution from 50 per cent less to 50 per cent greater than the stoichiometric quantity. Care was taken to eliminate or minimize other variables in the process of preparation. The surface area of each catalyst was measured by the BET method. A rate equation of the form $r = kp^n$ was used to correlate all the oxidation data. Individual reaction orders were determined and an overall average value was used in the rate expression. Finally the reproducibility of the catalysts was investigated (surface area, density, activity).

EXPERIMENTAL

Five groups of CuO catalysts were prepared distinguishable only in the amount of KOH used in the precipitation of $\text{Cu}(\text{OH})_2$ from $\text{Cu}(\text{NO}_3)_2$ solution. The catalysts prepared were:

A. Sample #1 (50% less than stoichiometric).

Four hundred and eighty four grams of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9% "Analytical Reagent") were dissolved in 2 liters of distilled water resulting in an approximately 0.5 M solution. The exact molality of the solution was determined gravimetrically by electroplating the copper from a known volume of solution on a platinum electrode. One hundred and thirty grams of 85 per cent KOH pellets were dissolved in 1 liter distilled water giving a 2M solution (the exact molality was determined by titration with 1 N HCl). The two solutions were separately heated to 80°C ; the KOH solution was then added, at the rate of 3 liters per hour, to the salt solution under constant agitation and constant temperature of 80°C .

The cupric nitrate solution changed to a light green suspension, cupric hydroxide, when the first few cubic centimeters of KOH solution were added, changing to green heavy precipitate with further addition of base. Subsequent to the addition of all the KOH, the mixture was kept at 80°C , under constant agitation, for 2 hours. At the end of this period the mixture changed from green to light brown. It was then suction filtered. The mixture before filtration had a pH of 3.8. The precipitate was then dispersed in 2 liters distilled water, brought to 50°C and filtered. The same washing procedure was repeated once more. Approximately 2 cc of the final precipitate was dispersed in 30 cc distilled water. This solution attained a pH of 5.7. The precipitate was air dried until it acquired the consistency of paste. With the aid of a stainless steel spatula the paste was forced into the 2 x 2 mm holes which were punched in the aluminum plate, placed in an electric oven and baked for fifteen

hours at 220°C. To insure the complete decomposition of $\text{Cu}(\text{OH})_2$ to CuO , a known weight of the resulting pellets was dissolved in concentrated nitric acid and the copper in the solution was gravimetrically determined by electroplating. The results showed complete conversion, within one per cent. There was no evidence of shrinkage in the resulting dry catalyst pellets, but they possessed rather poor mechanical strength. Upon compression they pulverized easily; however, there was adequate resistance to erosion to make them suitable for use in the catalytic bed.

B. Sample #2 (25% less than stoichiometric).

This catalyst was prepared identically as the #1 sample, except that 195 grams of KOH were used instead of 130 grams. The pH of this and the remaining samples were determined in the same manner as for sample #1. The pH of sample #2 was found to be 6.3. The resulting pellets showed no shrinkage. Although slightly stronger than those of sample #1, the mechanical strength of sample #2 pellets was poor.

C. Sample #3 (Stoichiometric).

In this case 242 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 130 grams of KOH were used. The preparation procedure was the same as above with the exception that instead of 2 hours, the resulting dark brown mixture after the addition of KOH, was kept at 80°C for only ten minutes. The pH of this sample was 6.8. The dried pellets showed no shrinkage and possessed good mechanical strength.

D. Sample #4 (25% above stoichiometric).

This catalyst was prepared identically as sample #3, except that 162.5 grams of KOH were used instead of 130 grams. The pH of the sample was 7.2. The pellets, after baking, showed no shrinkage and had exceptionally good mechanical strength.

E. Sample #5 (50% above stoichiometric).

For this sample 195 grams of KOH were used. The preparation procedure was the same as for sample #3. The pH of this sample was 8.8. The resulting pellets showed exceptional mechanical strength.

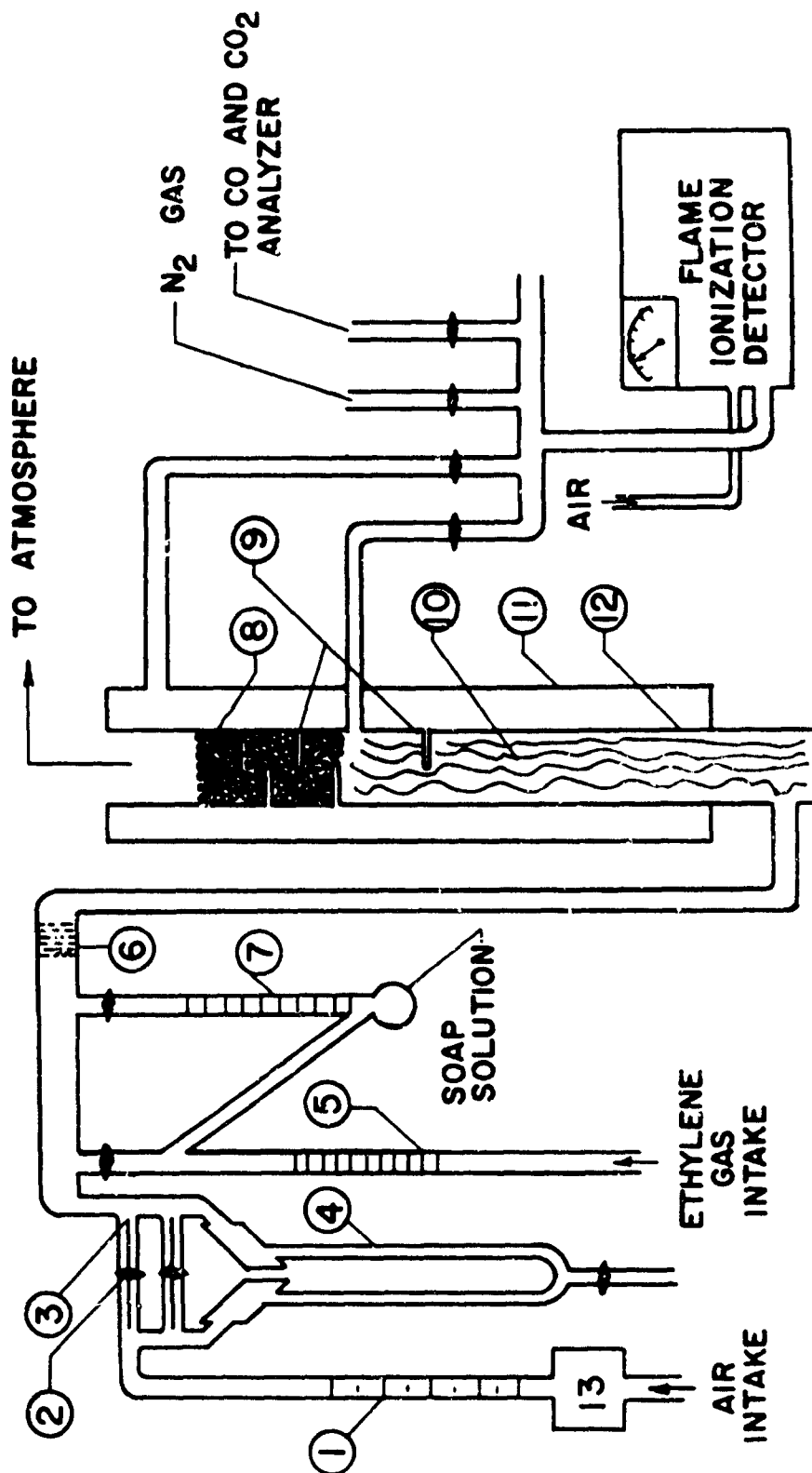
The surface area of all catalysts was measured by N_2 adsorption (BET method) at liquid N_2 temperatures. Samples of 2 to 4 grams were used. Surface areas ranged from 6.4 m^2 /gram to 28.5 m^2 /gram.

A schematic diagram of the apparatus used is shown in Figure 1. The entire apparatus (reactor tube and lines) were built of pyrex glass supplemented by tygon tubing connections where temperatures permitted.

The air stream was stripped of CO_2 and H_2O by passage through a molecular sieve column which was changed every six hours. Frequent tests were made for presence of CO or hydrocarbons in the air stream. The air flow rate was measured by a ball flowmeter which in turn was calibrated by a rotometer. The hydrocarbon concentration was also measured by a ball flowmeter which was checked at least twice a day by timing a rising soap bubble in a 10 cc burette. The two gases were then mixed in a mixing chamber and then introduced to the reactor. The latter was a pyrex cylinder 1.9 cm inside diameter, 60 cm long; it was equipped with 2 sampling outlets and 8 thermocouple wells. The entering mixture of gases was passed through 35 cm of packed glass rings to insure further mixing and to preheat the gas and then passed through the catalyst bed which ranged from 7.5 to 8.5 cm in length. The thermocouple wells were 2 mm O. D. pyrex cylinders extending from the walls of the reactor tube to the center of the tube. The latter end was sealed. The wells, spaced from 1 to 1 1/2 cm apart, were well staggered around the tube to minimize the disturbance of the flow pattern. The thermocouples were iron-constantan. A Honeywell recorder was used to continuously record temperature. The reactor tube was enclosed by an electric furnace consisting of two sections with two variable resistance controls in each section. Isothermal conditions within the bed were maintained both radially and axially within $\pm 1^\circ C$ at hydrocarbon concentrations below 1000 ppm and conversions below 50 per cent. At conversions above 50 per cent the temperature variation (axially) ranged from $\pm 1^\circ C$ to $\pm 8^\circ C$. The latter temperature gradient was observed at conversions above 90 per cent and at 1000 ppm hydrocarbon concentration.

FIGURE 1

1. Air Flow Meter
2. Teflon Stopcocks
3. Capillary Tube
4. Manometer
5. Hydrocarbon Flow Meter
6. Mixing Chamber
7. 10 cc Burette
8. Catalyst
9. Thermocouple Wells
10. Glass Rings
11. Furnace
12. Reactor Tube
13. Air Drier



OXIDATION APPARATUS

FIGURE 1

The radial variation of temperature was measured at 1/4 and 1/2 diameters from the reactor tube walls and never exceeded 2°C. The pressure drop across the bed was measured periodically by a manometer and at no time exceeded 0.5 per cent.

The hydrocarbon concentration, both inlet and outlet, were measured with the aid of a FIAD flame ionizer and recorded by a L & N recorder. When both temperature and concentration steady states were reached, the output hydrocarbon concentration reading was taken first and then the input, in order to avoid disturbance of the steady state. The linearity of the recorder, in changing scales of sensitivity, was checked regularly.

Each catalyst was activated before use, by passing air at 400°C through the bed for at least 48 hours.

Periodically a mass balance was taken by measuring the CO₂ in the outlet. In addition the outlet stream was analyzed frequently for CO, employing a CO analyzer sensitive between 0 and 2000 ppm.

The ethylene used in these experiments was Matheson's C P (99.9 per cent pure).

RESULTS

The experimental data of ethylene oxidation on all five catalyst samples are represented in Figures 6 to 13 of the Appendix. Conversion is plotted against bed temperature, giving the familiar S-shaped curves of hydrocarbon oxidation. The air flow rate used to determine the overall kinetics of ethylene combustion on each catalyst was 500 liters/hour (Figures 6 to 10). The ethylene initial concentration was varied from 200 to 1000 ppm. The experimental points represented in Figure 11 were obtained after 300 to 600 hours of use and demonstrate the consistency of the data for each catalyst since the continuous curves represent the data taken initially. In this figure only samples #1, #3 and #4 are depicted, but similar results were obtained from the other samples. An empirical rate equation of the form

$$r = k_p p_{O_2}^m p_E^n = k p_E^n \quad (1)$$

was used to represent the overall kinetics of the reaction. The reaction order, n , was determined by trial and error using temperatures resulting in 20 to 80 per cent conversion. Table 1 shows the variation of n within this range of conversions and also the average n for each catalyst.

