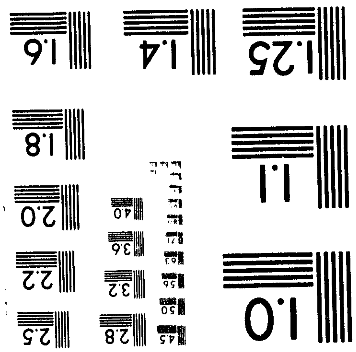
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INTERACTION OF CARBON AND SULFUR ON METAL CATALYSTS

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HYDROGASIFICATION OF CARBON ADSORBED ON SULFUR-POISONED DISPERSED METAL CATALYSTS

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ABSTRACT

The temperature programmed reaction of 1- to 10-atm hydrogen (TPRH) with carbon deposited on alumina supported Ni, Ru, and Co and on fused Fe catalysts has been developed to examine the effect of sulfur poisoning on coking rates and the nature of the deposited carbon. A new procedure, passivation by carbon deposition on clean reduced metals and low temperature (20°-50°C) exposure to recirculate dilute H_2S with moderate 0.1 atm partial pressure of CO_2 was used to slow the rate of sulfur chemisorption. This method facilitated slow uniform sulfur chemisorption to fractional saturation coverages. Fractional sulfur poisoning generally blocked sites of active surface carbon (or hydrocarbon fragments) while suppressing rates of hydrogasification as shown by the increasing temperatures in the TPRH hydrogasification rate versus temperature spectra. Fractional sulfur poisoning (e.g., half saturation) appears to inhibit H_2 gasification with surface carbon surprisingly without strongly affecting catalytic activity. Sulfur poisoning to saturation levels (defined here as ~1 ppm H_2S in 1-atm H_2 at 500°C) always results in complete loss of activity and is also marked by the growth of a very unreactive form of carbon.

EXPERIMENTAL SYSTEMS AND PROCEDURES

A versatile microreactor system (Figure 1) for the precise measurement of carbon chemisorption isosteres on dispersed catalysts was used for catalyst characterization and for preparation of coadsorbed carbon or CH_x fragments on supported Pt and on dispersed fused iron catalysts. Both catalysts were pretreated with fractional monolayers of chemisorbed sulfur. The microreactor was also used for determination of surface carbon gasification rates and for measurement of the thermodynamics of carbon adsorption or deposition.

