FE-2229-11
Distribution Category UC-90c

SURFACE STRUCTURE AND MECHANISMS OF GASIFICATION CATALYST DEACTIVATION

Quarterly Report for the Period
August 1, 1978 to October 31, 1978

P. J. Reucroft
E. B. Bradley
R. J. De Angelis
G. A. Sargent

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

December, 1978

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. EX-76-C-01-2229
(formerly E(49-18)-2229)

I. ABSTRACT

A sample preparation and gas treatment system has been assembled and attached to the ESCA spectrometer. This system will allow catalysts to be reduced, gas treated, and then analyzed without being exposed to air. A sulfided Ni-Cr/$MgAl_2O_4$ catalyst has been found to be chemically similar to a similarly treated Ni-Cr/$MgSiO_3$. The SO_4/S ratio is 10% higher in the $MgAl_2O_4$ supported catalyst. The sulfur uptake is also somewhat higher in this catalyst.

Raman spectra of CO adsorbed on Ni(110) and Ni(111) at -60°C show multiple CO bands in the 2020-2032 cm^{-1} region. The bands are assigned to linear bonded CO. Frequency shifts are observed in the spectra from Ni(110) with respect to Ni(111). These shifts are toward higher frequencies in accordance with what is expected for adsorption on the close-packed (111) plane as compared to (110). The CO bands disappear upon warming the Ni samples to 0°C.

Raman spectra of O_2 on Ni(111) have also been obtained with temperatures in the -130 to 0°C range. The O_2 band is located at 1551 cm^{-1} when the temperature is -60°C and at 1554 cm^{-1} with the temperature at 0°C. This O_2 band disappears upon warming the sample to 25°C.

Initial runs with a Ni(111) single crystal specimen have produced preliminary LEED and AES data on a clean Ni(111) surface, sulfur poisoned Ni(111), and sulfur poisoned Ni(111) with CO adsorption.

Preliminary studies on the sintering rate of a silica supported nickel catalyst (C150-1-01) in an atmosphere of hydrogen indicate that the rate is more rapid under hydrogen than under a nitrogen atmosphere. Alumina supported catalysts that are heated at 500°C for 24 hours are found to be less easily reduced subsequently, in comparison with samples that are reduced without a prior heat treatment.

II. OBJECTIVE AND SCOPE OF WORK

The objective of the program is to characterize the surface structure of methanation catalysts in order to relate structural features to catalytic activity and catalyst deactivation. Surfaces to be examined include (a) single crystal nickel with well-defined crystal planes and (b) dispersed samples of nickel and nickel alloys on alumina and silica supports. The chemical composition and surface concentration will be measured by ESCA and Auger Spectroscopy. Chemical bonding information will be determined by Raman and infrared spectroscopy. Structural changes in the surface lattice will be investigated by LEED characterization. The catalyst surface will be investigated in the presence of CO, H_2, CH_4 and H_2S in the initial stages of the program. Other potential poisons and deactivating agents, such as chlorides, cyanides, nitroge oxides and carbon depositors such as ethylene and benzene will be investigated as the program develops. The validity of currently accepted models of catalyst thermal deactivation i.e. sintering, will be evaluated and assessed for accurac and applicability. Parameters to be monitored include (a) particle size and particle size distribution, (b) the effect of temperature on particle size distribution and (c) the effect of particle size distribution on the rate of thermal sintering.

III. SUMMARY OF PROGRESS TO DATE

The status of the project to date is shown in Figure III.1. The experimental program is running approximately two to three months behind schedule. A time extension has been requested to extend the project beyond the present January 31, 1979 termination date, in order to complete the experimental project and assemble the final report. The project costs are running slightly below the budgeted level.

The following manuscripts describing work accomplished on the project have been recently published and/or accepted for publication.

1. J. M. Stencel, E. Heinz and E. B. Bradley, "Infrared and Raman Spectra of a Sulfur-resistant Methanation Catalyst", Appl. Spectrosc., in press.
2. E. B. Bradley and J. M. Stencel, "Infrared Spectra of Some Non-reduced Methanation Catalysts", Appl. Spectrosc., 32, 496 (1978).
3. J. M. Stencel and E. B. Bradley, "Raman Spectra of CO, H_2 and O_2 Adsorbed on Ni(111)", Spectrosc. Lett., II, 563 (1978).
4. J. M. Stencel, D. M. Noland, E. B. Bradley and C. A. Frenzel, "An Ultrahigh Vacuum Chamber for Raman Studies of Gases Adsorbed on Metals", Rev. Sci. Instr., 49, 1163 (1978).
5. R. B. Shalvoy, P. J. Reucroft and B. H. Davis, "Characterization of Coprecipitated Nickel in Silica Methanation Catalysts by X-Ray Photoelectron Spectroscopy", J. Catalysis, in press.
6. R. B. Shalvoy and P. J. Reucroft, "Characterization of a Sulfur Resistant Methanation Catalyst by X-Ray Photoelectron Spectroscopy", J. Vac. Sci. Tech., in press.

