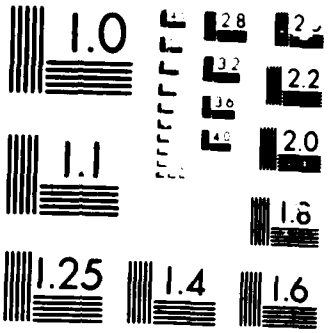
AD-A176 382 UV-LASER PHOTOLYSIS STUDIES OF REACTIONS OF HYDROCARBONS ON SUPPORTED METAL SURFACES(U) RICHMOND UNIV VA DEPT OF CHEMISTRY J T KEISER 28 JAN 87 1/1

UNCLASSIFIED N00014-84-K-0280 F/G 7/2 NL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3.6
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2.2
2.0
1.1
1.8
1.25
1.4
1.6

(12)

AD-A176 382

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED

1b. RESTRICTIVE MARKINGS:

2a. SECURITY CLASSIFICATION AUTHORITY:

3. DISTRIBUTION/AVAILABILITY OF REPORT: Unlimited

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE:

4. PERFORMING ORGANIZATION REPORT NUMBER(S):

5. MONITORING ORGANIZATION REPORT NUMBER(S):

6a. NAME OF PERFORMING ORGANIZATION: University of Richmond, Office of Sponsored Programs

6b. OFFICE SYMBOL (If applicable):

7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code): Richmond, VA 23173

7b. ADDRESS (City, State, and ZIP Code): 800 North Quincy Street, Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION:

8b. OFFICE SYMBOL (If applicable):

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-84-K-0280

8c. ADDRESS (City, State, and ZIP Code):

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
		NR 056-844	

11. TITLE (Include Security Classification): "UV-Laser Photolysis Studies of Reactions of Hydrocarbons on Supported Metal Surfaces" (unclassified)

12. PERSONAL AUTHOR(S): Joseph T. Keiser

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 84/4/1 TO 86/10/1	86/12/17	10

16. SUPPLEMENTARY NOTATION:

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Supported Metal Surfaces, Adsorbates, Laser, SMSI

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The adsorption of CO on both alumina supported rhodium and titania supported rhodium has been investigated by Fourier Transform Infrared Spectroscopy (FTIR), Thermal Desorption and Isotopic substitution methods. The titania support has been shown to interact chemically with the rhodium even though the surfaces were prepared under mild reducing conditions (H_2, 150C) compared to those normally used to induce the "Strong Metal Support Interaction (SMSI)"(H_2, T > 500C). Preliminary investigations into the adsorption of formaldehyde and acetone onto alumina supported rhodium surfaces has also been conducted. These systems were used to attempt to directly photolyze the adsorbates using an excimer laser. No evidence for decomposition of the molecularly adsorbed species was observed. This is believed to be due to low absorptivities of the surface species and rapid quenching by the metal substrate.

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DTIC ELECTE FEB 04 1987 S D E

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. David Nelson

22b. TELEPHONE (Include Area Code):

22c. OFFICE SYMBOL:

DD FORM 1473, 84 MAR — Previous editions may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

OFFICE OF NAVAL RESEARCH
FINAL REPORT

for

Contract N00014-84-K-0280
Task #NR 056-844

"UV - Laser Photolysis Studies of Reactions of Hydrocarbons on Supported Metal Surfaces"

Principal Investigator: Dr. J. T. Keiser
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January 28, 1987

Accession For	
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Unannounced	☐
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Distribution/	
Availability Codes	
Dist	Avail and/or Special
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Accomplishments and Conclusions:

The adsorption of formaldehyde, acetone and CO on supported rhodium surfaces was studied. The infrared adsorption spectra of formaldehyde adsorbed onto rhodium supported on alumina (Rh/Al_2O_3) was in qualitative agreement with the work reported by others (1). Acetone was observed to adsorb both molecularly and dissociatively at room temperature onto a Rh/Al_2O_3 surface. This is very interesting and to our knowledge has not been previously reported. A complete investigation of this system is planned.

