



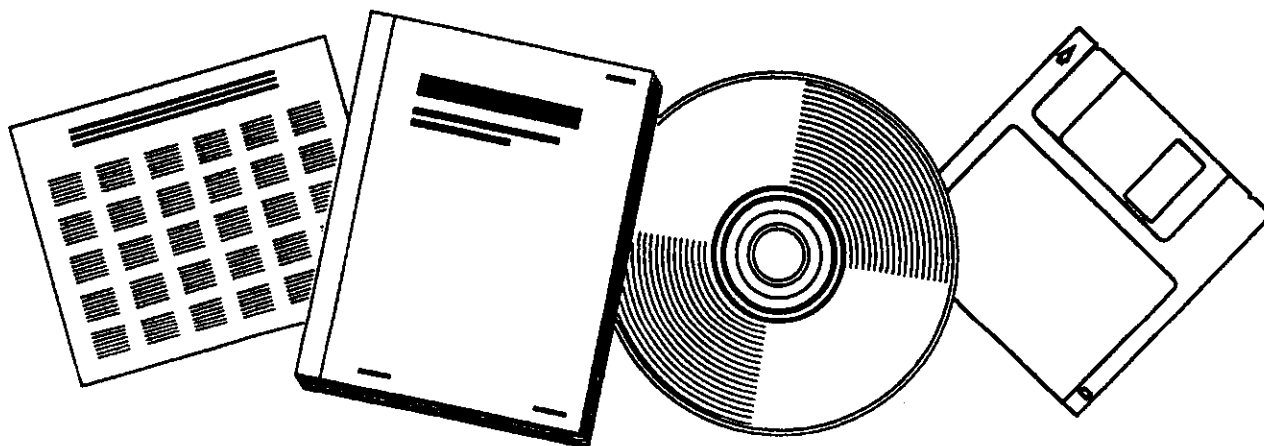
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**AUGER AND REACTION STUDIES OF POISONING BY
SULFUR AND REGENERATION OF METAL SYNTHESIS
GAS CATALYSTS. PROGRESS REPORT, DECEMBER
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SULFUR AND REGENERATION OF METAL SYNTHESIS
GAS CATALYSTS

Progress Report

For Period December 8, 1975, to December 8, 1976

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I. ABSTRACT

CO methanation rates have been measured in the all-glass internal recycle reactor developed for this work. The methanation rate over the cylinder Ni film catalyst at 400°C is 3.9 sec^{-1} initially, and the catalyst undergoes deactivation to a value of 1.8 sec^{-1} , comparable with a reported value of 2.5 sec^{-1} . The activation energy for Ni film on alumina is 24 kcal/mole, that for Ni film on silica is 17.8 kcal/mole comparable to values for Ni on these supports. The kinetics suggest that CO dissociation is rate limiting; carbon on the Ni is easily hydrogenated off. H_2S causes severe deactivation and regeneration after sulfur poisoning is not easily achieved by oxidation in the reactor. However sulfur is easily removed from Ni by oxygen from a molecular leak in the high-vacuum chamber of the Auger electron spectrometer. Atmospheric pressure studies using an ante-chamber connected to the spectrometer chamber show that sulfur cannot be removed from Ni under conditions similar to those in the reactor because of rapid oxide growth which buries the sulfur preventing removal. Standards allowing determination of concentration as well as chemical state for Ni, O, S and C have been developed.

II. RESEARCH OBJECTIVES AND SCOPE

The main objective of this work is to improve our currently incomplete understanding of the rate and mechanism of sulfur poisoning and of regeneration of metal catalysts used in converting synthesis gas ($CO+H_2$) to gaseous (CH_4) and liquid hydrocarbon products. Improved understanding of deactivation and of regeneration should result in development of catalysts with improved sulfur tolerance and the designation of improved operating procedures. A second objective is to bridge the gap between reaction studies at practical conditions and surface studies carried out under ultra-high vacuum conditions. This is required to allow quantitative interpretation of our surface concentration measurements in terms of the actual surface condition under steady-state reaction conditions and will be of value to others also. Rates of sulfur adsorption on metal films and rates and extents of deactivation of metal-film catalysts are being quantitatively measured, and mechanisms of sulfur deactivation are to be postulated based on the data obtained. Rates of reaction as a function of surface concentration of sulfur are to be determined. Rates and mechanisms of regeneration of sulfur deactivated metal foils and films in O_2 and H_2 as a function of temperature and gas-phase composition are being determined. The work will concentrate on Ni, Co and Fe but will also include other elements and combinations thereof (alloys).

