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WORKSHOP ON
"SURFACE SCIENCE AND CATALYSIS"
(4 - 8 May 1987)

MECHANISMS OF THE CARBON MONOXIDE OXIDATION AND NITRIC OXIDE REDUCTION REACTIONS OVER SINGLE CRYSTAL AND SUPPORTED RHODIUM CATALYSTS: HIGH PRESSURE RATES EXPLAINED USING ULTRAHIGH VACUUM SURFACE SCIENCE

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The demonstration that surface parameters obtained in UHV experiments are applicable to high pressure catalytic reactions has long been a goal of surface science studies. We will attempt to show directly in these lectures that, for an important class of reactions, the strongly-bound species present under the conditions of UHV studies are the same surface species reacting at high pressures. We have chosen two test reactions, CO oxidation ($2CO + O_2 \rightarrow 2CO_2$) and NO reduction ($2CO + 2NO \rightarrow 2CO_2 + N_2$) over rhodium, which are important in automotive exhaust catalysis. We will also discuss the water formation reaction ($2H_2 + 2O_2 \rightarrow H_2O$) on Rh when appropriate. An outline of the content of the lectures is as follows:

I. Motivation

II. Approach
  A. Measure High Pressure Reaction Rates
  B. Measure appropriate surface properties in ultrahigh vacuum
  C. Develop kinetic model based on UHV results
  D. Compare high pressure results with predictions based on UHV work

III. Equipment and Methods
  A. High Pressure Reaction Measurements
  B. Ultrahigh Vacuum Measurements
    a. Temperature Programmed Desorption (TPD)
    b. High resolution ($\Delta E \sim 40$ cm^{-1}) Electron Energy Loss Spectroscopy (EELS)
    c. Other surface science tools (XPS, UPS, ...)
  C. Example of determining an activation energy: NO(a) dissociation on Rh(111) or OH(a) formation on Rh(100)

IV. Carbon Monoxide Oxidation Reaction over Rhodium
  A. High pressure (1-100 Torr) kinetics over single crystal and supported Rh
  B. Low pressure (10^{-8}-10^{-4} Torr) kinetics over single crystal Rh
  C. UHV determination of activation energies of desorption and dissociation
  D. UHV determination of sticking coefficients for oxygen in the presence of CO(a)
  E. Derivation of a steady state reaction model based on UHV results
  G. F. Comparison of agreement between model results and reaction data
  H. G. What is the Rh surface like during CO oxidation?

V. Nitric Oxide Reduction Reaction over Rhodium
  A. High pressure (1-100 Torr) kinetics over single crystal and supported Rh
  ~~B. Low pressure (10^{-8}-10^{-4} Torr) kinetics over single crystal Rh~~ no time
  C. UHV determination of activation energies of desorption and dissociation
  D. Discussion of the steady state reaction model based on UHV results
  E. Comparison of agreement between model results and reaction data
  F. What is the Rh(111) surface like during the NO-CO reaction?
  G. How is the reaction different on supported Rh?

VI. The NO-CO-O_2 Reaction Over Rhodium
  A. High pressure (1-100 Torr) kinetics over single crystal and supported Rh
  B. Manifestations of NO inhibition of CO oxidation

VII. Conclusions

The similarity in the coverages of strongly-bound adsorbed species like NO and CO under UHV and high pressure conditions allows us to use UHV-obtained data to usefully explain high pressure kinetic data. We find that rate expressions based on UHV-determined intermediate steps using UHV-determined rate constants quantitatively predict the rates at high pressures for both the CO-O_2 and NO-CO reactions over single crystal Rh and supported Rh catalysts. Understanding the relative importance of intermediate steps in all of these reactions clarifies which steps need modification to improve overall reaction rates.

A good reference to begin with concerning these lectures is by S. H. Oh, G. B. Fisher, J. E. Carpenter, and D. W. Goodman in the Journal of Catalysis, Vol. 100 (1986), pp. 360-376.

CO OXIDATION

AND

NO REDUCTION

ON

RHODIUM SURFACES

OR

THE SUCCESSFUL PREDICTION OF HIGH PRESSURE REACTION RATES FROM PARAMETERS DETERMINED EXCLUSIVELY UNDER ULTRAHIGH VACUUM CONDITIONS: A VICTORY FOR SURFACE SCIENCE!

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MOTIVATION

- RHODIUM IS THE BEST [redacted] MATERIAL ADEQUATE AS A NITRIC OXIDE REDUCTION CATALYST IN AUTOMOTIVE EXHAUST ENVIRONMENTS
- RHODIUM IS ALSO AN EXCELLENT CATALYST FOR THE OXIDATION OF CARBON MONOXIDE
- WE NEED TO IDENTIFY THE IMPORTANT FACTORS IN THESE REACTIONS AT REALISTIC PRESSURES (~1% ATM OR 10 TORR) IN ORDER TO HOPEFULLY IMPROVE UPON PRESENT CATALYSTS

H

- WE WOULD LIKE TO UNDERSTAND IN DETAIL THE INTERMEDIATE STEPS OF THESE TWO REACTIONS BY USING A COMBINATION OF HIGH PRESSURE AND UHV SURFACE SCIENCE STUDIES

I) $$2CO + O_2 \xrightarrow[(Pd,Pt)]{Rh} 2CO_2$$

II) $$2NO + 2CO \xrightarrow{Rh} 2CO_2 + N_2$$

SAMPLE INTERMEDIATE STEPS ARE

$$CO(G) \underset{K_2}{\overset{K_1}{\rightleftarrows}} CO(A)$$

$$O_2(A) \xrightarrow{K_3} 2O(A)$$

$$CO(A)+O(A) \xrightarrow{K_4} CO_2(G)$$

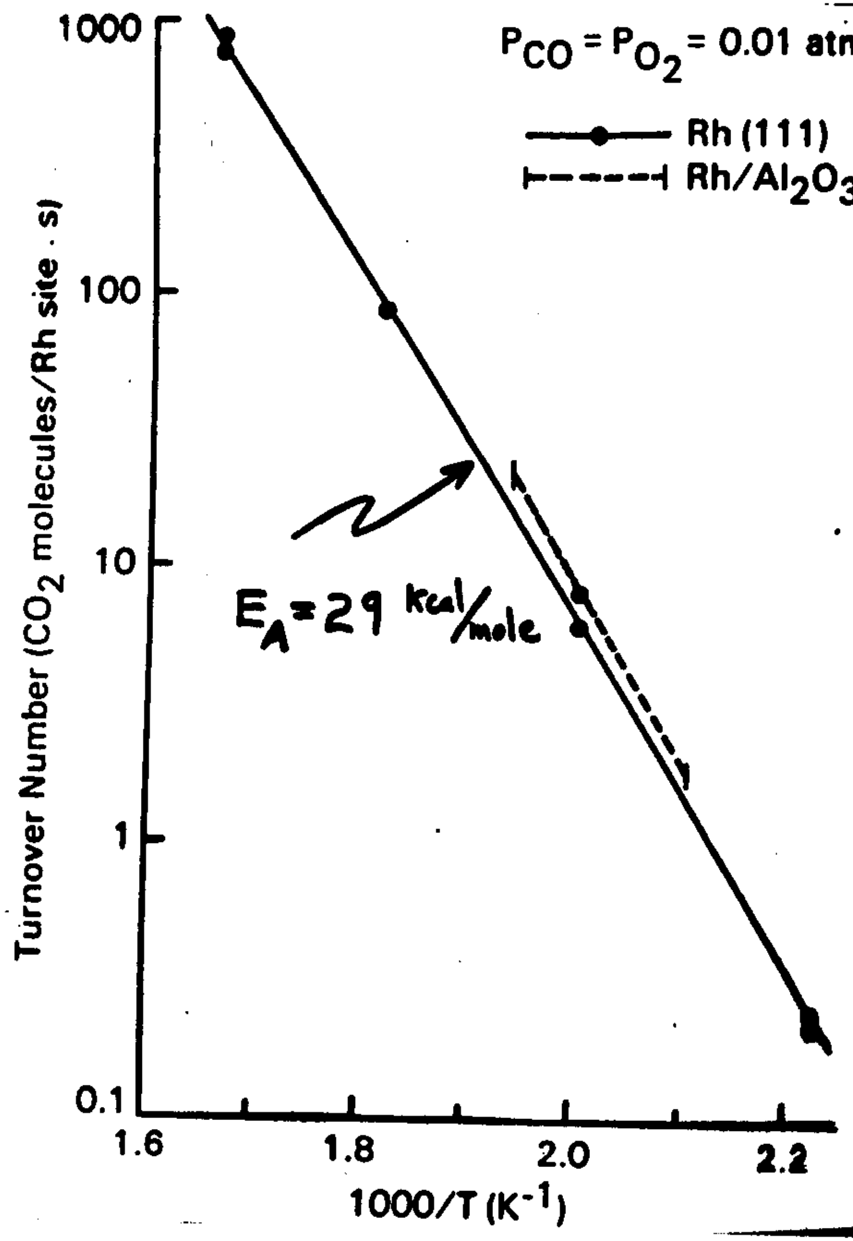
II. APPROACH

(1) MEASURE REACTION RATES AT REALISTIC PRESSURES ON SINGLE CRYSTAL AND SUPPORTED CATALYSTS.

(2) DETERMINE WITH ULTRAHIGH VACUUM (UHV) SURFACE SPECTROSCOPIES (E.G., TPD, EELS, XPS, UPS, LEED, ...) ALL OF THE INTERMEDIATE STEPS FOR THESE CATALYTIC SURFACE REACTIONS AND ALL OF THEIR RATE CONSTANTS.

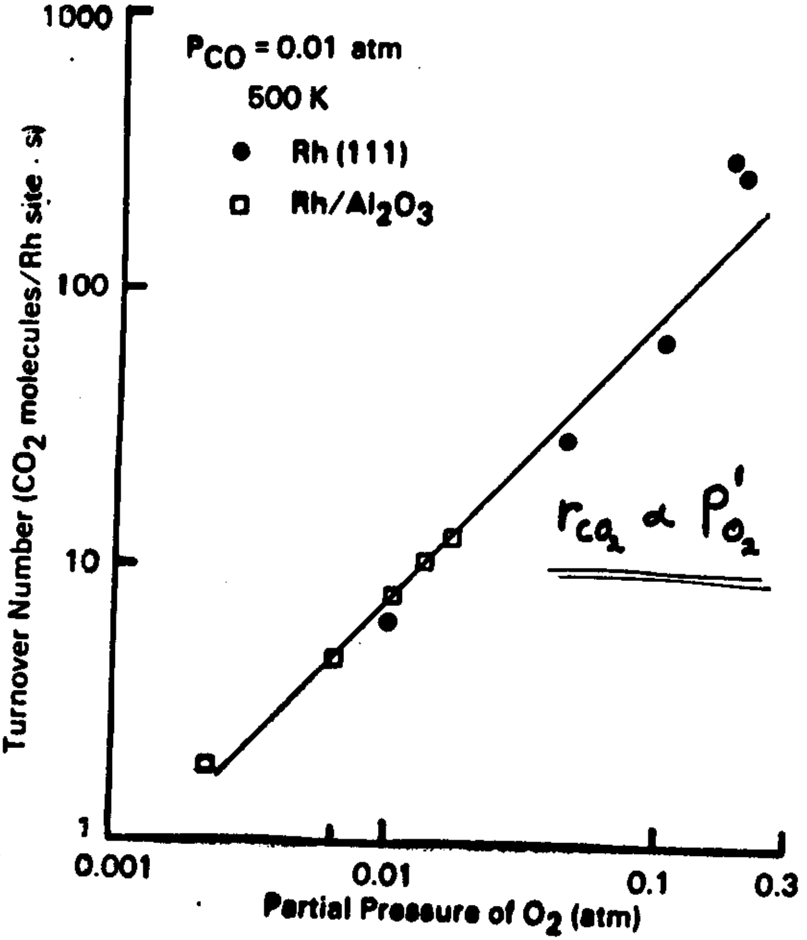
(3) USING KINETIC EXPRESSIONS BASED ON THE KNOWN INTERMEDIATE STEPS, PREDICT THE HIGH PRESSURE REACTION RATES USING ONLY UHV-DETERMINED PARAMETERS.

(4) COMPARE HIGH PRESSURE DATA WITH THE PREDICTIONS OF THE UHV-BASED KINETIC MODEL.



