

## Section 9

### SULFUR POISONING OF ALUMINA-SUPPORTED RUTHENIUM CATALYST

#### 9.1 Introduction

In the evaluation of catalysts for Fischer-Tropsch synthesis the sensitivity of the catalysts to sulfur-bearing feed gas contaminants is of major concern. Based on a theoretical analysis of irreversible surface poisoning<sup>1\*</sup> we have developed an experimental procedure to evaluate quantitatively the rate constant for catalyst deactivation. As shown in the appendix, a significant feature of this analysis is the "breakthrough time" ( $t_{1/2}$ ), an exposure interval at which the concentration of poison in the exit stream is just half that in the feed stream. By this analysis we can evaluate the rate constant for catalyst poisoning ( $k_p$ ) and the volumetric site density of poison acceptor sites ( $s_0$ ). For the experimental measurements of the intrinsic rate of catalyst deactivation we select operating conditions at which external and internal transport limitations become negligible,<sup>1</sup> such as low Thiele modulus, high Reynolds number, and large density ratio of catalyst sites to poison molecules.

#### 9.2 Experimental Details

The apparatus, operating under continuous flow conditions, contained the finely powdered catalyst (> 200 mesh) under study on a glass frit sealed into a small volume Pyrex reactor. The feed gas whose composition could be adjusted to yield the desired  $H_2/CO/H_2S$  ratio was fed into the

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\* References for Section 9 are given on page 9.4.

reactor and samples were withdrawn from the exit line and analyzed by gas chromatography (GC) to determine the concentrations of CO, CH<sub>4</sub>, and H<sub>2</sub>S.\* The space velocity ranged from 2 to 3 x 10<sup>5</sup> hr<sup>-1</sup>, the temperature was kept fixed at 553 K (thermocouple in catalyst bed). The catalyst was ground, and we chose a size fraction finer than 200 mesh for the catalytic measurements. The incoming H<sub>2</sub>S concentration was 4.5 ppm.

Preparation of 5% Ruthenium on Alumina—Granules of alumina Shell 10891-117 were ground and sieved to produce a powder finer than 150 Tyler mesh. The amounts of Ru Cl<sub>3</sub> (Fisher Scientific Company) and Al<sub>2</sub>O<sub>3</sub> necessary to ruthenium catalyst after reduction to the metal were weighed out in a dry box under nitrogen. The ruthenium trichloride was dissolved in a little water, a drop of 12 N HCl was added, and the volume of the solution was adjusted to give a stiff paste when added to the weighed alumina. The paste was stirred constantly over low heat until a dry powder formed. The powder was then heated in air to convert the ruthenium trichloride to a water insoluble form. The finished catalyst was reduced in hydrogen at 723 K before use in experiments. On the surface of the finished catalyst no chlorine was detectable by AES. For the purpose of comparison, we used a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (Girdler G-65, 25 wt% Ni) under identical conditions of feed gas composition, space velocity, and reaction temperature. This catalyst was reduced in flowing H<sub>2</sub> (1 atm) at 723 K for 18 hr before the start of the catalytic measurements.

### 9.3 Experimental Results

Typical data of the variation with time of the relative H<sub>2</sub>S concentration in the exit gas from the reactor are shown in Figure 9-1.

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\* For H<sub>2</sub>S analysis we used a flame-photometric detector with a sensitivity extending to 10 ppb.

As suggested by the theoretical analysis<sup>1</sup> we are plotting the function  $(n_1/n) - 1$ , where  $n_1$  represents the poison concentration in the inlet stream (kept constant at 4.5 ppm  $H_2S$  in these experiments) and  $n$ , that in the exit stream at time  $t$ . In this experiment the sulfur breakthrough occurred at  $t_{1/2} = 625$  min. Combined with the graphical analysis of the slope of the curve, which is proportional to  $k_p n_1$  in the semilogarithmic plot of Figure 9-1, we calculate for the  $Ru/Al_2O_3$  (5 wt%) catalyst the poisoning rate constants ( $k_p$ ) and acceptor site densities ( $s_o$ ) summarized in Table 9-1. The results for the  $Ru/Al_2O_3$  catalyst taken at two  $H_2/CO$  mixture ratios yield an average value of  $k_p = 1.42 \times 10^6 \pm 0.2$   $(mol/cm^3)^{-1} sec^{-1}$ , compared to a value of  $k_p = 2.47 \times 10^6 (mol/cm^3)^{-1} sec^{-1}$  for  $Ni/Al_2O_3$ . The apparent variation in  $k_p$  for  $Ru/Al_2O_3$  with  $H_2/CO$  ratio is within the experimental error of the measurements, estimated to be  $\pm 15\%$ .

#### 9.4 Discussion

Our results indicate that the  $Ru/Al_2O_3$  is somewhat less sensitive than  $Ni/Al_2O_3$  to  $H_2S$  poisoning as reflected in the relative magnitude of the poisoning-rate coefficients. If we compare the values of  $s_o$  (Table 9-1), we observe that this difference in sulfur sensitivity is not the result of differences in the initial number density of poison acceptor sites in the two catalysts. On Ni surfaces infrared adsorption measurements<sup>2</sup> have demonstrated that both bridge-bonded and linearly bonded adsorption of sulfur atoms occurs, similar to that observed during CO adsorption. Therefore, the number density of CO adsorption sites determined for the  $Ni/Al_2O_3$  catalyst under study yields a value of  $2.2 \times 10^{-4} mol/cm^3$  catalyst as compared to a value of  $2.7 \times 10^{-4} mol/cm^3$  catalyst evaluated from the  $H_2S$  poisoning experiments. The differences in  $k_p$  between  $Ru/Al_2O_3$  and  $Ni/Al_2O_3$  by a factor of nearly 2, therefore, indicate variation in the surface structure of the crystallites in the

supported catalysts, a property that may vary with catalyst preparation and catalyst aging.

