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INTERACTION OF CARBON AND SULFUR ON METAL CATALYSTS

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SUMMARY

Significant progress has been made in the development of the surface analysis by laser ionization (SALI) method for measurement of the thermochemical properties of carbon co-adsorbed with chemisorbed sulfur. Ni(100) has been examined as a reference system by using the SALI technique to measure the surface segregation of bulk carbon as a function of temperature. Preliminary results showed a very large background C^+ signal that limited the surface C sensitivity to about 0.01 monolayer, a level comparable to 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. Continued outgassing cycles and possibly the use of C^{13} dopant gas for the source of bulk carbon may allow C sensitivity to reach our original goal of 100 ppm. All systems necessary for completion of the segregation experiments with Ni(100), Pt(100), and polycrystalline Fe are in place.

Progress on the examination of carbon chemisorption on clean and partially sulfur covered dispersed metal catalysts has been slow, but future work on the carbon thermodynamic and H_2 and CO adsorption measurements is expected to proceed rapidly. Carbon isosteres were obtained for clean alumina-supported 5 wt% Pt, but unacceptable ambient air leaks (i.e., sources of molecular diffusion) developed in both the recirculation system designed to measure carbon thermodynamics and the sulfur treatment system. These leaks have been located and eliminated, and a difficulty with stability of the sensitive helium discharge ionization detector (DID) has been solved. The recirculation system is automated for 24-hour operation to maximize data acquisition. Considerable experience has been gained in the uniform treatment of dispersed metal catalysts with fractional monolayer sulfur. An environmental cell is now available for Fourier transform infrared (FTIR) examination of carbonaceous layers, and a supply of C^{13} -labelled methane is available for deposition on the catalyst surfaces for subsequent examination with C^{13} nuclear magnetic resonance (NMR).

The effect of chemisorbed sulfur on hydrogasification of carbonaceous overlayers has been determined for fused-iron catalysts by using temperature-programmed reaction with hydrogen (TPRH). 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. However, the sulfur treated fused-iron catalyst system has been found to be unsuitable for thermochemical examination of coadsorbed carbon because significant levels of potassium hydroxide and carbonate are present on its surfaces (Davis, 1988). Attempts to quantitatively measure CO and H₂ chemisorption were irreproducible. Sintering of precipitated iron during the sulfur treatment process make precipitated or powdered iron unattractive alternatives. Future work with dispersed iron will focus on MgO- or silica-supported iron.

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OBJECTIVE

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 re-forming, light alkane steam re-forming, 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, 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 examining the interaction of sulfur and carbon on metal surfaces. New analytical instruments with greatly improved sensitivity have recently been developed and applied: a helium discharge ionization detector (DID) is being used with our gas recirculation thermodynamic system and the surface analysis by laser ionization (SALI) technique (Becker and Gillen, 1984; Vajo and Becker, 1989) with our surface carbon segregation systems.

RESULTS

SINGLE-CRYSTAL CARBON SEGREGATION STUDIES

Experimental Apparatus and Procedures

The measurements were performed in a two-level ultrahigh vacuum system designed specifically for studies using electron- or ion-induced desorption together with time-of-flight (TOF) mass spectrometry. The upper level contains facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES) using a cylindrical mirror analyzer, and quadrupole mass spectrometry. The lower level contains pulsed electron and ion sources, laser entrance and exit windows, a laser ionization reflecting TOF mass spectrometer, and a doser assembly. As shown in Figure 1, the electron and ion sources are located on either side of the TOF mass spectrometer, while the laser windows are aligned so that photoionization occurs ~3 mm in front of the TOF optics and 1 mm in front of the sample. The pulsed source of ions or electrons is typically 5 μ s wide and has a repetition rate of 20-100 Hz. It desorbs both neutral molecules and secondary ions from the sample. Neutral species are ionized about 1 mm away from the surface by a focused, pulsed, untuned excimer laser operating at 193 nm and ~50 mJ and yielding approximately 3×10^9 W/cm³. This laser fires at the end of the electron or ion pulse. The path of the ions formed by laser ionization is shown schematically in Figure 1. After ionization, an ion optics column accelerates, focuses and deflects the ions into the TOF mass spectrometer, which operates at a drift potential of -1000 V. An electrostatic mirror reflects ions formed by laser ionization while secondary ions pass through the reflector and are not detected. Reflected ions are detected by micro-channel plates. The signal is amplified (15x) and recorded by a 100-MHz transient recorder that is triggered by the laser pulse and interfaced to an LSI 11/23 laboratory computer via CAMAC.