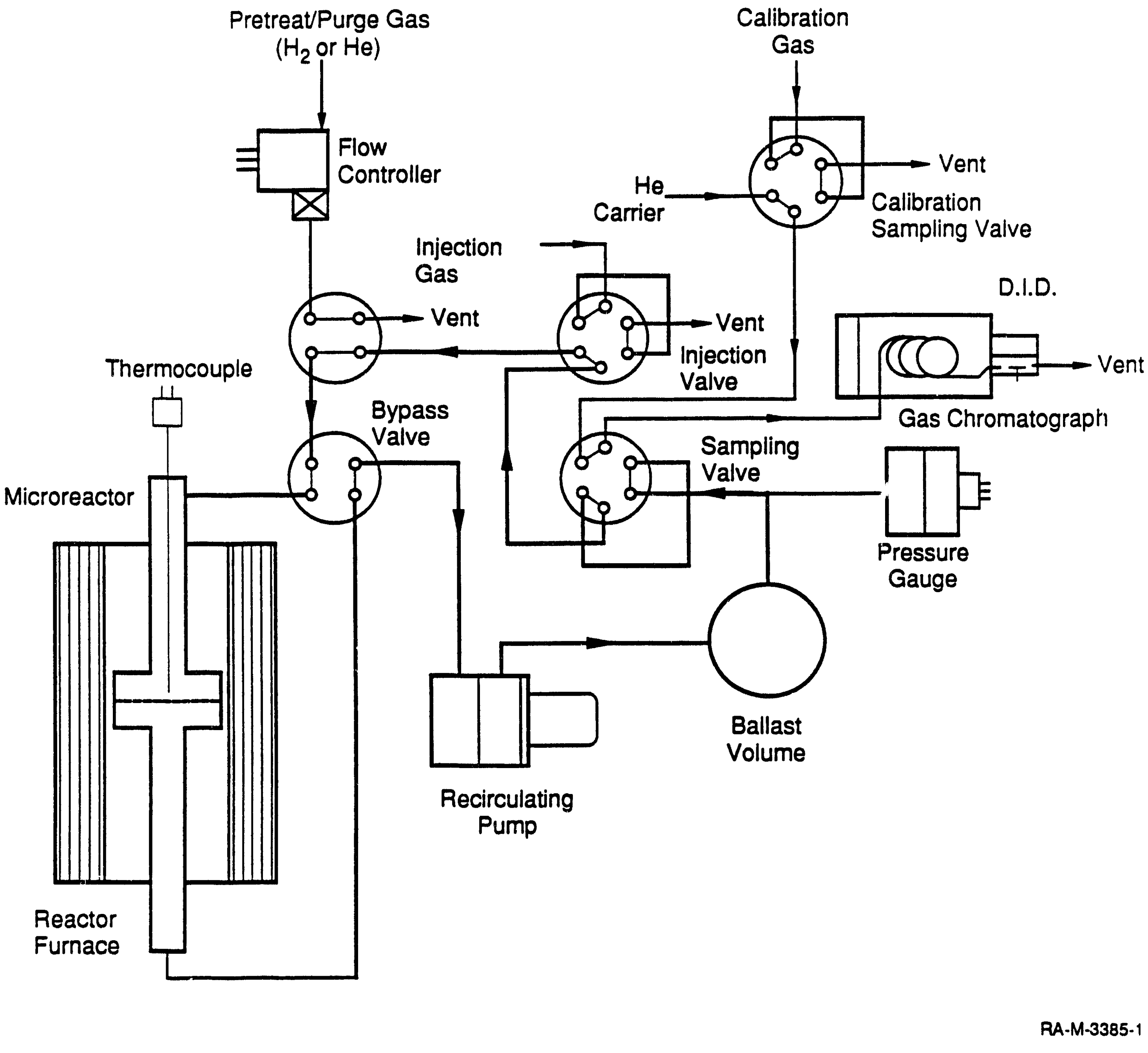

Figure 1. Experimental gas-recirculation microreactor system for measurement of carbon isosteres.
(D.I.D. = helium discharge ionization detector.)

Sensitive (ppm level) analysis of the recirculating gas is essential for the success of thermodynamic measurements. The gas chromatography (GC) used for thermodynamic analysis contains a carbon molecular sieve column, was equipped with a sensitive helium discharge ionization detector (DID) and a subambient attachment and was programmable to 575 K. The GC and DID instruments were capable of fully resolving and detecting levels below parts per million for methane, water vapor, oxygen, nitrogen, carbon monoxide, carbon dioxide, ethane, ethene, and acetylene in addition to 1-ppm levels of hydrogen. The DID was calibrated and found to have an ultimate sensitivity of about 1 ppm for H_2 and about 0.5 ppm for methane. However, sporatic appearance of noise and occasional off-scale zero shifts limited the useful sensitivity to levels at one order of magnitude higher.

HYDROGASIFICATION OF CARBON COADSORBED ON SULFUR-COVERED FUSED IRON

Thermally stabilized, clean-fused iron catalysts and those with uniform half-monolayer coverage of chemisorbed sulfur were prepared in a separate sulfur treatment system as reported previously. A sulfur-treated fused iron catalyst with monolayer sulfur coverage was successfully prepared by a technique developed previously (Tong and McCarty, 1989) to prepare fractional monolayer sulfur-treated iron Fischer-Tropsch synthesis catalysts. After gradual step-wise reduction in flowing H_2, the fused-iron surfaces were passivated by adsorption, dissociation, and disproportionation of CO and C_2H_4 into carbon and iron carbides at 573 K. Sufficient carbon was injected to produce approximately two monolayers of surface carbon. After passivation, aliquots of H_2S in hydrogen were injected into the closed recirculation loop at 473 K as the gas-phase H_2S concentration slowly fell, reaching 10 ppm after 2 hours. The system was then flushed with pure hydrogen at 473 K, and the passivating carbon, iron carbide, and adsorbed CO layers were removed by temperature programmed reaction (TPR) to 873 K in flowing 1-atm hydrogen. The catalyst was held at 773 K in recirculating hydrogen for 12 hours to allow local microscopic surface diffusion and equilibration of chemisorbed sulfur.