The following presentations have been recently delivered at scientific and engineering meetings:

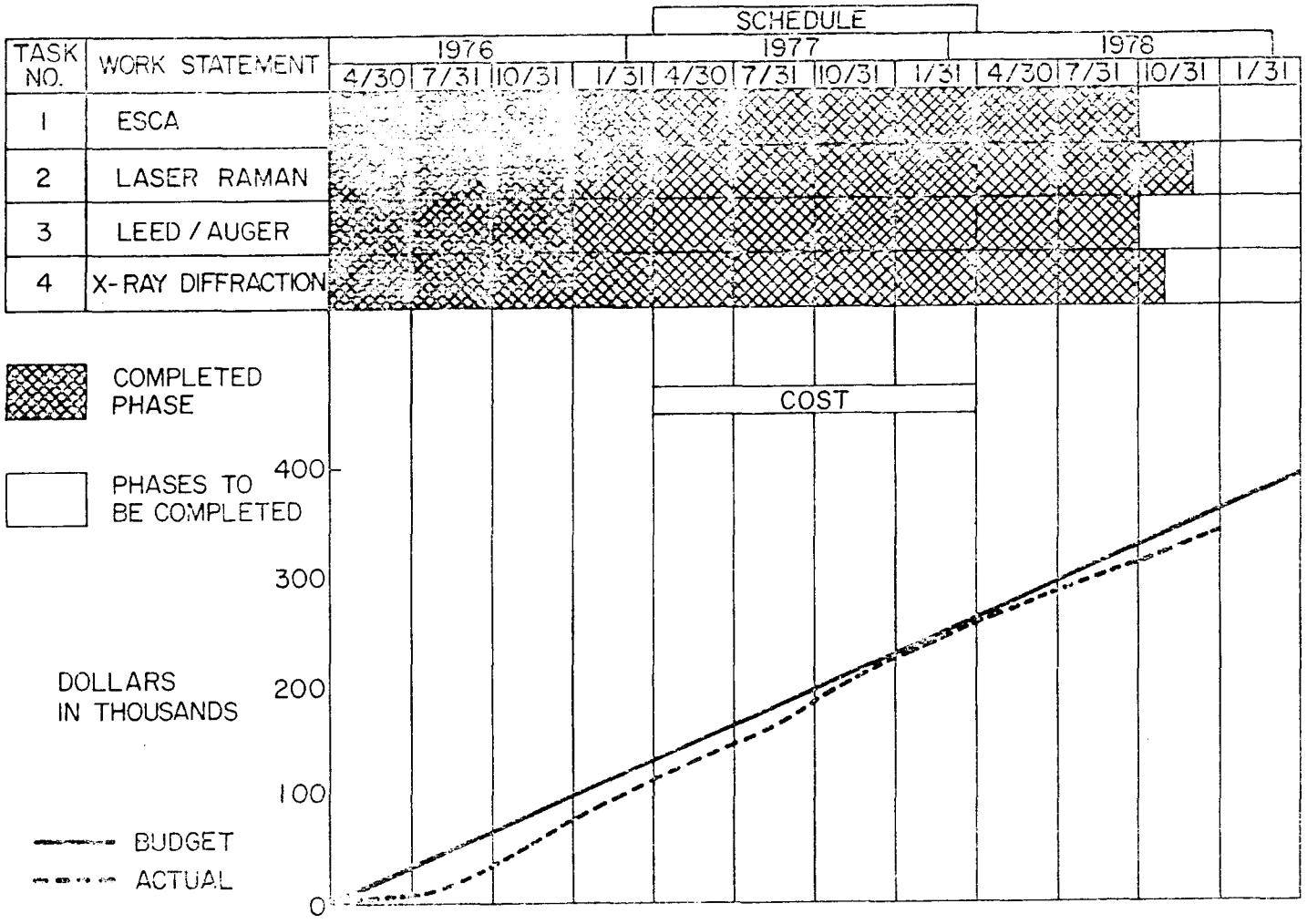

Figure III.1. Summary of Project Progress

1. "Surface Characterization of Methanation Catalysts", by P. J. Reucroft; presented by P. J. Reucroft at the Fifth Annual DOE/Fossil Energy Conference on University Coal Research, Lexington, Kentucky, August 23-24, 1978.