The directly photolysis of the molecularly adsorbed acetone and formaldehyde was attempted using an excimer laser operating at 193 nanometers. No evidence for the decomposition of the molecularly adsorbed species was observed. This is presumed to be due in part to the low absorptivity of the chemisorbed species. The uv spectra of these species is broad and fairly flat and is on top of the absorption spectrum of the pure metal. This makes it difficult to selectively pump the adsorbate. Also, the chemical bond between the metal and the adsorbate will result in rapid quenching of an excited adsorbate molecule. Multiphoton effects might still be possible but this was unlikely in our case since the power densities used in the experiments were not that high (typically around 1 megawatt/cm^2).

The adsorption of CO onto supported rhodium surfaces was studied extensively by Fourier Transform Infrared Spectroscopy (FTIR), Thermal Desorption and Isotopic substitution methods. Particular emphasis was placed on the effects of a titania support.

The use of titania supports is of interest for several reasons. Typical catalysts are supported on either alumina or silica. Both of these supports are insulators. Titania, in contrast, is a semiconductor. In 1972, it was first shown that photons which exceeded the band gap energy of titania

could be used to "assist" a catalytic process occuring on the surface (2). The experiment involved the photoassisted decomposition of water on titania. The mechanism for this reaction apparently involves the generation of electron hole-pairs by the action of photons on titania. Since the original experiment, other photoassisted catalytic reactions on metals supported on titania have been reported (3,4).

A second reason why titania supports are of interest is because of a phenomena which has been called the "Strong Metal Support Interaction (SMSI)". This phenomena was first observed in 1978 (5). Metal surfaces supported on titania which were prepared under vigorous reducing conditions (hydrogen gas at temperatures in excess of 500 C) had a reduced capacity to chemisorb CO. Other investigations have been conducted regarding the mechanism of this effect (6-8). There are at the moment two main theories which seem to be emerging. One suggests that the vigorous reducing conditions produces a reduced titanium oxide which has a lower vapor pressure that TiO_2. This oxide tends to creep and encapsulate the metal atoms. This incapsulation essentially reduces the exposed metal surface area and therefore the CO chemisorption. The second theory suggests that a reduced titania species interacts electronically with the metal. In this mechanism the reduced titania acts similarly to a lewis base and donates electron density to the metal to alter the metal/adsorbate interaction.

Interestingly, we have observed metal-support interactions between rhodium and titanium when these surfaces were prepared in hydrogen gas at temperatures of only 150 C. The table below gives a comparison of the infrared absorption bands observed for CO/Rh/Titania system compared to the CO/Rh/Alumina system (Figure 1). Both surfaces are peresent in the same cell and therefore have been exposed to identical reduction conditions (H_2, 150 C) and exposure to CO (50 Torr).

Vibrational Mode	CO/Rh/Al_2O_3	CO/Rh/TiO_2	Δcm-1
Symmetric stretch of the gem dicarbonyl [$Rh(CO)_2$]	2112 cm-1	2107cm-1	-5
Asymmetric stretch of the gem dicarbonyl [$Rh(CO)_2$]	2047	2042	-5
CO stretch of the "A-top" species [RhCO]	2079	2078	-1
CO stretch of the Bridge bonded species [Rh_2CO]	≈1900 (broad)	≈1900 (broad)	--
Previously unobserved CO species	----	2004	--

It was also observed that the ratio of the intensities of the bands assigned to the assymetric and the symmetric stretch of the double carbonyl peaks was different on the titania support compared to the alumina support (Figure 1). This ratio is believed to be indicative of the CO-Rh-CO bond angle. When an alumina support is used the ratio of these bands is usually close to 1 which indicates a 90 degree angle (9). In our work this ratio was 0.94 when an alumina support was used indicating an angle of 88 degrees. In contrast, when the titania support was used, the ratio of these bands was 0.59 indicating an angle of approximately 75 degrees.

Isotopic substitution experiments were conducted in order to futher investigate this system. $C_{13}O$ was first chemisorbed onto a rhodium surface supported onto titania. The spectra obtained is consistent with the expected isotopic shift (Figure 2). The system was then evacuated and the sample exposed to 50 Torr of $C_{12}O$. The exchange was very rapid and by the time that a new spectra was taken (several minutes) the surface had been

completly exchanged and only bands due to $C_{12}O$ species were detected by FTIR.