III. DESCRIPTION OF RESEARCH EFFORT

The research involves a three-part experimental program. In the first part quantitative kinetics of CO hydrogenation are being determined in a flow-reactor system in the absence of sulfur and as a function of sulfur (H_2S) concentration. The reactor developed for this work is an all-glass or all-quartz internal recycle reactor. The catalyst is a metal film thrown on the outside of an alumina or glass cylinder. Film thickness can be varied so that quantitative kinetic studies can be made on a thick film which can also be studied by Auger electron spectroscopy, giving quantitative surface composition without support interference to relate to observed catalytic activity. Thin, discontinuous films which approximate real supported metal catalysts can also be studied for activity and surface composition.

In the second part of the program the same or an identical metal film to that used to determine catalytic activity is contacted under the same conditions used in the kinetic studies with $H_2/CO/H_2S$ in an ante-chamber attached to the Auger electron spectrometer to reproduce the same surface condition on the metal film as was present in the kinetic studies, and Auger electron spectroscopy is used to measure the sulfur concentration on the surface of the metal

film. Thus, a direct relationship can be established for the first time between the sulfur concentration on a metal surface and the catalytic activity of the surface. Activity measurements are not being made in the ante-chamber because of the inability to obtain quantitative kinetics on a small metal surface area in such a chamber. Sulfur removal (catalyst regeneration) studies are being done on the metal films in the ante-chamber.

The third part of the program involves in situ studies of sulfur adsorption on and removal from the same metal film catalysts in the main vacuum chamber of the Auger electron spectrometer. A molecular leak system allows the metal surface to be contacted with an $H_2/CO/H_2S$ mixture at widely varying conditions with simultaneous Auger analysis of the metal surface. This part of the research is used to establish sulfur adsorption isotherms, and sulfur removal rates and removal mechanisms. It is also being used to allow us to bridge the gap between the atmospheric pressure measurements and measurements made at ultra-high vacuum. Development of an understanding of how to translate surface measurements made at ultra-high vacuum conditions to the conditions which exist at the surface under higher-pressure steady-state reaction conditions is essential to the effective exploitation of electron spectroscopy in this and other catalysis research.

The essential features of the experimental program are: (a) quantitative measurements of catalytic activity are being related directly to surface sulfur concentrations, and (b) high and low pressure surface studies are being done to help define mechanisms of catalyst deactivation and of catalyst regeneration and to help bridge the gap between ultra-high vacuum conditions and higher pressure conditions. When the system has provided a quantitative picture for nickel under CO hydrogenation conditions, studies will be directed toward establishing directions which could lead to the development of a sulfur tolerant catalyst and the development of practical regeneration procedures.

IV. PROGRESS TO DATE

The flow reactor system, including an all-glass and an all-quartz internal recirculation reactor, has been developed and is operating. Initial studies showed that H_2S (even in low concentrations, e.g., 1 ppm, in H_2) reacted with glass to form a sulfide species of unknown form. This species gave up sulfur at a level of about 0.4 ppm H_2S only in the presence of H_2 and did so for very long periods of time resulting in back contamination in "clean" runs. In the presence of helium no sulfur species appeared; adsorbed H_2S was not responsible for the back contamination, but re-admission of H_2 resulted in reappearance of H_2S in the reactor.

This problem is markedly reduced by quartz. Such back-contamination may be an unrecognized problem in other sulfur poisoning studies. To really understand sulfur deactivation it is necessary to determine methanation kinetics as a function of gas-phase sulfur (H_2S) concentration to levels of tens of parts per billion requiring quantitative control of H_2S concentrations in this range. Our analytical scheme (flame-photometric G.C.) can measure 10 parts per billion. Required film preparation and characterization techniques have been developed. Precleaning procedures for the alumina supports including heating in air to $1300^\circ C$ did not provide adequately clean alumina. Even after this high-temperature treatment very small amounts (a few ppm) of magnesium sulfate remained; this apparently underwent slow reduction by hydrogen under reaction conditions leading to a slow sulfur poisoning of the Ni film. Thus very pure alumina is required, and studies with glass supports have also been conducted to compare with the alumina-supported Ni film and to help elucidate the problems. All equipment and operational procedures for film-catalyst preparation and for reaction studies have been developed and are operating in accordance with the contract requirements.

The Auger electron spectroscopy system including the ante-chamber and molecular leak system into the main vacuum

chamber of the Auger electron spectrometer has been constructed, a quadrupole mass spectrometer has been added to the system for residual gas analysis, and a PDP-8 computer is being interfaced with the Auger electron spectrometer to allow a 10^3 - to 10^4 -fold reduction in electron beam current. The entire system with the exception of the computer interfacing has been completed, and the system has been used to study sulfur adsorption on and removal from nickel films and foils. This portion of the system is also now completed and currently all components of it are being used in these studies in accord with the contract requirements.