The effect of coadsorbed sulfur on the hydrogasification of surface carbon was determined by TPR with 1-atm H_2. Carbon was deposited on 0.1-g samples of both clean and sulfur-treated fused iron catalysts by exposure in the TPR apparatus to a stream of 2% C_2H_4/He at 900 K for 1200 s. The same exposure was repeated for the clean catalyst at 700 and 800 K. The appearance of methane and hydrogen as major gaseous products during the C_2H_4 exposure indicated the formation of hydrocarbon fragments that deposited carbon on the catalyst surface. After the reactor had been cooled to room temperature, the stream of helium was replaced by a stream of hydrogen and a H_2-TPR apparatus was used to identify the quantity and reactive state of the deposited carbon.

For the clean-fused iron catalysts, the peak temperatures for methane formation from deposited carbon correspond approximately to the temperatures at which the carbon deposition occurred (Table 1). In each case, all the surface carbon reacted with H_2 during the TPR experiment. By way of contrast, the low-level sulfur-treated (50% monolayer sulfur coverage) fused iron catalysts exhibited a shoulder at 923 K and continuous evolution of methane up to 1123 K during H_2-TPR (Figure 2). This result indicated that a portion of the carbon deposit was in the same reactive state as that on the clean catalyst, but that a large amount of additional carbon was present in less reactive states. In the case of the high-level sulfur-treated (100% saturation coverage) fused iron catalyst, the peak temperature for methane formation was completely shifted to 1123 K. Clearly, the presence of sulfur on the surface not only increased the quantity of subsequently deposited carbon but also caused this carbon to assume a less reactive state.

Table 1
H_2-TPR OF CARBON DEPOSITED ON FUSED IRON CATALYSTS BY EXPOSURE TO C_2H_4

Sulfur Coverage (% Saturation)	Exposure Temperature (K)	Amount of Carbon Deposited (mmol/g catalyst)	Peak Temperature of H2-TPR (K)
0 (clean)	700	202.1	700
0 (clean)	800	442.7	850
0 (clean	900	2184.8	910
50	900	3182.3	920,1073
100	900	1079.5	1073

The presence of sulfur poison on an iron catalyst slightly decreases its tendency to deposit coke by significantly increasing the temperature required to avoid continuous accumulation of coke in a reducing atmosphere. Thus in 1-atm H_2, clean-fused iron could be exposed to low levels of carbonizing gas without continuous coking at temperatures above 670 K. Upon complete sulfur poisoning, coke accumulation could occur at temperatures below 850 K. Similar behavior has been noted by our laboratory for Ru/Al_2O_3 steam re-forming catalysts in other studies.