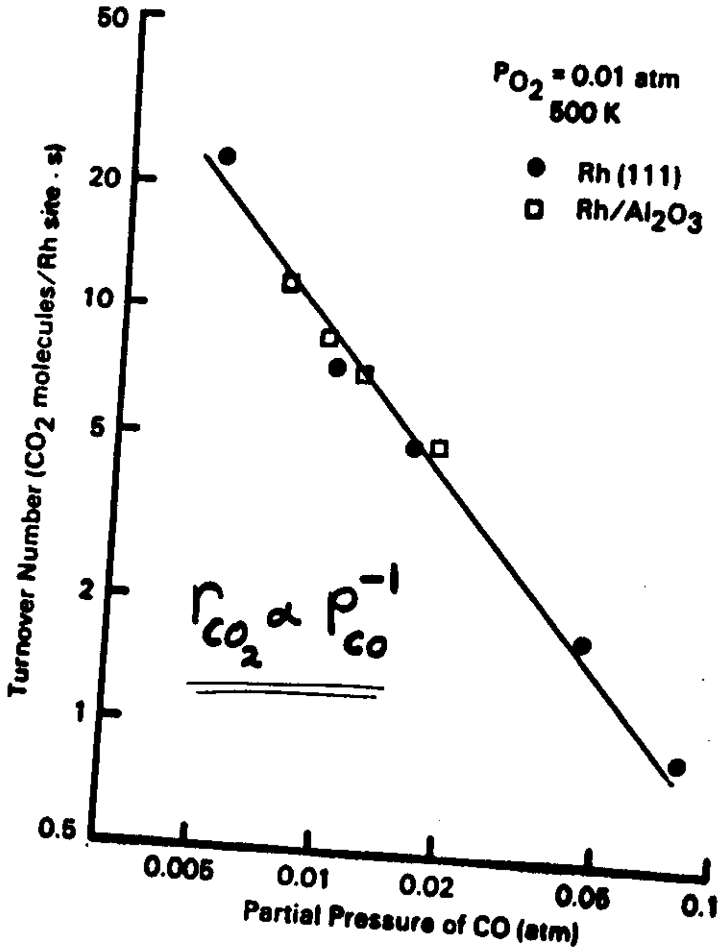
$E_A = 29$ kcal/mole

structure-insensitive



$r_{CO_2} \propto P_{O_2}^{1}$

IV.A.



$r_{CO_2} \propto P_{CO}^{-1}$

IV.A. CONCLUSIONS FOR CO-O_2 ON Rh(111) AND Rh/Al_2O_3

- CO OXIDATION IS A STRUCTURE-INSENSITIVE REACTION, IDENTICAL ON BULK AND SUPPORTED CATALYST.
- CO OXIDATION REACTION IS FIRST ORDER IN OXYGEN PRESSURE.
- REACTION IS NEGATIVE FIRST ORDER IN CARBON MONOXIDE PRESSURE. CO IS THE MAIN INHIBITING SPECIES.

IV. C. Begin Determining Rate Constants of These Elementary Steps.

CO OXIDATION REACTION STEPS

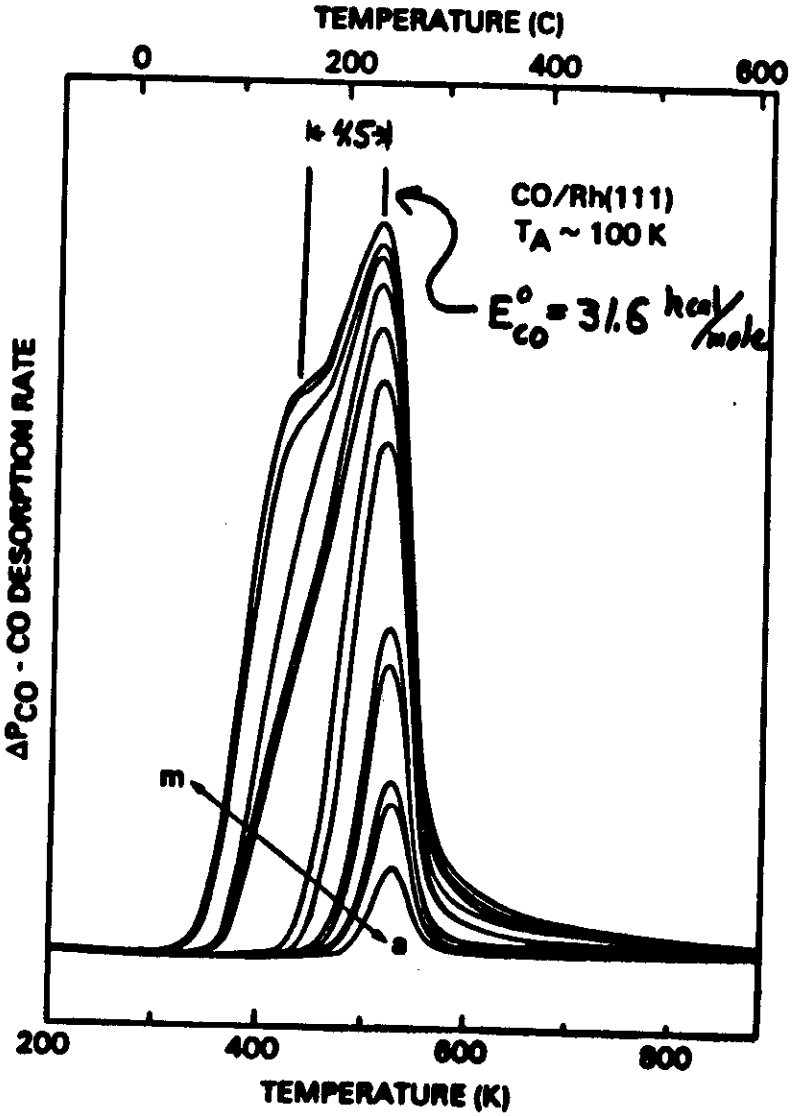
$$2CO + O_2 \xrightarrow{Rh} 2CO_2$$

$$S + CO(g) \underset{2}{\overset{1}{\rightleftharpoons}} CO(A)$$

$$S + O_2(g) \xrightarrow{3} 2O(A)$$ (FIRST ORDER ADSORPTION)

$$O(A) + CO(A) \xrightarrow{4} CO_2(g) + 2S$$

IV. C



IV. C. Parameter Values Used in Model Calculations for CO-O_2 Reaction

	This Work	Literature Value
1) **CO Adsorption**		
S_{CO}	0.5	0.5
2) **CO Desorption**		
k (s^{-1})	1.6×10^{14}	$1 \times 10^{13.6 \pm 0.3}$
E^{o}_{CO} (kcal/mol)	31.6	31.6 ± 1
α_{CO} (kcal/mol)	4.5	$- \; E_{CO}^{des} = (E^{o}_{CO} - \alpha_{CO}\theta_{CO})$ $\simeq 27$ kcal/mole
3) **O_2 Adsorption**		
S_O (500 K)	0.01	0.01
4) **L-H Reaction**		
k (s^{-1})	1×10^{12}	3×10^{5}
E (kcal/mol)	14.3	14.3
α_O (kcal/mol)	4.4	4.4

IV. E. Derive Reaction model for high pressures,

using elementary steps

$$\frac{d\theta_{CO}}{dt} = \underbrace{k_1 P_{CO}(1-\theta_{CO}-\theta_O)}_{\text{CO ads}} - \underbrace{k_2\theta_{CO}}_{\text{CO des}} - \underbrace{k_4\theta_O\theta_{CO}}_{CO_2\text{ form.}}$$

$$\frac{d\theta_O}{dt} = \underbrace{k_3 P_{O_2}(1-\theta_{CO}-\theta_O)}_{O_2\text{ ads}} - \underbrace{\cancel{k\theta_O^2}}_{O_2\text{ des}} - \underbrace{k_4\theta_O\theta_{CO}}_{CO_2\text{ form.}}$$

because $\theta_O \sim 0$, $\theta_{CO} \sim 1$, $\theta_v = 1-\theta_{CO}$

CO is in ads-des equilibrium

$$\frac{d\theta_{CO}}{dt} = k_1 P_{CO}\theta_v - k_2\overset{(\sim 1)}{\theta_{CO}} - \overset{\text{small,}}{\cancel{k_4\theta_O\theta_{CO}}}$$

$$= k_1 P_{CO}\theta_v - k_2$$

$$\frac{d\theta_O}{dt} = k_3 P_{O_2}\theta_v - k_4\theta_O\theta_{CO}$$

Then in steady state, $\frac{d\theta_{CO}}{dt} = \frac{d\theta_O}{dt} = 0$

IV. E.

FOR STEADY STATE CONDITIONS, THE CO_2 FORMATION RATE BECOMES

$$R_{CO_2} = k_4 \cdot \Theta_{CO} \cdot \Theta_{O} = k_3 \cdot \Theta_{V} \cdot P_{O_2}$$

$$= k_3 \cdot \frac{k_2(T)}{k_1 P_{CO}} \cdot P_{O_2}$$

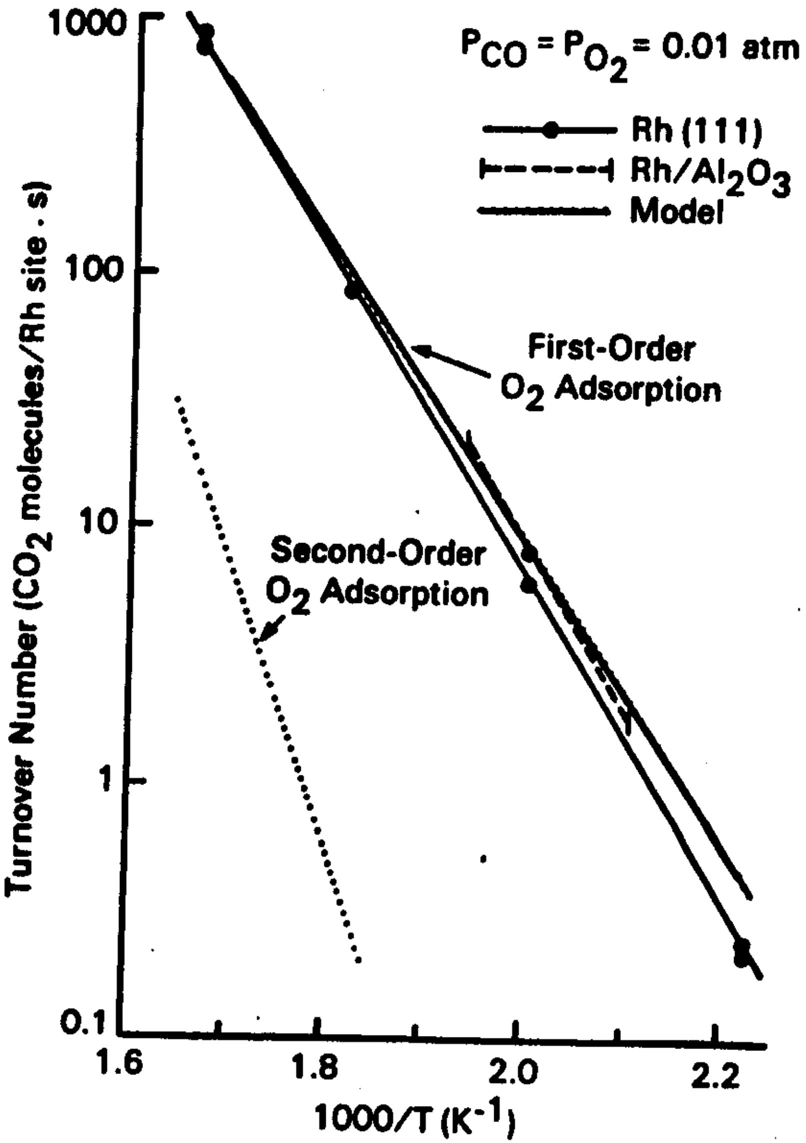
- $$\boxed{R_{CO_2} = \frac{K^{ADS}_{O_2}}{K^{ADS}_{CO}} \cdot \frac{P_{O_2}}{P_{CO}} \cdot \underline{R^{DES}_{CO}(T)}}$$

$$= \frac{K^{ADS}_{O_2}}{K^{ADS}_{CO}} \cdot \frac{P_{O_2}}{P_{CO}} \cdot \underline{K^{DES}_{CO}\, e^{-(E^{0}_{CO} - \alpha_{CO}\Theta_{CO})/RT}}$$

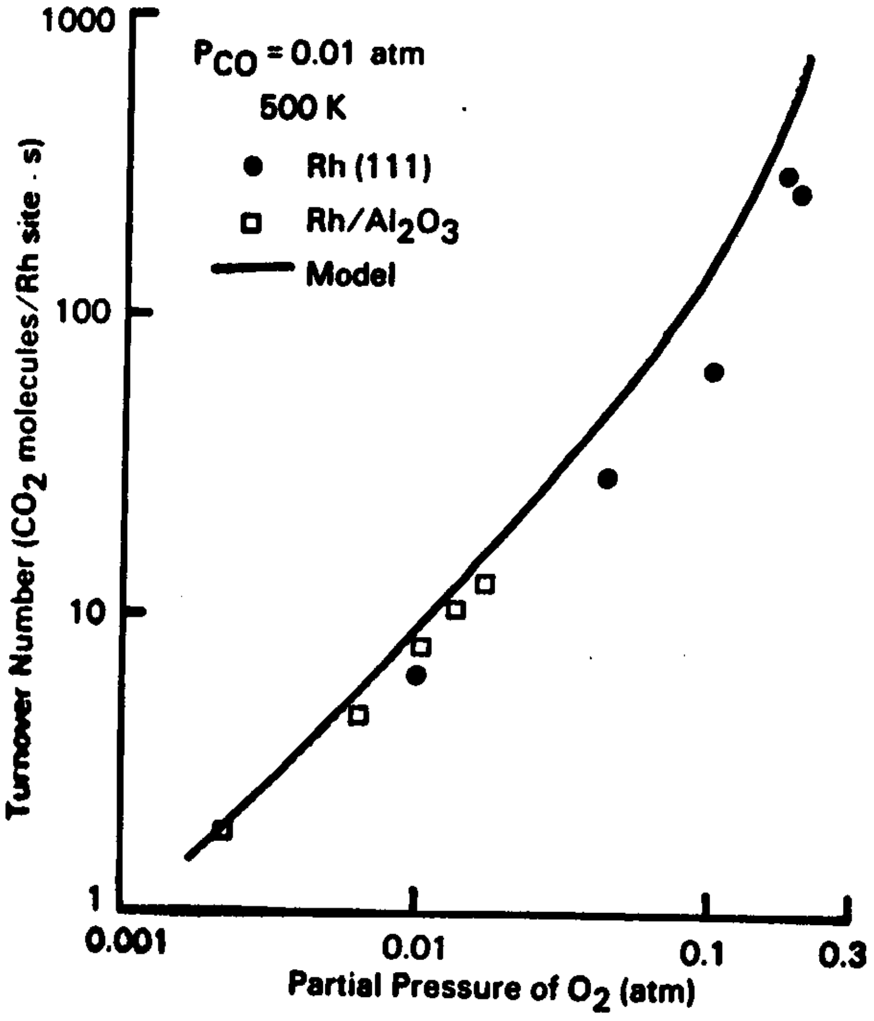
- HIGH PRESSURE APPARENT ACTIVATION ENERGY IS ALSO THE UHV HEAT OF DESORPTION FOR CO(A).
- HOLDING THE RATIO OF REACTANT PRESSURES CONSTANT KEEPS THE REACTION RATE CONSTANT.