The vacuum chamber, which has a base pressure of 2×10^{-10} torr is pumped by a 200-L/s ion pump and a titanium sublimation pump (TSP). In addition, the ion source is differentially pumped by a 50-L/s turbomolecular pump and the drift region of the TOF mass spectrometer is pumped by a 50-L/s TSP. Differentially pumping the ion source limits the pressure rise at the sample to $< 2 \times 10^{-9}$ torr of argon while the ion source is operating at 5×10^{-5} torr.

Molybdenum clips are used to mount the sample on a Mo platen ~65 mm off the center axis of the vacuum chamber. The platen is attached to a long travel manipulator with x, y, rotary, and

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Figure 1. Schematic of apparatus for stimulated desorption studies showing configuration of the sample, electron, and Ar^+ sources and time-of-flight (TOF) mass spectrometer.

azimuthal motion. Electron bombardment heating from behind the Mo platen and conductive cooling by a copper braid from a liquid nitrogen cooled copper block is controlled by Chromel-Alumel thermocouples spot welded to the edge of the sample. Constant temperatures or linear temperature ramps are achieved with a commercial microprocessor temperature controller.

For the measurements reported here, ion stimulated desorption (ISD) TOF mass spectra were collected using a 2000-eV pulsed Ar^+ ion beam with a dc current density of $0.5\text{--}1.0\ \mu\text{A}/\text{cm}^2$ and a pulse width of $5\ \mu\text{s}$ at $20\text{--}100\ \text{Hz}$, which yielded a time-averaged current density of $50\text{--}500\ \text{pA}/\text{cm}^2$. Time-resolved experiments were performed by collecting ISD TOF mass spectra as the crystal temperature was varied between set-points. Typically, 2000 mass spectra were collected and the peak areas for up to 20 selected masses computed in real time by numerical integration. The contribution of the background gas in the vacuum chamber to the mass spectrometric signal was automatically subtracted by pulsing the ion source at half the frequency of the photoionization pulse. The gas phase signal that was collected on alternate pulses (without the ion beam) was continuously subtracted.

Experimental Results and Discussion

Ni(110). The initial SALI measurements were performed on a Ni(110) crystal that had been thoroughly cleaned of carbon and sulfur and used for about 1 year for methanol decomposition experiments. After the crystal was equilibrated at $650\ \text{K}$ for > 12 hours, the amount of segregated carbon was measured by AES (Figure 2a). On the basis of a calibration for the $\text{C}(272)/\text{Ni}(102)$ peak-to-peak ratio, the carbon coverage, Θ_{C} , was 0.17 monolayer relative to the number of nickel atoms in the outermost (110) plane. An equilibrium carbon coverage of 0.17 represents an extremely low bulk carbon atom concentration at $650\ \text{K}$ compared with that for Ni(100), with $\Theta_{\text{C}} = 0.33$. The surface carbon atom concentration was recorded for $m/e = 12$ amu without normalization by time resolved ISD-TOF measurements.

As the crystal temperature was raised from about 650 to $800\ \text{K}$, the surface carbon atom concentration declined rapidly. A slow decline in the mass 12 intensity at constant temperature was attributed to degradation of the photoionizing laser pulse characteristics, namely, the total pulse energy and the temporal and spatial energy distributions. We have since used an on-line gas purifier to extend the lifetime of an individual gas fill in our excimer laser. The purifier has reduced the problem of signal variation due to changes in the laser pulse.

Ni(100). To investigate a system that had been characterized previously, we removed the Ni(110) sample and installed in its place a Ni(100) sample that had earlier been used for carbon segregation studies by AES (Ramanathan et al., 1984). As shown in Figure 2, the Ni(100) crystal

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Figure 2. A portion of the Auger spectrum between approximately 100 and 600 eV (a) for Ni(110) that had been equilibrated at 650 K for > 12 hours and (b) for Ni(100) that had been equilibrated at ~590 K for 1 hour. The incident electron energy was 2000 eV and the electron current 4 μ A.

contained substantially more carbon than the Ni(110) crystal. For the Ni(100) crystal, the surface carbon coverage after equilibration at 590 K for about 1 hour was 0.50 monolayer. The carbon layer had a carbidic AES line shape and a $p(2 \times 2)$ LEED pattern.

An ISD-TOF mass spectrum with the gas phase subtracted for $\Theta_c = 0.33$ on Ni(100) is shown in Figure 3. The peaks at masses 58, 60, 61, 62, and 64 represent the isotopic distribution of nickel. The intensity of masses 58 and 60 are off scale on this plot, while, for example, mass 64 occurs with an isotopic abundance of 1.08%. The peaks at masses 27, 46-50, 52-56, 63, and 65 are due to Al from alumina, doubly ionized molybdenum, stainless steel, and copper, respectively, and originate from the edges of the Ar^+ beam hitting the sample holder around the Ni(100) sample. We estimate that only about 1% of the beam contributes to signal from surfaces other than the Ni crystal. The sensitivity to Al is unusually high because of a coincidental 1-photon autoionizing resonance.