CO hydrogenation to methane over our cylinder Ni film catalyst has a turnover number at 400°C of 3.90 sec^{-1} initially, and the catalyst undergoes deactivation to a value of 1.80 sec^{-1} in about 15 hours, based on a roughness factor of 2.0. This compares with a value of 2.52 sec^{-1} at 400°C reported by Vannice [J. Catal. 37, 449 (1975)] for supported Ni. For Ni on glass the activity behavior was reproducible within $\pm 8\%$ over four separate films; for Ni on Al_2O_3 reproducibility has not been as good because of apparent sulfur deactivation from the support Al_2O_3 . The steady-state activity in the absence of sulfur problems undergoes only very slow activity decline with time, about 5% per 24-hour day. Most if not all of the deactivation was

reversible by hydrogenation (reduction in hydrogen but in the absence of CO) under reaction conditions; it is inferred that the deactivation observed was due to carbon formation on the surface of the nickel, and that in the presence of hydrogen only this was readily hydrogenated off as methane leaving a clean Ni surface.

Our activation energy for Ni film on Al_2O_3 is 24 Kcal/mole (200-400°C) which is equivalent to that reported by Vannice and others for supported Ni/ Al_2O_3 catalysts. Ni films on glass gave a value of 18.4 ± 0.2 Kcal/mole for four different catalysts comparable to a value of 18 ± 0.5 given by Fontaine (Ph.D. Thesis, Cornell Univ., 1973) for Ni/ SiO_2 . Thus our Ni-film catalysts give the same specific catalytic activity and the same activation energy as observed for nickel supported on both Al_2O_3 and SiO_2 and even reproduces the activity differences observed for the supported systems. It is extremely important that this be the case in order that observations made in this work where quantitative surface measurements can be done can be directly translated to the real supported metal catalyst systems.

Introduction of H_2S at levels in excess of 1ppm results in rapid deactivation to levels below our minimum level of detection in about seven hours. Catalyst activity has not been regenerable after such an experiment even after

several high-temperature oxidation-reduction cycles; this has been consistently observed in a series of runs. Similarly before sulfur (H_2S) was introduced into the reactor so that back-contamination could have been a problem, Ni film catalysts with sulfur on the metal could not be regenerated by either mild or severe oxidation-reduction cycles.

Sulfur removal from Ni films and foils has also been studied in the ante-chamber at conditions used in regeneration attempts in the internal recycle reactor. A large number of different experiments all indicated that sulfur removal did not occur under these conditions. For example, in one set of experiments a single layer of sulfur segregated on the surface of Ni (a two-dimensional surface nickel sulfide) was treated with oxygen at various conditions, ~10 torr to 760 torr and 25°C to 350°C without indication of sulfur removal. A nickel oxide formed which upon Ar ion sputtering away showed a region which contained sulfur at a depth dependent on the severity of the oxidation treatment. The integrated intensity over depth of the sulfur peak was about the same as the intensity of the sulfur peak for the monolayer of sulfur on the surface of the Ni indicating that sulfur removal by oxidation had not occurred. Further calibration standards have shown that the sulfide peak shape differs markedly from the sulfate peak shape. The

observed peak shape was always that of nickel sulfide even after oxidation, indicating that the sulfur (originally as sulfide) was not oxidized to a stable sulfate. It simply remained as an unreactive sulfide buried in nickel oxide after the oxidation cycle to immediately appear on the surface again upon reduction. Thus the Auger-ante-chamber studies have presented to this point a pretty clear picture of why the sulfur deactivated catalysts could not be regenerated in the reactor.

However under the ultra-high vacuum conditions of the main vacuum chamber of the Auger electron spectrometer a monolayer of sulfur nickel could be easily removed by oxidation using the molecular leak system built into the chamber. Sulfur removal was verified by the reduction of the sulfur signal and the appearance of SO_2 in the mass spectrometer. This seems contradictory. Others have reported sulfur removal from metal surfaces by oxygen under high vacuum conditions, but no previous studies have been done at higher pressures.

The apparent explanation is that there are two competing processes occurring: a) oxidation of the sulfur to SO_2 and (b) oxidation of the Ni to nickel oxide. At low oxygen pressures a monolayer of nickel oxide forms slowly, and the sulfur is oxidized to SO_2 and removed at a comparable rate. At the higher oxygen pressures the formation of nickel

oxide is markedly faster resulting in the rapid growth of nickel oxide which rapidly buries the sulfide, and conversion to SO_2 and removal does not occur. Studies are continuing to further our understanding of the sulfur removal process and to use this understanding to develop regenerable catalysts and successful regeneration procedures.

