

Section 1

KINETIC STUDIES OF CATALYST POISONING DURING METHANOL SYNTHESIS AT HIGH PRESSURES

1.1 Introduction

Both low-pressure and high-pressure catalytic processes are now being used industrially to convert CO/H₂ gas mixtures (syngas) to methanol. Qualitatively, the high pressure process catalysts have been reported to have a higher resistance to poisoning by sulfur-containing contaminants in the feed gas than the low pressure process catalyst. But no quantitative poisoning data are available for either catalytic process. We have examined several methanol synthesis catalysts to obtain data on catalytic deactivation by sulfur-bearing contaminants. Our measurements were performed at temperatures and pressure typical of industrial usage.

For these measurements we used a high-pressure bench-scale apparatus that incorporates a Berty gradientless reactor (described in Section 1.2). We have determined methanol yield as a function of temperature, space velocity, total pressure, and exposure to feedstocks containing gaseous sulfur compounds. Our objectives were

- To quantitatively evaluate the sulfur-poisoning kinetics of typical methanol synthesis catalysts by hydrogen sulfide, carbonyl sulfide and thiophene.
- To identify the mechanism of interaction of sulfur-bearing feedstock contaminants with the catalyst surface.

1.2 Experimental Program

This section describes in detail the high-pressure, gradientless reactor system designed and constructed for use on this project (Figure 1-1).

1.2.1 Gas Supply Section

The gas supply section contains three separate sources of gas. One is a cylinder of high pressure nitrogen used to purge the system and to set pressures on dome-loaded regulators. A second source contains two cylinders, one of nitrogen and one of hydrogen, used to supply hydrogen-in-nitrogen mixtures (1 to 10% hydrogen) to reduce and activate the catalysts. The third source is the gaseous feedstock composed of 33 vol% CO, 65 vol% H₂, and 2 vol% CO₂ supplied in special aluminum cylinders (84 ft³ STP pressurized to 1650 psig).

The gas flow and pressure control system is designed to supply

- The nitrogen purge gas at the desired pressure with flow monitored and controlled by the vent rotameter at the outlet of the system
- The nitrogen-hydrogen mixture for catalyst activation by separate flow regulators and rotameters followed by in-line mixing before admission to the reactor system
- The reaction gas mixture with pressure control achieved with special dome-loaded regulators manufactured by Grove Regulator Company. (These regulators were chosen for their wide range of pressure selection, and because the parts that contact the gas are primarily aluminum, which is inert to H₂S.)

1.2.2 Compressor

To achieve pressures greater than those available from the gas cylinders (1650 psig), we installed a model 46-13421 diaphragm compressor manufactured by Aminco (American Instrument Company) of Silver Spring,

Maryland. It has maximum output pressure of 10,000 psi. At the most severe reaction conditions experienced under this project (5000 psi), this compressor delivers 11 scf/hr with a 500 psi suction pressure. The system includes a bypass to allow operation without the compressor (i.e., for low pressure studies or during compressor failures), and a surge vessel to dampen the pressure fluctuations from the compressor. A Grove regulator maintains proper downstream pressure. Constant flow is assured by maintaining a constant regulated upstream pressure and a constant compressor stroke.

1.2.3 Reactor

The catalyst test reactor is a gradientless reactor designed by Berty^{1*} and manufactured by Autoclave Engineers. The reactor contains a stationary draft tube catalyst basket. The gas mixture is stirred with a turbine blade impeller driven by a variable speed Magnedrive assembly. The manufacturers supplied three concentric draft tube cylinders, and we found that the capacity of the smallest inner cylinder was about 150 grams of catalyst. Since the methanol synthesis studies were performed at high hourly space velocities (5,000-80,000 hr⁻¹), we needed a smaller catalyst load. For this purpose we fabricated an additional cylinder to fit inside the smallest draft tube supplied by the manufacturer. With this cylinder, we could operate with as little as 10 cm³ of catalyst and greatly reduce our use of the expensive synthesis gas mixture.

1.2.4 Product Handling

The effluent from the Berty reactor flows through a needle valve

* References to Section 1 are listed on page 1.15.

to reduce the pressure. A portion of the low-pressure effluent stream is diverted to the gas chromatograph. The remaining gas enters a cooling coil (immersed in tap water). The cooled stream flows into a 1-liter stainless steel cylinder where any liquid products are separated and collected. The gas continues through a rotameter to the vent.

1.2.5 Product Analysis

The methanol yield is determined by gas chromatographic analysis of aliquots taken from the effluent stream. Methanol is separated from the other components on a Porapak S column and detected in a thermal conductivity cell. Methanol yields are reported in terms of the fraction of carbon monoxide converted.

A flame photometric detector was used to measure the concentration of hydrogen sulfide in the reactor effluent by allowing an aliquot of gas to pass through a Porapak QS column. The detector response was calibrated against a wet chemical collection and titration technique (NIOSH Analytical Method for Hydrogen Sulfide, No. S4, validated by SRI).

1.2.5 Procedure

Before each experimental run, the reactor was charged with a weighed mass of catalyst, then purged with dry nitrogen. The catalyst was reduced by slowly raising the reactor temperature to 500 K while a dilute hydrogen stream (2 vol% H₂ in dry N₂) flowed through the bed at a total pressure of 1 atm. The flow of reducing gas was sustained for at least 24 hr.

To test the gradientless operation of the Bertly reactor we made some initial runs with a low pressure process catalyst. Under constant reaction conditions (temperature, pressure, and space velocity), the

methanol yield remained constant as the reactor impeller velocity was varied over the range 500 to 1500 rpm. In all subsequent runs, we used an impeller velocity of ≥ 1000 rpm.

1.2.6 Catalysts

For our study we obtained samples of two low pressure process industrial catalysts: one was manufactured by Catalysts and Chemicals, Inc., Louisville, Kentucky, and was designated C79-1. It was supplied in the form of 1/4 x 1/8 inch cylindrical pellets. The other, of identical dimensions and form, was a proprietary formulation and we have designated it catalyst "B".

We have also examined one high pressure process catalyst designated Zn-0312 T, supplied in the form of 1/4 x 1/4 inch zinc chromite pellets by the Harshaw Chemical Company, Cleveland, Ohio.

1.2.7 Sulfur Bearing Contaminants

The sulfur compounds used as feedstock contaminants were hydrogen sulfide (H_2S), carbonyl sulfide (COS) and thiophene (C_4H_4S). In all cases, the sulfur-bearing impurity was admixed to the syngas by the gas supplier* and stored in aluminum alloy cylinders. Hydrogen sulfide was supplied in a number of concentration levels in the range 0.06 to 75 ppm; COS , 0.2 to 2 ppm; and C_4H_4S , 3 to 5 ppm. The contaminant concentration in each cylinder was determined at the time the unit was put into service. Although the sulfur impurity level often differed from the nominal value, it did not vary between the filled and

* Airco Industrial Gases, Santa Clara, California

near-empty state of a particular cylinder, indicative of good mixing and little loss by reaction with the cylinder walls.

1.2.8 Catalyst Surface Examination

Samples of catalyst pellets were examined by Auger electron spectroscopy (AES) before and after reaction. Fractional surface concentrations were derived from the measured peak-to-peak heights I_i of the Auger-electron first-derivative peaks (Figure 1-2). Such a procedure² is meaningful in the interpretation of AES spectra, provided line-shape changes do not occur, and the spectra are obtained with a constant set of instrumental parameters and a fixed specimen geometry. Our AES spectra conform to these conditions. Consequently, the fractional surface concentration X of component i is given by

$$X_i = \alpha_i I_i / \sum_j \alpha_j I_j \quad (1)$$

where the denominator is the sum over the major peaks of all the elements that appear in the spectrum. The inverse relative AES yield, α , is a correction factor that accounts for differences between elements in ionization cross section, electron escape depth, and the transmission of the AES analyzer. In principle, values of α can be determined empirically from surfaces of pure elements or from compounds of known stoichiometry. To a reasonable approximation, however, AES peak heights for a pure substance are proportional to $1/\sqrt{E}$, where E is the energy of the AES peak.³ It is convenient to select one element as an arbitrary standard for which $\alpha = 1$. Then,

$$\alpha_i = I_i^0 / I_i^0 \text{ standard} = \sqrt{E_i} / \sqrt{E_i \text{ standard}} \quad (2)$$

where superscript o refers to the pure element. We estimated values of α_i by Equation (2), choosing oxygen ($E = 510$ v) as our standard.