The CO adsorpion on Rh/TiO_2 was also investigated as a function of the CO pressure. It can be seen from Figure 3 that upon exposure to 0.5 Torr of CO, all of the surface species are observable. As the pressure is increased, their is a marked increase in the intensity of the bands assosciated with the gem dicarbonyl species but almost no increase in the intensity of the 2004 cm-1 band (an unknown CO species). It is unclear if the band associated with the a-top CO species is increasing in intensity. But, the location of this band does shift to higher wavenumbers as the CO pressure is increased. This is believed to be due to the fact the a-top species is formed on islands of rhodium atoms (10). As the coverage is increased, the increased concentration of near neighbors distorts the vibration. In contrast, there is no significant shift in the bands due to the gem dicarbonyl species or to the unknown CO species at 2004 cm-1. The gem dicarbonyl species is reportedly formed on isolated atoms of Rhodium or possibly on the edges of islands where there is room for two CO molecules per rhodium atom (10, 11). The fact that the 2004 cm-1 band also does not shift with increasing CO pressure suggests that it also is associated with isolated rhodium atoms or the edges of islands.

The stability of the chemisorbed CO species as a function of temperature was also investigated. After exposing a freshly prepared Rh/TiO_2 surface to CO at room temperature, the surface was slowly heated to 85 C. Spectra were taken at various temperatures as shown in Figure 4. The intensity of the gem dicarbonyl species and the a-top species are markedly decreased as the temperature is increased. However, there is litt'e change in the intensity of the 2004 cm-1 band up to 85 C. This suggests that this species is more stable than the other species.

Based on this work, we have concluded the following:

a) It appears that at least the three CO/Rh species previously seen in the CO/Rh/Al_2O_3 system are present in the CO/Rh/TiO_2 system.

b) TiO_2 appears to chemically interact with the Rhodium surface. This is supported that there are observable shifts in basically all of the CO species, and by the presence of the new band at 2004 cm-1 and by the alteration in the relative intensities of the gem dicarbonyl bands.

c)Regarding the 2004 cm-1 band it appears to be

1) a CO species of some type
2) rapidly exchangeable at moderate pressures of CO
3) associated with isolated or edge sites
4) less easily desorbed thermally than either the gem dicarbonyl or the a-top species

d)Regarding the CO-Rh-CO angle in the gem dicarbonly species, the angle is altered from 90 degrees in the CO/Rh/Al_2O_3 case to approximately 75 degrees in the CO/Rh/TiO_2 case.