no total press dependence

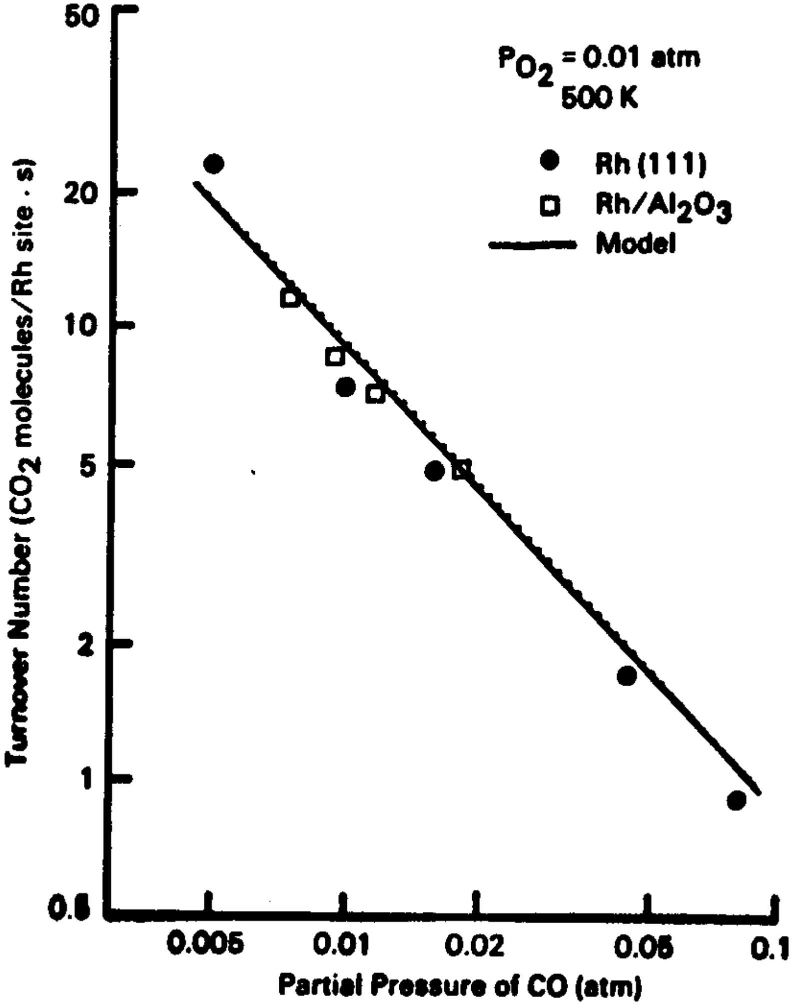
IV. F. Comparison Between Predictions & Measurements



IV. F.



IV. F.

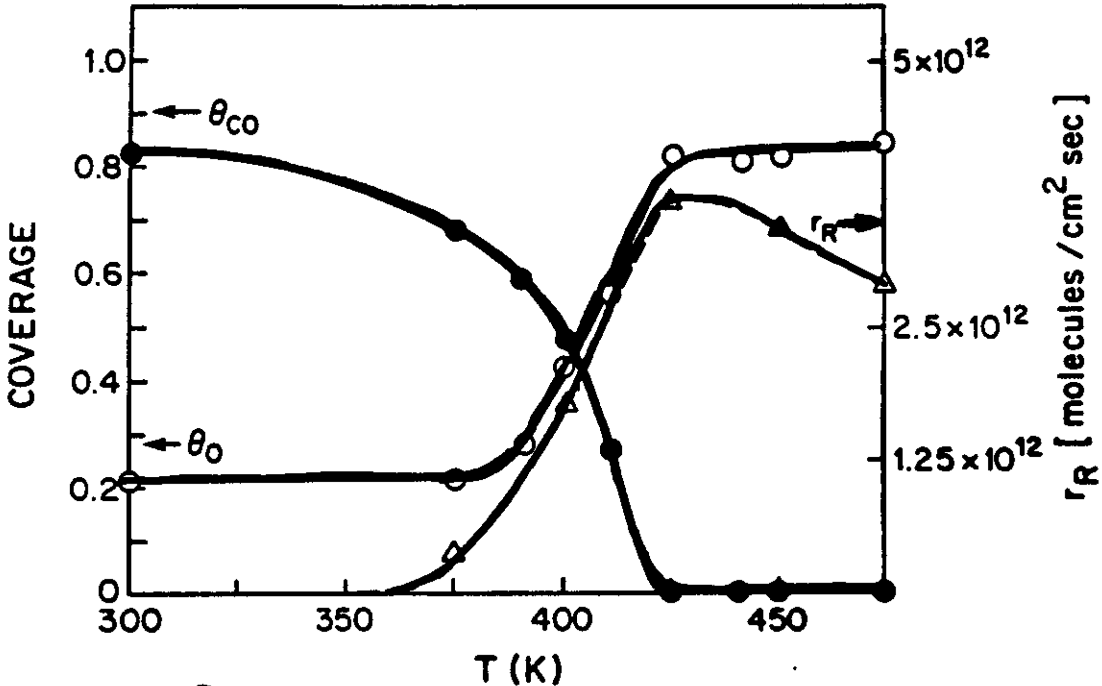


Absolute

IV.G

CO + O_2 Reaction Rate Measured Simultaneously with coverages by XPS

at low pressures



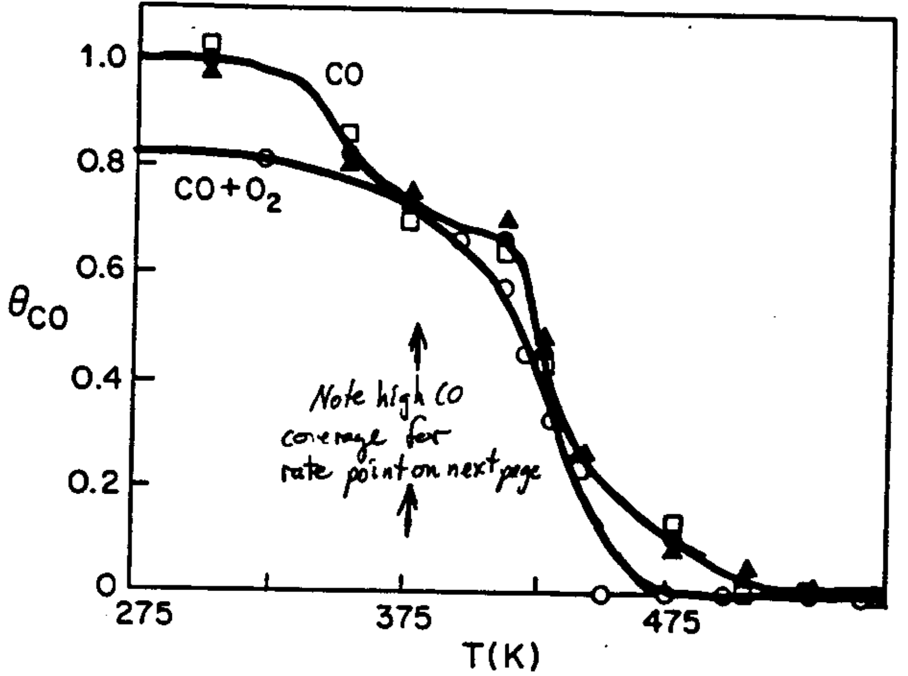
$P_{CO} = 5 \times 10^{-8}$ Torr

$P_{O_2} = 1 \times 10^{-7}$ Torr

IV.G

Coverage of CO with (—) and without (—) oxygen as a function of temperature

Shows CO is in ads-des equilibrium even at 2×10^{-7} Torr

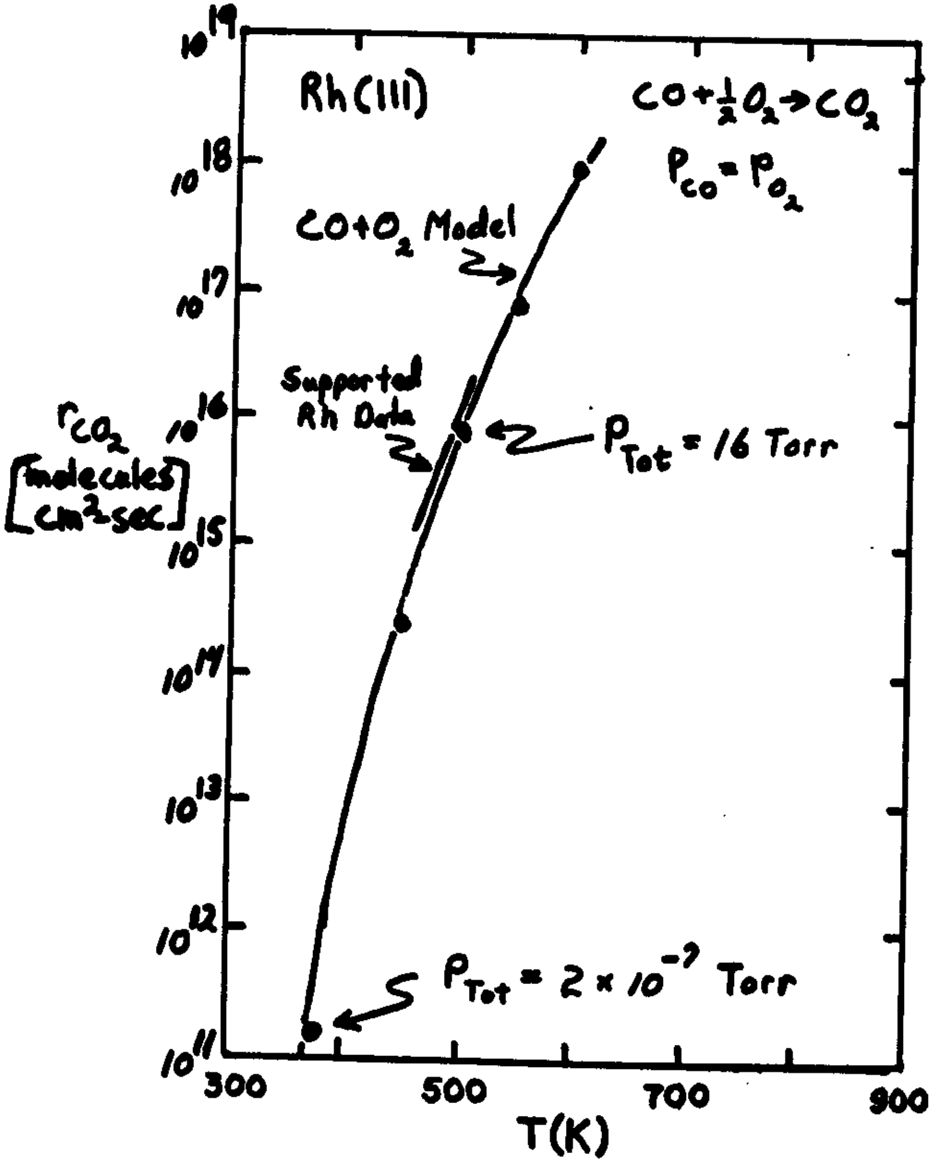


Note high CO coverage for rate point on next page

$P_{CO} = 1.0 \times 10^{-7}$ Torr

$P_{O_2} = 1.0 \times 10^{-7}$ Torr

IV. G. Bridging the Pressure Gap



IV. H.

CONCLUSIONS

- THE CO_2 FORMATION RATE OVER A WIDE RANGE OF CONDITIONS IS GIVEN BY:

$$R_{CO_2} = \frac{K^{ADS}_{O_2}}{K^{ADS}_{CO}} \cdot \frac{P_{O_2}}{P_{CO}} \cdot R^{DES}_{CO}\ (T)$$

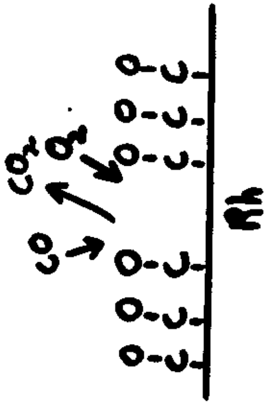
- THE AGREEMENT BETWEEN THIS EXPRESSION AND THE DATA IS QUANTITATIVE, PROVIDING THE CORRECT ABSOLUTE RATE PER SURFACE Rh ATOM FOR BULK AND SUPPORTED Rh.

