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Progress Report

INTERACTION OF CARBON AND SULFUR ON METAL CATALYSTS

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SUMMARY

We have assembled, tested, calibrated, and successfully operated an automated, external gas recirculating microreactor system designed specifically for measurement of carbon isosteres on metal catalysts. The experimental system is used for catalyst characterization, preparation of coadsorbed carbon on metal catalysts with fractional monolayers of chemisorbed sulfur, and determination of carbon gasification rates as well as measurement of the thermodynamics of carbon adsorption or deposition. The discharge ionization detector essential to the success of the thermodynamic measurements has been calibrated for hydrogen and found to have a sensitivity of 1 ppm for H_2 in a helium carrier. The gas chromatograph used in the studies of carbon and sulfur interaction on dispersed catalysts is capable of detecting levels below parts per million of methane, water vapor, oxygen, nitrogen, carbon monoxide, carbon dioxide, ethane, ethene, and acetylene, in addition to hydrogen. Measurement of carbon deposition isosteres, CO and H_2 chemisorption isosteres, and carbon hydrogasification on clean Pt/Al_2O_3 catalysts is under way.

A 2 wt% platinum catalyst with platinum impregnated on a moderate ($80\text{ m}^2/\text{g}$) surface area alumina support has been synthesized and characterized and is under study in the new thermodynamics system. Thermally stabilized clean fused iron catalysts and those with uniform half-monolayer coverage with chemisorbed sulfur have been prepared in a separate sulfur treatment system. These catalysts, along with a well-characterized 5 wt% nickel on alumina catalyst that will serve as a reference catalyst for the C-S interaction system, are available for further experimentation. By the end of the first project year in March, we expect to complete the preparation and characterization of fully and fractionally sulfur-covered supported Pt/Al_2O_3 and fused iron catalysts.

OBJECTIVE

At high coverage, sulfur generally deactivates metal catalysts, but at low coverage, chemisorbed sulfur can have a more subtle effect on 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. Our laboratory has developed special methods, such as reversible sulfur chemisorption on supported metals (McCarty and Wise, 1980, 1981, and 1983) and temperature-programmed reaction characterization of catalyst carbon (McCarty et al., 1982, and McCarty and Wise, 1979), that are well-suited to examining the interaction of sulfur and carbon on metal surfaces.

RESULTS

Most of the initial activity for this project has been directed toward assembly and testing of a new, leak-tight, automated, and versatile microreactor system (Figure 1) for the precise measurement of carbon chemisorption isosteres on dispersed catalysts. This experimental system is also used for catalyst characterization, for preparation of coadsorbed carbon or CH_x fragments on supported Pt and Pd, and on dispersed Fe catalysts pretreated with fractional monolayers of chemisorbed sulfur. The microreactor is also used for determination of surface carbon gasification rates as well as for measurement of the thermodynamics of carbon adsorption or deposition. The system has been assembled, tested, and calibrated and is fully operational.

The discharge ionization detector (DID), which is essential for the success of the thermodynamic measurements, has been calibrated for hydrogen and found to have a sensitivity of about 1 ppm for H_2 and about 0.5 ppm for methane. The gas chromatograph (GC) used for analysis contains a carbon molecular sieve column, is equipped with a subambient attachment, and is programmable to 575 K. The GC and DID are capable of fully resolving and detecting levels below parts per million of methane, water vapor, oxygen, nitrogen, carbon monoxide, carbon dioxide, ethane, ethene, and acetylene in addition to 1 ppm levels of hydrogen. Maximum concentration levels are about 3 vol% for a dynamic range of nearly 10^5 . An exponential dilution flask is available to determine the DID linearity for H_2 and CH_4 over the full dynamic range.

A number of clean and partially sulfur-covered catalysts have been prepared for study in the new thermodynamics system. A 2 wt% platinum on moderate ($80 \text{ m}^2/\text{g}$) surface area alumina support has been synthesized and characterized and is being studied. The $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst has a specific metal surface area of $85 \text{ m}^2/\text{g}$ based on H_2 and CO chemisorption at 300 K following reduction in flowing hydrogen at 800 K. Measurement

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Figure 1. Experimental gas-recirculation microreactor system for measurement of carbon isosteres.

of carbon deposition isosteres, CO and H₂ chemisorption isosteres, and carbon hydrogasification rates on the clean and sulfur-covered Pt/Al₂O₃ catalyst are under way and should be completed by the end of the first project year.

Thermally stabilized, clean-fused iron catalysts and those with uniform half-monolayer coverage of chemisorbed sulfur have been prepared in the separate sulfur treatment system (Figure 2). A sulfur-treated fused iron catalyst monolayer sulfur coverage was successfully prepared by a technique developed previously (Tong and McCarty, 1987) to prepare fractional monolayer sulfur-treated iron Fischer-Tropsch synthesis catalysts. After gradual reduction, the fused iron surfaces were passivated by CO adsorption, dissociation, and disproportionation into carbon and iron carbides at 573 K. Aliquots of CO were injected into a closed gas recirculation loop containing several grams of the reduced fused iron catalyst, while the CO/CO₂ ratio was followed with the GC system described above. Sufficient CO was injected to produce approximately two monolayers of surface carbon.