2. "An Ultrahigh Vacuum Cell for Infrared Reflection Studies of Gases Adsorbed on Metals", by J. M. Stencel, E. B. Bradley and E. Heinz; presented by E. Heinz at the APS Southeastern Section Meeting, Blacksburg, Virginia, October 26, 1978.

3. "Raman Spectra associated with Gas Adsorption on Nickel (110)", by J. M. Stencel and E. B. Bradley; presented by E. B. Bradley at the National Meeting, Optical Society of America, San Francisco, Calif., November 3, 1978.

4. "Auger Electron Spectroscopy and Desorption Studies of CO on Sulfur Poisoned Nickel (111) Simple Crystal Surfaces", by G. A. Sargent, G. B. Freeman and J. L. Chao; presented by G. B. Freeman at the 176th National ACS Meeting, Miami, Florida, September 11-14, 1978.

5. "Characterization of a Sulfur Resistant Methanation Catalyst by X-Ray Photoelectron Spectroscopy", by R. B. Shalvoy and P. J. Reucroft; presented by R. B. Shalvoy at the 25th National Vacuum Symposium, American Vacuum Society, San Francisco, California, November 28 - December 1, 1978.

Research personnel who have participated in the project in addition to the co-principal investigators, include Drs. J. M. Stencel and P. Zanzucchi (Postdoctoral Research Fellows), Drs. P. Ganesan, R. B. Shalvoy, G. B. Freeman and B. H. Davis (Institute for Mining and Minerals Research) and H. K. Kuo, J. Chao, D. M. Noland, E. Heinz and J. W. Park (Graduate Assistants).

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. REPORTING CATEGORY 1 - ESCA STUDIES (Prepared by R. B. Shalvoy and P. J. Reucroft)

(i) Work Accomplished

The work in this quarter has focussed increasingly on analysis of the results obtained to date and the preparation of papers on these findings. The preliminary findings on the sulfided Ni and Ni-Cr/$MgSiO_3$ catalysts have been presented in a paper submitted to the Journal of Vacuum Science and Technology. These catalysts show the presence of NiS in the inactive catalysts (Ni only) and a variable mixture of NiS and $NiSO_4$ in the catalysts that are still active (Ni-Cr). $NiSO_4$ has not been observed in any of these catalysts except the Ni-Cr catalysts. The total sulfur uptake in the Ni-Cr/$MgSiO_3$ catalysts is about one half that of the Ni/$MgSiO_3$ catalysts.

The improved methanation activity in the Ni-Cr catalysts correlate with the presence of Cr_2O_3, $NiSO_4$ and a lower sulfur uptake. It appears that at the elevated temperature (600°C) for which the improved activity is observed, Cr_2O_3 is promoting the formation of $NiSO_4$ which is a less effective poison than NiS and which is less likely to remain on the catalyst. The result is an incompletely poisoned catalyst even after high sulfur exposure. As the reducing and methanation environments are not conducive to the oxidation of NiS, this speculation on the role of $NiSO_4$ in the increased activity of the Ni-Cr catalyst must be confirmed by the observation of $NiSO_4$ in a methanation tested sample which has not been exposed to air. This sample should be received from United Catalysts in the coming quarter. A more complete paper on the sulfided catalysts will be prepared on completion of the studies on the sulfided Ni-Cr/$MgAl_2O_4$ catalysts.

The sample preparation chamber (SPC) has been secured on a permanent framework and a number of problems have been solved. The gas admission manifold is being assembled and will be complete in the next quarter. Test reductions and treatments of the C150 catalysts will then be attempted.

Experimental work has been limited in this quarter. A reduced, sulfided, nitrogen stored, then air exposed Ni-Cr/$MgAl_2O_4$ catalyst was examined. The spectra obtained from this sample were similar to those obtained for a similarly treated Ni-Cr/$MgSiO_3$ catalyst. The SO_4 to S ratio was 10% higher than for the $MgSiO_3$ supported catalyst. The ratio decreased significantly as the sample was etched to reveal the bulk. The sulfur uptake appears to be significantly greater than for the $MgSiO_3$ supported catalyst. This finding is preliminary, however, as only this one sample has been studied. A more complete examination of these catalysts will be performed in the coming quarter.