The specific rate constant was determined from the design equation¹¹

$$k = \frac{Q(p_E^o)^{(1-n)}}{W(1-n)} \cdot \left[1 - (1-X)^{(1-n)} \right] \quad (2)$$

for each temperature and each one of the catalysts. From plots such as Figure 16 in the Appendix, the activation energy, E , and frequency factor A , were determined and the specific rate constant was expressed as a function of temperature according to the Arrhenius equation

$$k = A e^{-E/RT} \quad (3)$$

Table 1

PHYSICAL AND KINETIC DATA OF COPPER OXIDE CATALYSTS USED FOR THE COMBUSTION OF ETHYLENE

Sample	CuO-Alumina (1:1)			
	#1	#2	#3	#4
Mechanical Strength	Poor	Poor	Good	Excellent
Size of pellets (cylinders)	2 x 2 mm	2 x 2 mm	2 x 2 mm	2 x 2 mm
Density, pellets/gram	74	75	101	111
BET Surface area, m ² /gram	6.4	7.1	18.6	22.6
Bed void fraction	0.53	0.49	0.46	0.42
Reynold's No. for 500 liters/hour*	136	126	126	120
Space velocity, hr. ⁻¹	25000	25000	25000	25000
Range of Temperatures (°C) for conversions of 20 to 80 percent using w/F = 10 ³ gr. -hr. /mole Ethylene	240-300	220-265	210-240	200-245
Range of Reaction Order, n,	0.70	0.50-0.70	0.35-0.70	0.55-0.75
Average Reaction Order	0.70	0.60	0.65	0.60
Frequency factors (with actual n, values), moles Ethylene, hr. ⁻¹ , gr. catal. ⁻¹ , atm. ⁻ⁿ	5 x 10 ⁶	6 x 10 ⁸	6.8 x 10 ¹⁰	2.1 x 10 ¹⁰
Frequency factors (with overall n = 0.60), moles Ethylene, hr. ⁻¹ , gr. catal. ⁻¹ , atm. ⁻ⁿ	2.5 x 10 ⁶	6 x 10 ⁸	2.1 x 10 ¹⁰	2.1 x 10 ¹⁰
Activation energies (actual n), kcal. /mole	19500	24200	27200	22200
Activation energies (n = 0.60), kcal. /mole	19600	24200	26600	22200

* Reynolds No. was determined according to equation $Re = \frac{Gd_p}{\mu(1-\delta)}$

To test the validity of equation (1) data were taken by varying the air flow rates. Figures 12 and 13 depict data taken on samples #1 and #4 with air flow rates other than 500 liters/hour. Similar results were obtained with the rest of the samples. The experimental points taken at air flow rates of 600 and 400 liters/hour are in good agreement with the curves determined by equation (2).

The data taken at 700 liters/hour air flow rate is unreliable since the catalytic bed was partially fluidized at this flow rate hence, the observed discrepancy. The poor agreement between the experimental data and the predicted values at 300 liters/hour air flow rate can be attributed to the fact that the plug flow assumption implied in equation (2) was no longer valid in this case. At 300 liters/hour the Reynolds number of the flow through the reactor tube used was 87. According to Schwartz¹² and Dorweiler¹³ the velocity distribution of flow through packed beds becomes a strong function of the flow rate for Reynolds numbers smaller than 69, where the plug flow assumption does not hold. From Figure 13, however, it seems that even at a Reynolds number of 87 such an assumption is a poor one. Accomazzo¹⁴ in his work with light hydrocarbons reports similar discrepancies at low flow rates between the experimental data and values predicted from an empirical equation based on plug flow.

The reproducibility of the catalysts is shown in Figures 14 and 15. Sample #6 was prepared identically as sample #3; the same is true of samples #5 and #7. The solid lines represent the data for catalysts #3 and #5, and the data points represent the results obtained with catalysts #6 and #7. The reproducibility is excellent. Surface area measurements and density determination also showed good reproducibility for all samples.

The BET surface areas, per unit weight of catalyst, are shown in Table 1. These values were obtained from plots such as in Figure 17.

DISCUSSION

Figures 6 to 10 show that the conversion increases with temperature and with decreasing initial concentration of ethylene for all five catalysts studied. This is in accord with the results obtained by other investigators using various other catalysts.^{10, 14, 15} A comparison of these five graphs shows also that at a given temperature conversion increases with the amount of KOH used in the preparation of the catalyst, with the exception of sample #5. This latter effect is more apparent in Figure 2, where the data for only one ethylene initial concentration are compared.

For comparison purposes an overall reaction order, $n = 0.60$, was used in equation (2). This apparent order is equal to the average n for three of the catalysts and differs only slightly from the other two. A check of the reasonableness of this choice of the reaction order with the experimental data for all the catalysts is shown in Figure 3. Equation (2) was rearranged and p_E^0 replaced by $X_0 \cdot 10^{-6}$ where X_0 is the initial ethylene concentration in ppm; thus

$$\frac{W}{F} X_0^n k = \left(\frac{10^6}{1-n} \right) \left[1 - (1-X)^{(1-n)} \right] \quad (4)$$

where $F = Q \rho p_E^0 / P_t$ and $n = 0.60$. Figure 3 is a plot of equation (4). The slope of this curve should be constant, independent of flow rate, initial concentration of ethylene, and the catalyst used. Figure 3 indicates that equation (4) correlates all the experimental data quite well. With the exception of the data taken at 300 and 700 liters per hour the agreement appears good up to almost a conversion of 80 per cent. At higher conversions the pressure drop between ambient gas and the catalyst surface becomes appreciable and the kinetic mechanism becomes affected by diffusion.¹⁴ Thus, the experimental values of conversion at higher conversions are lower than the predicted ones. The deviations for the 300 and 700 liters per hour flow rates have been discussed earlier.