- THIS AGREEMENT ALSO INDICATES THAT ALL OF THE IMPORTANT INTERMEDIATE STEPS AND THEIR RATE CONSTANTS HAVE BEEN IDENTIFIED CORRECTLY.

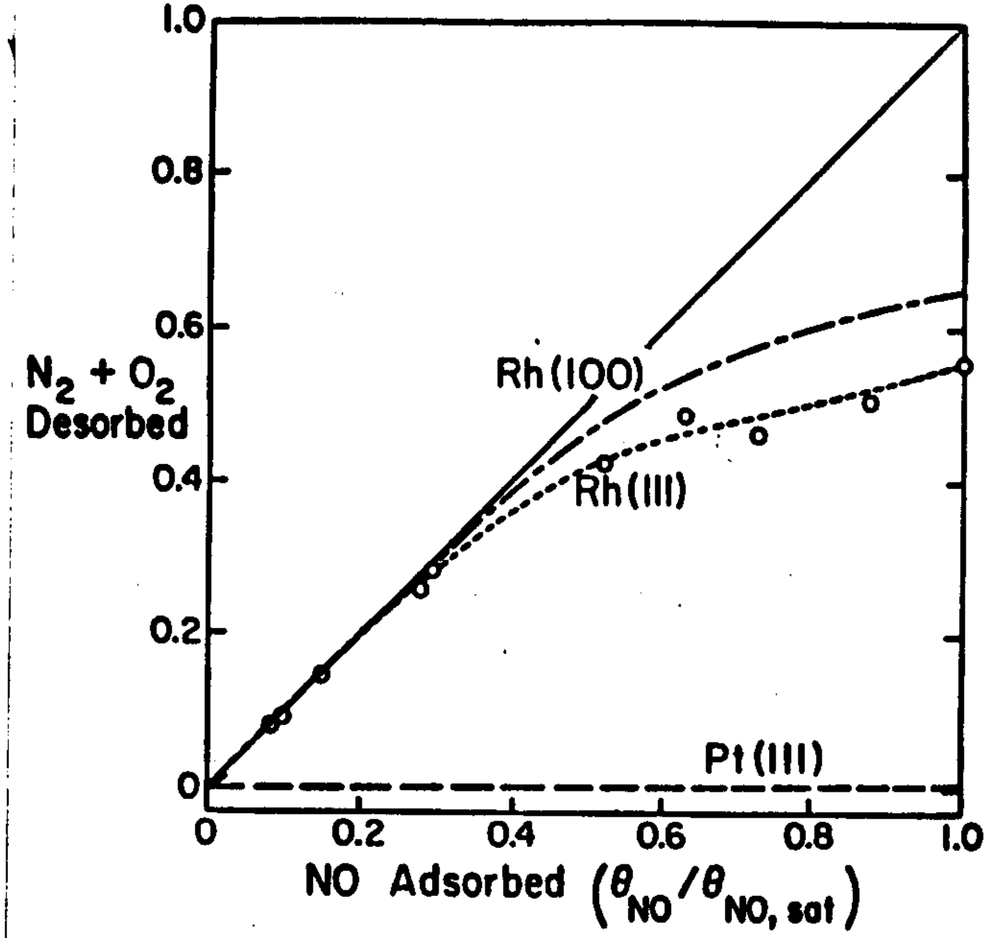
- THIS IS THE FIRST TIME A MODEL USING ONLY UHV-DETERMINED PARAMETERS HAS CORRECTLY PREDICTED A CATALYTIC REACTION AT HIGH PRESSURES

IV. #4, $CO-O_2$ REACTION MECHANISM

- AT LEAST FOR HIGH CO AND O_2 PRESSURES, THE Rh SURFACE IS NEARLY COVERED WITH CO AND THE $CO-O_2$ REACTION RATE IS CONTROLLED BY THE CO DESORPTION RATE **WHICH DETERMINES THE CO COVERAGE AND THE OXYGEN ADSORPTION RATE.**
- OXYGEN COMPETES WITH CO TO ADSORB AT THE LIMITED NUMBER OF VACANT SITES.

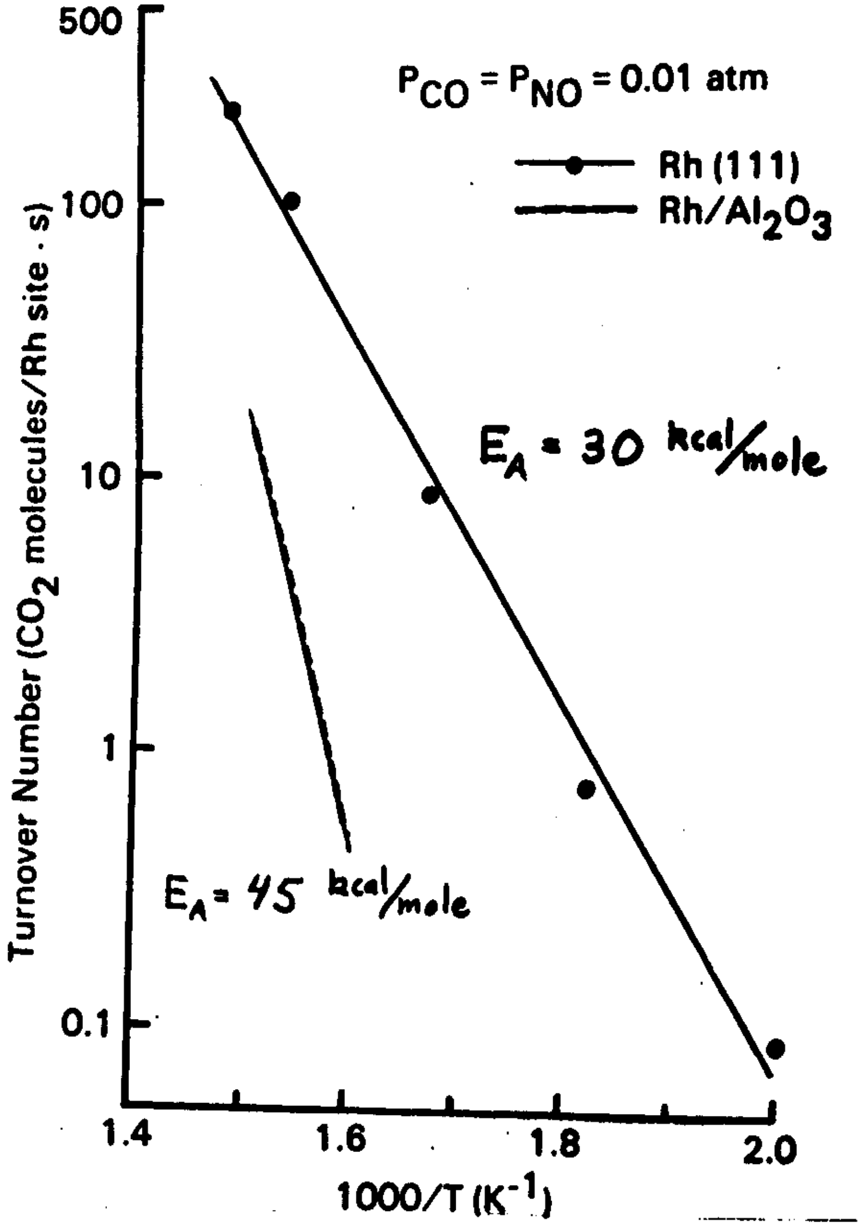


V. The NO-CO Reaction



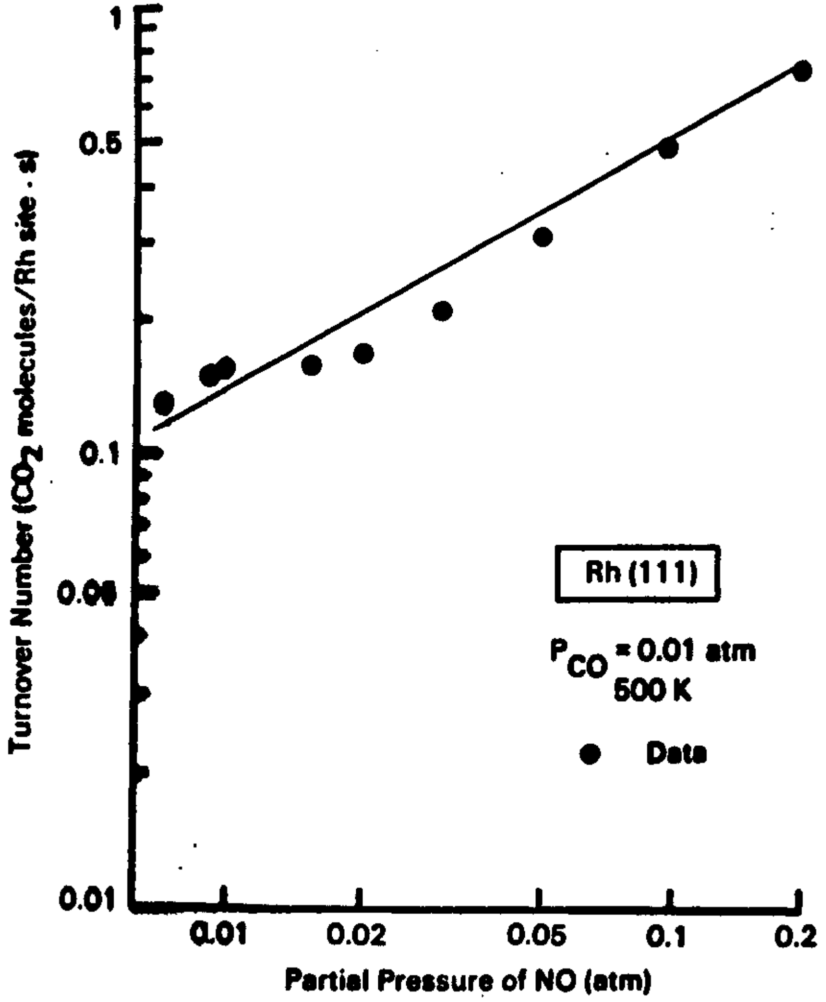
Why Rh? – All the Rh surfaces Dissociate NO more effectively in UHV than any Pt surface studied.

V.A. High Pressure Results

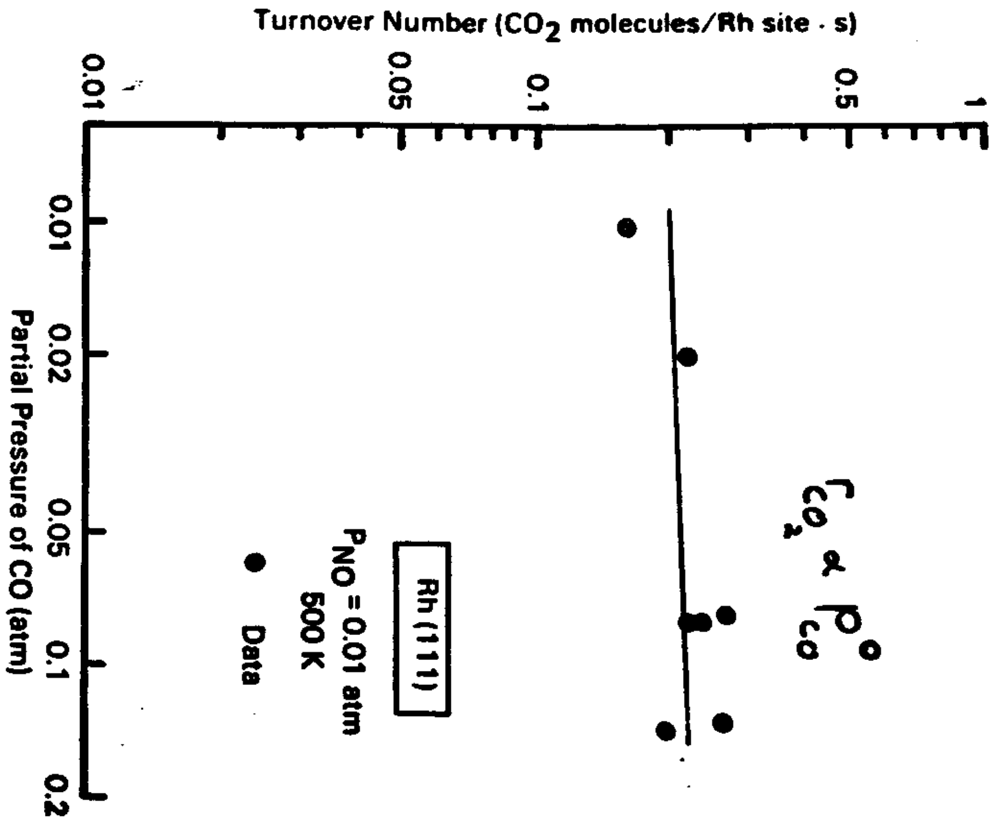


Structure-sensitive

V.A.