Figure 1

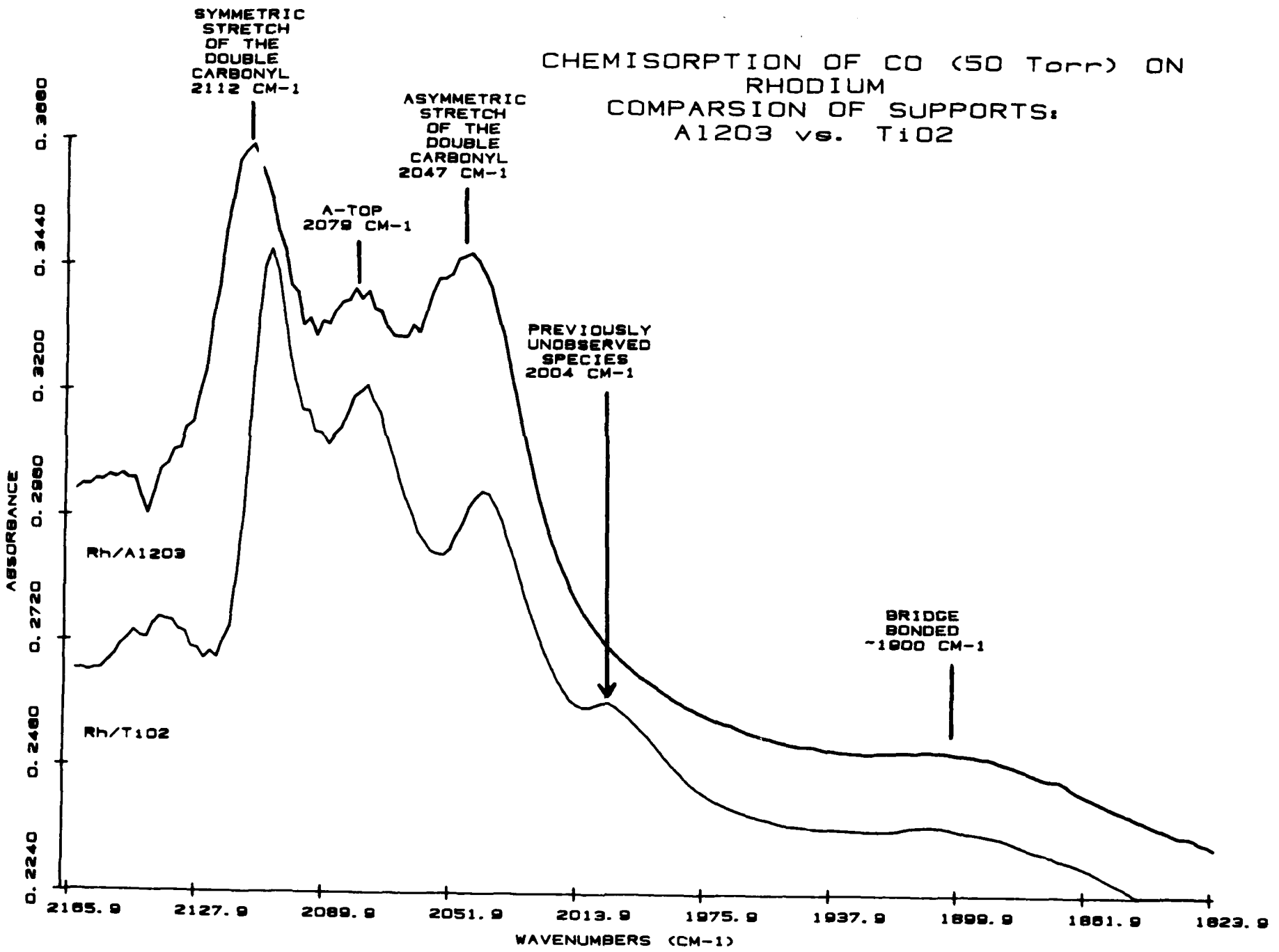

CHEMISORPTION OF CO (50 Torr) ON RHODIUM
COMPARSION OF SUPPORTS:
A1203 vs. Ti02
SYMMETRIC STRETCH OF THE DOUBLE CARBONYL 2112 CM-1
ASYMMETRIC STRETCH OF THE DOUBLE CARBONYL 2047 CM-1
A-TOP 2079 CM-1
PREVIOUSLY UNOBSERVED SPECIES 2004 CM-1
BRIDGE BONDED ~1900 CM-1
Rh/A1203
Rh/Ti02
ABSORBANCE
0.3680
0.3440
0.3200
0.2960
0.2720
0.2480
0.2240
2165.9
2127.9
2089.9
2051.9
2013.9
1975.9
1937.9
1899.9
1861.9
1823.9
WAVENUMBERS (CM-1)