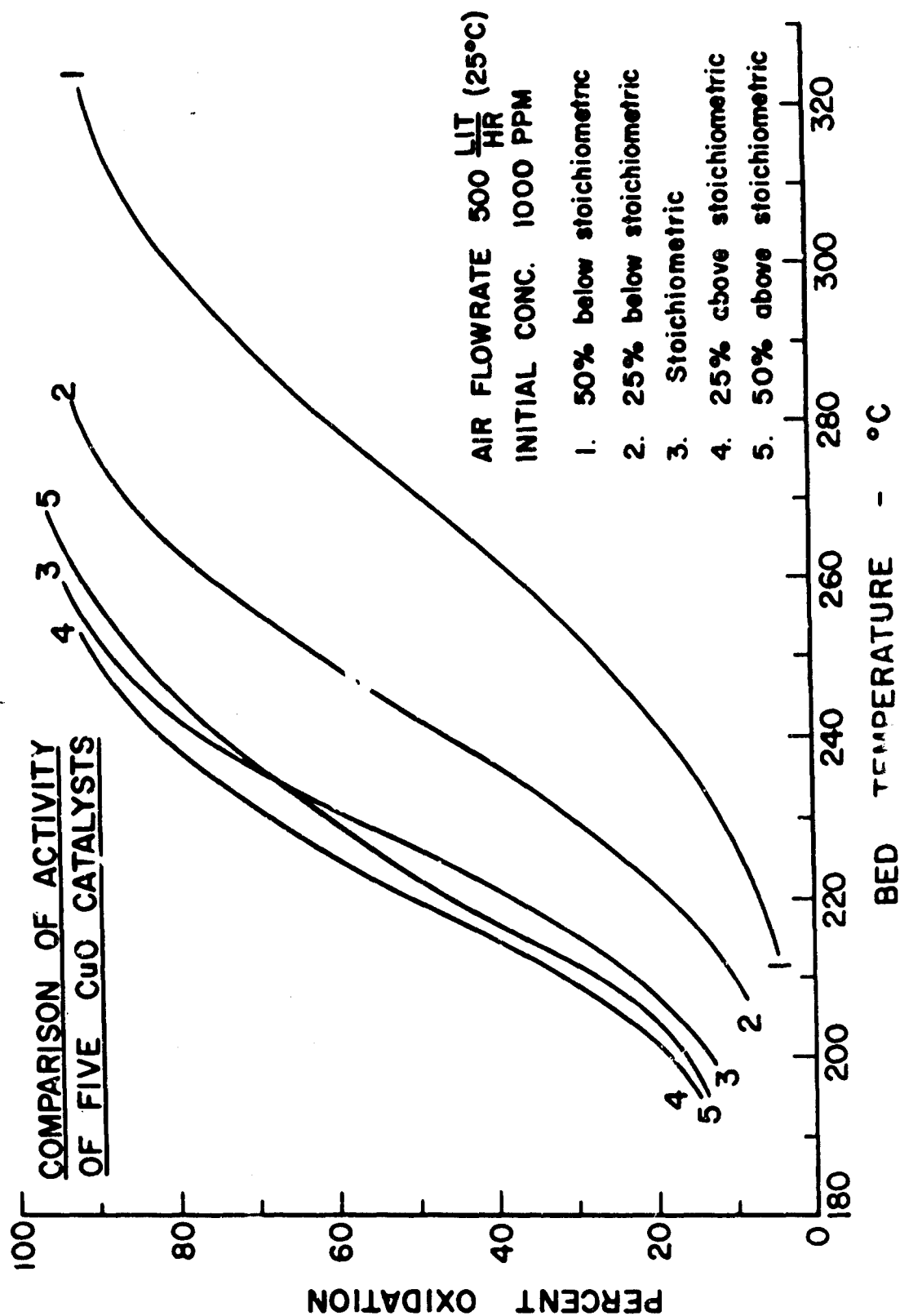


FIGURE 2

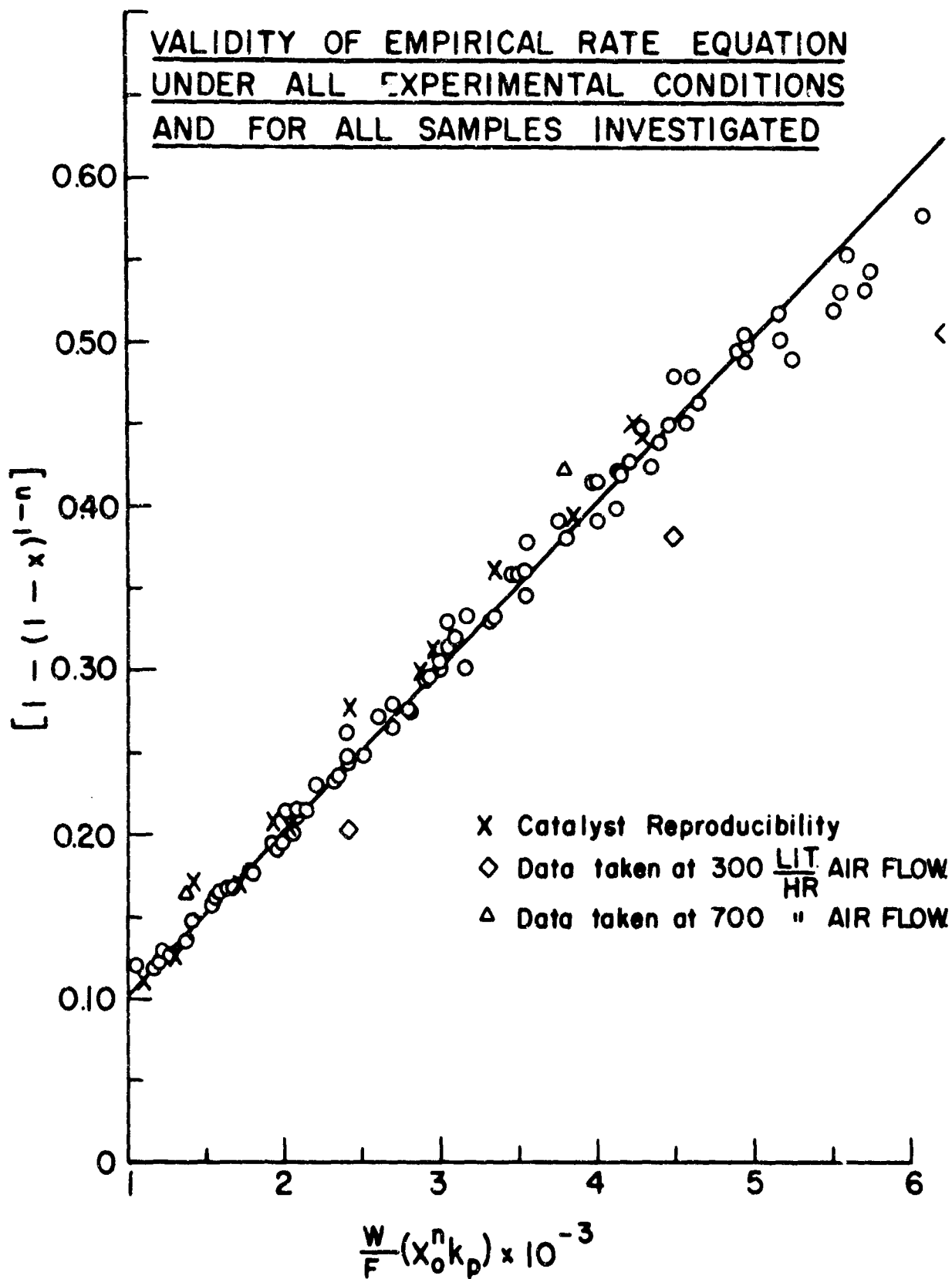


FIGURE 3

Table 1 is a summary of the physical and kinetic data for all five catalysts. Table 2 compares conversions, reaction rate constants and reaction rates at 340°C , and also surface areas and activation energies. Table 2 shows that an increase in the amount of KOH used in the preparation of the catalysts results in an increase in the mechanical strength of the catalyst, the conversion and the reaction rate constant (frequency factor) at a given temperature, the apparent activation energy of the reaction and the surface area of the catalyst. The only exception to this trend is catalyst #5.

According to the experimental results then, catalyst #4 (the least acidic of the 4 samples) is the best of the five catalysts for the combustion of ethylene. The superiority of catalyst #4 is apparently due to its relatively high surface area. The magnitude of the surface area of a catalyst depends not only on the amount of KOH used, but also on a number of other variables in the preparation procedure as, for example, the temperature at which precipitation takes place, the pressure applied during the molding process, the decomposition temperature and the gas environment at which decomposition takes place. Pella¹⁶ reports that CuO of very high surface area can be obtained when the $\text{Cu}(\text{OH})_2$ is decomposed, at 850°C , in the presence of pure oxygen instead of air.

In order to relate the pH of the catalyst to its catalytic activity the effect of surface area should be eliminated. In this study the specific rate constant per unit surface area is taken as a measure of the activity of the catalyst. Another quantity that is independent of surface area is the apparent activation energy; it has also been used as a means of comparison of catalytic activity in various other studies, but it is a less reliable experimental quantity in this study.

The last entry in Table 2 indicates that the catalytic activity of CuO increases with acidity of the catalyst up to 25% less than stoichiometric CuO. In the case of sample #1 (50% less than stoichiometric CuO) the activity reaches an unexpected minimum. This, however, can be explained.

Table 2

COMPARISON OF ACTIVITY OF CuO CATALYSTS AT 240°C*

Sample	#1	#2	#3	#4	#5	CuO-Alumina (1:1)
Percent Conversion	19	46	79	81	73	10
Specific Rate constant, moles ethylene converted hr., gm. catalyst, atm. 0.60	1.3×10^{-2}	3.5×10^{-2}	6.9×10^{-2}	7.3×10^{-2}	6.1×10^{-2}	5.3×10^{-3}
Rate of reaction moles ethylene converted hr., gm. catalyst	1.8×10^{-4}	3.8×10^{-4}	4.3×10^{-4}	4.4×10^{-4}	4.4×10^{-4}	
Activation Energy, kcal./mole	19.6	24.2	26.6	27.0	22.2	18.0
Surface Area, m ² /gm.	6.4	7.1	18.6	28.5	22.6	86
pH of catalyst samples	5.7	6.3	6.8	7.2	8.8	
Specific Rate constant/unit surface area moles ethylene converted hr., atm. 0.60, m ²	2.1×10^{-3}	4.9×10^{-3}	3.7×10^{-3}	2.6×10^{-3}	2.7×10^{-3}	6.2×10^{-4}

* $\frac{W}{F} = 10^3$ gm.-hr./mole ethylene for all samples

at least partly, by the fact that the error in the calculation of the BET surface area at such low values becomes large (0.2 cc uncertainty in the volume measured could result to approximately 20% uncertainty in BET surface area). The small discrepancy at the other end (sample #5) can be attributed to experimental error. Although no linear relationship has been developed between catalytic activity and catalyst acidity, the results of this study indicate that catalytic activity increases with acidity, with the effect being most evident in the range of 25% less than to 25% greater than stoichiometric CuO.

When the apparent activation energies for the combustion of ethylene are compared, the same trend as above is observed up to sample #4. Thus, the activation energy for the process decreases with increasing pH of the catalyst or KOH used in its preparation. In Figure 4 activation energies and rate constants, at 240°C, are plotted against the catalyst samples.

The results of this investigation are consistent with those reported in literature for various other reactions and catalysts. Most of the previous studies on this subject have been on the strongly acidic catalysts used in the petroleum industry. A. Clark et al⁴ studied the effect of the acidity of silica-alumina catalyst on its activity in the polymerization of propylene and in the hydrogen transfer reaction between decalin and isobutene. They report increased catalytic activity with acidity.

M. S. Boreesova et al⁵ studied the dehydration of isopropyl alcohol and the dimerization of propylene and isobutylene using the following catalysts: silica-alumina, aluminum oxide, silica gel, calcium silicate and phosphoric acid-silica gel. They report an increase of catalytic activity with an increase in acid sites on each of the above catalyst surfaces.

J. B. Fisher and F. Sebba⁶ report that the activation energy for the formic acid decomposition reaction decreases with increasing acidity of the silica-alumina catalyst used. The decrease in the activation energy is pronounced as the acidity is changed from 0 to 0.05 meq./gm., leveling off at higher acidities (about 0.25 meq./gm.).

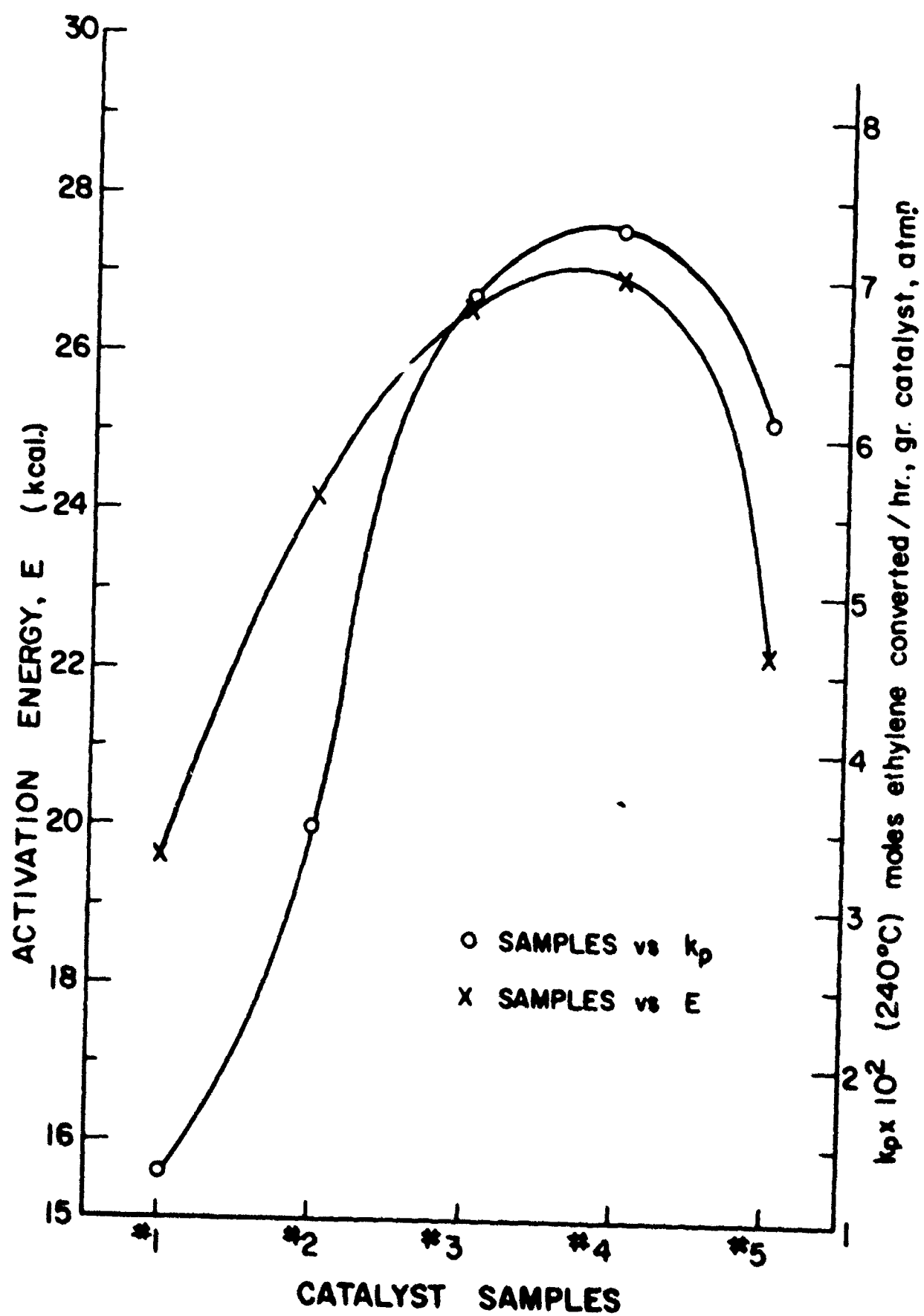


FIGURE 4

J. Blumenthal¹⁰ studied the effect of the amount of KOH used in the preparation of CuO on its catalytic activity in CO oxidation. He also reports increased activity with acidity.

Studies, underway by A. Cohen at UCLA, on CO oxidation with NiO catalyst indicate a similar relationship between the amount of KOH used in the preparation of the catalyst and its activity.