(ii) Work Forecast

In the coming quarter studies on the variously treated Ni-Cr/$MgAl_2O_4$ catalysts will be completed. The sample preparation chamber will be activated and preliminary reducing tests will be performed. Papers on the Ni/Al_2O_3 and sulfided Ni-Cr/$MgSiO_3$ and $MgAl_2O_4$ catalysts will be prepared.

B. REPORTING CATEGORY 2 - LASER RAMAN AND INFRARED SPECTROSCOPY

(Prepared by J. M. Stencel and E. B. Bradley)

(i) Work Accomplished

Raman spectra of CO adsorbed on Ni(111) and Ni(110) were obtained with the Ni crystals at temperatures from -150 to 0°C using 60mW of 5145Å excitation. Adsorption of CO enhances the visual brightness of the scattered radiation but no Raman bands could be observed until the CO pressure was approximately 0.5 atmospheres with the sample at -150°C. The bands for CO/Ni(110) are located at 2020, 2025, 2029 and 2032 cm^{-1} and for CO/Ni(111) at 2022, 2027 and 2032 cm^{-1}. Thus, the band frequencies are shifted to higher frequencies (by $2cm^{-1}$) in going from the Ni(110) to Ni(111).

Interpretation of these bands is difficult due to the absence of Raman data on adsorbed CO. Raman spectra of CO on Raney Ni indicates 16 bands in the 200-2100cm^{-1} region with bands in the 2040 and 2020 cm^{-1} region assigned to $Ni(CO)_4$.[1] However, contrary to this study, increasing the laser power from 60 to 150mW does not decrease the intensities of the CO modes on Ni(110) or Ni(111) as it does for $Ni(CO)_4$. The CO frequencies are also lower than that expected for CO gas (2143 cm^{-1}) which indicates considerable interaction with the Ni surface. Tentatively, we assign the observed bands to linearly bonded CO; the multiplicity could be related to different adsorption sites of a stepped surface and to interactions between adjacent CO molecules.

Raman bands due to adsorbed O_2 on Ni(111) were also investigated during this period. In correspondence with previous studies, the intensity of the broad-band scattered radiation decreases with O_2 adsorption in the -130 to -50°C region; as the temperature increases above -50°C the scattered radiation intensity increases. At -60°C the band due to adsorbed O_2 is located at 1551 cm^{-1},

at -40°C it is shifted to 1553 cm^{-1}, and at 0°C it is located at 1554 cm^{-1}. It is most intense at 0°C, and no trace of the O_2 band could be found when the temperature of the Ni crystal was raised to 25°C.

Gaseous O_2 produces a Raman band at 1553·3 cm^{-1}. Thus, the -40°C and 0°C Raman data indicates a gaseous O_2 species which is closely associated with the Ni surface. The frequency shift is indicative of surface interaction but even at -60°C the adsorbed O_2 is essentially in its gaseous form.

(ii) Work Forecast

In the next period Raman spectra will be obtained for CO on Ni(100) and then compared with the results obtained for Ni(110) and Ni(111). Infrared spectra are also expected to be obtained from adsorption on Ni(111) under UHV conditions.

(iii) References

1. W. Krasser, A. Ranade and E. Koglin, J. Raman Spec. 6, 209 (1977).

C. REPORTING CATEGORY 3 - SURFACE ANALYSIS BY LOW ENERGY ELECTRON DIFFRACTION (LEED) AND AUGER SPECTROSCOPY (AEA)

(Prepared by P. Zanzucchi and G. Sargent)

(1) Work Accomplished

A vacuum leak in the LEED/AES sample holder has now been repaired by Varian Corporation. With this sample holder in the vacuum system, a base pressure in the range of 10^{-10} torr was obtainable. Initial runs with a Ni(111) single crystal specimen have produced preliminary LEED and AES data on a clean Ni(111) surface, sulfur poisoned Ni(111), and sulfur poisoned Ni(111) with CO adsorption. Changes in the LEED patterns with CO adsorption were observed and photographed.

While the sample holder was being repaired, a temperature controller, which drives a power supply that heats the specimen, was built to control the temperature of the specimen either in a linear ramp upwards or to maintain it at a constant value. The purpose of this unit is to produce desorption data which can be readily analyzed. With a proper thermocouple connection to the specimen, satisfactory performance was delivered by this unit.