The signal to noise ratio, S/N , for the carbon $m/e = 12$ peak shown in Figure 3 is approximately 2500. From this value, a surface carbon coverage of 5×10^{-4} monolayer would yield a S/N of 5. We estimate that coverages lower than about 10^{-4} monolayer can may be measured with a good S/N by increasing the number of spectra averaged, the photoionizing pulse energy, or both. In comparison with this detection limit of $\sim 10^{-4}$ monolayer, the detection limit commonly found using AES is $\sim 10^{-2}$.

A difficult problem that we have discovered and investigated concerns the accurate subtraction of the gas phase signal at $m/e = 12$ when the crystal temperature is high, (~ 1000 K). The gas phase signal at $m/e = 12$ originates from photofragmentation during photoionization of background CO in the vacuum chamber. The spectra shown in Figure 3 was collected with the crystal at ~ 500 K. Under these conditions, the ratio of the gas phase background to the surface signal intensity at $m/e = 12$ is only about 0.1. Therefore, subtraction of the gas phase intensity is reliable and accurate. However, as the sample is heated, the surface coverage of carbon decreases and the partial pressure of CO in the background increases because of outgassing of the sample holder and the manipulator assembly. At crystal temperatures near ~ 1000 K, the ratio of gas phase intensity to surface $m/e = 12$ intensity was ~ 10 , which represents a considerable loss in S/N . Under these conditions, it is increasingly difficult to accurately extract the surface component of the TOF signal.

This problem was recently minimized by modifications to our sample holder to reduce manipulator outgassing. The crystal was previously heated by thermal conduction from a Mo platen, but is now heated directly by electron bombardment and separated from the sample holder

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Figure 3. Ion stimulated desorption TOF mass spectrum for Ni(100) with $\Theta_c = 0.33$. The spectrum consists of 2000 averaged spectra with the gas phase contribution subtracted on alternate averages.

by alumina spacers. This heating arrangement reduces the surface area that becomes hot when the crystal is heated.

A comparison of the equilibrium surface carbon coverages obtained from ion stimulated desorption TOF and AES measurements of Ni(100) is shown in Figure 4. The TOF measurements are referenced to the Auger measurements at 800 K. Figure 4 also shows our previous AES results obtained in another vacuum system with the same Ni(100) crystal (Ramanathan et al., 1984). The shift to higher carbon coverages in the present study was probably caused by increased bulk carbon due to intervening exposure of the crystal to unsaturated hydrocarbons.

Because a complete ion induced TOF mass spectrum is collected for each ion pulse, temporal variations in the surface carbon coverage can be monitored with a time resolution on the order of seconds. Therefore, kinetic parameters, namely, activation energies and preexponential factors for carbon diffusion and segregation, can be obtained in addition to equilibrium thermodynamic properties. Kinetic measurements are helpful for estimating the time required for equilibration at a particular temperature and may yield insight into how coadsorbates, including carbon itself, affect carbon segregation.

An example of the time resolved segregation of carbon to the Ni(100) surface during a decreasing temperature profile is shown in Figure 5. The surface carbon coverage (shown as the mass 12 intensity in Figure 5a) increases as the temperature (shown in Figure 5b) decreases over the temperature range from ~950 to 800 K. The rate of increase of the surface carbon concentration illustrates that, for these temperatures, the rate constant for segregation is on the order of 60, which is fast relative to the rate of temperature change. Equilibrium is therefore established nearly as soon as the crystal temperature reaches steady state, and little kinetic information can be determined. For lower temperatures, the rate of carbon segregation will be much slower and, moreover, slow compared to the rate of the temperature change. Under these conditions, accurate kinetic parameters may be obtained for the rates of carbon segregation.

CARBON-SULFUR COADSORPTION STUDIES

Experimental Systems and Procedures

As reported previously, the assembly, testing, calibration, and automation of a versatile microreactor system (Figure 6) for the precise measurement of carbon chemisorption isosteres on dispersed catalysts was completed last year. This experimental system is also used for catalyst characterization and for preparation of coadsorbed carbon or CH_x fragments on supported Pt and on dispersed fused iron catalysts, both pretreated with fractional monolayers of chemisorbed

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Figure 4. Equilibrium carbon coverage on Ni(100) obtained from both Auger and stimulated desorption measurements. Auger measurements made previously on this crystal in another vacuum system are also shown.

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Figure 5. Time resolved ion stimulated desorption TOF measurements of carbon segregation on Ni(100). The mass 12 intensity and the crystal temperature are shown as a function of time in (a) and (b), respectively. Each point consists of 2000 averaged spectra obtained at 20 Hz, with the gas phase contribution subtracted on alternate averages.