Ryland, Tamele and Wilson,¹⁷ in an article on cracking catalysts, give an excellent review of the results of investigations on acidity vs activity of acid catalysts. In all cases reported, catalytic activity increases with acidity. In most cases the rate of increase is high at moderate acidities leveling off with increase in acidity. Unfortunately, in many of these studies, activity is expressed in terms of conversion, overall rate constants, or conversion temperatures with no mention of the procedure of preparation of the catalyst or its surface area; thus, the effect of acidity on the activity of the catalyst independent of its surface area is not known making comparison between investigations very difficult. The recent development of quantitative methods for the determination of acid site concentration and distribution over the catalytic surface, in the case of high acidity catalysts, have offered an effective tool for comparison between various studies and subsequently should lead to a better understanding of the effect of acidity. The results obtained from measurements of the concentration of acid sites also indicate that activity increases with acidity.

Ryland et al¹⁷ also report that adsorbed alkali metal cations reduce the activity of the catalyst. The same effect is observed when aluminum atoms are replaced by alkali atoms on silica-alumina catalyst surface. The deactivation is proportional to the concentration and the size of the cation. This phenomenon has been interpreted as being the result of the adsorption of cations on the active acid sites, thus rendering them inactive.

Recently, Malinowski et al⁸ studied the basicity of silica gel catalysts impregnated with various quantities of NaOH. Their results were only

semiquantitative, since in contrast to strong acid catalysts, there were no quantitative methods for determining the basic site concentration or distribution on the surface of a basic catalyst. They report the presence of both acid and basic sites on the surface and conclude that the basicity measured is a net value. This conclusion is based on the assumption that basic and acid sites interact on the surface of the catalyst neutralizing each other. It was assumed that the basic sites corresponded to -ONa groups on the surface.

In the case of acid catalyzed reactions (cracking, isomerization, alkylation, etc) it is generally accepted that the reaction mechanism involves the formation of carbonium ions (in the hydrocarbon dissociation step) and that the acid sites are directly responsible for the catalytic activity. If it is assumed that ethylene oxidation follows the same mechanism-involving the formation of carbonium ions - the higher activity of the more acidic CuO observed in this study seems reasonable (Jenkins and Rideal¹⁹ report that ethylene when adsorbed on Ni surfaces decompose to a C_1H_3 complex). The deactivation effect due to blocking of acid sites on silica-alumina by alkali metal cations as reported by Ryland et al,¹⁷ offers a reasonable explanation for the decline in activity of CuO with the amount of KOH used in its preparation. The fact that the basic CuO was not completely inactive could be explained from the results of Malinowski's⁸ experiments. According to the latter results, a catalyst surface with a net basic pH retains a number of acid sites which are still distinct and therefore catalytically active.

Pines and Schaap¹⁹ report that isomerization and alkylation reactions of olefins, believed until recently to be catalyzed only by acids, are also catalyzed by bases. Similar catalysis for hydrocarbon oxidation have not, however, been reported.

One of the purposes of this study was to compare the activity of pure CuO and CuO -alumina (1:1) investigated by Accomazzo. The results are depicted in Figure 5 where ethylene conversion is plotted against temp-

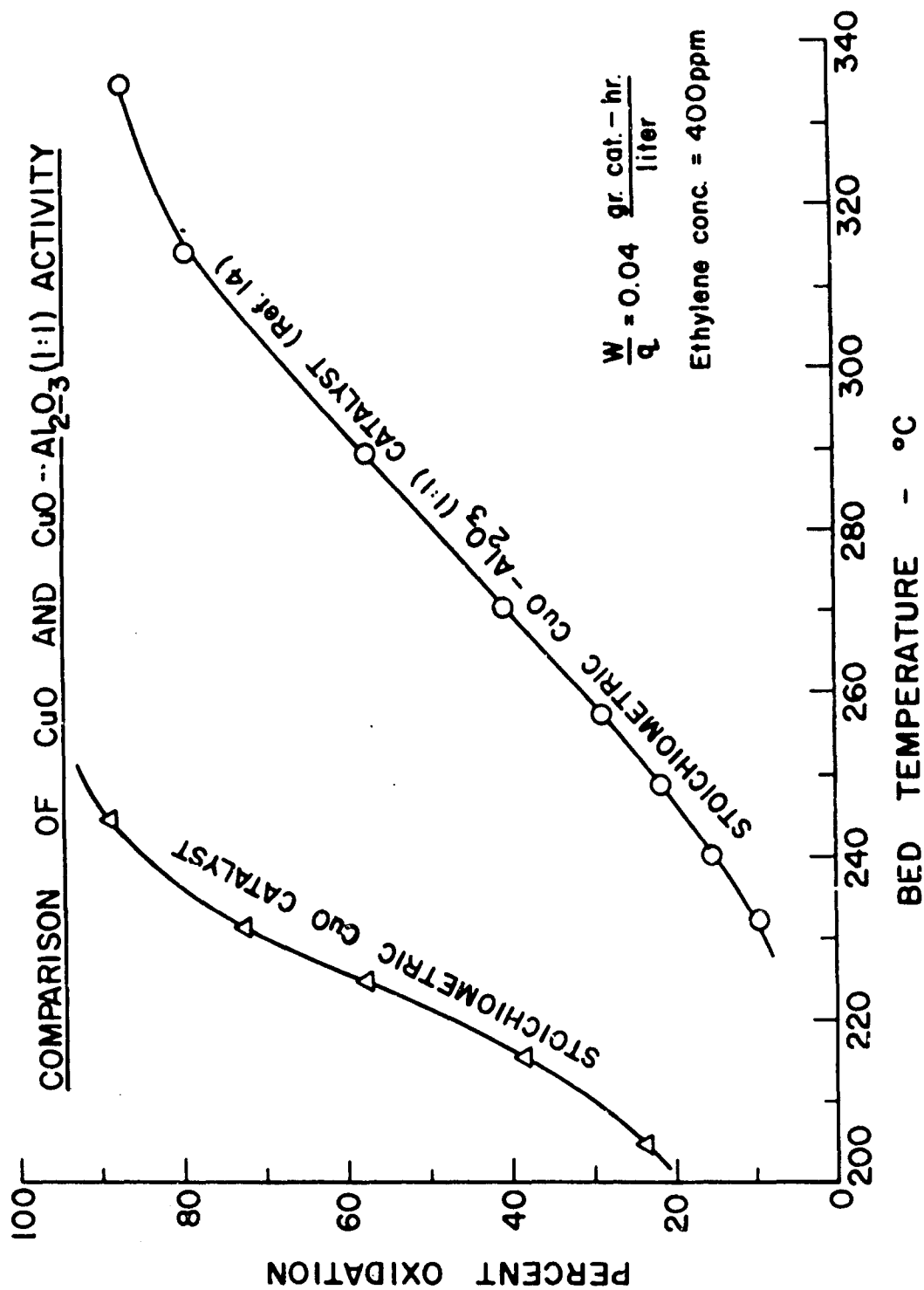


FIGURE 5

eratures. It is seen that pure CuO has a much higher activity than the supported one. When activities are compared on the basis of unit surface area the results again favor the pure CuO (Table 2). A better comparison would have been possible if the degree of CuO coverage of the alumina surface were known. Such data, however, were not available.

CONCLUSIONS

The results of this investigation have resulted in the following conclusions:

- 1) The catalytic activity of stoichiometric CuO catalyst as prepared in this study was much higher than the stoichiometric CuO-Ammonia (1:1), prepared by similar methods, in the combustion of ethylene; this was indicated by the higher specific rate constant and the lower conversion temperatures.
- 2) The amount of KOH used in the precipitation of $\text{Cu}(\text{OH})_2$ from $\text{Cu}(\text{NO}_3)_2$ played an important role in the activity of the resulting copper oxide catalyst. The experimental results indicated that CuO was a very active catalyst for ethylene combustion. The temperature for a specified conversion decreased with increasing amount of KOH used up to 25 per cent above the stoichiometric quantity.
- 3) The surface area of the catalyst increased with increasing amount of KOH used.
- 4) The mechanical strength of the catalyst pellets increased with increasing amount of KOH used.
- 5) The catalytic activity of CuO, represented by the specific rate constant per unit surface area, increased with decreasing pH of the catalyst. The apparent activation energy increased with increasing pH and is in accord with the results obtained in a number of investigations.
- 6) The overall kinetics of the reaction for all the catalysts between 20 and 80 per cent conversions were described by the empirical rate expression $r = k p_E^{0.60}$. For conversions below 20 per cent the uncertainty in k due to experimental error is greater than 6 per cent; for conversions above 80 per cent the reaction is affected by diffusion and the experimental values

of conversion are lower than those predicted by the above equation.

- 7) The method of preparation used in this study produced catalysts of high activity. The reproducibility of the catalytic activity by the preparation procedures was good. The catalyst activity remained at the same level for at least 500 hours of continuous use (initial conversions were reproduced within $\pm 2\%$ conversion after 500 hours of continuous use).

BIBLIOGRAPHY

1. Trambouze, Y. J., Perrin, M., and DeMourgues, L., Advances in Catalysis, Academic Press, New York 1957. Vol 9, p. 544.
2. Tamele, M. W., Disc. Faraday Soc., 8:270 (1950).
3. Johnson, O., J. Phys. Chem., 59:327 (1955).
4. Holm, V. C. F., Bailey, G. C., and Clark, A., J. Phys. Chem. 63:129 (1959).
5. Boreesova, M. S., Dzeesco, V. A., and Cheeredneek, E. M., Kinetics and Catalysis, (Sept. - Oct. 1962) 3:643.
6. Fisher, J. B., and Sebba, F., Actes du 2me Congres Inter. de Catalyse, technip, Paris, 1960. Vol 1, p. 711.
7. Hirschler, A. E., J. Catalysis, 2:428 (Oct. 1963).
8. Malinowski, S., and Szczepanska, S., J. Catalysis, 2:310 (Aug. 1963).
9. Boreesova, M. S., Dzeesco, V. A., Kinetics and Catalysis, 4:337 (May - June 1963).
10. Blumenthal, J. L., Ph. D. Thesis, Depart. of Engineering, University of California, Los Angeles, (Jan. 1963).
11. Smith, J. M., Chemical Engineering Kinetics, New York, McGraw-Hill, 1956, p. 318.
12. Schwartz, C. E., and Smith, J. M., Ind. Eng. Chem., 45:1209 (1953).
13. Dorweiler, V. P., and Fahien, R. W., A. I. Ch. E. Journal, 5:139 (1959).
14. Accomazzo, M. A., Ph. D. Thesis, Depart. of Engineering, University of California, Los Angeles, (June 1963).
15. Caretto, L. S., Masters Thesis, Depart. of Engineering, University of California, Los Angeles, (Jan. 1963).
16. Pella, E., Z. Anal. Chem., 192:397 (1963).
17. Ryland, L. B., Tamel, M. W. and Wilson, N. J., Catalysis, Reinhold Publishing Corp., New York, 1960, Vol. VII p. 75.
18. Jenkins, G., L., and Rideal, E., J. Chem. Soc., London, 1955, p. 2490.
19. Pines, H., and Schaap, L. A., Advances in Catalysis, Academic Press, New York, 1960. Vol. 12, p. 117.
20. Benson, S. W., Foundations of Chemical Kinetics, New York, McGraw-Hill, 1960. p. 87.

APPENDIX

EXPERIMENTAL DATA

The following figures represent the complete data taken in this study.