### 9.5 References

1. C. M. Ablow and H. Wise, Kinetic Analysis of Catalyst Deactivation by Irreversible Surface Poisoning (Appendix)
2. R. T. Rewick and H. Wise, Study of H<sub>2</sub>S and CO adsorption on Alumina Supported Nickel Catalysts by Infrared Spectroscopy, Preprint Am. Chem. Soc., Div. of Petroleum Chemistry, 22 (4), 1324 (1977).

Table 9-1

CATALYST POISONING REACTION KINETICS IN THE PRESENCE OF H<sub>2</sub>S AT 553 K

Catalyst	$U$ $\text{hr}^{-1} \times 10^{-5}$	H <sub>2</sub> /CO	$k_p$ $(\text{mol}/\text{cm}^3)^{-1} \text{sec}^{-1} \times 10^{-6}$	$n_i^*$ (mol/cc)	$s_o$ (mol/cc) cat
Ru/Al <sub>2</sub> O <sub>3</sub> (5 wt%)	1.80	4.40	1.55	2.0	3.8
Ru/Al <sub>2</sub> O <sub>3</sub> (5 wt%)	1.69	2.95	1.30	2.0	3.1
Ni/Al <sub>2</sub> O <sub>3</sub> (25 wt%)	2.34	2.95	2.47	2.0	2.7

\* H<sub>2</sub>S inlet concentration corresponding to 4.5 ppm.

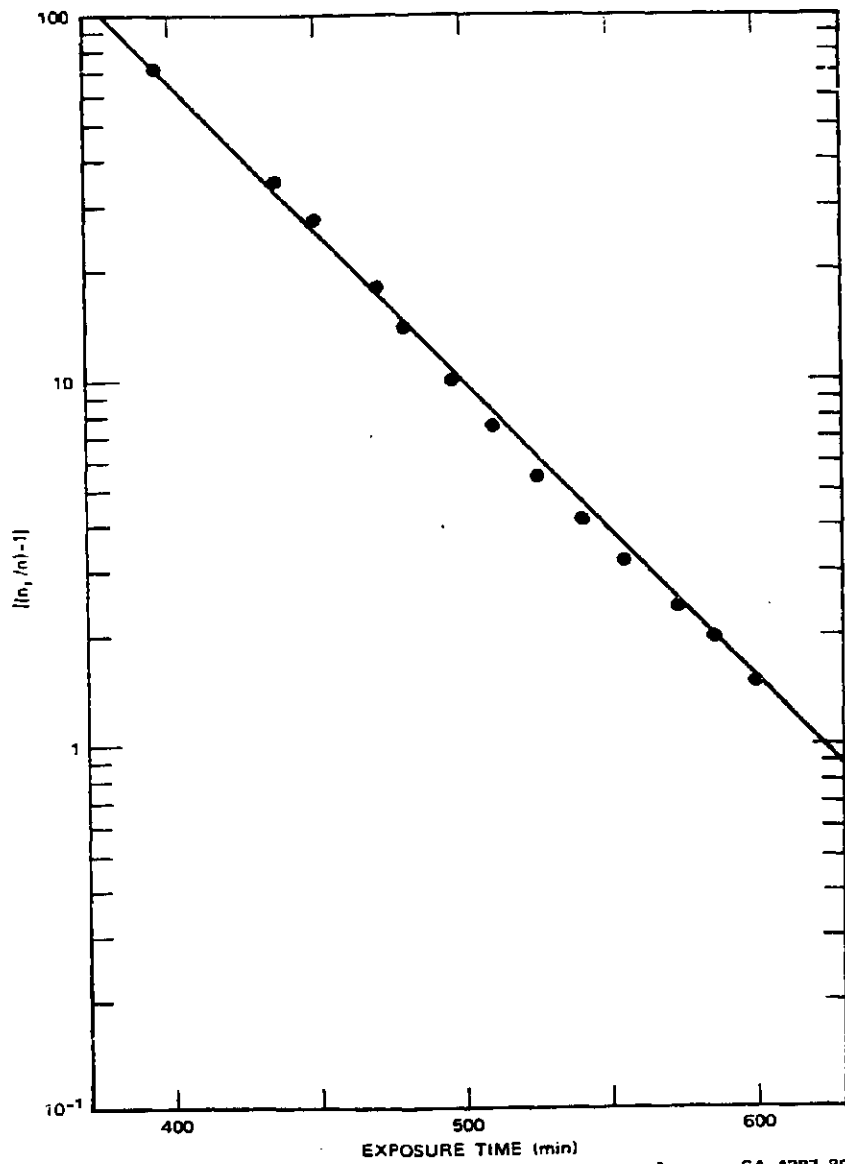


FIGURE 9-1 KINETIC ANALYSIS OF CATALYST POISONING BY H<sub>2</sub>S (4.4 ppm H<sub>2</sub>S: 553 K; H<sub>2</sub>/CO = 4.4 b.v.)