Figure 2

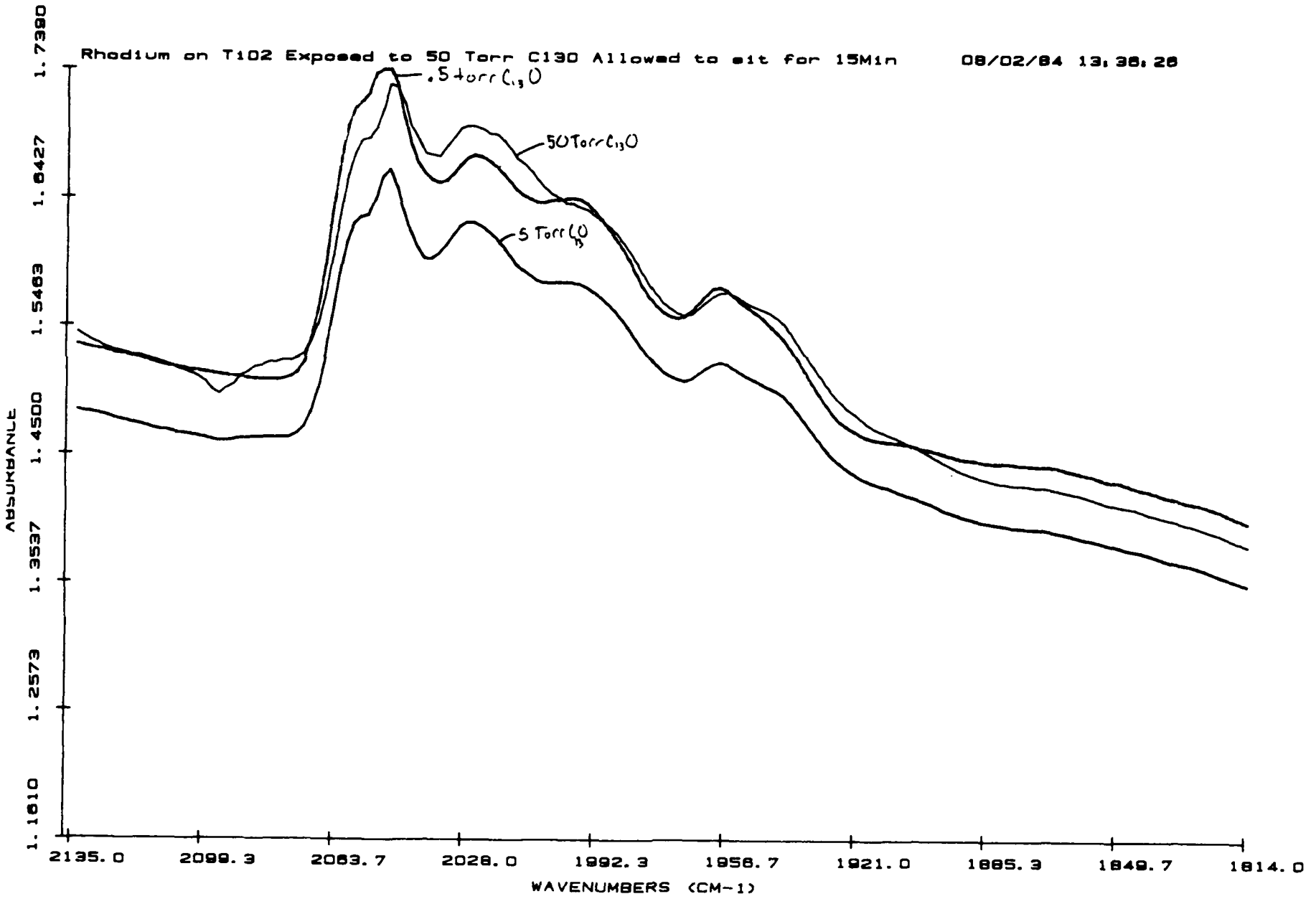