V.A.



very hard to understand

V.A. CONCLUSIONS FOR NO-CO ON Rh(111) AND Rh/Al_2O_3

- NO REDUCTION OVER RHODIUM IS A STRUCTURE-SENSITIVE REACTION, DEPENDENT ON THE ENVIRONMENT OF THE RHODIUM.
- Rh(111) (PER SURFACE Rh ATOM) IS A SUPERIOR CATALYST TO SUPPORTED Rh.
- THE NO-CO REACTION HAS A ZERO ORDER DEPENDENCE ON CO PRESSURE.

IV.C. We need rate constants for these steps

NO REDUCTION REACTION STEPS

$$2NO + 2CO \xrightarrow{Rh} 2CO_2 + N_2$$

$$S + CO(G) \overset{1}{\underset{2}{\rightleftharpoons}} CO(A)$$

$$S + NO(G) \overset{3}{\underset{4}{\rightleftharpoons}} NO(A)$$

$$S + NO(A) \xrightarrow{5} N(A) + O(A)$$

$$CO(A) + O(A) \xrightarrow{6} CO_2(G) + 2S$$

$$N(A) + N(A) \xrightarrow{7} N_2(G) + 2S \qquad (\beta - N_2)$$

$$NO(A) + N(A) \xrightarrow{8} N_2(G) + O(A) + S \qquad (\delta - N_2)$$

UNDER STEADY STATE CONDITIONS:

$$R_{CO-NO} = r_{LH} = 2\, r_{N_2,\,\delta} + r_{N_2,\,\beta}$$

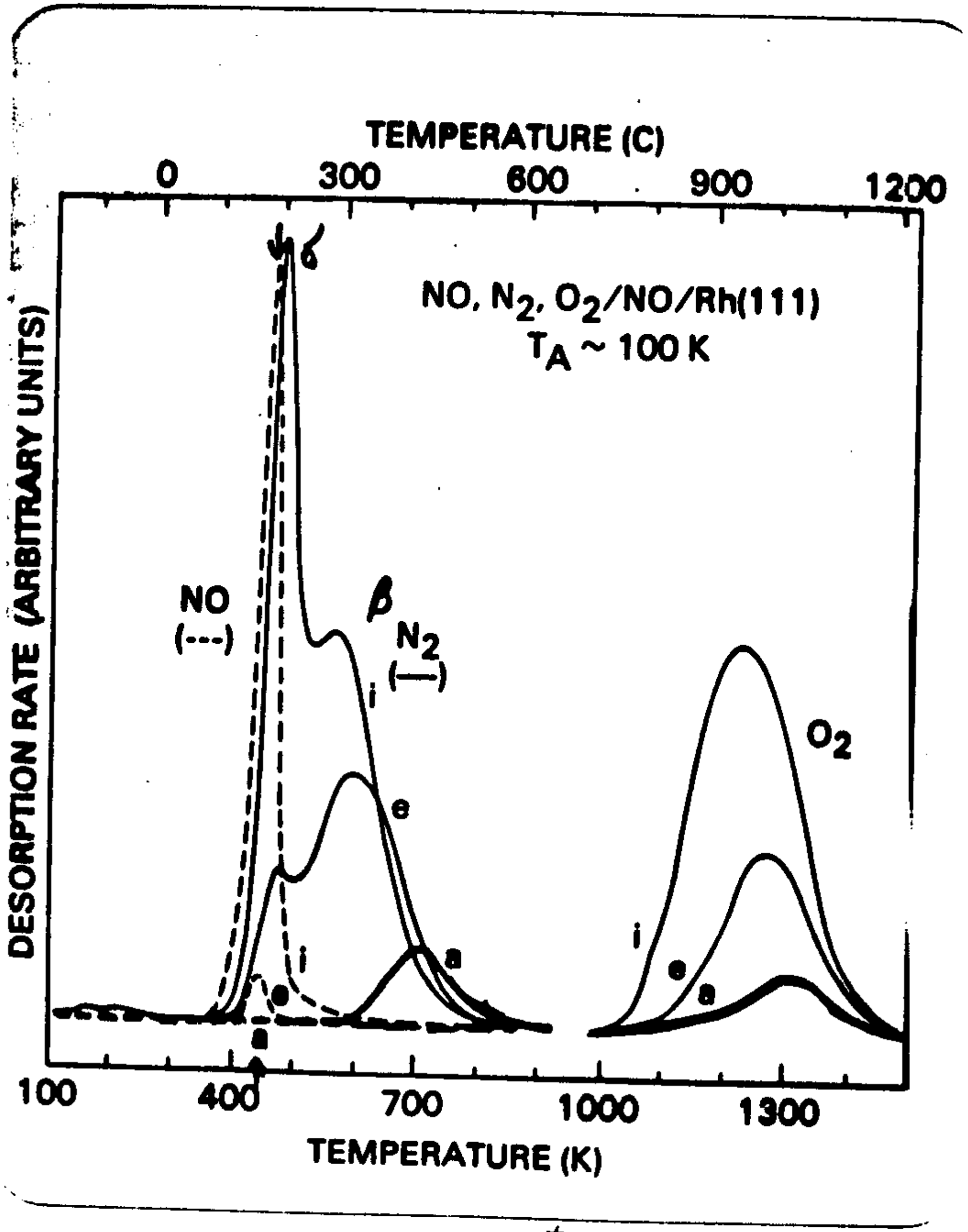
- ON Rh(111) THE REACTION IS CONTROLLED BY THE NITROGEN DESORPTION RATE.

IV.C.

Parameter Values Used in Model Calculations for CO-NO Reaction

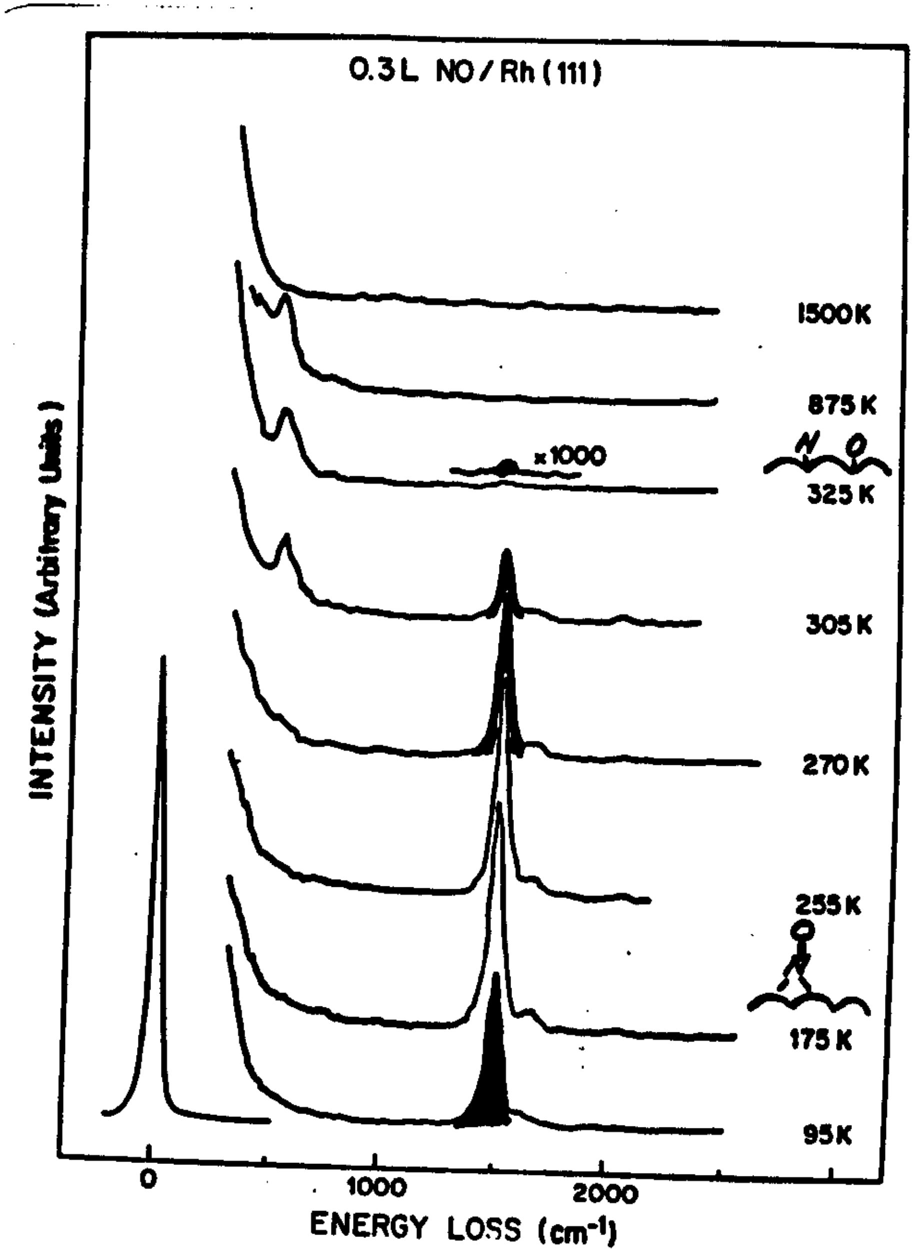
	This Work	Literature Value	
CO Adsorption			
s_{CO}	0.5	0.5	
CO Desorption			
k (s^{-1})	1.6×10^{14}	$1 \times 10^{13.6\pm0.3}$	
E (kcal/mol)	31.6	31.6 ± 1	← (obtain this second)
α_{CO} (kcal/mol)	4.5	-	
α_N (kcal/mol)	$\boxed{10}$	10	
L-H Reaction			
k (s^{-1})	1×10^{12}	3×10^{5}	
E (kcal/mol)	14.3	14.3	
α_O (kcal/mol)	4.4	4.4	
NO Adsorption			
s_{NO}	0.5	~1	
NO Desorption			
k (s^{-1})	5×10^{13}	2×10^{12}	
E (kcal/mol)	26	26	
NO Dissociation			
k (s^{-1})	6×10^{13}	6×10^{13}	← (obtain This first)
E (kcal/mol)	19	19	
δ-N_2 Desorption			
k (s^{-1})	2×10^{9}	2×10^{9}	
E (kcal/mol)	21	21	
β - N_2 Desorption			
k (s^{-1})	3×10^{10}	3×10^{10}	
E (kcal/mol)	$\boxed{31}$	31	
α_N (kcal/mol)	4 (estimated)	-	

V.C.

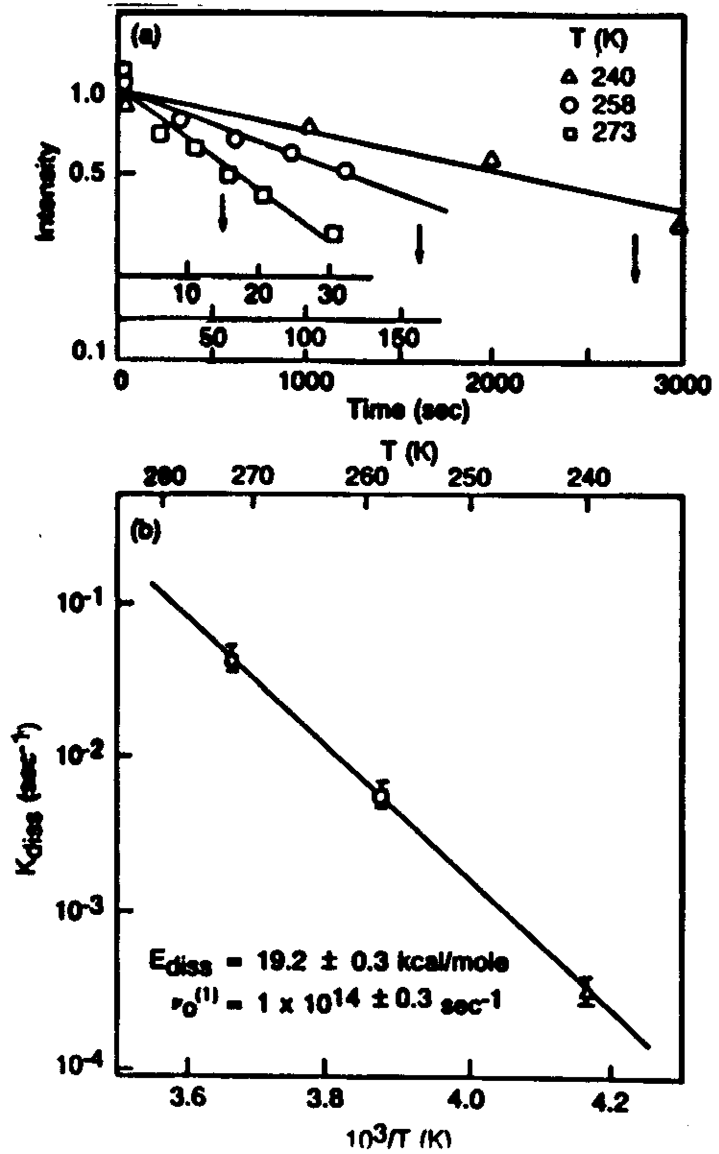


at low Θ NO diss., but at what T?