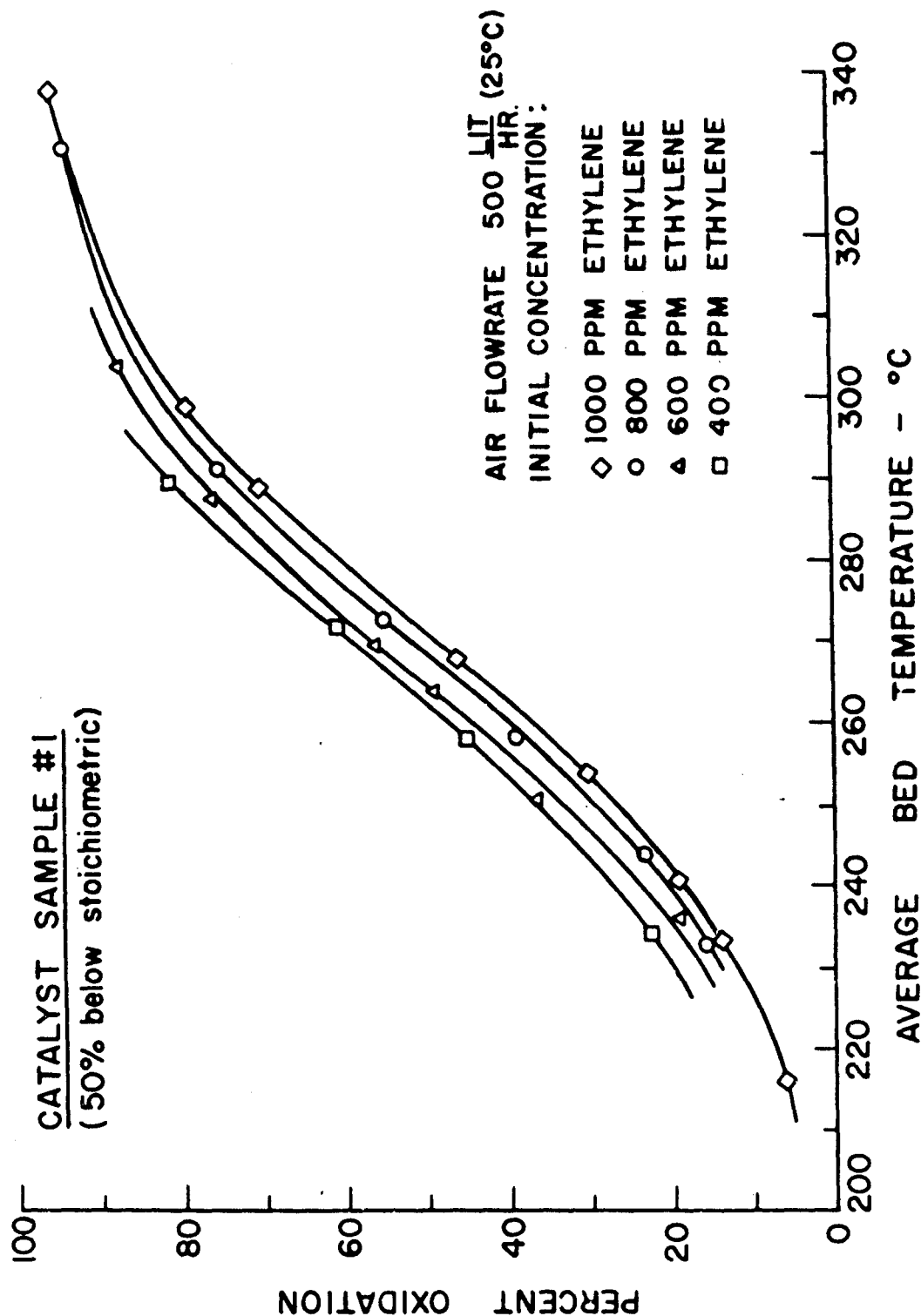


FIGURE 6

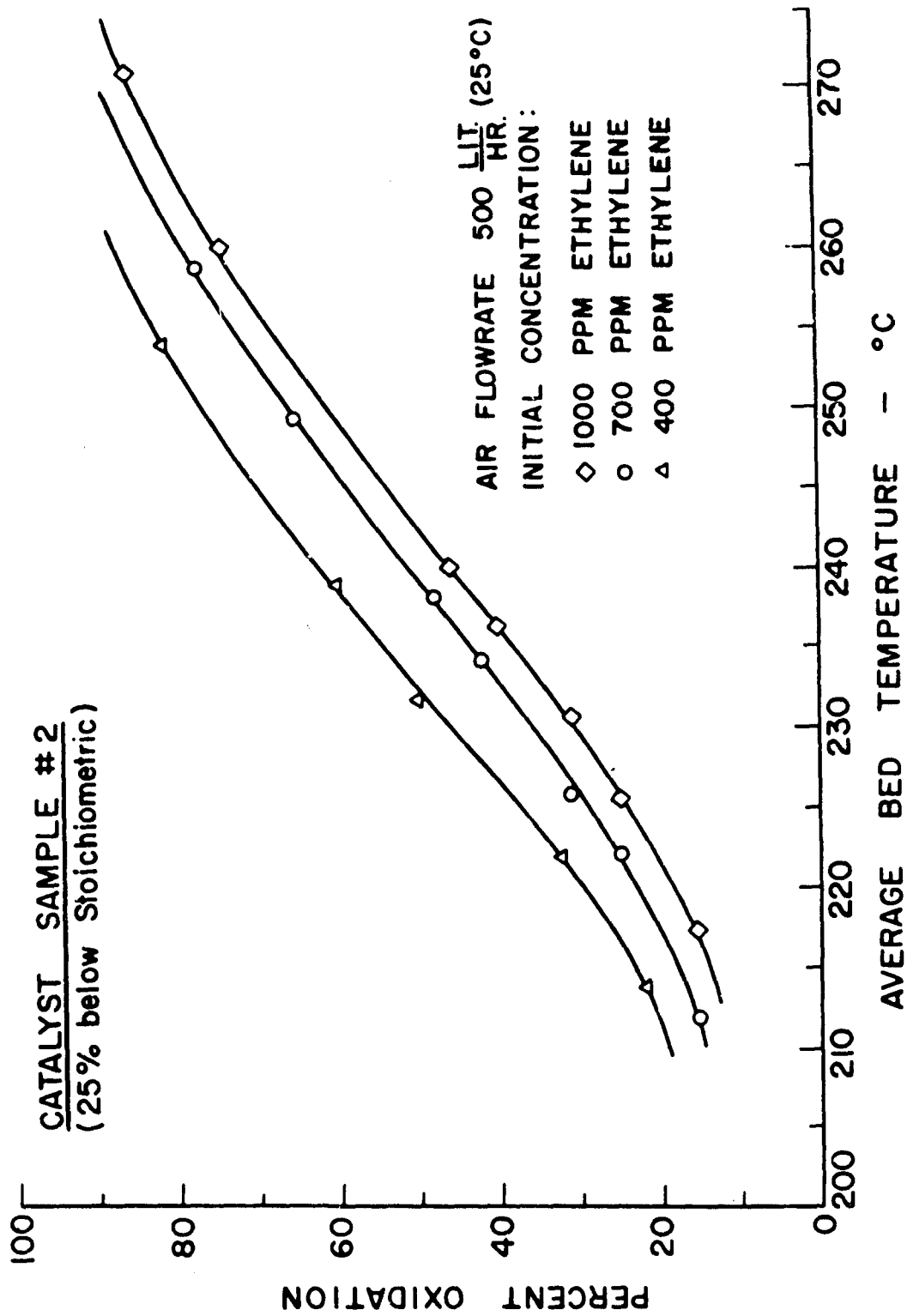


FIGURE 7

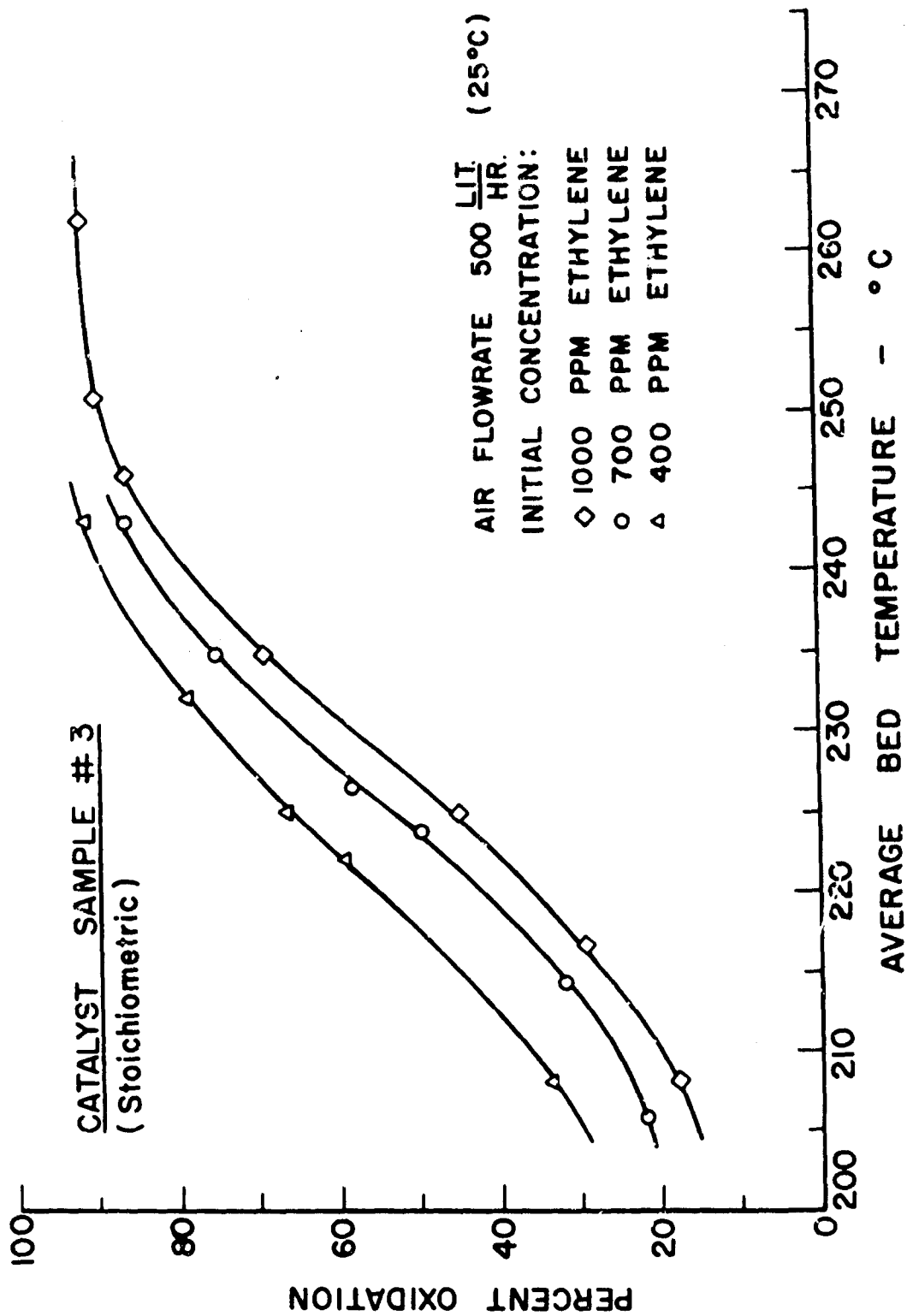


FIGURE 8