(ii) Work Forecast

Work will continue in correlating the LEED patterns with CO adsorption of the sulfur poisoned single crystal Ni surface. Thermal desorption data will also be taken in measuring the CO coverage and in measuring the energy of both desorption and decomposition.

D. REPORTING CATEGORY 4 - X-RAY DIFFRACTION CHARACTERIZATION OF CATALYST MATERIALS (Prepared by P. Ganesan and R. J. DeAngelis)

(1) Work Accomplished

During this report period the initial series of sintering experiments on the reduced nickel catalyst C-150-1-01 under a hydrogen atmosphere have been initiated. The results obtained thus far indicate that the sintering rate is more rapid under hydrogen than under nitrogen. Additional work is needed before definite statements concerning the magnitude of the differences in sintering rates under the hydrogen and nitrogen atmospheres can be made.

During this period the TGA work on the reduction of nickel oxide supported on alumina and silica was completed.

The alumina supported catalysts C150-1-03 and C150-4-03 showed similar behavior, as reported previously, in that the rate of reduction and the amount of reduction decreases at 500°C compared to 450°C. This is most likely due to stronger interaction of NiO with the alumina support at higher temperature resulting in decreased reduction kinetics. During this report period further work has been done to clarify this point. The alumina supported catalysts were sintered at 500°C for 24 hours and then reduced at 500°C using a pure hydrogen flow rate of 8cc/min. Under the same conditions of temperature and hydrogen flow rate the sintered samples showed lesser amounts of reduction compared to samples reduced without sintering. For example, after 30 minutes of reduction the sintered C150-1-03 and C150-4-03 catalysts reduced only about 15% and 45%, respectively, as compared to the non-sintered samples. The latter samples showed 32% and 50% reduction. This indicates that the sintering at 500°C prior to reduction probably results in the formation of nickel aluminates which are more difficult to reduce than NiO and the effect is greater in the case of the C150-1-03 catalyst. Because of the foregoing, it can be concluded that the amount of reduction at 500°C is less than that observed at 450°C

because of stronger interaction of NiO with the alumina support at the higher temperature.

(ii) Work Forecast

During the next quarter the following work is planned:

(a) Complete the hydrogen sintering experiments with reduced nickel catalysts.

(b) Complete the analysis of the total TGA data set.

V. CONCLUSIONS

A. REPORTING CATEGORY 1 - ESCA STUDIES

1. A Ni-Cr/$MgAl_2O_4$ catalyst when sulfided forms both $NiSO_4$ and NiS. The ratio of SO_4 to S is 10% higher for this catalyst than for a similarly treated Ni-Cr/$MgSiO_3$ catalyst. The sulfur uptake also appears to be higher in this catalyst.
2. The presence of Cr_2O_3 appears to promote the formation of $NiSO_4$ in the sulfided Ni-Cr/$MgSiO_3$ catalysts. The sulfur uptake is about half that observed for a similarly sulfided Ni/$MgSiO_3$.

B. REPORTING CATEGORY 2 - LASER RAMAN AND INFRARED SPECTROSCOPY

1. CO Raman bands for CO on Ni(110) and Ni(111) are located in the 2020-2032 cm^{-1} region with temperatures from -60 to 0°C. These bands are assigned to linear bonded CO.
2. O_2 Raman bands for O_2 on Ni(111) are located in the 1550 cm^{-1} region with temperatures from -130 to 0°C. These bands shift to higher frequencies upon warming the Ni crystal to 0°C.

C. REPORTING CATEGORY 3 - SURFACE ANALYSIS BY LEED AND AES

1. LEED patterns of CO adsorption can be measured and characterized by this system.
2. The temperature controller has worked in a satisfactory manner.

D. REPORTING CATEGORY 4 - X-RAY DIFFRACTION CHARACTERIZATION OF CATALYST MATERIALS

1. The sintering rate of a silica supported nickel catalyst is more rapid in a hydrogen atmosphere compared to a nitrogen atmosphere.
2. Heat treatment of alumina supported nickel catalysts prior to reduction leads to a decrease in the fraction of nickel that becomes reduced.

VI. ACKNOWLEDGEMENTS

Catalyst samples and general information were supplied by A. L. Hausberger and associates at United Catalysts, Inc., Louisville, Kentucky.

☆U.S. GOVERNMENT PRINTING OFFICE: 1979—640-014/4576