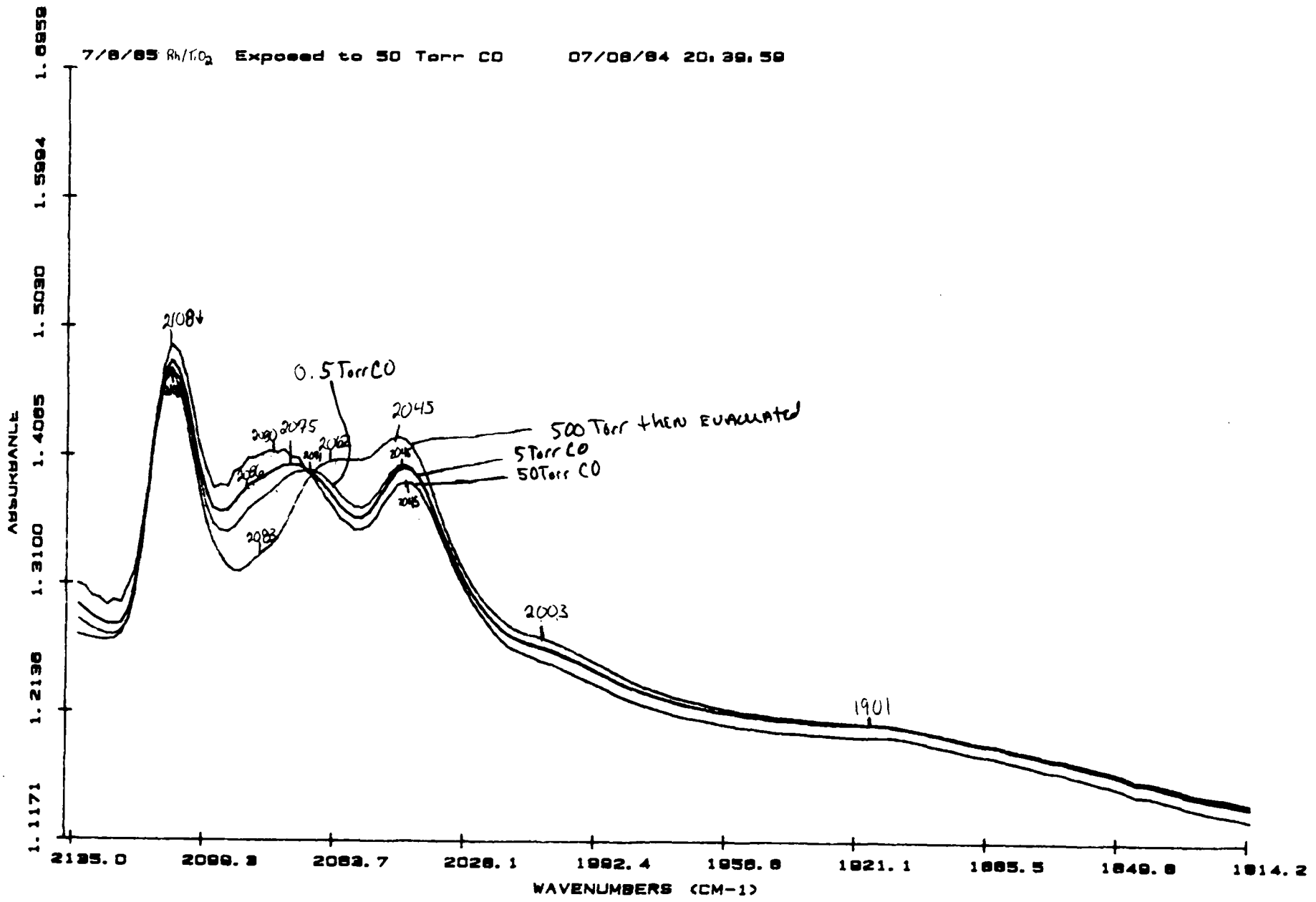
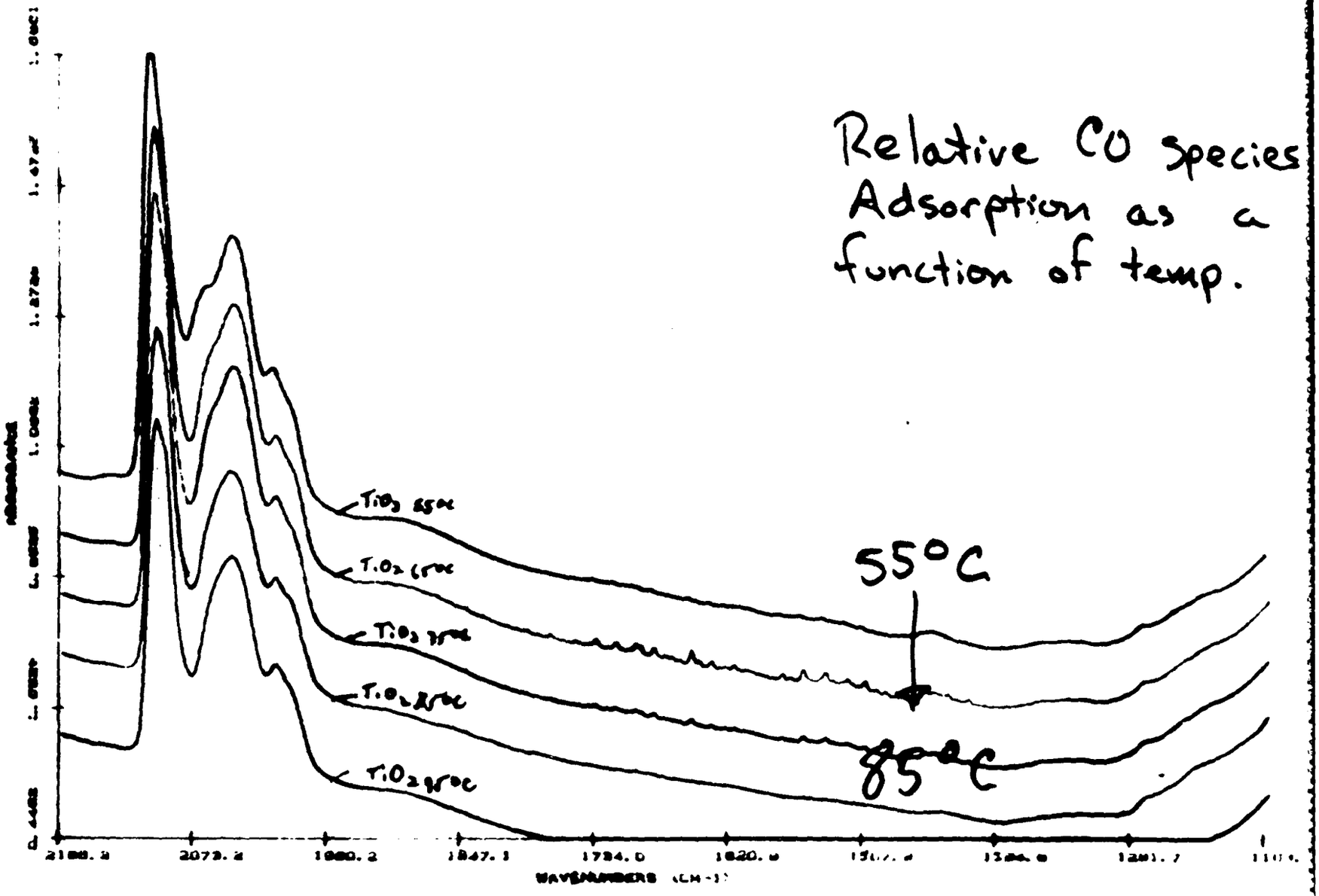