V.C. Find Temp. Range where NO diss. w/ EELS

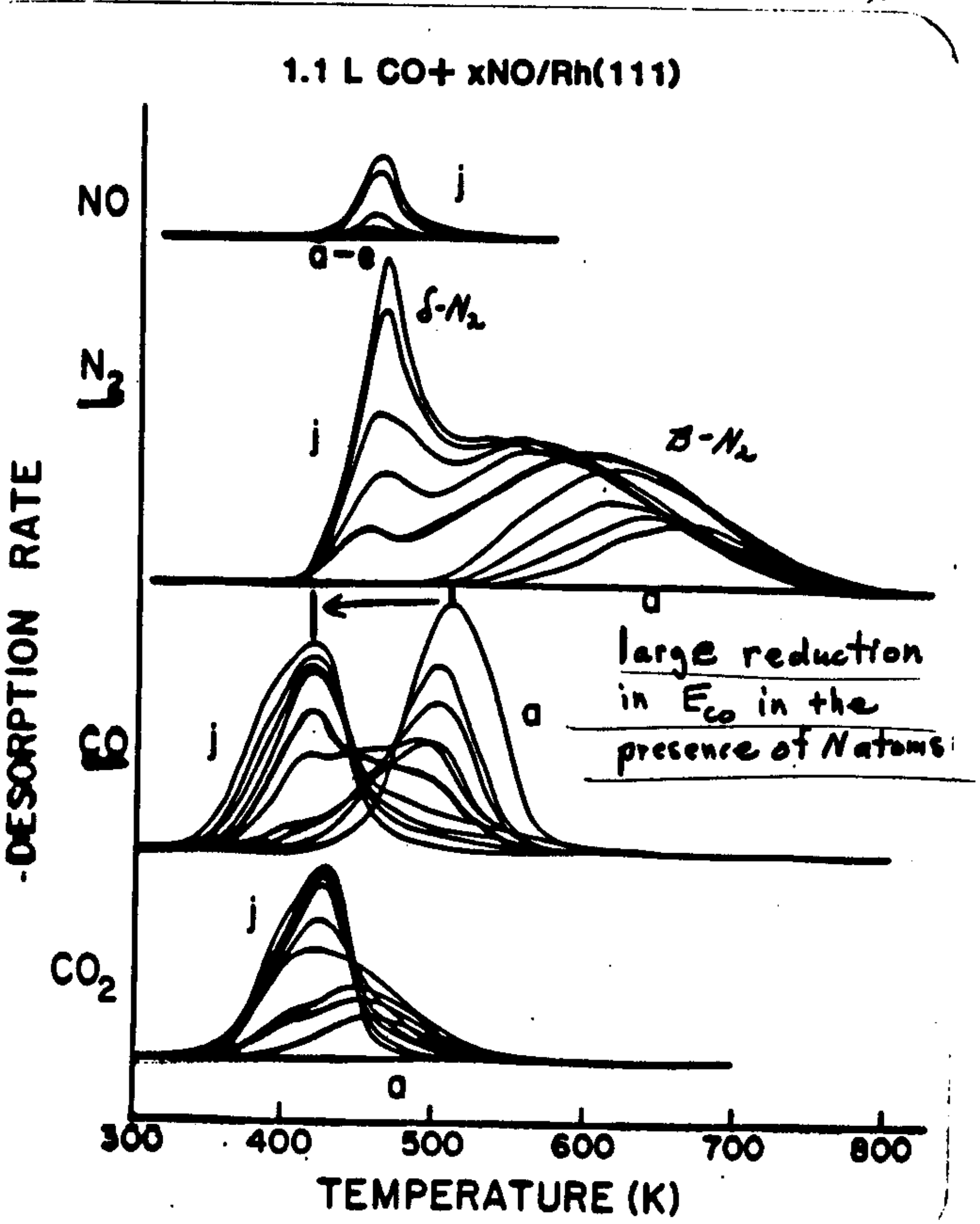


V.C. Use decay of NO stretch to get E_{diss}(NO)

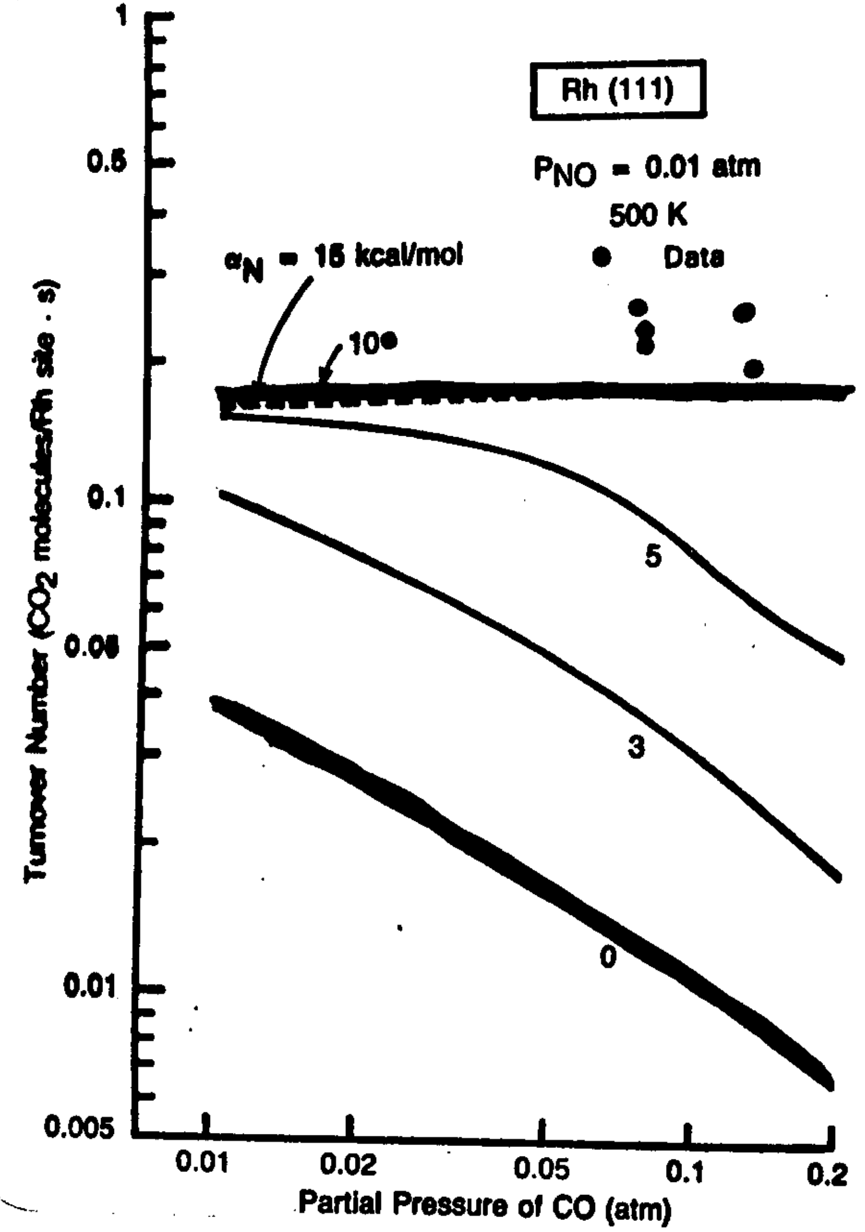


- R^{DIS}_{N-O} IS TOO FAST TO BE A RATE-LIMITING STEP FOR THE NO-CO REACTION ON Rh(111).

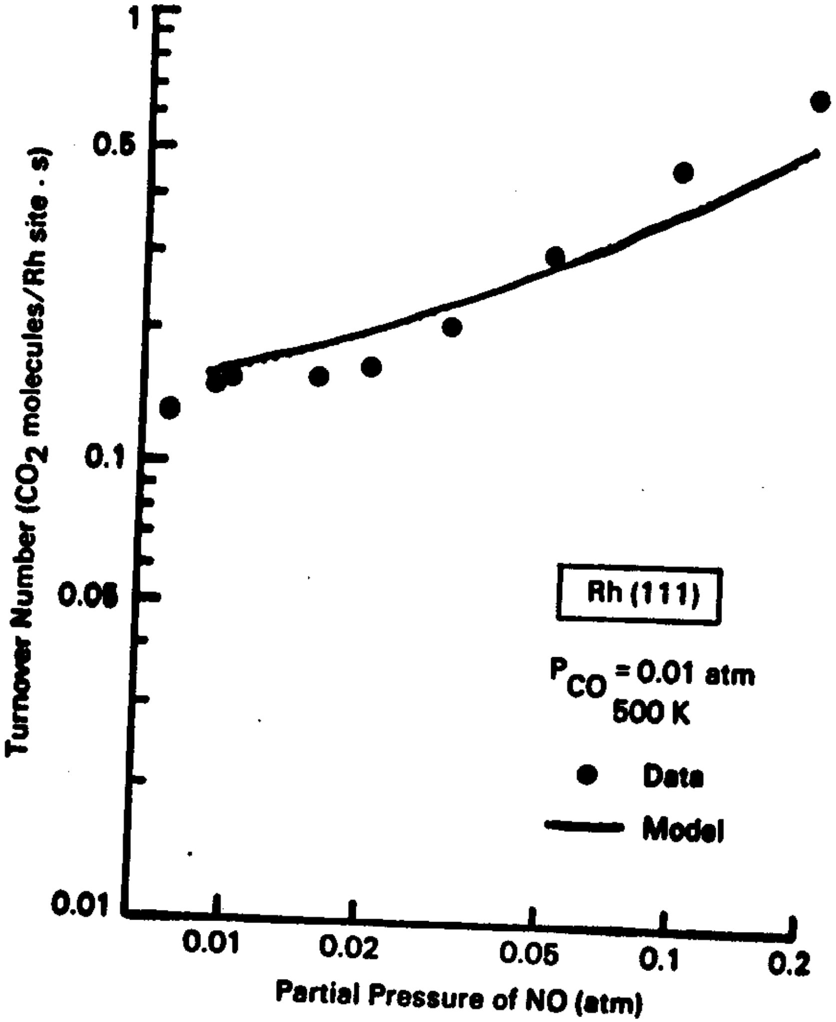
V.C. N atoms reduce CO heat of desorption



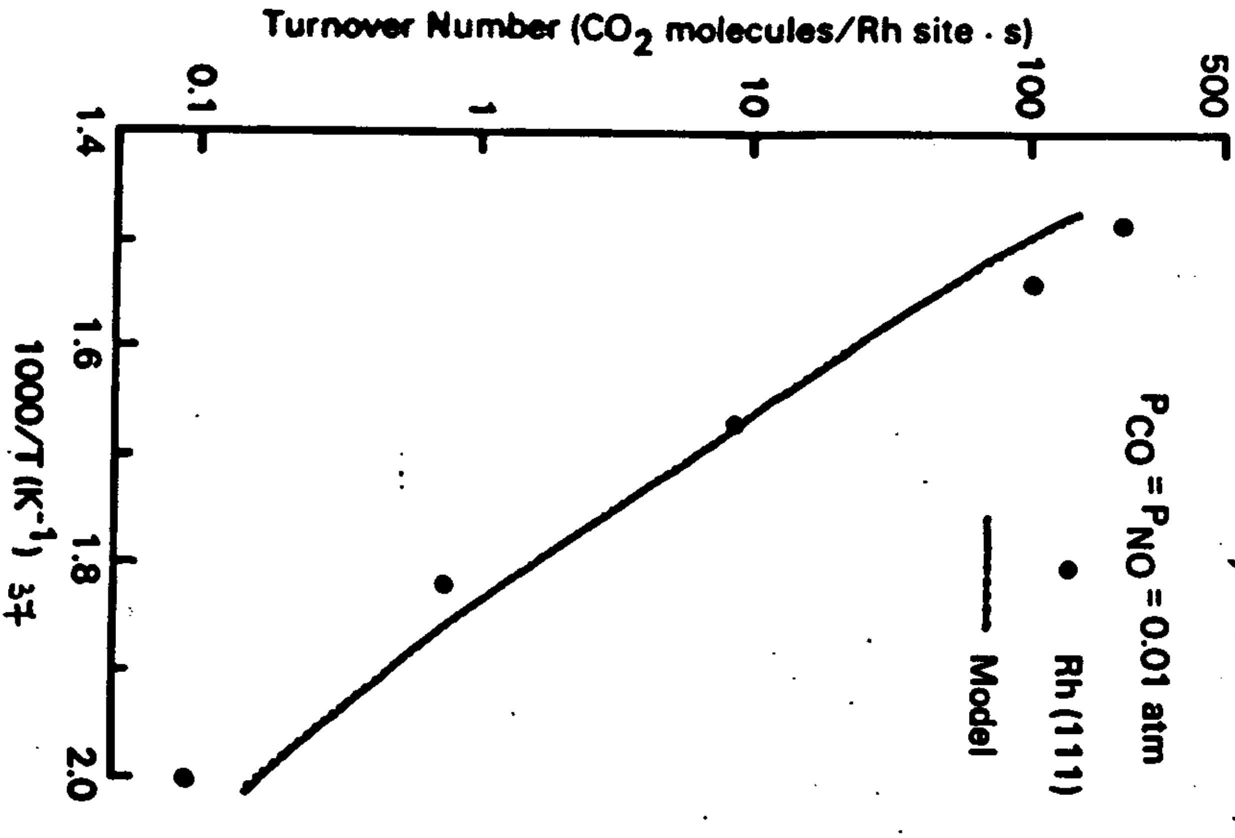
V.D.E. E_{des} [N_{ad}] gives correct absolute rate
& functional dependence on P_{CO}