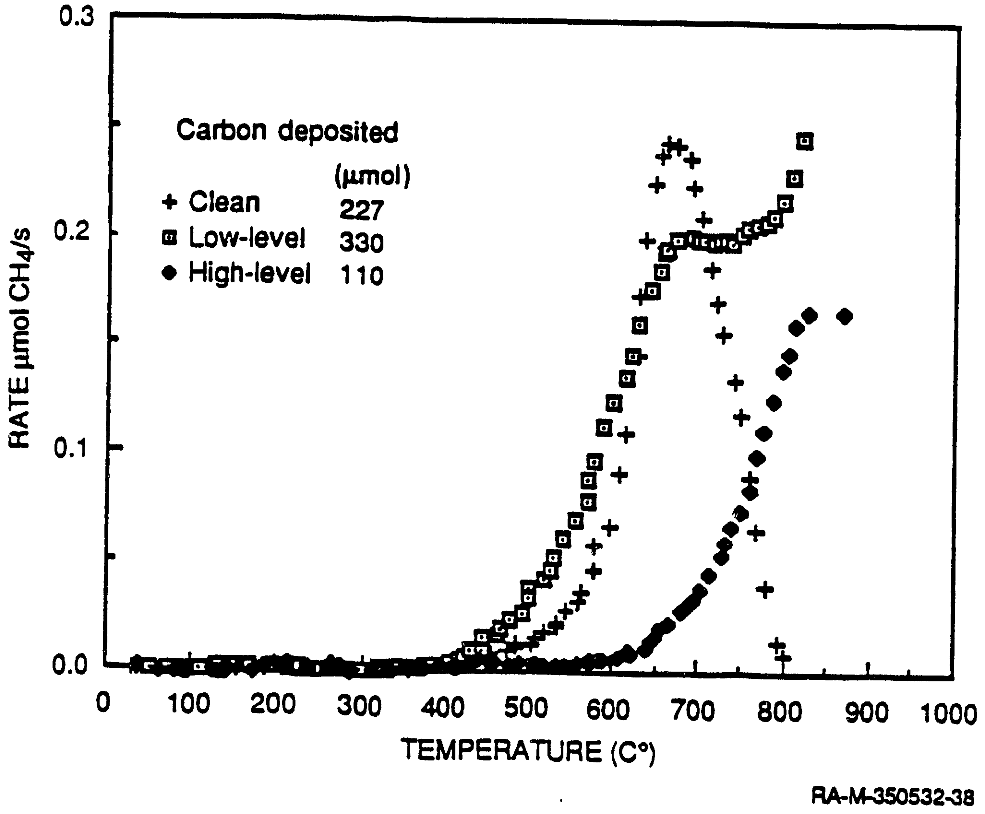

Figure 2. H_2 TPR (temperature programmed reaction of clean and sulfur-treated fused iron catalysts exposed to 2 vol% C_2H_4 at 900 K for 1200 s. (~0.10 g catalyst used, approximately 21.0 µmol surface.)

RESEARCH SUMMARY

OBJECTIVES

At high coverage, sulfur generally deactivates metal catalysts, but at low coverage, chemisorbed sulfur can have a more subtle effect on catalyst activity and selectivity. The general goal of the current project is to examine fundamental aspects of selective poisoning by fractional monolayers of chemisorbed sulfur on a variety of metal catalysts used for commercially important reactions such as hydrocarbon reforming, light alkane steam reforming, and hydrocarbon synthesis. Specific objectives of the research program are to experimentally measure as a function of coverage the influence of chemisorbed sulfur on the thermodynamics, reactivity, and structure of surface and bulk carbon occupying both dispersed and well-characterized metal catalyst surfaces.

In previous DOE-BES supported work, our laboratory has developed special methods, such as reversible sulfur chemisorption on supported metals (McCarty and Wise, 1979b, 1981, 1982, and 1985; McCarty et al., 1983) and temperature-programmed reaction (TPR) characterization of catalyst carbon (McCarty et al., 1982; McCarty and Wise, 1979a), that are well suited to examine the interaction of sulfur and carbon on metal surfaces. In this final project for DOE-BES, a new analytical instrument with greatly improved sensitivity, the surface analysis by laser ionization (SALI) technique (Becker and Gillen, 1984; Vajo and Becker, 1989), was used in surface carbon segregation to examine the effect of sulfur on the thermodynamics of carbon chemisorbed on single-crystal surfaces.

REPORTING PERIOD

1 April 1986 to 31 December 1992.

PARTICIPATING PERSONNEL

Jon G. McCarty (Principal Investigator; C+S/Ni single crystals; C/dispersed Fe, Co, Ni and Ru; FTS with S/Fe).

Bernard J. Wood (C/dispersed Fe, Co, Ni and Ru).

John J. Vajo (C+S/Ni single crystals).

Gilbert T. Tong (C/dispersed Fe, Co, Ni and Ru; FTS with S/Fe).

Christopher H. Becker (C+S/Ni single crystals).

Victor L. Wong (C/dispersed Ru).

Ramurthy Ramanathan[1] (C+S/Ni single crystals).

Henry Wise[2] (C+S/Ni single crystals).

MANUSCRIPTS

"Thermodynamic Stability of Carbon Atoms (Carbidic) in the Presence of Coadsorbed Sulfur on a Ni(111) Surface," R. Ramanathan, H. Wise, and J. G. McCarty (manuscript to be submitted for publication in 1994).

"Thermodynamics of Carbon Coadsorbed with Sulfur on Ni(100)," J. J. Vajo and J. G. McCarty, *Applied Surface Science*, **47**, 23-33 (1991).

"The Role of Sulfur in the Deposition of Carbon on Ruthenium and Nickel Steam Reforming Catalysts," B. J. Wood, G. T. Tong, and J. G. McCarty with M. Masuda, T. Tabata, and O. Okada of Osaka Gas Company, in *Catalyst Deactivation 1991*, pp. 185-193, C. H. Bartholomew and J. B. Butt, Eds., Elsevier (1991).