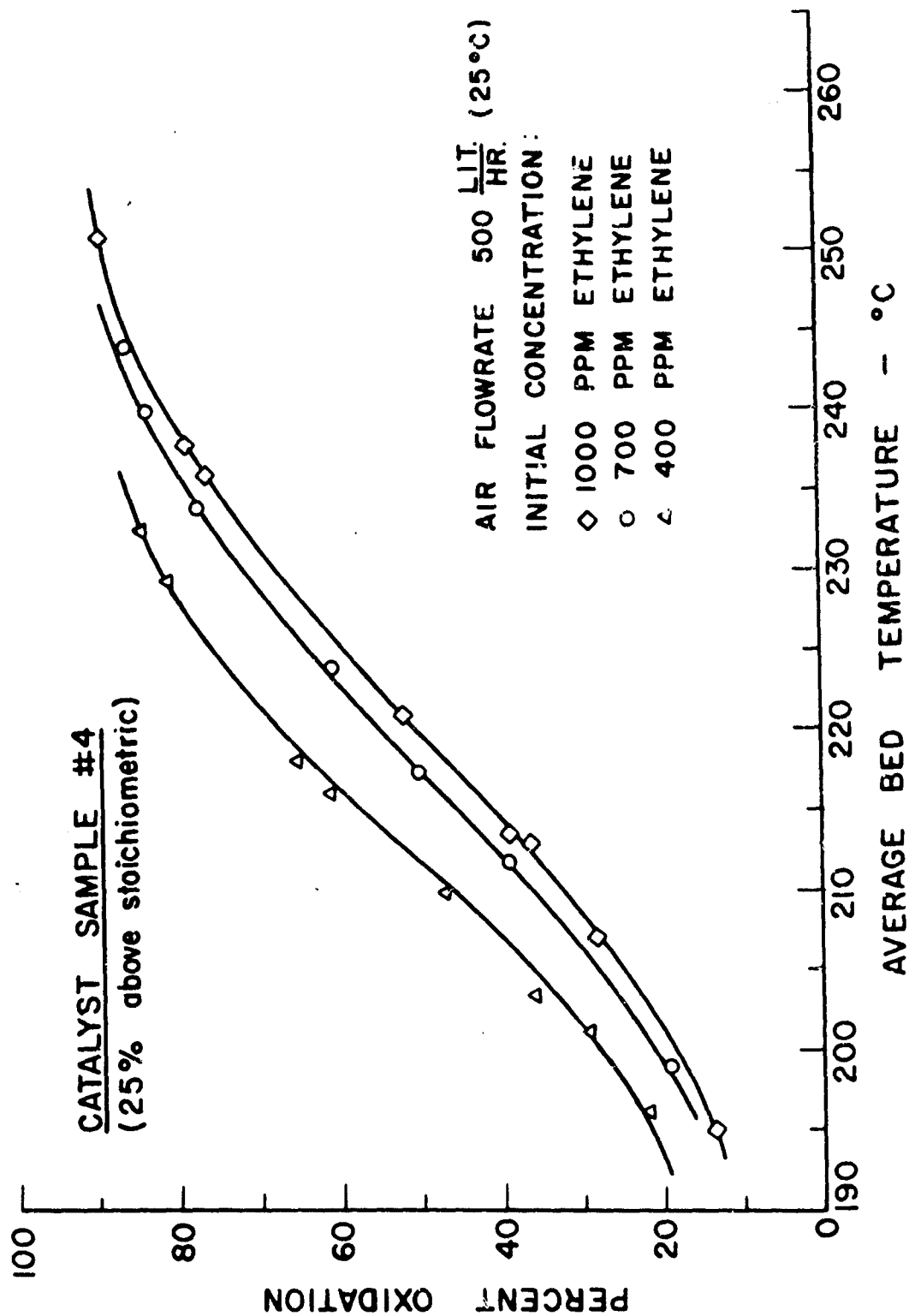


FIGURE 9

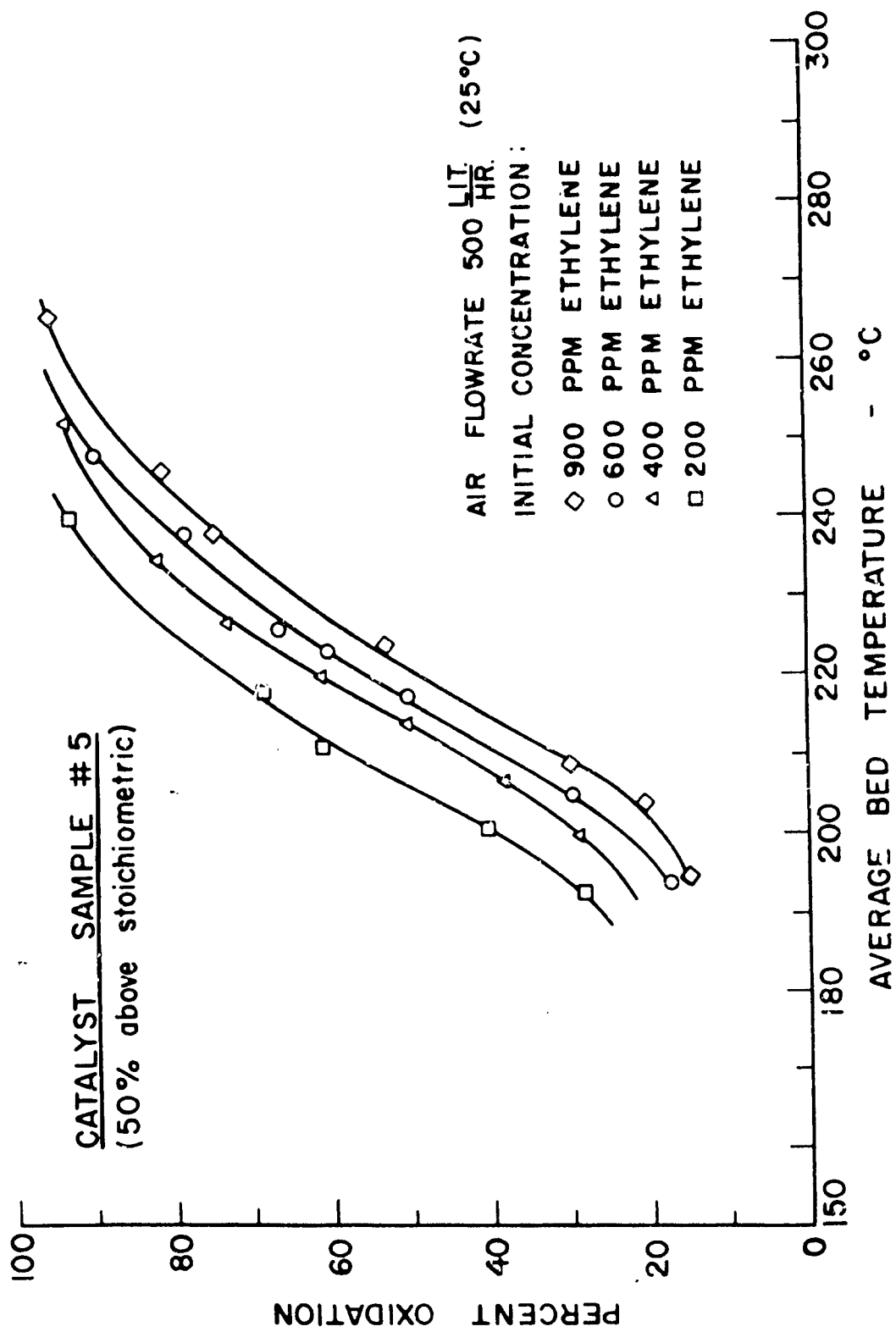


FIGURE 10

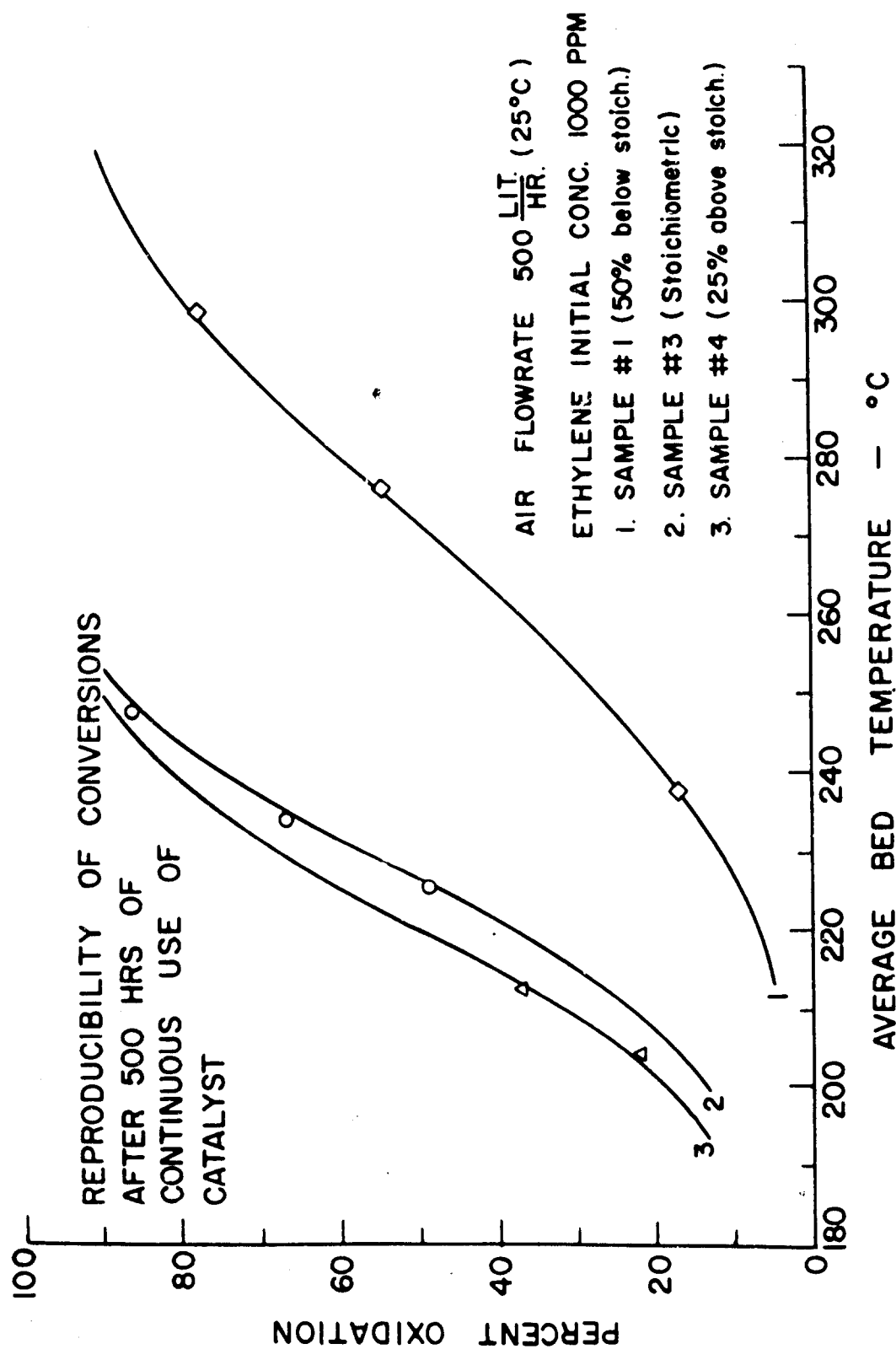


FIGURE II

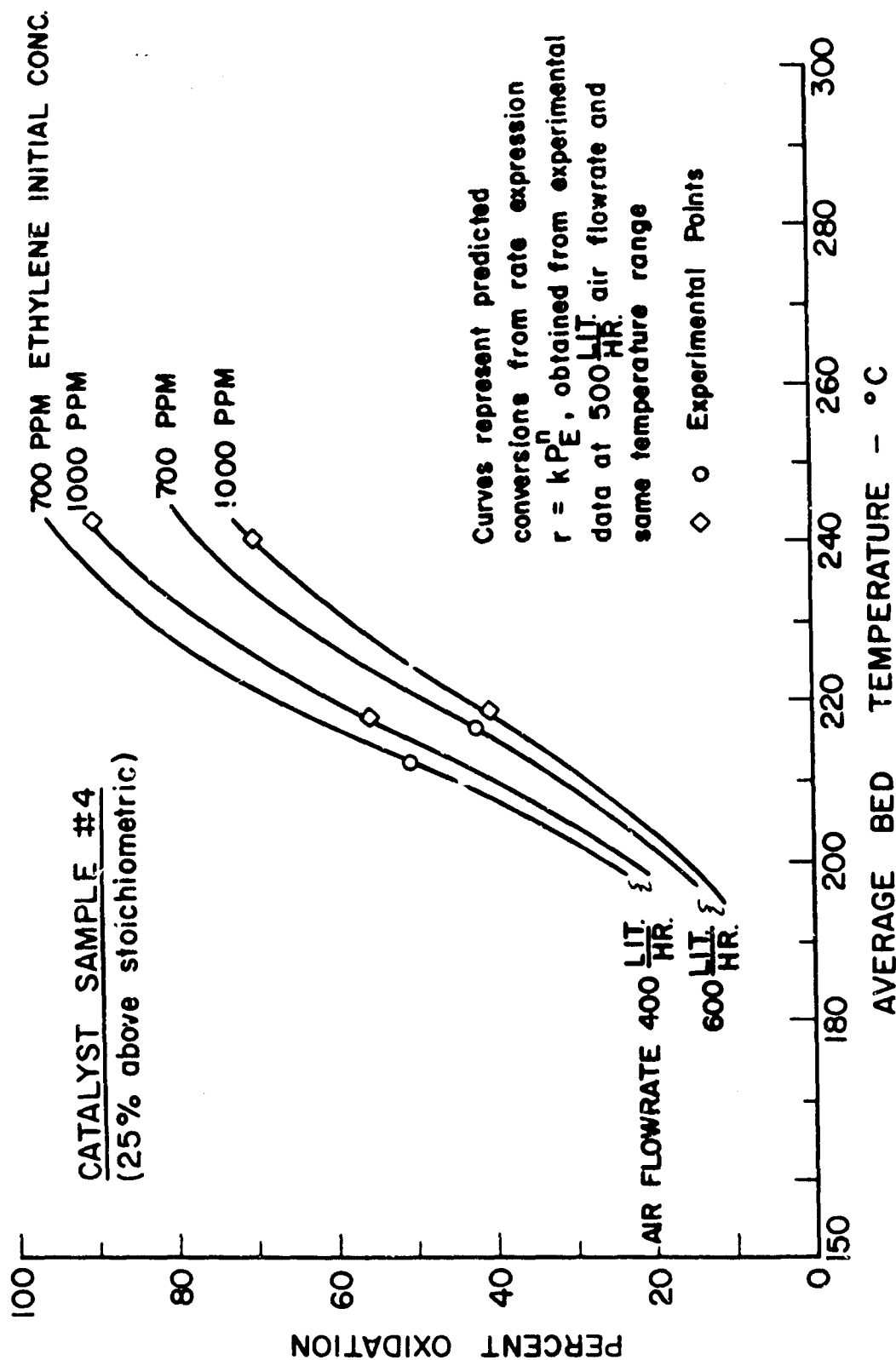