V.D.E. Dependence on NO pressure



II.D.E. overall rate agreement on Rh(111)

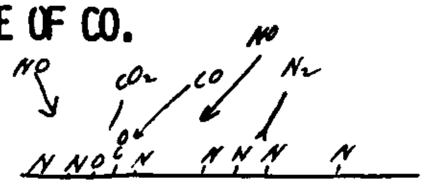


II.D,E,F CONCLUSIONS FOR THE NO-CO REACTION ON Rh(111)

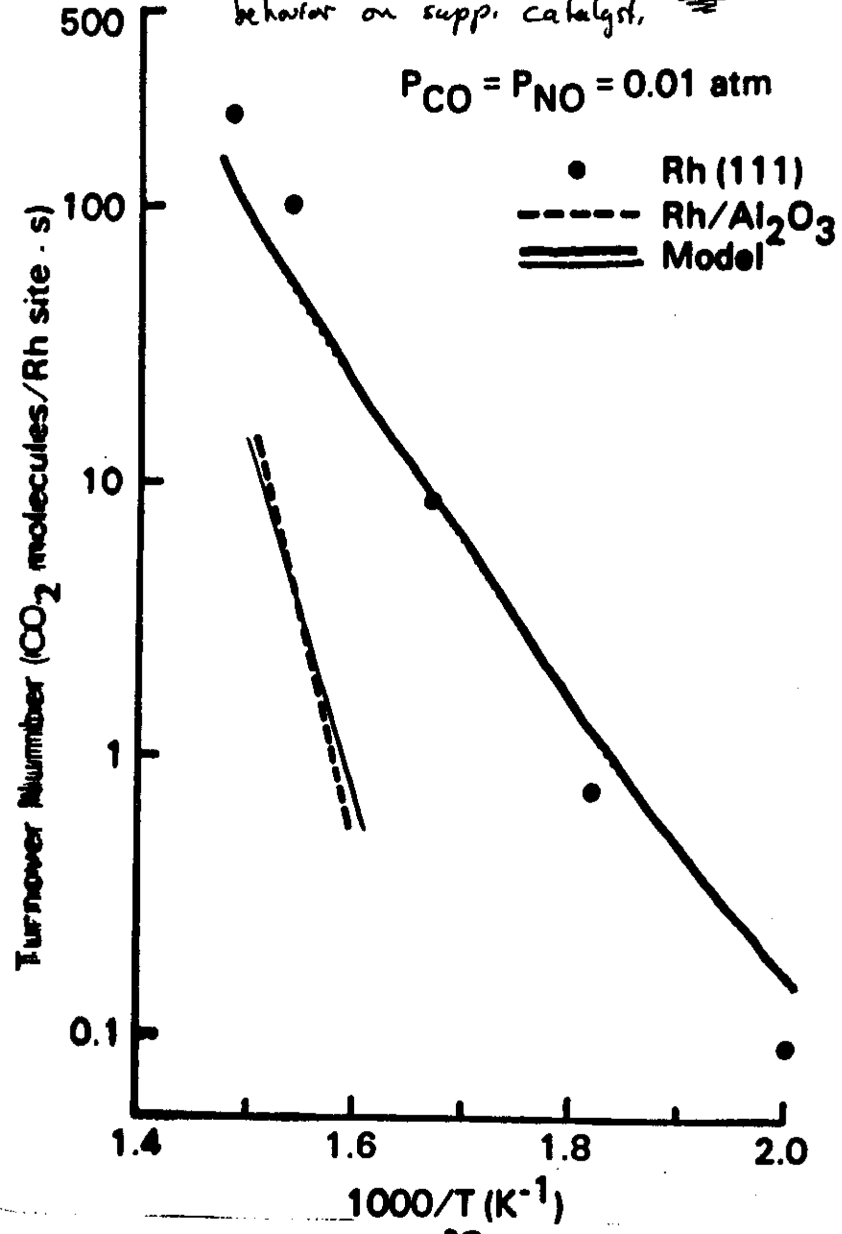
- THE UNEXPECTEDLY LARGE REDUCTION OF ABOUT 10 KCAL/MOLE IN THE HEAT OF DESORPTION FOR CO IN THE PRESENCE OF NITROGEN ATOMS ON Rh IS SIGNIFICANT FOR THE NO-CO REACTION AT HIGH PRESSURES.

- THIS REDUCED HEAT OF DESORPTION FOR CO IS CRITICAL FOR OBTAINING THE CORRECT ABSOLUTE RATE AND FUNCTIONAL DEPENDENCE ON CO PRESSURE.

- AT HIGH PRESSURES THE Rh(111) SURFACE IS COVERED WITH N ATOMS AND THE REACTION RATE IS CONTROLLED BY THE DESORPTION RATE OF NITROGEN, AND HENCE, THE ADSORPTION RATE OF CO.



V.G. Using $r_{diss}(NO)_{supp} = \frac{1}{2000}\left[r_{diss}(NO)_{Rh(111)}\right]$
Then the model work for all of the NO-CO behavior on supp. catalyst.

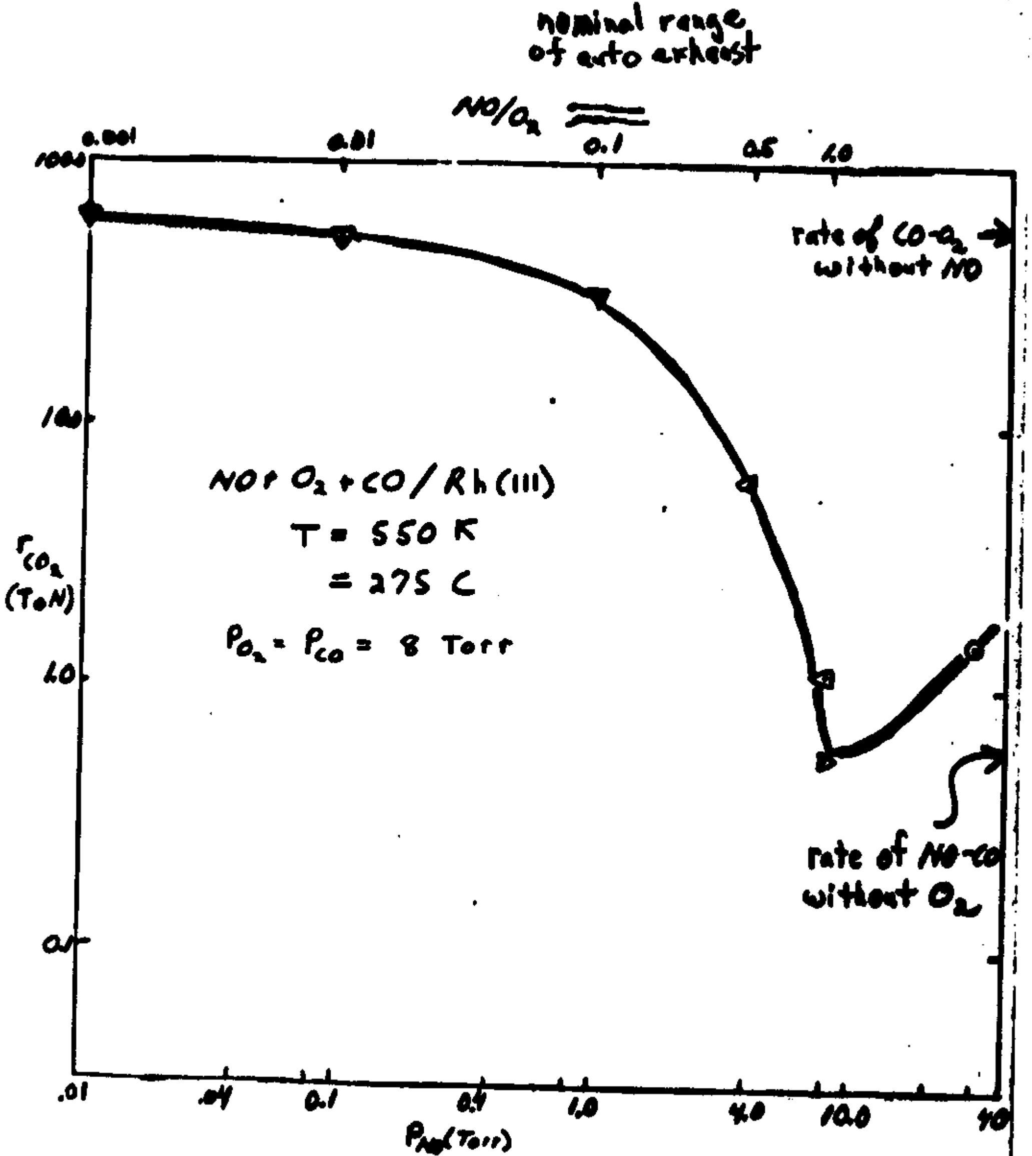


V.G.

CONCLUSIONS FOR NO-CO REACTION ON SUPPORTED Rh

- BY USING A REDUCED RATE OF NO DISSOCIATION (BY A FACTOR OF 1000) FOR Rh ON THE SUPPORT, ALL OF THE BEHAVIOR OF THE NO-CO REACTION ON ALUMINA-SUPPORTED Rh IS PREDICTED.
- THIS AGREEMENT SUGGESTS THAT THE REACTION ON THE SUPPORT IS LIMITED BY NO DISSOCIATION AND NOT NITROGEN DESORPTION AS ON Rh(111).

VI. NO inhibits CO oxidation on Rh(111) for $P_{NO} > .1\ P_{CO}, P_{O_2}$ but has even more effect on supp. Rh.



OVERALL CONCLUSIONS

- INSIGHTS AND DATA OBTAINED IN UHV EXPERIEMNTS ON RHODIUM TRANSFER QUANTITATIVELY TO EXPLAIN THE $CO-O_2$ AND NO-CO REACTIONS AT REALISTIC PRESSURES.
- FOR A CERTAIN CLASS OF REACTIONS, WE CAN CROSS THE PRESSURE GAP!
- WE NOW KNOW THE INTERMEDIATE STEPS FOR THE $CO-O_2$ AND NO-CO REACTIONS AND THEIR RELATIVE IMPORTANCE ON SINGLE CRYSTALS AND SUPPORTED RHODIUM
- THE NEXT STEP IS THE IMPROVEMENT OF OVERALL REACTION RATES BY THE MODIFICATION OF CRITICAL REACTION STEPS.

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The molecular and atomic states of oxygen adsorbed on Rh(100): Adsorption

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The adsorption of oxygen at 100 K on Rh(100) has been studied with temperature-programmed desorption and photoelectron spectroscopy. Oxygen adsorbs with a sticking probability of about 0.8 up to a near saturation coverage of 1.1×10^{15} atoms/cm^2 or three-fourths of a monolayer coverage on Rh(100). Initial adsorption is dissociative. However, for coverages above half a monolayer a low temperature molecular state, denoted α, which does not exhibit isotopic exchange, desorbs at 150 K. Dissociated oxygen recombines and desorbs in three high temperature or β states. At low coverages oxygen desorbs in a second order state, β_3, between 1200 and 1325 K with an activation energy for desorption of 360 kJ/mole (85 kcal/mole). At coverages above half a monolayer, two first order states, β_1 and β_2, appear at 820 and 920 K, respectively. Their respective heats of desorption are 210 kJ/mole (50 kcal/mole) and 260 kJ/mole (62 kcal/mole). In contrast with previously reported results, *no* bulk diffusion of adsorbed oxygen atoms into Rh is observed for temperatures up to the onset of oxygen desorption.

J. Vac. Sci. Technol. A 1 (2), Apr.–June 1983 pp. 1064-1069

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North-Holland Publishing Company

ADSORPTION AND REACTION OF NITRIC OXIDE AND OXYGEN ON Rh(111) *

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Adsorption of NO and O_2 on Rh(111) has been studied by TPD and XPS. Both gases adsorb molecularly at 120 K. At low coverages ($\theta_{NO} < 0.3$) NO dissociates completely upon heating to form N_2 and O_2 which have peak desorption temperatures at 710 and 1310 K, respectively. At higher NO coverages NO desorbs at 455 K and a new N_2 state obeying first order kinetics appears at 470 K. At saturation, 55% of the adsorbed NO decomposes. Preadsorbed oxygen inhibits NO decomposition and produces new N_2 and NO desorption states, both at 400 K. The saturation coverage of NO on Rh(111) is approximately 0.67 of the surface atom density. Oxygen on Rh(111) has two strongly bound states with peak temperatures of 840 and 1125 K with a saturation coverage ratio of 1 : 2. Desorption parameters for the 1125 peak vary strongly with coverage and, assuming second-order kinetics, yield an activation energy of 85 ± 5 kcal/mol and a pre-exponential factor of 2.0 cm^2 s^{-1} in the limit of zero coverage. A molecular state desorbing at 150 K and the 840 K state fill concurrently. The saturation coverage of atomic oxygen on Rh(111) is approximately 0.83 times the surface atom density. The behavior of NO on Rh and Pt low index planes is compared.