1.3 Experimental Results

1.3.1 Low Pressure Process Catalysts

Under our experimental conditions (475 to 500 psig, 460 to 515 K) and in the absence of sulfur contaminants the freshly reduced catalysts exhibited typical aging characteristics, exemplified by high initial activity followed by a gradual decrease to a constant conversion level after about 4.5 hr, with a methanol yield about one-half that observed initially. In some runs with sulfur-free syngas, we allowed the feed stream to continue during the daytime but interrupted it each night and replaced it with a stream of dry nitrogen at 1 atm pressure. When the reactor was repressurized with syngas after these overnight intervals, the catalytic activity matched closely the activity observed before the feed stock flow was interrupted. In one case only, after an interruption of several days, impaired, yet stable catalytic activity was observed.

Methanol yield varied predictably with space velocity. Figure 1-3 shows typical yield variation as a function of the reciprocal space velocity, τ (a measure of residence time). The deviation from linearity in these plots for large values of τ (i.e., low space velocities) cannot be attributed to the approach to equilibrium conversion. At 517 K and 475 psig the calculated equilibrium yield⁴ of methanol is about 40 vol%. More likely these results reflect the appearance of desorption limited rate processes or inhibition by reaction products.⁵

While mass transport in the gas phase in the Berty reactor is fast relative to chemical reaction rate at sufficiently high space velocities (Figure 1-3), the relative magnitude of intrapellet (pore) diffusion had to be established separately. Intraparticle mass transport can be characterized empirically by evaluation of the Weisz-Prater criterion ϕ ,⁶ which specifies that diffusional effects are negligible if

$$\bar{\phi} = (dn/dt)(1/C)(R^2/D) \leq 0.3$$

where (dn/dt) is the observed reaction rate per unit volume of catalyst, C is the reactant concentration (outside the pellet), R is the pellet radius, and D is the diffusivity of the reactant in the gaseous medium. All these parameters were measured for our system with the exception of D , which was estimated for our reaction conditions from Gilliland's empirical formula.⁷ We calculate for the highest methanol-formation rate observed in our experiments with a pelleted catalyst,

$$\bar{\phi} = 0.03$$

indicating that intraparticle diffusional resistance is absent. Parallel experiments with catalysts of widely different particle sizes supported this conclusion. As shown in Table 1-1, methanol formation rate varied little when the mean particle size of the catalyst was reduced by nearly an order of magnitude.

Space velocities used in our experiments ranged from 5000 to 10,000 hr^{-1} . In these ranges in a gradientless reactor,⁸ the fractional conversion of reactant under steady-state conditions is a linear function of the reaction rate r , the mass of catalyst W , and the feed rate of reactant F :

$$(X_1 - X_0) = rW/F \quad (3)$$

where X_1 and X_0 are the CO concentrations in the feed stream and the effluent, respectively. The fractional yield of methanol $Y = (X_1 - X_0)/X_1$, hence Equation (1), becomes

$$r = YX_i F/W \quad (4)$$

In our experiments, $X_i = 0.0147$ mole/liter (STP), and W was in the range 5 to 30 g. Consequently, we calculated values of reaction rate in units of $\text{mole}\cdot\text{hr}^{-1}\cdot(\text{g catalyst})^{-1}$ from measured values of yield and feed rate.

During our experiments with the C79-1 catalyst, we varied the reactor temperature in the range 460 to 515 K. The measured values of reaction rate fit an Arrhenius plot (Figure 1-4), which suggests an overall activation energy $E = 25.6$ kcal/mole for methanol synthesis in the absence of sulfur compounds in the feed stream.

After we had established a steady methanol yield at specified temperature, pressure, and space velocity, we began catalyst poisoning experiments. The sulfur-free syngas was replaced with a $\text{CO}/\text{H}_2/\text{CO}_2$ gas mixture of the same composition but with a known concentration of a sulfur-containing impurity. The rate of catalyst poisoning was determined by monitoring the decrease in methanol yield as a function of time. At inlet concentrations of H_2S in the range from 1.6 to 40 ppm catalyst activity, decay followed a logarithmic law (Figure 1-5).

An exponential decay in activity caused by catalyst surface poisoning is characteristic of a heterogeneous reaction system in which deactivation occurs by a first-order reaction in a kinetically controlled regime, i.e., where diffusional transport is not rate limiting. One model⁹ for such a process is applicable to the gradientless reactor, in which the catalyst is bathed in a gaseous environment of uniform composition. We have developed a more versatile model that includes convective flow of gas through a fixed catalyst bed and therefore takes into account concentration gradients of poison in the bed. The mathematical development of this model is presented in an Appendix to this report.

According to both models, the slope of the exponential decay of reaction rate with exposure is the product of the poisoning rate constant k and the concentration n_i of the sulfur contaminant in the reactor inlet stream. However, if the decay rate deviates from an exponential curve, then the mass transport processes may have begun to affect the poisoning rate. Such behavior might occur with pelleted catalysts when the active sites on the outer surfaces of the pellet are completely poisoned. At this point further loss in activity will be governed by the rate at which poison diffuses into the pore structure of the pellet. Factors that determine the time (measured from the onset of poisoning) required for such intraparticle diffusion to become rate-controlling, include the mass of the bed, the pore structure of the catalyst, the size of the pellets, and the concentration of the poison in the feedstock. We observed exponential decay for periods as long as 55 hr with 1/4 x 1/8-inch pellets of C79-1 catalyst exposed to syngas containing 3 ppm H_2S or less (Figure 1-5). However, with a 40 ppm feed-stream-concentration of H_2S , deviation from the exponential decay law was observed in less than 1 hr (Figure 1-6). Consequently, we have used the model to evaluate poisoning rate constants from experimental runs in which less than 40 ppm H_2S was added to the feedstock. The analysis of our data for the low pressure process catalysts yields the values of k presented in Tables 1-2 and 1-3. These results allow us to compare the sulfur resistance of the catalysts quantitatively and to evaluate catalyst life in the presence of various sulfur compounds in the feed stream.

1.3.2 High Pressure Process Catalyst

To compare the sulfur resistance of high- and low-pressure process catalysts, we made measurements with the Zn-0312 catalyst at 3000 psig and 573 K. Under these typical industrial conditions, we found it necessary to reduce the mean catalyst particle diameter to 0.85 mm (16 to 24 mesh)

and to increase the space velocity to values greater than $40,000 \text{ hr}^{-1}$ to attain gradientless conditions in the reactor during methanol synthesis (Figure 1-7). Catalyst activity decayed exponentially with time of exposure to feedstocks containing sulfur-bearing contaminants in the concentration range 0.08 to 1.5 ppm. The deactivation rate as a function of H_2S concentration is shown in Figure 1-8, and the average values of poisoning rate constant for H_2S and thiophene are summarized in Table 1-3.

1.4 Discussion

Significant quantitative differences exist in the sulfur poisoning resistance of the catalysts examined in this study. In the absence of sulfur contaminants, catalyst "B" exhibits an average specific conversion ($12 \pm 2 \times 10^{-3} \text{ mole hr}^{-1} \cdot \text{g catalyst}^{-1}$) about twice that of C79-1 (Figure 1-4) at 503 K. However, the poisoning rate constant for catalyst "B" exposed to H_2S is more than five times that of C79-1. Hence, the enhanced activity of catalyst "B" is gained at the expense of a considerably greater sensitivity to poisoning by H_2S . The high pressure process catalyst, Zn-0312, exhibited a poisoning rate constant comparable to that of C79-1 (Table 1-3).

The respective magnitudes of the poisoning rate constants (Table 1-3) indicate that thiophene is comparable to hydrogen sulfide as a catalyst poison for the low pressure process catalyst, but only about half as effective as H_2S for the high pressure process catalyst.