"Carbon Deposition on Steam Reforming Catalysts. I. TPR Studies of Carbon Deposits on Clean- and Sulfur-Poisoned Ruthenium Catalysts," B. J. Wood, J. G. McCarty, and G. T. Tong with O. Okada, T. Tabata, and M. Masuda of Osaka Gas Company, (submitted for publication).

"Fischer-Tropsch Synthesis with Sulfur-Treated Iron Catalysts," G. T. Tong and J. G. McCarty (unpublished manuscript).

"Hydrogasification of Carbon Adsorbed in Sulfur-Poisoned Dispersed Metal Catalysts," J. G. McCarty (unpublished manuscript).

PUBLICATIONS FROM THE PRECEDING CONTRACT (1977-1986)

"Thermodynamics of Sulfur Chemisorption on Transition Metals," (Abstract), J. G. McCarty, B. J. Wood, and H. Wise, *J. Vacuum Sci. and Tech.* **16**, 566 (1979).

"Thermodynamics of Sulfur Chemisorption on Metals, I. Alumina-Supported Nickel," J. G. McCarty and H. Wise, *J. Chem. Physics*, **72**, 6332 (1980).

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[1] Dr. Ramanathan left SRI International at the end of 1985.

[2] Dr. Wise has been a consultant for SRI since joining the Materials Science Department at Stanford University in 1984.

"Thermodynamics of Sulfur Chemisorption on Metals, II. Alumina-Supported Ruthenium," J. G. McCarty and H. Wise, *J. Chem. Physics*, **74**, 5877 (1981).

"Thermodynamics of Sulfur Chemisorption on Metals, III. Iron and Cobalt," J. G McCarty and H. Wise, *J. Chem. Physics*, **76**, 1162 (1982).

"Thermodynamics of Sulfur Chemisorption on Metals, IV. Alumina-Supported Platinum," J. G. McCarty, K. M. Sancier, and H. Wise, *J. Catalysis*, **82**, 92 (1983).

"Sulfur Diffusion of Chemisorbed Sulfur on Ni(111)," B. J. Wood, C. M. Ablow, and H. Wise, *Applied Surface Science*, **18**, 429 (1984).

"Thermodynamics of Sulfur Chemisorption on Metals, V. Alumina-Supported Iridium," J. G. McCarty and H. Wise, *J. Catalysis*, **94**, 543 (1985).

SUMMARY OF RESULTS

The thermodynamic stability of adsorbed carbon atoms (carbidic) in the presence of coadsorbed S atoms, on a Ni(111) surface, was determined using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) in the temperature range $300\ K < T < 800\ K$. The principle of equilibrium carbon segregation under near equilibrium conditions, was used to obtain the experimental results. The overlayer structure and segregation behavior of carbon atoms were studied for various constant coverages of adsorbed S atoms. Our results show higher thermodynamic stability for adsorbed C atoms in the presence of coadsorbed S atoms. These results are presented in the attached manuscript, "Thermodynamic Stability of Carbon Atoms (Carbidic) in the Presence of Coadsorbed Sulfur on a Ni(111) Surface," as a temperature versus coverage (T vs $\theta_S{}^*$) diagram showing the region of stability of carbidic C atoms. The practical implications of our findings relevant to heterogeneous catalysis and grain boundary segregation are also discussed in the manuscript.

Progress was made in the development of the surface analysis by laser ionization (SALI) method for measurement of the thermochemical properties of carbon coadsorbed with chemisorbed sulfur. Ni(100) was examined as a reference system by using the SALI technique to measure the surface segregation of bulk carbon as a function of temperature. Our initial results showed a very large background C^+ signal that limited the surface C sensitivity to about 0.01 monolayer, a level comparable to and perhaps two times more sensitive than that obtainable with Auger electron spectroscopic (AES) measurements. The crystal holder was then redesigned and modified to allow higher crystal outgassing temperatures (to 1273 K) and to minimize heating of the crystal support materials. Additional outgassing and subtraction of the C^+ signal during alternate cycles of the

Ar^+ ion beam improved the sensitivity at least an order of magnitude, to less than 1000 ppm (on the surface layer) at 1000 K, although we were unable to reach our original goal of 100 ppm.