Rhodium on TiO2 Exposed to 50 Torr CO Allowed to sit for 15Min
08/02/84 13:38:28
.5 torr CO
50 Torr CO
5 Torr CO
ABSORBANCE
1.7380
1.6427
1.5463
1.4500
1.3537
1.2573
1.1610
2135.0
2099.3
2063.7
2028.0
1992.3
1956.7
1921.0
1885.3
1849.7
1814.0
WAVENUMBERS (CM-1)

Figure 3



7/8/85 Rh/TiO2 Exposed to 50 Torr CO 07/08/84 20:39:59
ABSORBANCE
1.6959
1.5994
1.5030
1.4065
1.3100
1.2136
1.1171
2135.0
2099.3
2063.7
2028.1
1992.4
1956.8
1921.1
1885.5
1849.8
1814.2
WAVENUMBERS (CM-1)
2108
0.5 Torr CO
2045
500 Torr then evacuated
5 Torr CO
50 Torr CO
2075
2083
2003
1901

Figure 4


Relative CO Species Adsorption as a function of temp.
55°C
85°C
TiO2 55°C
TiO2 65°C
TiO2 75°C
TiO2 85°C
TiO2 95°C
2073.2
1980.2
1847.1
1734.0
1820.0
1281.7
WAVENUMBERS (CM-1)

References

1. J. T. Yates, Jr., and R. R. Cavanagh, J. of Cat. 74, 97 (1982).
2. A. Fujishima and K. Honda, Nature 238, 37 (1972).
3. S. Tsai, C. Kao, and Y. Chung, J. of Cat., 79, 451 (1983).
4. S. Sato, and J. M. White, J. Amer. Chem. Soc. 102, 7206 (1980).
5. S. J. Tauster, S. C. Fung, and R. L. Garten, J. Amer. Chem. Soc. 100, 170 (1978).
6. S. M. Spencer, J. Catal. 93, 216 (1985).
7. S. C. Fung, J. Catal., 76, 225 (1982).
8. D. N. Belton, Y.-M. Sun, J. M. White, J. of Phys. Chem. 88, 5172 (1984).
9. S. F. A. Kettle and I. Paul, Adv. Organomet. Chem. 10, 199 (1972).
10. J. T. Yates, Jr., T. M. Duncan, S. D. Worley, and R. W. Vaughan, J. Chem Phys. 70(3), 1219 (1979).
11. A. C. Yang and C. W. Garland, J. Phys. Chem. 61, 1504 (1957).

Listing of all technical reports and journal articles:

An article on the adsorption of CO on supported rhodium comparing the alumina versus the titania supports is in preparation. A copy will be sent to ONR as soon as preprints are available. No other technical reports have been issued.

Personnel:

The following undergraduate students have worked on this project:

John Randolph - June '84 to May '85

Rich Rounds - January 85 to May '85

Phil Schultz - May '85 to December '85

Sean Tutton - September '85 to Present

Phil Merrill - January '85 to Present

END

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