An experiment with feed gas containing 1.20 ppm COS and less than 60 ppb H_2S showed the contribution of COS to the decay rate of the catalysts to be negligibly small relative to that of H_2S . No measurable decay in methanol synthesis activity was noted over a period of about 4 hr. Actually, the COS was detected in the exit stream from the reactor at concentrations comparable to those in the feed stream. Apparently

COS conversion by reaction with H_2 ($COS + H_2 \rightleftharpoons CO + H_2S$) did not occur to a measurable degree although it is favored thermodynamically.

The absence of catalyst poisoning by COS under the conditions of our study must be due to kinetic limitations, since on the basis of thermodynamic calculations, the metal sulfides could form (Table 1-4). As discussed in some detail in Section 4 of this report, we need to consider the stability of surface sulfides rather than bulk metal sulfides if we are to completely explain catalyst deactivation by sulfur poisons.

To provide some insight into the mechanism of catalyst poisoning, we measured the surface and bulk characteristics of the fresh and the used catalyst pellets by AES and x-ray diffraction. AES is a highly surface selective technique that gives the elemental composition of the outermost atomic layers of a solid, typically to a depth of less than 20 Å. Comparison of the AES results of a catalyst surface before and after exposure to H_2S -containing feed gas show some striking changes in surface composition after exposure. The elemental surface compositions of a fresh catalyst (run A) and reduced samples (runs B-D) before exposure to the $CO/H_2/CO_2$ mixture are comparable (Table 1-5). Similarly, little change is noted when the catalyst has come into contact with syngas nearly free of sulfur compounds (run E) in the Bertly reactor at 500 psig. When the catalyst is exposed to H_2S -containing feed gas at low levels (< 4 ppm), the sulfur signal increases and the signals associated with copper, zinc, and oxygen (runs F, G) decrease. Thiophene produces similar effects (run H). These AES results, in combination with the x-ray diffraction data, suggest that surface sulfur builds up gradually. In contrast, in runs I-L involving higher partial pressures of H_2S , a significant surface enrichment with Cu relative to Zn becomes apparent.

At the Auger electron energies of the elements under study (Figure 1-2), the AES data represent the composition of the first four

or five atomic layers nearest the catalyst surface. A decrease in the concentration of one component with the appearance or increase of another, therefore, may be interpreted as selective deposition of a surface phase. Thus, a decrease in Cu and Zn with the appearance of sulfur on the catalyst composed of copper and zinc oxide, strongly suggests the formation of a multilayer adsorbate of sulfur on the surface (Table 1-5, Runs F and G). At the low concentrations of H_2S used in these runs, the formation of surface sulfur adspecies on copper is favored. Indeed, the negative heat of adsorption of sulfur on copper is reported¹⁰ to be about 10 kcal/mole greater than the heat of formation of bulk Cu_2S . At higher concentrations of H_2S , however, the ZnO phase in the catalyst is converted to ZnS, and concurrently, the surface concentration of copper increases beyond that of the freshly reduced catalyst (Table 1-5, Runs I-L). Also, the oxygen content of the surfaces of these catalysts is diminished to the degree expected as a result of sulfidation of ZnO. These data suggest that a surface reconstruction has occurred during which copper atoms have diffused selectively to the surface. The driving force for this process may be the formation of a microcrystalline copper sulfide phase undetectable by x-ray diffraction because of line broadening. The surface enrichment with copper detectable by AES at relatively high levels of H_2S generally agrees with observations made by low energy electron diffraction (LEED) during exposure of single oriented crystals of copper to H_2S .¹¹ These studies indicated that the process of dissociative adsorption with localization of sulfur atoms at sites of maximum coordination is followed, at a critical surface coverage, by the sequential formation of islands of sulfur atoms and subsequently, by a two-dimensional surface sulfide with copper atoms interspersed in the surface layer. This sequence of surface processes suggests that, first, the copper atoms disappear because of the prevalence of a sulfur adlayer, and that, then, the copper reappears as the two-dimensional surface sulfide begins to form.

Catalyst "B" exhibits similar behavior, although the AES data for the fresh sample (Run M, Table 1-5) indicate a much higher copper content (Zn/Cu = 1.1) than for the other catalyst (Zn/Cu = 1.9). As observed previously with C79-1, surface sulfiding at low levels of H₂S (< 1 ppm) in the feedstock causes a general decrease in the surface concentration of Zn and Cu. However, at an H₂S level > 40 ppm, total depletion of Zn occurs from the surface of this catalyst, a change in the same direction but of much greater magnitude than that encountered with C79-1.

The AES examination of the high pressure process catalyst (Harshaw Zn-0312) demonstrated the buildup of sulfur on its surface during exposure to H₂S or C₄H₄S (Table 1-6).

To gain some insight into the surface distribution of the components of C79-1 catalyst a sample was examined by scanning electron microscopy (SEM). In addition to micrographic examination to reveal the structure of the surface, energy dispersive x-ray analysis was used to examine the lateral distribution of the major surface components. The results (Figure 1-9) indicate that the Al-containing phase is dispersed throughout a Cu- and Zn-containing matrix. Within the limit of resolution of the instrument it is not possible to differentiate between Cu and Zn phases, but it is quite apparent that Cu and Zn are highly interdispersed. The formation of a solid solution¹² between copper and Al₂O₃ or ZnO cannot be excluded. Indeed, the strong surface enrichment with Cu exhibited during sulfidation of the C79-1 catalyst suggests that dispersed Cu and ZnO phases exist in intimate contact with each other. Possibly, the ZnO acts as a "sink" for the S-species and thereby retards the sulfidation of the copper crystallites. An indication that such selective distribution of sulfur might occur is found in the absence of a bulk copper sulfide phase after extensive H₂S exposure of the catalysts

(Table 1-5). The smaller poisoning rate constant C79-1 compared with catalyst "B" (Table 1-2) may be actually related to the difference in Zn/Cu (Table 1-5).

In summary, catalyst C79-1 operating at 500 psig, and catalyst Zn-0312, operating at 3000 psig, have sulfur poisoning rate constants of similar magnitude. As a result, in choosing a catalytic system for methanol synthesis, operating factors other than sulfur sensitivity need to be taken into consideration. In the low-pressure process the catalyst with the higher methanol-synthesis activity (catalyst "B") is much more susceptible to H_2S poisoning than catalyst C79-1. In this case, the effort expended in feed gas cleanup (removal of sulfur compounds) must be weighed against reduced catalyst activity when a catalyst is selected for industrial methanol synthesis. Our studies provide basic kinetic information on catalyst poisoning in terms of absolute rate constants. These data may be used in catalyst and process selection for a wide range of operating conditions with various sulfur contaminants in the feedstock.

1.5 References

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Table 1-1

CATALYST EFFECTIVENESS ASSESSMENT^a

| Mean Pellet Diameter (mm) | Bulk Density (g·cm ⁻³) | Mass of Charge (g) | Flow Rate (STP L·hr ⁻¹) | CH ₃ OH Formation Rate (mol·hr ⁻¹ ·g·cat ⁻¹) |
|------------------------------|---------------------------------------|-----------------------|--|---|
| 6.3 x 3.1 (cylinders) | 1.05 | 10.5 | 125-250 | 6.2 x 10 ⁻³ |
| 2.9 (6-8 mesh) | 1.12 | 5.0 | 55-160 | 7.1 x 10 ⁻³ |
| 0.85 (16-24 mesh) | 1.22 | 5.0 | 42-120 | 6.3 x 10 ⁻³ |

^aCatalyst: C79-1; T = 503 K, P = 500 psig.

Table 1-2

DEACTIVATION OF LOW PRESSURE PROCESS CATALYSTS BY
HYDROGEN SULFIDE DURING METHANOL SYNTHESIS^a

| Catalyst | H ₂ S Concentration ^b n ₁ (mole.l ⁻¹) · 10 ⁶ | Activity Decay Rate kn ₁ (hr ⁻¹) × 10 ² | Poisoning Rate Constant k (l.mole ⁻¹ hr ⁻¹) × 10 ⁻⁴ |
|----------------------|---|--|--|
| C79-1 (T = 503 K) | 1.3 | 1.1 | 0.85 |
| | 2.6 | 2.5 | 0.96 |
| | 26. | 15.3 | 0.59 |
| | | | $\bar{k} = 0.80 + 0.14$ |
| "B" (T = 514 K) | 0.07 | 0.50 | 7.4 |
| | 0.86 | 3.05 | 3.6 |
| | | | |

^a Space velocity: 10⁴ hr⁻¹; pressure: 500 psig; feedstock: 32 CO, 66 H₂, 2 CO₂ (vol%);
1/4 x 1/8-inch catalyst pellets.