Following passivation, aliquots of H₂S in hydrogen were injected into the closed recirculation loop at 473 K, while the gas-phase H₂S concentration was monitored with a sensitive photoionization detector. The hydrogen sulfide injected into the system represented approximately 50% of the sulfur capacity of the catalyst. The gas-phase H₂S concentration slowly fell, reaching 10 ppm after 2 hours. The system was then flushed with pure hydrogen at 473 K. The deposited carbon, iron carbide, and adsorbed CO were removed by temperature programmed reaction (TPR) to 873 K in 1-atm flowing hydrogen. Methane was observed during the TPR and reached a maximum at 710 K. Evolution of H₂S to a level of 1 ppm was observed at 700 K, but the gas was quickly readsorbed at higher temperature. The catalyst was held at 773 K in recirculating hydrogen for 12 hours to allow local microscopic surface diffusion and equilibration, while the gas-phase H₂S concentration was measured continuously.

Figure 2. Catalyst sulfur treatment system.

FUTURE WORK

During the second project year and continuing through the third project year, we will examine in detail the thermodynamics and reactivity of carbon deposited on clean supported platinum, on clean fused iron, and on those same surfaces uniformly covered with fractional monolayers of chemisorbed sulfur. The results of this study will provide the enthalpy and entropy of coadsorbed carbon as a function of temperature, sulfur coverage, and carbon coverage. Additional properties to be determined include:

- Temperature-programmed hydrogasification of the carbon deposit to determine the reactive nature of the carbon and its gasification kinetics as a function of temperature, sulfur coverage, carbon coverage, and sample history. Temperature-programmed desorption experiments will detect the decomposition of surface CH_x fragments.
- Low-temperature hydrogen and carbon monoxide isotherms or isosteres on catalysts with specified sulfur and carbon coverage to determine the adsorption capacity and adsorption thermodynamics of the coadsorbed layers.
- FTIR spectroscopic examination in an environmental cell of the CH_x fragments at selected sulfur and carbon coverage.
- C^{13} solid-state NMR spectroscopy to examine the nature of C^{13} -enriched carbon coadsorbed under selected conditions of temperature, sulfur coverage, and carbon coverage.

The C^{13} solid-state NMR experiments appear especially promising for the quantitative identification of adsorbed hydrocarbon fragments. The BES-sponsored work at the University of Illinois, under the direction of Prof. C. P. Slichter, has examined the adsorption and decomposition of C_2H_2 and C_2H_4 on $\text{Pt}/\text{Al}_2\text{O}_3$ by C^{13} NMR and $\text{C}^{13}\text{-H}^1$ double resonance (Slichter, 1987). This research verifies our approach to the adsorption and isosteric measurements of carbon on supported platinum by observing the irreversible decomposition of adsorbed hydrocarbons into isolated

highly mobile carbon atoms on platinum with conversion of most of the hydrogen atoms into methane. This work also provides helpful results for the identification of adsorbed CH_x^- and C_2H_y^- hydrocarbon radicals at low temperature through solid-state C^{13} NMR and the $\text{C}^{13}\text{-H}^1$ doublet resonance NMR techniques.

During the last half of the second year, we also will begin experiments with single crystalline platinum and, for reference, limited experiments with single crystalline nickel using the surface analysis by laser ionization (SALI) technique developed by another laboratory at SRI (Becker and Gillen, 1984). The objective of this work is to measure the (low level) coverage of segregating carbon as a function of coadsorbed sulfur coverage, temperature, and chemical potential of bulk dissolved carbon. Auger electron spectroscopy will be used to calibrate the SALI measurements and to examine the nature of surface carbon at coverages above 0.05 monolayer. Low-energy electron diffraction experiments will be used to determine the structure of the chemisorbed sulfur layer and to determine possible two-dimensional order-disorder phase boundaries. This work will continue into the third project year.

Our segregation experiments in the third year will extend these studies from Ni and Pt single-crystal faces to polycrystalline Fe. Prof. J. M. White of the University of Texas (White, 1987), has suggested that oriented Fe films on W single crystals obviate the difficulties of working with impure, fragile single crystals of Fe. The University of Texas work has shown that uniform Fe films can be deposited (with care) on W single crystals, and we may adopt this approach.

REFERENCES

- Becker, C. H. and K. J. Gillen, 1984. Anal. Chem., 56, 1971.
- McCarty, J. G. and H. Wise, 1979. J. Catal., 57, 406.
- McCarty, J. G. and H. Wise, 1980. J. Chem. Phys., 76, 6332.
- McCarty, J. G. and H. Wise, 1981. J. Chem. Phys., 76, 1162.
- McCarty, J. G. and H. Wise, 1983. J. Chem. Phys., 74, 5877.
- McCarty, J. G., P. Y. Hou, D. Sheridan, and H. Wise, 1982. In Coke Formation on Metal Surfaces, L. F. Albright and R.T.K. Baker, Eds., ACS Symposium Series, 202, 253.
- Slichter, C. P., 1987. Presentation before the DOE 6th Catalysis and Surface Science Chemistry Research Conference, Gaithersburg, MD.
- Tong, G. T. and J. G. McCarty, 1987. Presentation before the 10th Meeting of the North American Catalysis Society, San Diego, CA.
- White, J. M., 1987. Presentation before the DOE 6th Catalysis and Surface Science Chemistry Research Conference, Gaithersburg, MD.

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