FIGURE 12

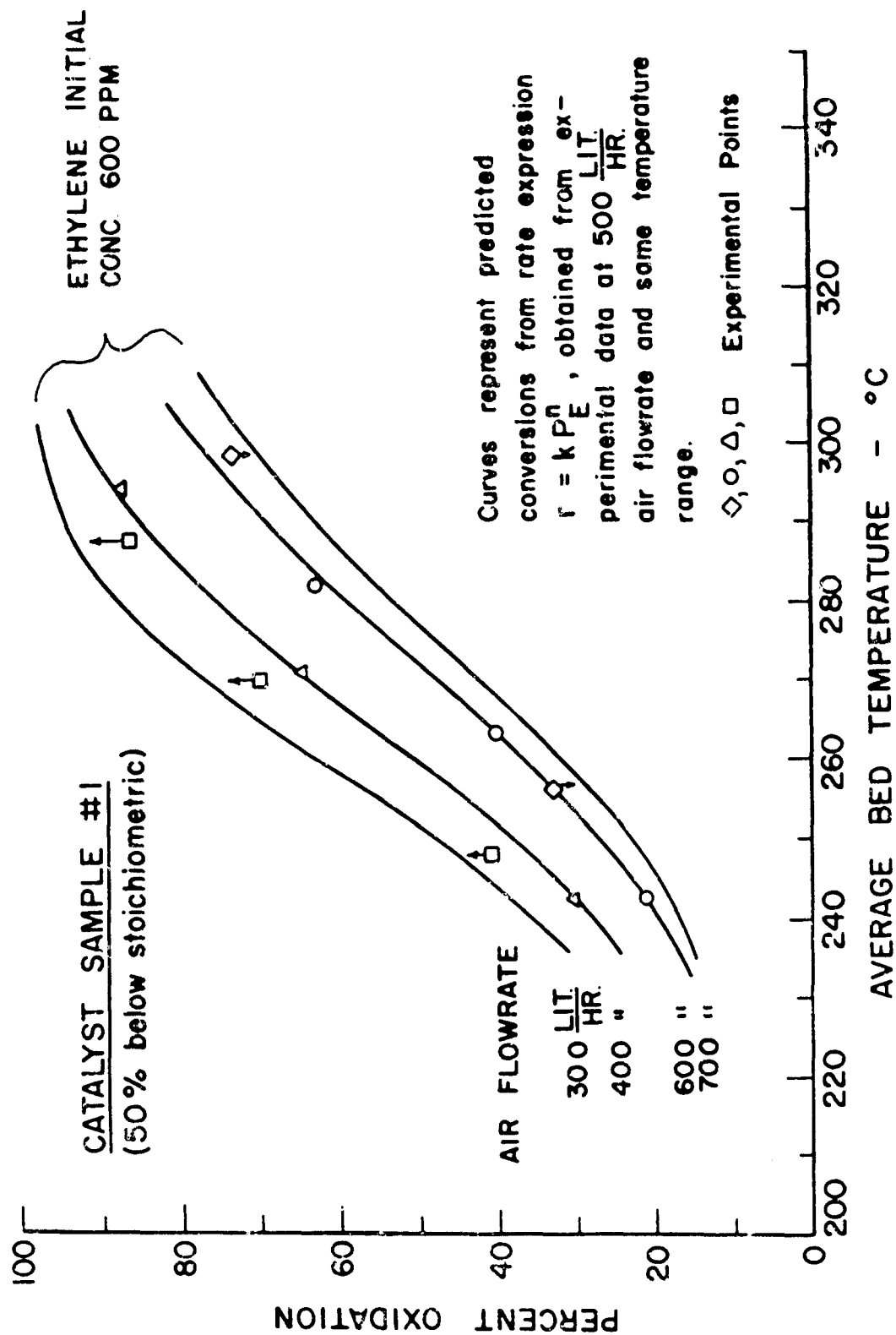


FIGURE 13

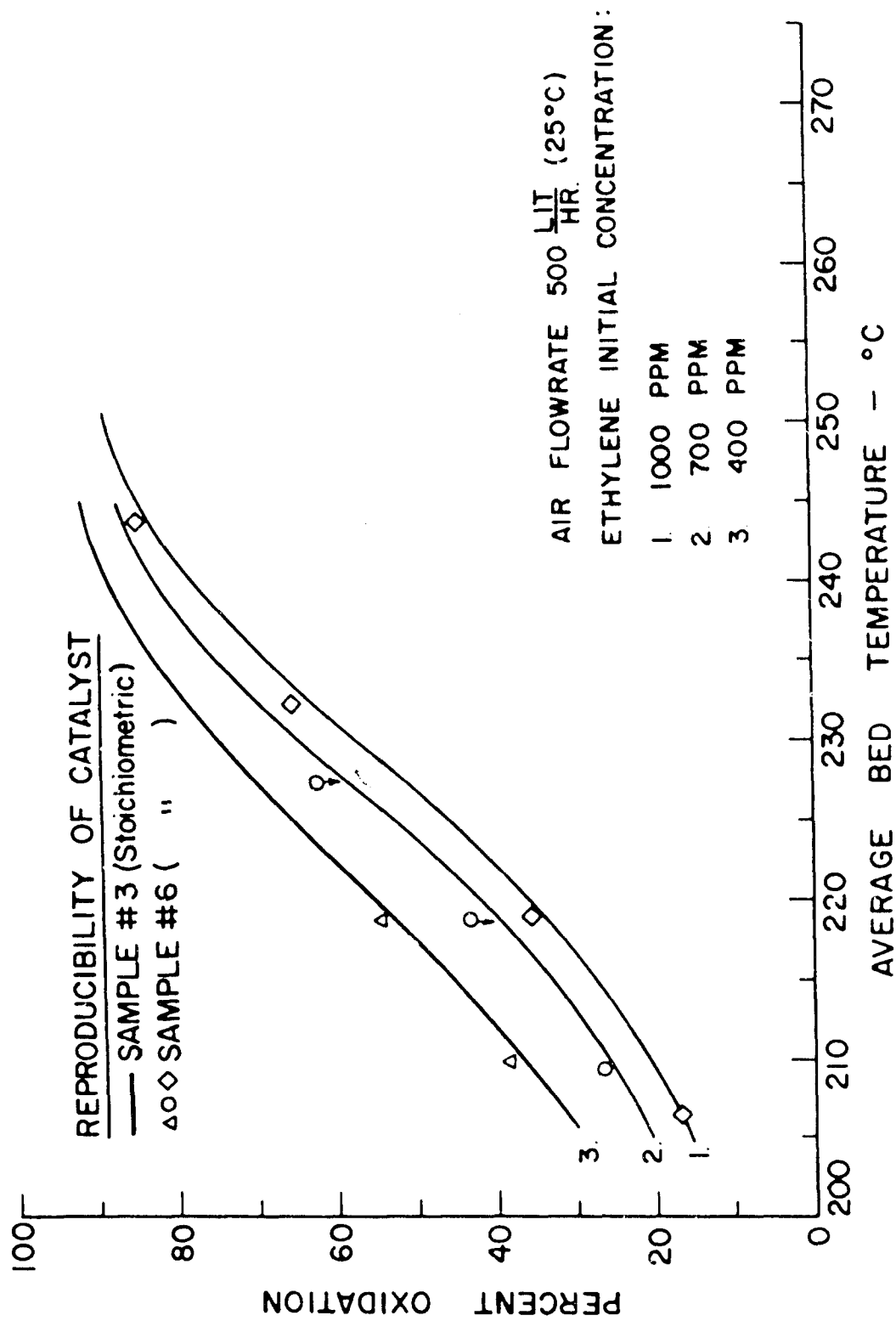


FIGURE 14

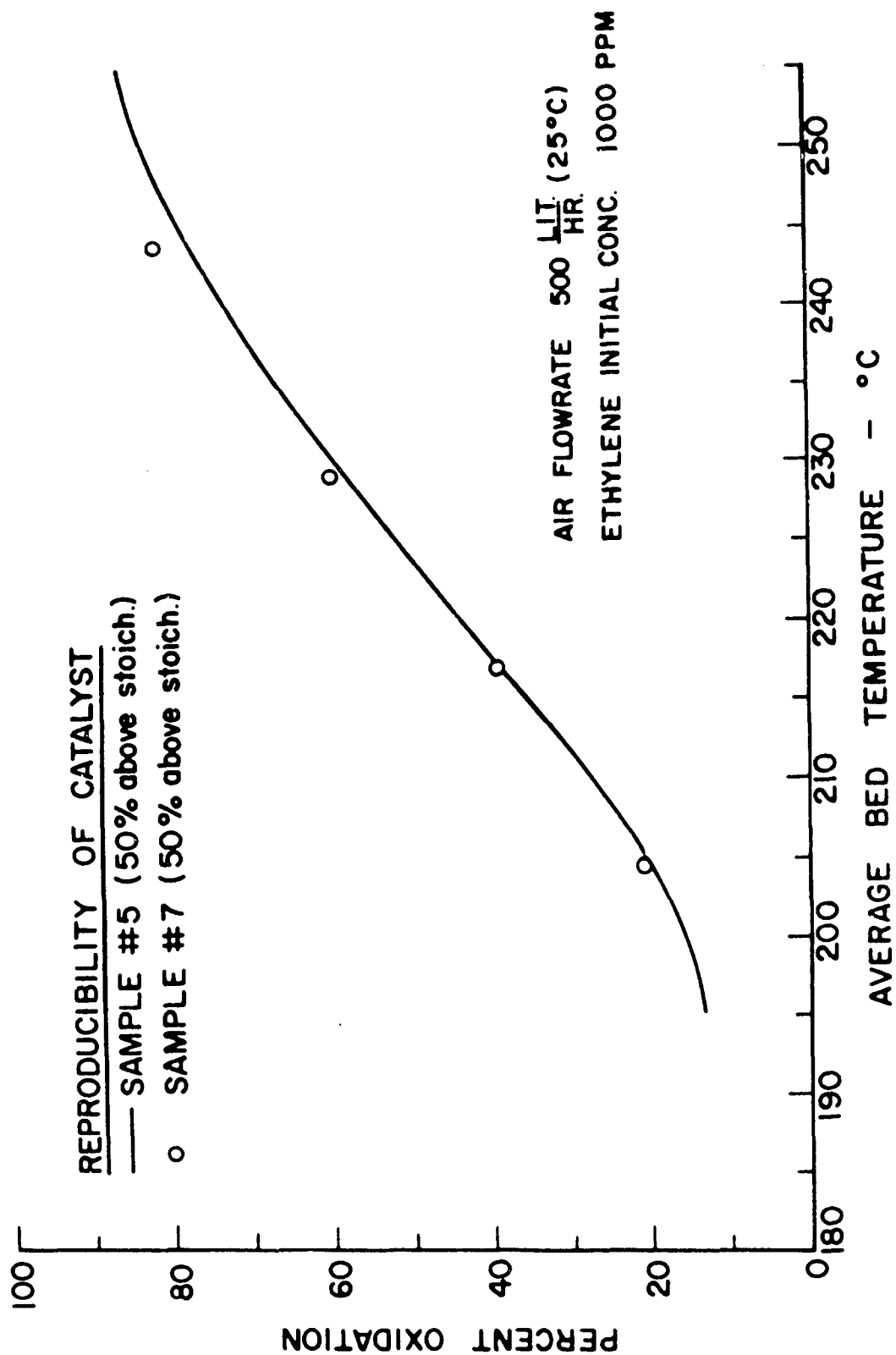