^b At temperature and pressure of reactor.

Table 1-3

COMPARISON OF POISONING RATE CONSTANTS FOR METHANOL SYNTHESIS CATALYSTS^a

| Process Type | Catalyst | Feedstock Contaminant | | Reaction Temperature (K) | Poisoning Rate Constant k ^b (ℓ -mole ⁻¹ ·hr ⁻¹) x 10 ⁻⁶ |
|---------------|----------|-----------------------|---------------------|--------------------------|---|
| | | Type | Concentration (ppm) | | |
| Low pressure | C79-1 | H ₂ S | 1.6-33 | 503 | 0.80 ± 0.14 |
| | | COS | 0.6-9 | 503 | 0 |
| | | Thiophene | 3-5.4 | 503 | 1.02 ± 0.18 |
| High pressure | 'B' | H ₂ S | 0.08-40 | 514 | 5.5 ± 1.9 |
| | | COS | 0.01-7 | 514 | 0 |
| | Zn-0312 | H ₂ S | 0.08-1.5 | 573 | 0.77 ^c |
| | | | | 573 | 0.33 ^c |
| | | Thiophene | 5.2 | 573 | 0.77 ^c |
| | | | | 573 | 0.33 ^c |

^a Evaluated at space velocity = 10⁴ hr⁻¹.

^b Average values.

^c Space velocity = 8.07 x 10⁴ hr⁻¹.

Table 1-4

EQUILIBRIUM H₂S LEVELS OVER CATALYST COMPONENTS UNDER SYNTHESIS CONDITIONS^a

| Reaction | Equilibrium Constant K _p | S-Component Threshold ^b (ppm) |
|--|--|---|
| (1) 2 Cu + H ₂ S = Cu ₂ S + H ₂ | 3.26 × 10 ⁵ | 2.0 |
| (2) 2 Cu + COS = Cu ₂ S + CO | 4.20 × 10 ⁵ | 0.8 |
| (3) Cu + H ₂ S = CuS + H ₂ | 44.9 | 1.4 × 10 ⁴ |
| (4) Cu + COS = CuS + CO | 57.7 | 5.4 × 10 ³ |
| (5) ZnO + H ₂ S = ZnS + H ₂ O ^c | 7.1 × 10 ⁷ | 7 × 10 ⁻⁷ |
| (6) ZnO + COS = ZnS + CO ₂ | 8.2 × 10 ¹⁰ | 2.4 × 10 ⁻⁷ |

^a At 503 K and mole fractions of N_{H₂} = 0.66, N_{CO} = 0.32, and N_{CO₂} = 0.02.

^b H₂S (or COS) level above which the metal sulfide would be favored thermodynamically.

^c Initial water mole fraction of 46 ppm calculated from water-gas shift equilibrium of reactant gas.

Table 1-5

SURFACE COMPOSITION OF METHANOL SYNTHESIS CATALYST BY AUGER ELECTRON SPECTROSCOPY

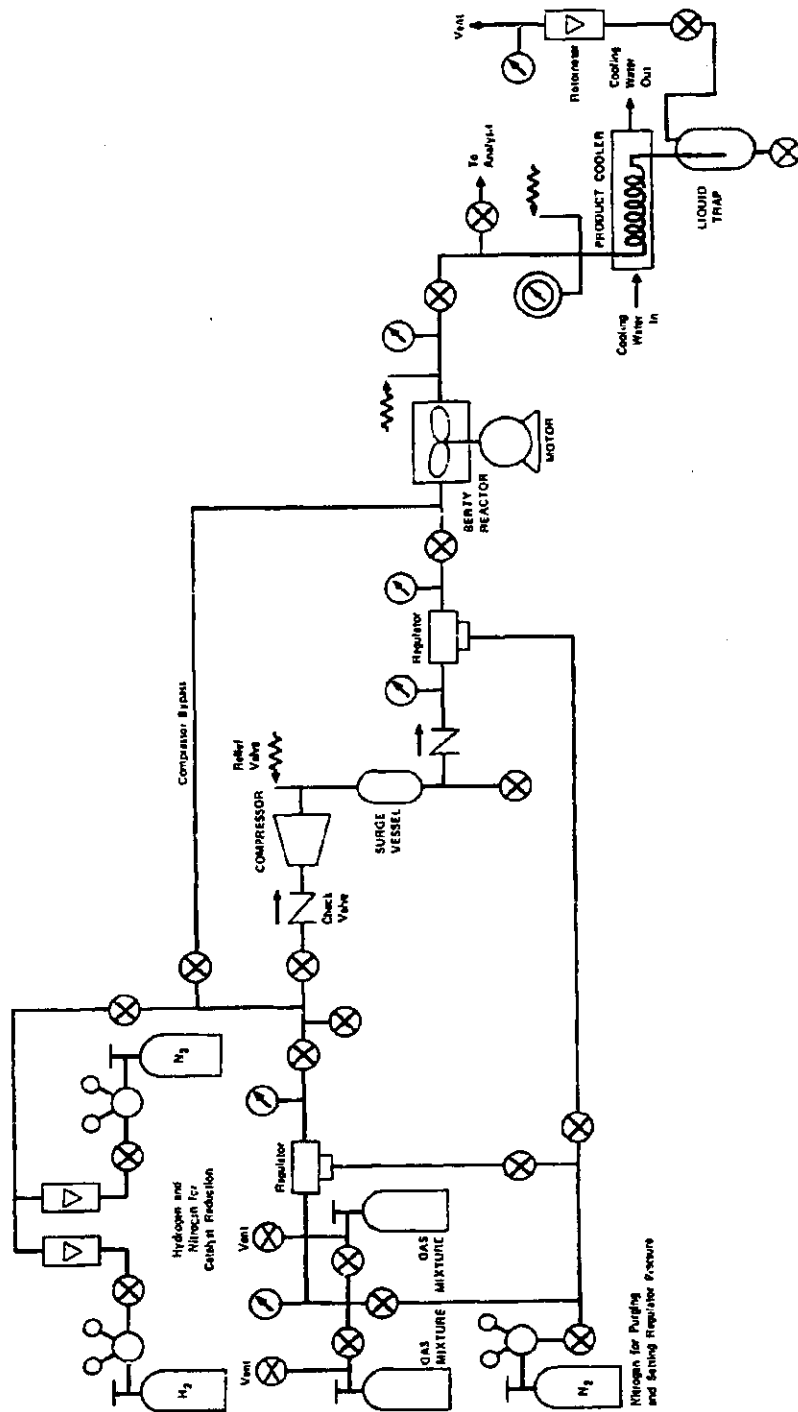
| Catalyst Run | Catalyst History | Total Exposure (mole H ₂ /g cat) x 10 ³ | Surface Composition (%) | | | | | | | Bulk Composition ^a | |
|--------------|------------------------------------|--|-------------------------|----|----|----|----|----|-----|-------------------------------|--------------|
| | | | S | Cl | C | O | Cu | Zn | Al | | Zn/Cu |
| C78-1 | A | 0 | 0 | 0 | 2 | 46 | 14 | 27 | 12 | 1.9 | CuO, ZnO |
| | B | 0 | 0 | 5 | 40 | 11 | 26 | 19 | 2.4 | Cu, ZnO, CuO (trace) | |
| | C | 0 | 0 | 4 | 41 | 12 | 29 | 14 | 2.5 | Cu, ZnO, CuO (trace) | |
| | D | - | 0 | 2 | 44 | 13 | 26 | 15 | 1.9 | Cu, ZnO | |
| | E | 0 | 1 | 0 | 2 | 44 | 14 | 27 | 10 | 2.0 | Cu, CuO, ZnO |
| | F | 0 | 15 | 2 | 8 | 31 | 9 | 23 | 12 | 2.6 | Cu, ZnO, ZnS |
| | G | 0.09 | 22 | 4 | 4 | 30 | 7 | 18 | 15 | 2.5 | Cu, ZnO |
| | H | 0.11 | 3 | 2 | 2 | 43 | 9 | 23 | 18 | 2.6 | - |
| | I | 0.50 | 16 | 0 | 3 | 28 | 21 | 20 | 12 | 1.0 | Cu, ZnS |
| | J | 0.58 | 33 | 0 | 11 | 16 | 23 | 6 | 12 | 0.3 | Cu, ZnS, ZnO |
| | K | 0.41 | 24 | 4 | 8 | 24 | 15 | 10 | 15 | 0.7 | - |
| | L | 0.78 | 27 | 1 | 4 | 19 | 23 | 18 | 7 | 0.8 | Cu, ZnS, ZnO |
| "D" | | | | | | | | | | | |
| M | fresh | 0 | 0 | 0 | 47 | 21 | 22 | 10 | 1.1 | CuO, ZnO | |
| N | syngas (H ₂ S = 40 ppm) | 0.02 | 20 | 0 | 12 | 34 | 16 | 0 | 19 | 0 | Cu, ZnS, ZnO |
| P | syngas (H ₂ S < 1 ppm) | - | 6 | 3 | 1 | 39 | 14 | 19 | 17 | 1.4 | Cu, ZnO |