The thermodynamics of the segregation of dissolved carbon to a Ni(100) surface containing adsorbed sulfur was examined by stimulated desorption using a low-current pulsed Ar^+ beam at 2 keV, followed by laser ionization at 193 nm of the desorbed neutral species and reflecting time-of-flight mass spectrometry of the resulting C^+ photo ions. Equilibrium surface-carbon coverages were measured for fractional sulfur coverages of 0, 0.1, 0.16, and 0.26 monolayer over a temperature range of 700 to 1100 K. Absolute carbon and sulfur coverages were calibrated by Auger electron spectroscopy of saturated, ordered overlayer structures. Identical carbon-segregation coverages obtained for both increasing and decreasing temperature profiles indicated that the measured carbon coverages represented equilibrium values. For fractional carbon coverages >0.15 monolayer with respect to the number of surface nickel atoms, the heat of formation of adsorbed carbon on Ni(100) was -28 ± 7 kJ/mol; the Langmuir-McLean model was used to describe the segregation. The heat of formation of adsorbed carbon increased with increasing carbon coverage. Coadsorbed sulfur did not affect the heat of formation of adsorbed carbon for sulfur coverages ≤0.16 monolayer. For a sulfur coverage of 0.26 monolayer, the heat of formation of adsorbed carbon increased (weakened) to -7 ± 2 kJ/mol. Coadsorbed sulfur reduced the maximum coverage of segregated carbon on Ni(100) from 0.5 with no coadsorbed sulfur to 0.24 with a sulfur coverage of 0.26 monolayer. These results and the likely influence of coadsorbed sulfur on carbon during methanation on nickel are discussed further in the attached reprint, "Thermodynamics of Carbon Coadsorbed with Sulfur on Ni(100)."

The effect of chemisorbed sulfur on hydrogasification of carbonaceous overlayers was examined for fused-iron and alumina supported ruthenium catalysts by using temperature-programmed reaction with hydrogen (TPRH) to qualitatively and quantitatively examine surface carbon (see attached manuscripts, "The Role of Sulfur in the Deposition of Carbon on Ruthenium and Nickel Steam Reforming Catalysts," and "Carbon Deposition on Steam Reforming Catalysts. I. TPR Studies of Carbon Deposits on Clean- and Sulfur-Poisoned Ruthenium Catalysts"). Multilayers of bulk carbon deposited on fused-iron by extended exposure to C_2H_4 exhibited higher characteristic TPRH peak temperatures with the partially (about 50% saturation coverage) and fully sulfur poisoned catalyst.

We investigated the role of contaminant sulfur on the deposition of carbon on a Ru/Al_2O_3 catalyst during naphtha reforming in laboratory experiments and in long-term bench-scale tests. The results showed that sulfur levels typically present in industrial steam reformer feedstocks (~1 ppm) will poison the Ru catalyst. Furthermore, the poisoning contributes significantly to the accumulation of surface carbon, especially with feedstocks containing long-chain alkanes and alkyl aromatic components. In contrast to the limited level of catalyst carbon produced on a fresh catalyst exposed to a sulfur-free feedstock, continuous carbon deposition occurs on a sulfur-poisoned catalyst. As a result, steam reforming activity is reduced, the pressure drop across the catalyst bed increases, and coke fouling of the reactor may occur. Correspondence between bench-scale and laboratory results indicates that the laboratory method is a reliable tool for evaluating the coke-forming tendency of a catalyst and predicting its long-term performance.

The FTS selectivity of the partially poisoned fused iron catalyst showed greatly suppressed methane formation and high olefin to paraffin product ratios with a lower chain growth factor. Sulfur poisoning also suppressed short-term deactivation of the catalyst with very low H_2/CO ratio feed gas. This sulfur-treated catalyst appears to have excellent properties for production of light olefins with CO-rich synthesis gas at moderately high temperatures ($T \geq 300°C$) and moderate pressure ($P \leq 20$ atm), as discussed in the attached manuscript, "Fischer-Tropsch Synthesis with Sulfur-Treated Iron Catalysts."

Our examination of carbon chemisorption on clean and partially sulfur covered dispersed metal catalysts produced disappointing results. Carbon isosteres were obtained for clean alumina-supported 5 wt% Pt, but the stability of the sensitive helium discharge ionization detector (DID) used to measure trace levels of H_2 in methane and helium gas. Considerable experience has been gained in the uniform treatment of dispersed metal catalysts with fractional monolayer sulfur. We were unable to measure the thermodynamics of carbon coadsorbed with sulfur at fractional monolayer coverage on the supported catalysts, thereby linking the results with single crystals to dispersed metal catalysts.

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