We have also developed techniques and standards which allow us to identify the chemical nature of sulfur and carbon on the surface of Ni from peak shape and peak position so that we can get more information than just chemical composition from our surface analysis work. Using standards to calibrate peak shapes and intensities we can quantify monolayer sulfide, bulk NiS, bulk NiS_2 , Ni sulfate, and bulk or surface oxide. Ni peak shape in the valence band region can also be used to identify oxide versus sulfide species. We have shown that a carbon species formed on the surface on Ni at high temperature is not reactive with H_2 , and is similar to the carbon in the bulk of the nickel, whereas carbon formed on the surface from CO during reaction readily reacts with H_2 under similar conditions. These two different carbon species have different peak shapes, and a catalyst under steady-state reaction conditions contains high concentrations of reactive carbon on its surface. These results are consistent with our observed kinetics which indicates that the reaction mechanism may involve dissociation of CO.

During the past year the principle investigator has spent approximately 25% of his time on this project, and the amount of effort to be expended during the remainder of the current term of the project will be from 15 to 20%.

V. CONTINUING WORK

The continuing work will concentrate on nickel. We are now determining the rates and extents of adsorption of sulfur (sulfur adsorption isotherms) on nickel using two molecular leaks and various temperatures and various ratios of H_2 - H_2S - CO . Simultaneously studies in the ante-chamber are being carried out at similar temperatures and ratios of H_2 - H_2S - CO . The objectives of this work are: (a) to determine adsorption isotherms for sulfur (H_2S) at high and low (in situ) pressures, (b) to determine how best to go from the high-pressure steady-state environment and surface condition in the ante-chamber through evacuation and movement into the main vacuum chamber of the Auger electron spectrometer for analysis with the least alteration of the steady-state surface condition, (c) to determine what changes in the surface condition occur upon evacuation and movement into the main vacuum chamber, and (d) to develop correlations between the observed surface composition in the Auger chamber and that under actual steady-state reaction conditions if a one-to-one relation does not exist. Current work

suggests that it does. A variety of experiments will be performed, and the results of each evaluated to allow determination of what happens to the surface during evacuation and movement for analysis and thus to indicate how UHV measurements should be interpreted with respect to higher-pressure steady-state surface conditions present during reaction. The results of this work provide the base for our future work and should be useful to the efforts of other groups doing surface analysis and attempting to relate it to catalytic observations.

When we are certain how to translate from UHV conditions to high-pressure conditions, we will complete our studies of the surface sulfur concentration on Ni as a function of reaction conditions using the ante-chamber. The measured catalytic activities as a function of reaction conditions will then be related to the surface sulfur concentrations observed for these conditions to give a direct relationship between surface sulfur concentration and catalytic activity.

We are studying the effect of sulfur on the methanation activity in the all-quartz internal recycle reactor system. This will provide quantitative information on the rates of deactivation and the steady-state methanation activity as a function of feed gas H_2S concentration. This

work will use the same catalyst and will exactly duplicate the conditions used in the ante-chamber studies so that a quantitative relationship between surface sulfur concentration and catalytic activity can be established.

The third activity being pursued is a study of the regeneration of sulfur-deactivated nickel catalysts. This involves the films used in the ante-chamber poisoning studies and those used in the all-quartz microreactor studies. The emphasis of this work is to determine the rate and mechanism of sulfur removal and to determine the conditions for regeneration. We feel that regeneration of sulfur-deactivated catalysts is possible, but that it is not as straightforward as the ultra-high vacuum studies suggest.

VI. PUBLICATIONS

"An All-Glass Internal-Recycle Reactor" submitted to Ind. Eng. Chem., Fundamentals (by W. D. Fitzharris & J. R. Katzer).

"AES Study of H₂ Reduction of Oxidized Polycrystalline Ni Films," Chem. Phys. Letters in print (by H. M. Windawi and J. R. Katzer).

"Reaction of H₂S with Glass in Sulfur Poisoning Studies," to be submitted to J. Catalysis (by W. D. Fitzharris and J. R. Katzer).

"AES Depth Profiling with N₂⁺ Ion Sputtering," Phys. Letters 59 (1976) 62-64 (by H. M. Windawi, J. R. Katzer and C. B. Cooper).

"Depth Profiling Unit," J. Vac. Sci. Technol. 13 (1976) in print (by H. M. Windawi).