^a By x-ray diffraction

Table 1-6

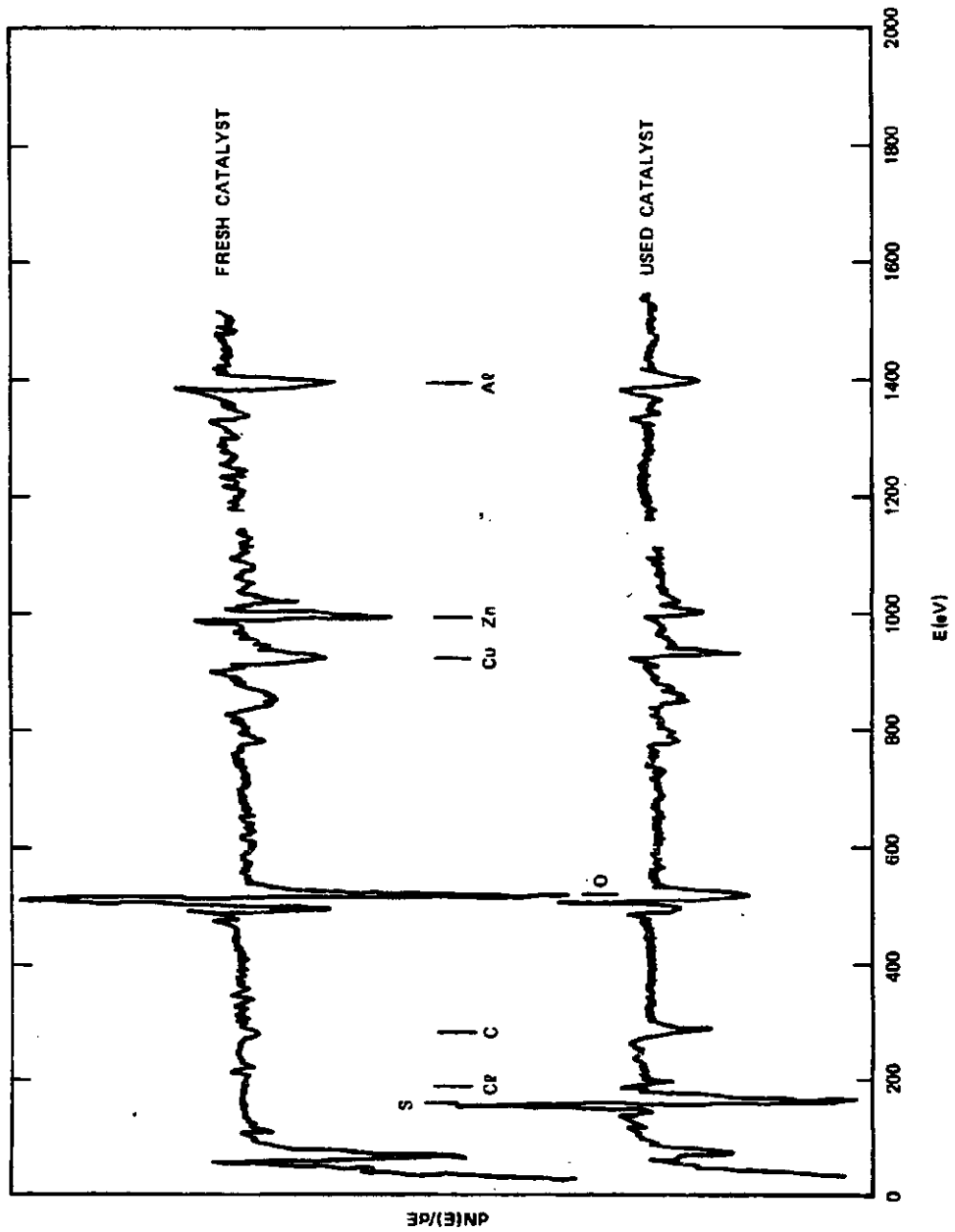
SURFACE COMPOSITION OF Zn-0312
METHANOL SYNTHESIS CATALYST BY AES

| Catalyst History | Surface Composition (%) | | | | | | |
|----------------------------------|-------------------------|-----|-----|----|----|-----|-------|
| | S | Cl | C | O | Zn | Cr | Zn/Cr |
| Fresh (activated) | 0 | 0 | 6.1 | 60 | 29 | 4.6 | 6.3 |
| Syngas, 1.5 ppm H ₂ S | 4.5 | 2.2 | 2.0 | 59 | 26 | 6.2 | 4.2 |
| Syngas, thiophene: 5.2 ppm | 0.42 | 1.2 | 3.9 | 57 | 33 | 4.9 | 6.7 |