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Figure 6. Experimental gas-recirculation microreactor system for measurement of carbon isosteres.
(D.I.D = helium discharge ionization detector.)

sulfur. The microreactor is also used for determination of surface carbon gasification rates and for measurement of the thermodynamics of carbon adsorption or deposition.

Sensitive (ppm level) analysis of the recirculating gas is essential for the success of the thermodynamic measurements. The gas chromatograph (GC) used for analysis contains a carbon molecular sieve column, is equipped with a sensitive helium discharge ionization detector (DID) and 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 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 a sensitivity of about 1 ppm for H_2 and about 0.5 ppm for methane.

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 H₂ 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 H₂-TPR (Figure 7). 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.

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 H₂, 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/Al₂O₃ steam re-forming catalysts in other studies.

Table 1

H₂-TPR OF CARBON DEPOSITED ON FUSED IRON CATALYSTS
BY EXPOSURE TO C₂H₄

Sulfur Coverage (% saturation)	Exposure Temperature (K)	Amount of Carbon Deposited (mmol/g catalyst)	Peak Temperature of H ₂ -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

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Figure 7. H₂ TPR (temperature programmed reaction of clean and sulfur-treated fused iron catalysts exposed to 2 vol% C₂H₄ at 900 K for 1200 s. (~0.10 g catalyst used, approximately 21.0 μmol surface).

THERMODYNAMIC STUDIES OF CARBON ADSORBED ON DISPERSED CATALYSTS

The examination of carbon chemisorption on clean and partially sulfur covered dispersed metal catalysts has shown slow progress over the past year. Carbon isosteres were obtained for clean alumina-supported 5 wt% Pt, but unacceptable ambient air leaks (from sources of molecular diffusion) developed in both the recirculation system designed to measure carbon thermodynamics and the sulfur treatment system. These leaks have been located and eliminated, but detection and control of diffusional oxygen leakage is exacerbated by the low conductance tubing and remains a concern with the recirculation system. The discharge ionization detector sporadically showed a large decline in sensitivity that was probably caused by long-term exposure of the 1-atm helium discharge electrodes to ppm levels of oxygen and water vapor in the helium carrier gases.

The time lost because of these technical difficulties may be recovered during the remaining 15 months of the project. The recirculation system is automated for 24-hour operation to maximize data acquisition. Considerable experience has also been gained in the uniform treatment of dispersed metal catalysts with fractional monolayer sulfur. An environmental cell is now available for Fourier transform infrared (FTIR) examination of carbonaceous layers, and a supply of C^{13} -labeled methane is available for deposition on the catalysts so that they can undergo subsequent C^{13} nuclear magnetic resonance (NMR) examination.

Despite observation of the effect of chemisorbed sulfur on hydrogasification of carbonaceous overlayers, the sulfur treated fused-iron catalyst system has been found to be unsuitable for thermochemical examination of coadsorbed carbon because the catalyst system contains significant levels of potassium hydroxide and carbonate at the surface (Davis, 1988). Attempts to quantitatively measure CO and H_2 chemisorption were irreproducible. Sintering of precipitated iron during the sulfur treatment process makes precipitated or powdered iron an unattractive alternative. Future work with dispersed iron will focus on MgO- or silica-supported iron.

FUTURE WORK

During the remainder of the second year, we will conclude our SALI carbon segregation experiments with single crystalline nickel and begin experiments with single crystalline platinum. 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. Low-energy electron diffraction experiments will be used as necessary to determine the structure of the chemisorbed sulfur layer and to determine possible two-dimensional order-disorder phase boundaries in the last project year. Construction of a two-dimensional electron multiplier array and position sensitive collector plate is planned to examine the order-disorder boundaries at moderate temperatures.

Continuing through the third project year, we will examine in detail the thermodynamics and reactivity of carbon deposited on clean alumina-supported platinum, on clean magnesia-supported 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. The following additional studies are planned:

- FTIR spectroscopic examination of the CH_x fragments at selected sulfur and carbon coverage in an environmental cell.
- Solid-state NMR spectroscopy to examine the nature of C^{13} -enriched carbon coadsorbed under selected conditions of temperature, sulfur coverage, and carbon coverage.
- 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.
- 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.

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 Professor C. P. Slichter has examined the adsorption and decomposition of C_2H_2 and C_2H_4 on Pt/Al_2O_3 by C^{13} NMR and C^{13} - H^1 double resonance NMR spectroscopy (Wang et al., 1984, 1985, 1986). This research validates 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 -hydrocarbon radicals at low temperature through solid-state C^{13} NMR and the C^{13} - H^1 double resonance NMR techniques.

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