# SULFUR POISONING OF CATALYSTS: A STUDY OF ACTIVITY DECAY IN METHANOL SYNTHESIS AND FISCHER--TROPSCH CATALYSIS. FINAL REPORT

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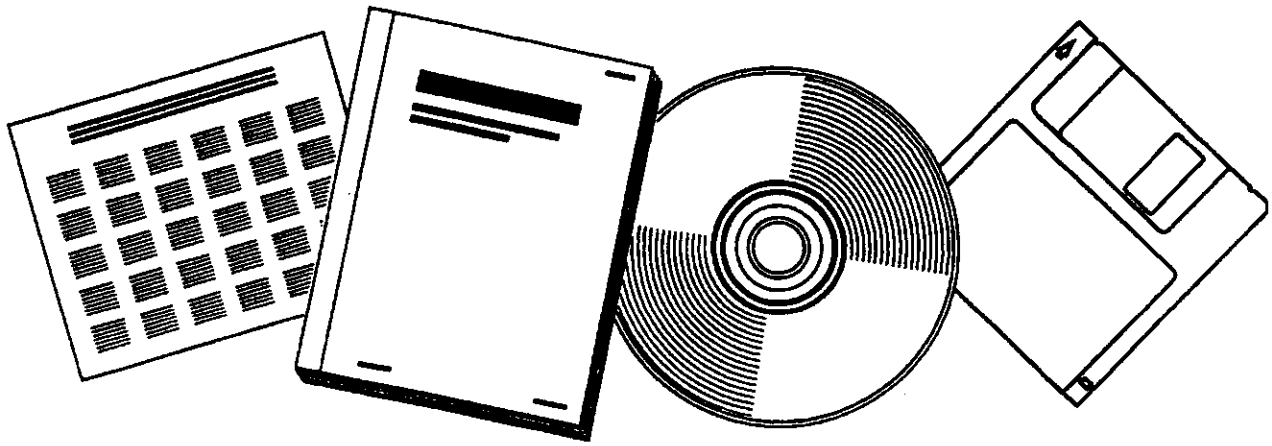

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*Final Report PERC-0050-8*

# SULFUR POISONING OF CATALYSTS: A Study of Activity Decay in Methanol Synthesis and Fischer-Tropsch Catalysis



*By:* B. J. GIKIS, W. E. ISAKSON, J. G. McCARTY, K. M. SANCIER, S. SCHECHTER, P. R. WENTRCEK, B. J. WOOD, and H. WISE (Project Leader)

*Prepared for:*

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Attention: Daryl B. Morse
Sr. Contract Administrator

Contract No. E936-2-0060
SRI Project No. PYU 4387

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## SUMMARY

The objective of this research program was to study the deactivation of commercial catalysts used for the production of liquid fuels from carbon monoxide and hydrogen. This final report describes the two main areas of research:

Part I: Sulfidation of Methanol-Synthesis Catalysts

Part II: Carburization of Fischer-Tropsch Catalysts

The research is divided into a number of specific tasks, discussed and described in detail in separate and self-contained sections within each part of the report. A brief summary of the results of our study is given below.

In methanol synthesis (Part I) significant effort was devoted to the problem of sulfur poisoning of several commercial high-pressure and low-pressure catalysts at space velocities and pressures encountered in industrial practice (Section 1). This work was supplemented (Section 2) by studies of sulfur segregation and distribution on catalyst surfaces measured by Auger electron spectroscopy (AES) and by surface area "titration" measurements (Section 3). In the investigation of reactivation of sulfur-poisoned catalysts, we examined the thermodynamics of bulk and surface sulfur in equilibrium with $H_2$ for the copper and iron systems (Section 4). In addition, we carried out some preliminary studies on oxidative reactivation of a sulfur poisoned methanol synthesis catalyst.

In the area of Fischer-Tropsch catalysis (Part II), we examined the processes of bulk carburization and of surface carbon deposition on

promoted iron-based catalysts (Section 5). This work included kinetic studies by thermogravimetric analysis (TGA), thermomagnetic analysis (TMA), and electron spin resonance spectrometry (ESR). We addressed the problems of catalyst swelling and breakup in addition to the kinetics of carbon deposition. By AES we evaluated the depth distribution of promoter near the catalyst surface during carburization. We supplemented this experimental effort with thermochemical calculations to establish the phase-boundary compositions of the stable products (CO, $CO_2$, $H_2O$, $H_2$, $CH_4$) in equilibrium with Hagg carbide, cementite, and magnetite (Section 6). Recent interest in the application of ruthenium-based catalysts for Fischer-Tropsch synthesis led to studies of carbon buildup (Section 7) and sulfur poisoning (Section 8) of alumina-supported ruthenium catalysts.

During this study, we have:

- Obtained quantitative data on the sensitivity of low-pressure and high-pressure methanol synthesis catalysts to hydrogen sulfide, carbonyl sulfide and thiophene feedstock impurities
- Gained insight into the mechanism of sulfur deposition on catalyst surfaces by different sulfur-bearing contaminants
- Assessed the regeneration potential of sulfur-poisoned catalysts
- Quantitatively evaluated the rates of carburization and carbon deposition on iron catalysts and characterized the equilibrium catalyst composition under synthesis conditions

- Estimated the carbon-fouling tendency and sulfur resistance of alumina-supported ruthenium catalysts

The following SRI staff members participated in this research effort: B. J. Gikis, W. E. Isakson, J. G. McCarty, K. M. Sancier, S. Schechter, P. R. Wentrcek, H. Wise (project leader) and B. J. Wood.

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