SA-AMT-1

FIGURE 1-1 SCHEMATIC DIAGRAM OF CATALYST TEST SYSTEM



SA-4387-9

FIGURE 1-2 TYPICAL AUGER ELECTRON SPECTRA OF C79-1 CATALYST

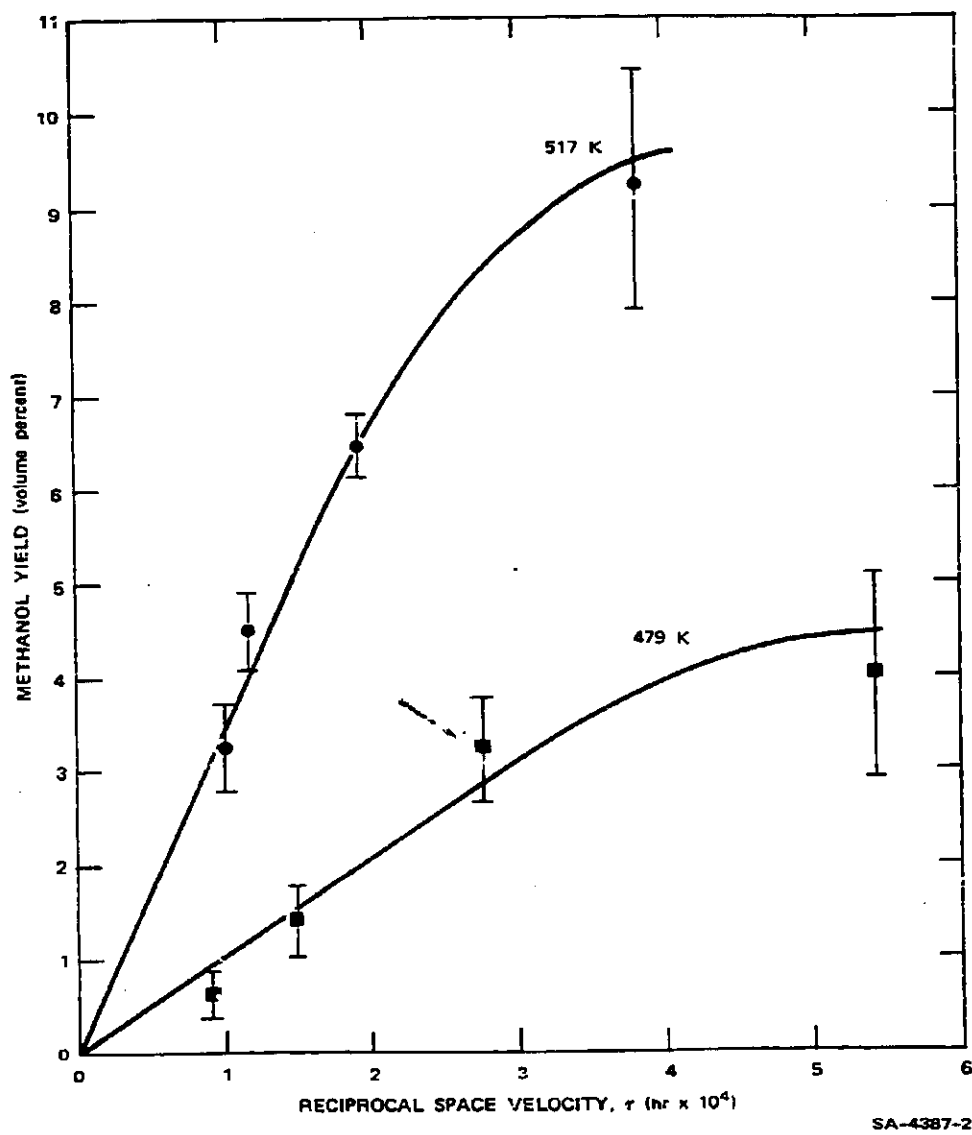
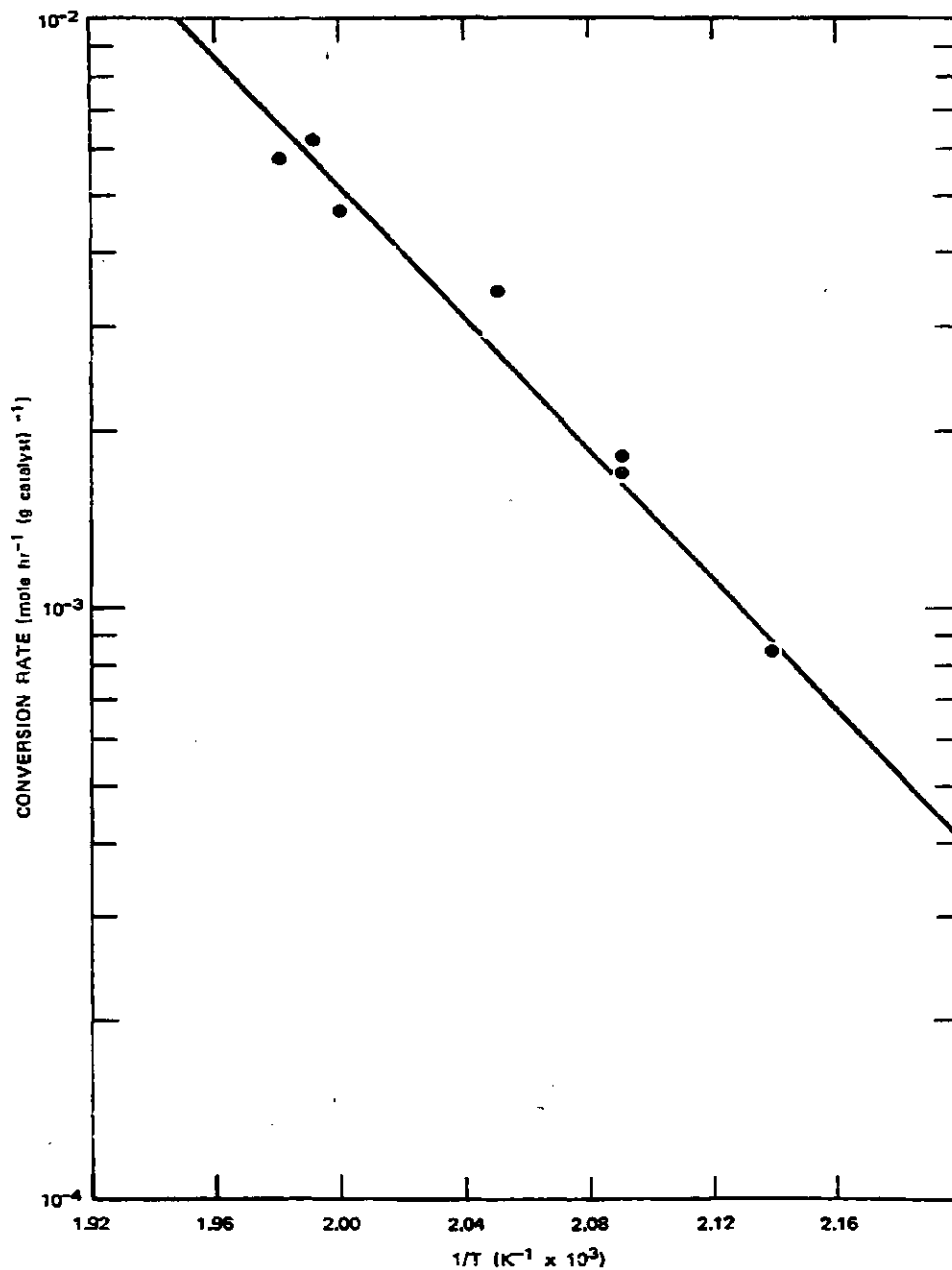


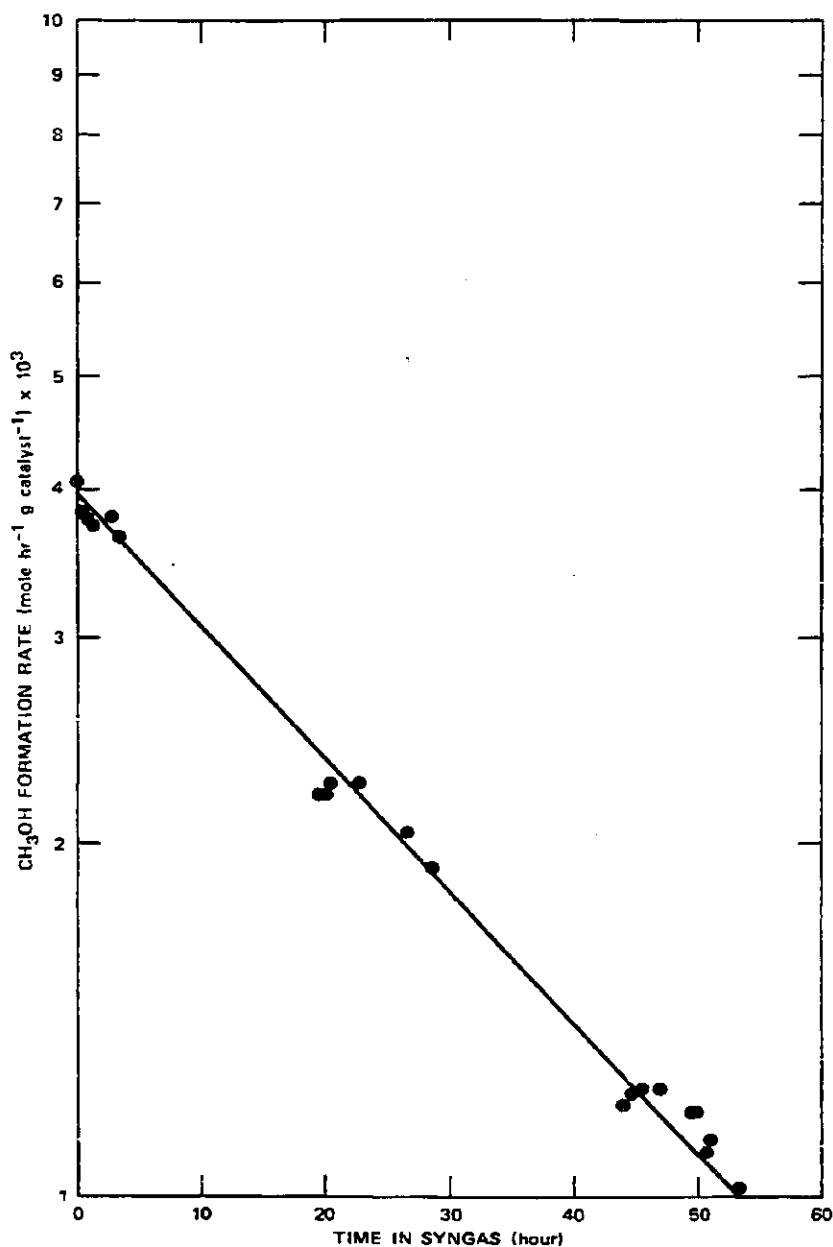
FIGURE 1-3 METHANOL YIELD AS A FUNCTION OF RECIPROCAL SPACE VELOCITY
 Feed Gas: 33% CO, 65% H₂, 2% CO₂. P = 475 psig. Catalyst: C79-1,
 1/4 x 1/8-inch pellets.