FIGURE 15

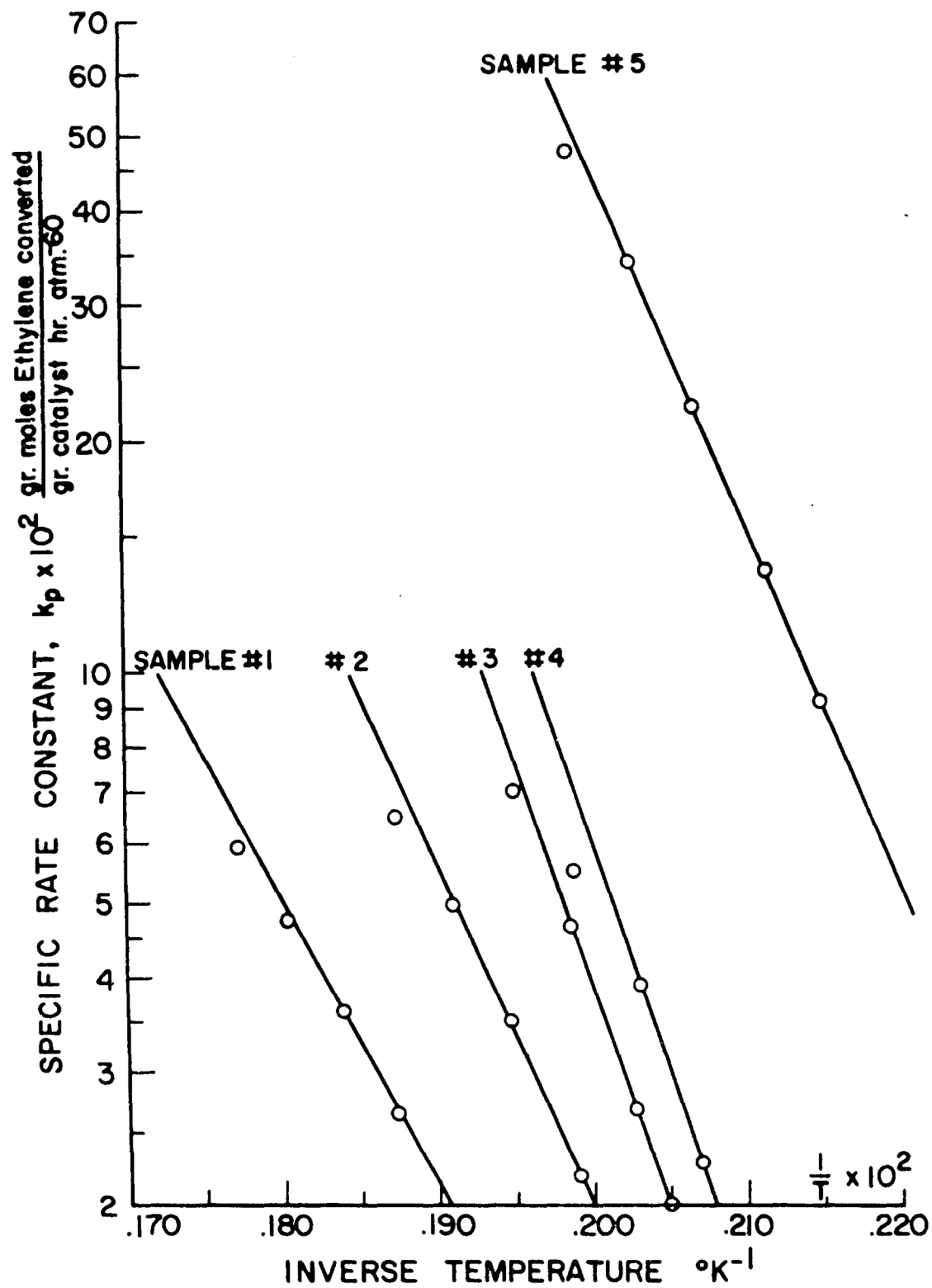


FIGURE 16

SURFACE AREAS OF CuO CATALYSTS
(B. E. T. METHOD)

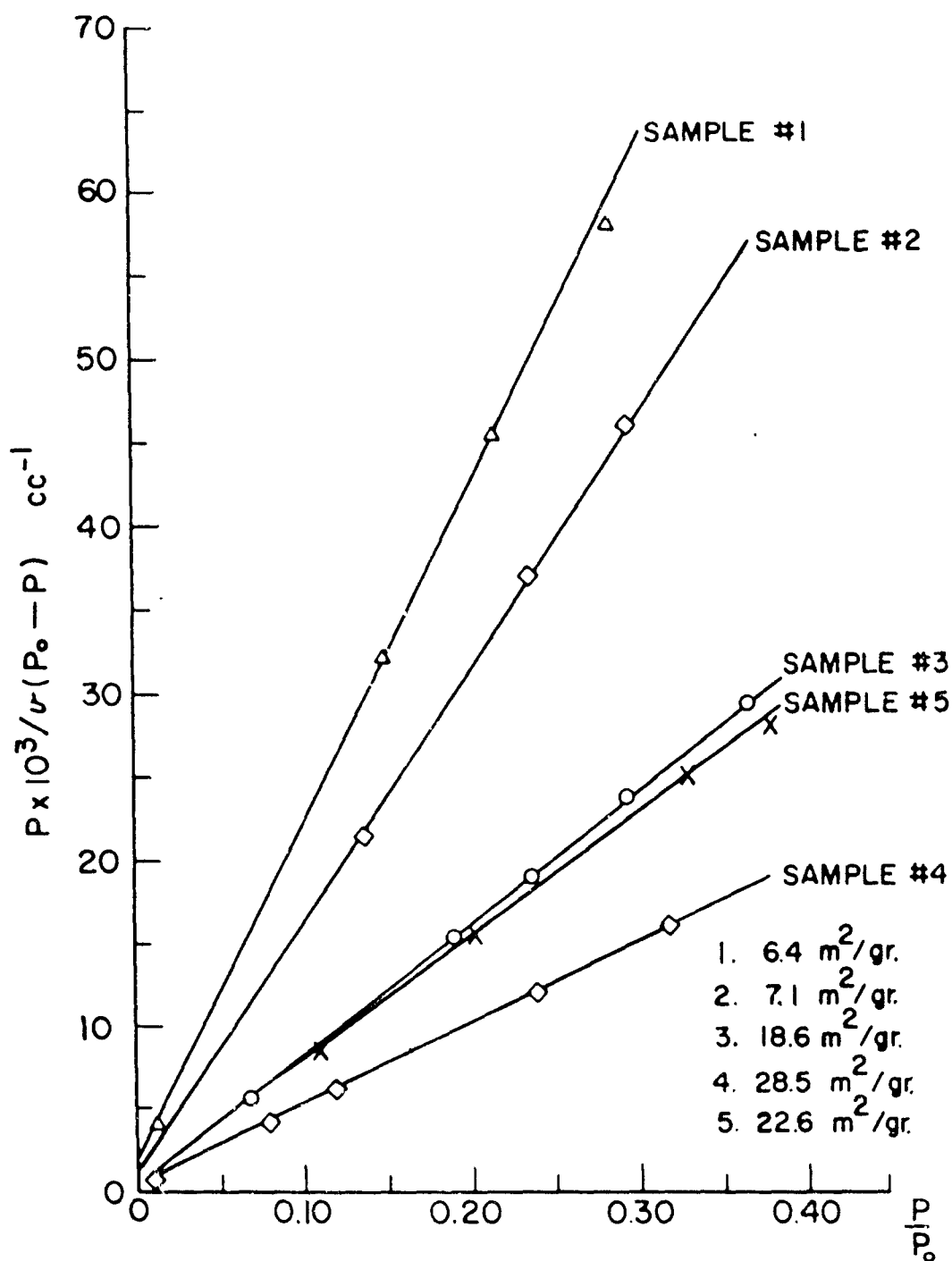


FIGURE 17