SA-4387-4

FIGURE 1-4 EFFECT OF TEMPERATURE ON RATE OF CONVERSION OF CO TO METHANOL

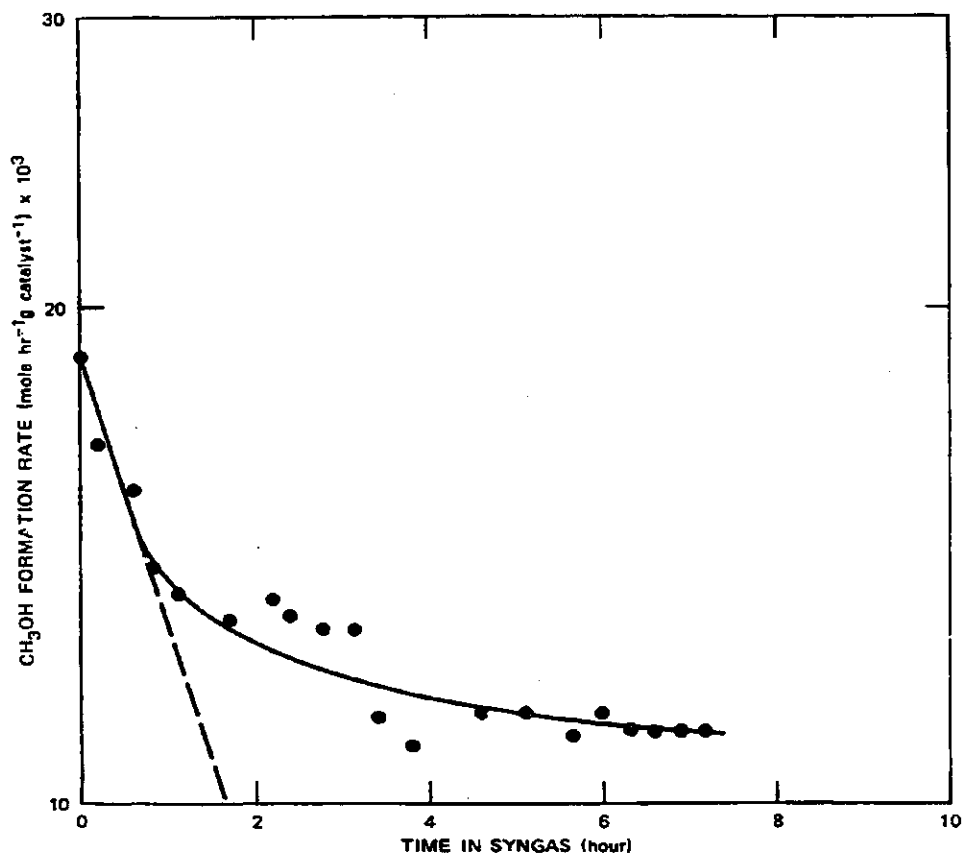
Feed Gas: 33% CO, 65% H₂, 2% CO₂. P = 475 psig. Catalyst: C79-1, 1/4 x 1/8-inch pellets.



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FIGURE 1-5 TYPICAL DECAY IN CATALYTIC ACTIVITY DURING METHANOL SYNTHESIS WITH H₂S-CONTAMINATED FEEDSTOCK

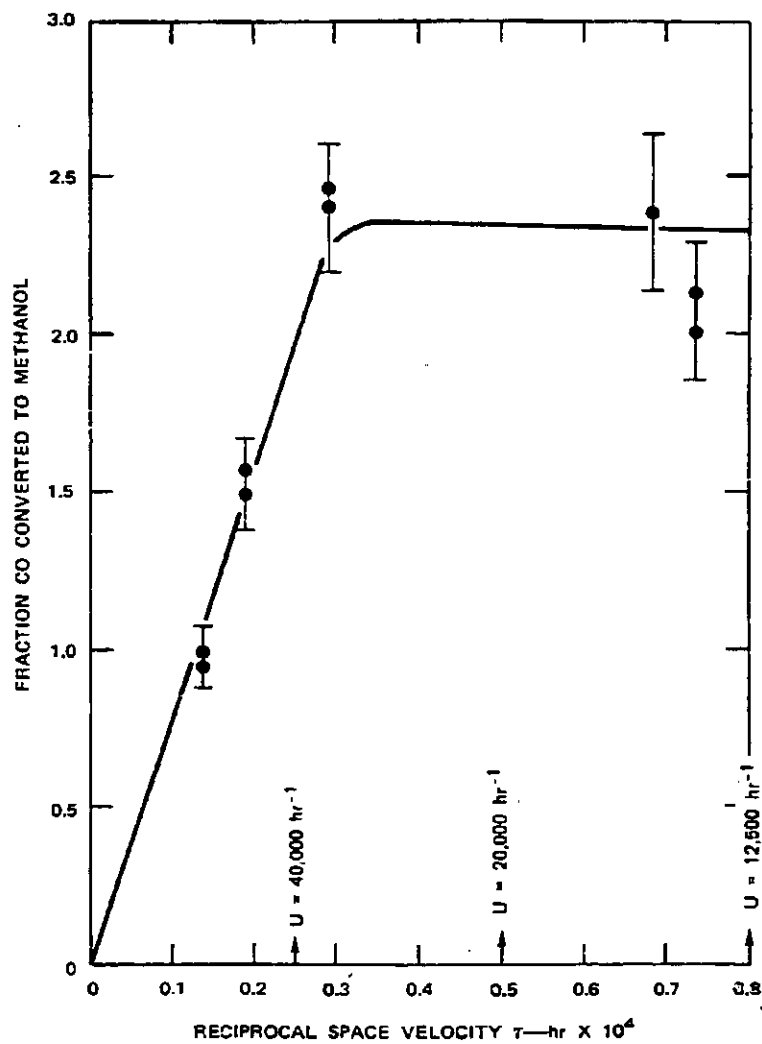
Feed Gas: 33% CO, 65% H₂, 2% CO₂, 3.2 ppm H₂S. Space Velocity = 10⁴ hr⁻¹, T = 503 K, P = 500 psig. Catalyst: C79-1 1/4 x 1/8 inch pellets.



SA-4287-69

FIGURE 1-6 METHANOL SYNTHESIS ACTIVITY DECAY WITH HIGH LEVEL H₂S FEEDSTOCK CONTAMINATION

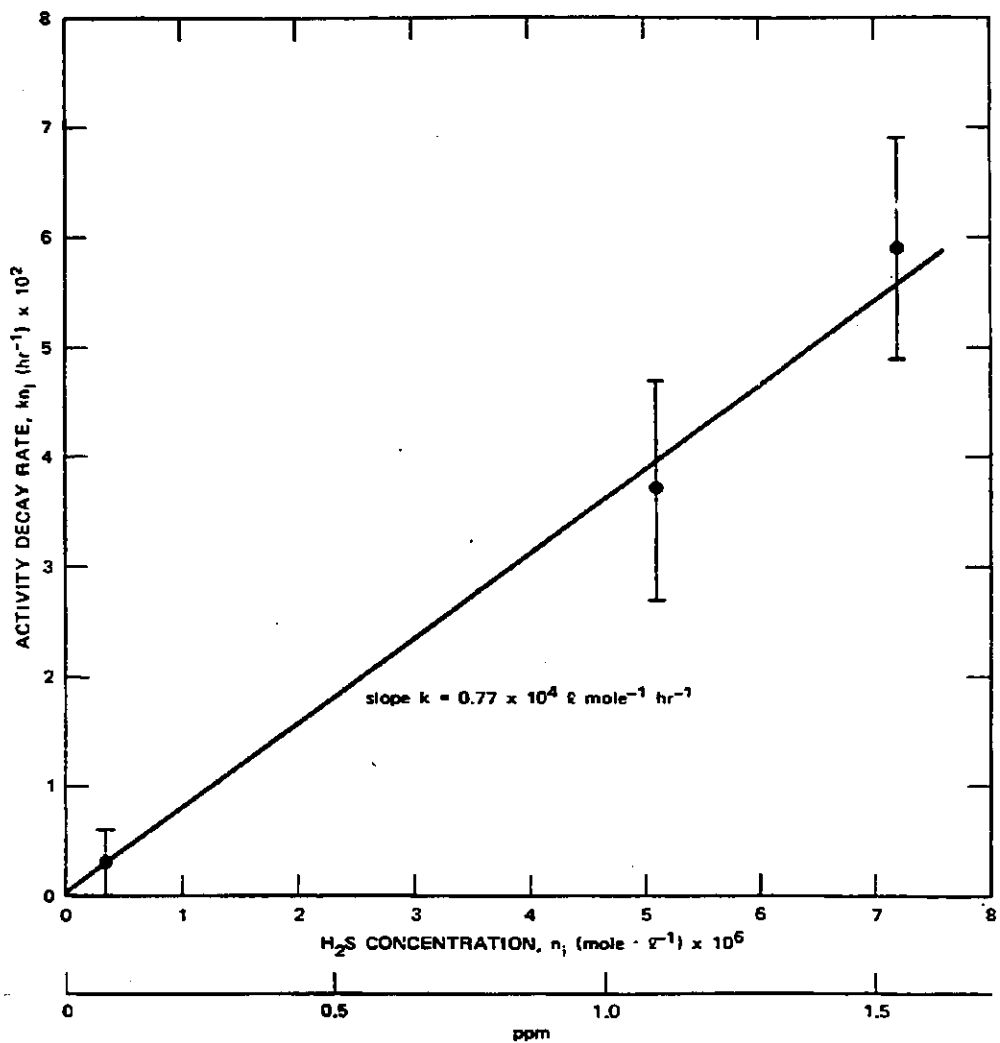
Feedgas: 33% CO, 65% H₂, 2% CO₂, 40 ppm H₂S. Space Velocity: 10⁴ hr⁻¹,
 T = 514 K, P = 500 psig. Catalyst: "B" 1/4 x 1/8 inch pellets.



SA-4387-11

FIGURE 1-7 METHANOL YIELD AS A FUNCTION OF RECIPROCAL SPACE VELOCITY

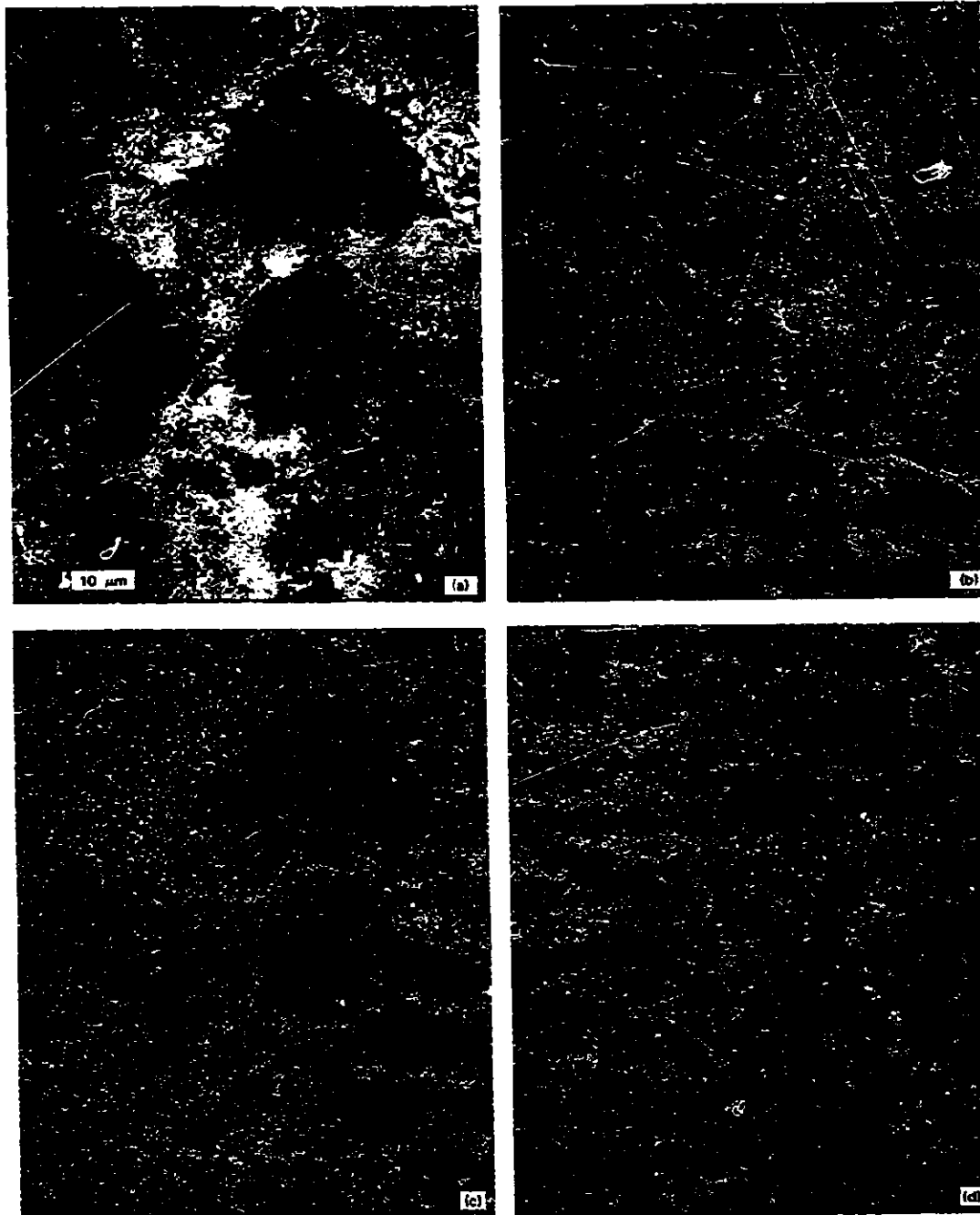
Feedstock: 33 vol% CO, 2 vol% CO₂, Balance H₂. Pressure: 3000 psig.
 Temperature: 566 K. Catalyst: Zn-0312, 0.7-1 mm particles.



SA-4387-70

FIGURE 1-8 DEACTIVATION OF METHANOL SYNTHESIS CATALYST Zn-0312 AT DIFFERENT H₂S CONCENTRATIONS IN FEED STREAM

Space Velocity: 80650; Synthesis Gas: 32 CO, 66 H₂, 2 CO₂ (vol %);
 Temperature: 573 K., Pressure: 3000 psig.



SA-4387-36

FIGURE 1-9 SCANNING ELECTRON MICROGRAPH (a) AND ENERGY DISPERSIVE X-RAY ANALYSIS (b, c, d) OF C79-1 METHANOL SYNTHESIS CATALYST

Dark regions in micrograph (a) are revealed to be particles of Al_2O_3 immersed in a Cu/Zn matrix by the x-ray maps for Al (b), Zn (c), and Cu (d).