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NITRIC OXIDE REDUCTION BY CO ON Rh(111): TEMPERATURE PROGRAMMED REACTION *

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The reaction of NO with CO on Rh(111) has been studied with temperature programmed reaction (TPR). Comparisons are made with the reaction of O_2 with CO and the reaction of NO with H_2. The rate-determining step for both CO oxidation reactions is $CO(a)+O(a) \rightarrow CO_2(g)$. Repulsive interactions between adsorbed CO and adsorbed nitrogen atoms lead to desorption of CO in a peak at 415 K which is in the temperature range where the reaction between CO(a) and O(a) produces $CO_2(g)$. Thus the extent of reaction of CO(a) with NO(a) is less than that between CO(a) and O(a) due to the lower coverage of CO caused by adsorbed N atoms and NO. A similar repulsive interaction between NO(a) and H(a) suppresses the $NO+H_2$ reaction. CO + NO reaction behavior on Rh(111) is compared to that observed on Pt(111).

JOURNAL OF CATALYSIS 100, 360–376 (1986)

✳ This has most of the high pressure data so far.

Comparative Kinetic Studies of CO–O_2 and CO–NO Reactions over Single Crystal and Supported Rhodium Catalysts

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The kinetics of the CO–O_2 and CO–NO reactions over single crystal Rh(111) and over alumina-supported Rh catalysts have been compared at realistic reactant pressures. For the CO–O_2 reaction, there is excellent agreement between both the specific rates and activation energies measured for the two types of Rh catalysts. The CO–NO reaction, on the other hand, exhibits substantially different activation energies and specific reaction rates between the single crystal and supported catalysts. This indicates that the kinetics of the CO–NO reaction, unlike the CO–O_2 reaction kinetics, are sensitive to changes in catalyst surface characteristics. The kinetic data for the CO–O_2 and CO–NO reactions over Rh(111) and Rh/Al_2O_3 were analyzed using mathematical models which account for the individual elementary reaction steps established from surface chemistry studies of the interactions of CO, NO, and O_2 with Rh surfaces. The model, when used with the parameter values similar to those reported in the surface chemistry literature, can *quantitatively* fit the CO oxidation rate data over both the single crystal and supported Rh catalysts. The kinetics of the CO–NO reaction over Rh(111) can also be well described by a reaction model using parameter values taken from surface chemistry studies. However, the rate data for the CO–NO reaction over supported Rh can be rationalized by assuming that the dissociation of molecularly adsorbed NO occurs much more slowly on supported Rh than on Rh(111).

Electron energy loss characterization of NO on Rh(111). I. NO coordination and dissociation[a)]

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Electron energy loss spectroscopy (EELS) has been used to study the adsorption of nitric oxide on Rh(111). NO adsorbs in twofold bridge sites at all coverages. The dissociation rate of NO on this surface at low coverage has been measured directly using EELS. The first order dissociation rate parameters are $E_a = 19.2 \pm 0.3$ kcal/mol and $\nu_0^{(1)} = 1 \times 10^{14 \pm 0.3}$ s^{-1} at $\theta_{NO} \approx 0.2$. Ordered low energy electron diffraction (LEED) patterns are observed only for partially dissociated NO adlayers and not for NO adsorbed molecularly at 95 K. Because NO adsorbs in twofold bridge sites at all coverages, the N–O stretching frequency exhibits a 150 cm^{-1} shift from zero to saturation coverage.

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Electron energy loss characterization of NO on Rh (111). II. Coadsorption with oxygen and CO[a)]

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High resolution electron energy loss spectroscopy has been used to examine the effects of coadsorbed oxygen and carbon monoxide on the bonding of nitric oxide adsorbed on the Rh (111) surface. NO is converted from twofold bridge sites (1500–1600 cm^{-1}) to linear sites (1840 cm^{-1}) when annealed to 275 K in the presence of coadsorbed oxygen. Terminally bound linear NO does not dissociate, but desorbs molecularly, a finding consistent with the commonly observed oxygen inhibition of NO dissociation over noble metals. Coadsorbed CO does not significantly inhibit or promote the dissociation of a low coverage of nitric oxide compared to the clean Rh (111) surface. CO and NO appear to segregate and form islands of each species at 95 K if CO is adsorbed first. Annealing this adlayer above 250 K disperses the islands and mixes the adsorbate layer at temperatures below where NO dissociation and reaction with CO are significant. The Rh–CO bond is weakened in well-mixed CO + NO adlayers, indicating that the NO–CO repulsive interaction acts through the Rh substrate rather than directly between the adsorbed molecules.

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$CO + O_2$ Reaction on Rh(111): Steady-State Rates and Adsorbate Coverages

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Steady-state kinetics of CO oxidation on clean Rh(111) were measured over a wide range of CO and O_2 gas-phase compositions and surface temperatures for pressures between 10^{-4} and 10^{-8} Torr. Coverages were measured by XPS during steady-state reaction. Below 425 K the reaction rate increases with temperature with an activation energy of 20 kcal/mol, while above 450 K the rate decreases with temperature with an activation energy of −7 kcal/mol. At low temperatures and in excess CO, the reaction rate is proportional to $P_{O_2}P_{CO}^{-1}$, while in excess O_2 and at high temperatures the reaction rate is negative order in P_{O_2} and more than first order in P_{CO}. Near stoichiometric reactant ratios XPS shows that CO is the dominant adsorbed species below 400 K, while from 425 to 900 K the surface is nearly saturated with oxygen. Experimental rates and coverages are fit qualitatively by using a simple Langmuir–Hinshelwood model assuming competitive adsorption, although adsorption parameters for CO and O_2 are not in agreement with clean surface values. Modified Langmuir–Hinshelwood models involving strong inhibition of oxygen adsorption by adsorbed CO, either through coverage-dependent sticking coefficients or a dependence of the heat of adsorption of oxygen on the CO coverage, give good agreement with UHV parameters, measured CO and oxygen coverages, and reaction rates.

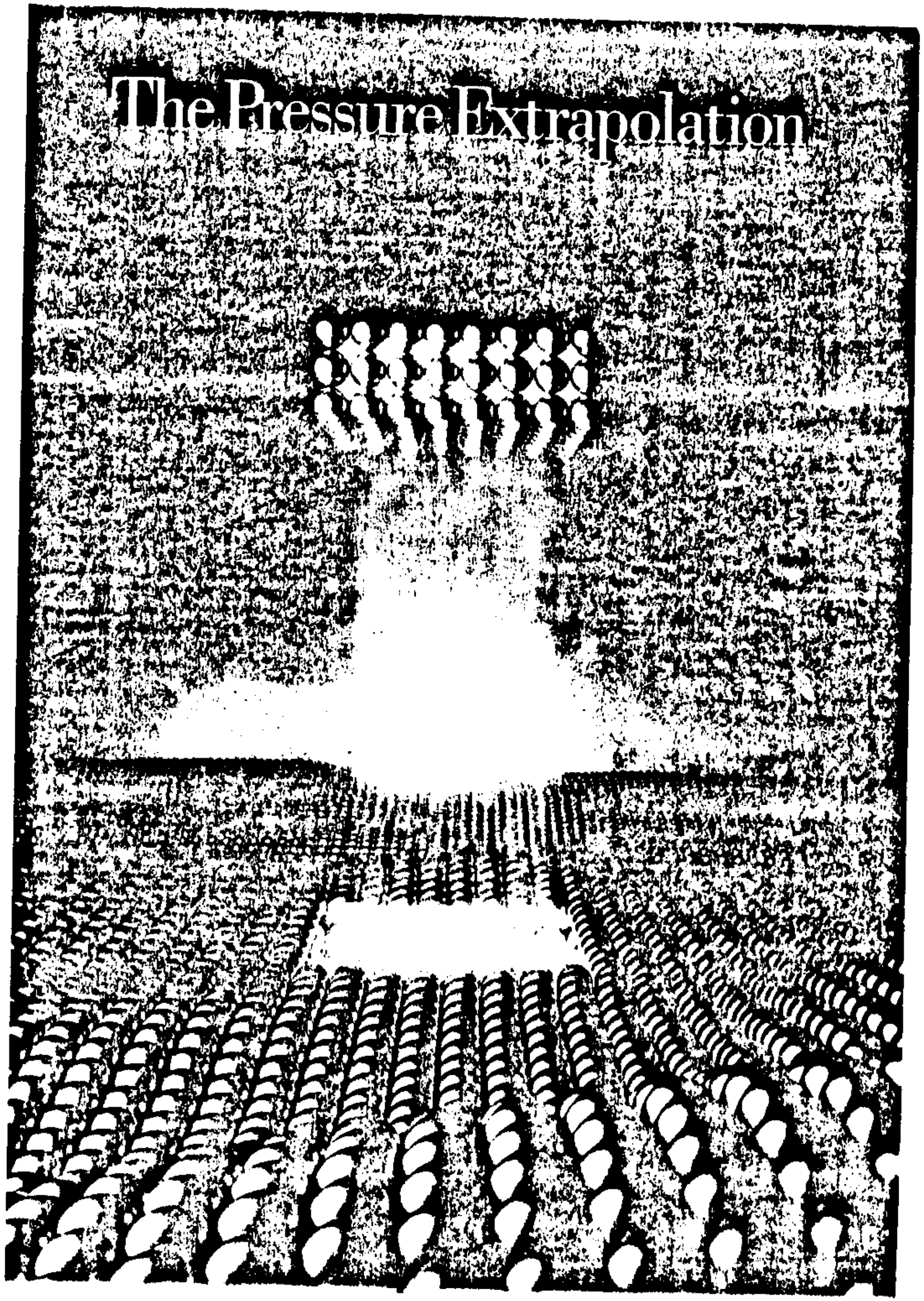
and

the following reference, which is an advertisement

G. B. Fisher & Se H. Oh, Scientific American 255 (1986) pp. 69-71.

or in German in

Spektrum Der Wissenschaft, February, 1987, pp. 35-37



The Pressure Extrapolation

Modern automotive catalytic converters contain rhodium which promotes chemical reactions to remove pollutants from a car's exhaust. Scientists at the General Motors Research Laboratories have recently made discoveries about one such chemical reaction, the reaction between nitric oxide and carbon monoxide, pointing the way toward new or improved catalysts.

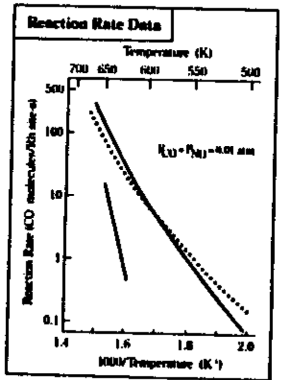


Figure 1: Rate comparisons for the NO-CO reaction. Measured data over single crystal Rh(111) (solid red line) and over supported Rh (blue line); model predictions (dotted red line).

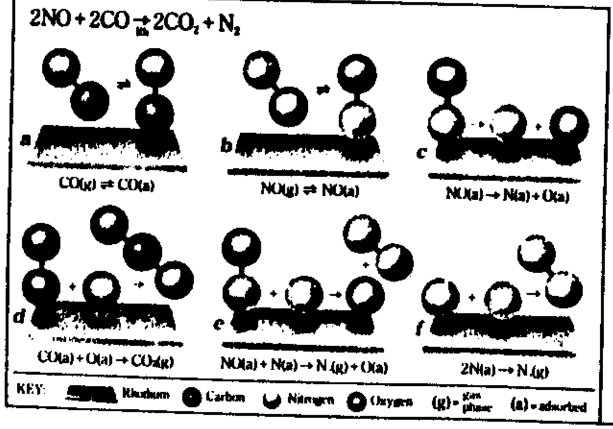


Figure 2: Schematic representation of the elementary intermediate steps for the NO-CO reaction.

MOST FUNDAMENTAL catalytic studies using surface science techniques require an ultrahigh vacuum environment (10^{-13} atm). They are best suited for studying well characterized materials, such as metal single crystals. Catalytic reactions of practical interest, however, involve polycrystalline materials, in the form of small metal particles dispersed on supports. And they take place at atmospheric pressures rather than in an ultrahigh vacuum.

Now Dr. Galen B. Fisher and Dr. Se H. Oh have demonstrated how the wealth of chemical information obtained from ultrahigh vacuum (UHV) studies of ideal, single-crystal catalysts can be applied to the understanding of real-world systems that have different catalyst environments and that operate at much higher pressures.

These researchers concentrated their studies on the major chemical reactions that occur in modern automotive catalytic converters. One such reaction is the reduction of nitric oxide (NO) by carbon monoxide (CO) over a rhodium (Rh) catalyst to yield carbon dioxide (CO_2) and nitrogen (N_2) (Figure 2).

Dr. Fisher used various surface science spectroscopies in ultrahigh vacuum to study all of the elementary reactions over a rhodium single crystal [Rh(111)] that might be involved in this specific reaction. Over several years he measured the rates and determined the activation energies of each of these reactions. For most of these reactions, this was the first time these parameters had been measured. Based upon these results, Dr. Fisher hypothesized that the elementary reactions shown in Figure 2(a-f) were the significant steps involved in the NO-CO reaction and that nitrogen recombination and desorption (Figure 2f) was the rate-controlling step on Rh(111).

Dr. Fisher and Dr. Oh also initiated kinetic studies of this reaction at realistic reactant partial pressures and temperatures using two different catalysts—one was a rhodium single crystal [Rh(111)], and the other consisted of rhodium particles supported on alumina [Rh/Al_2O_3]. The rhodium concentrations on the support were similar to those used in an automotive catalytic converter. The studies with the single crystal at realistic, high pressures were done in collaboration with Dr. D. Wayne Goodman of Sandia National Laboratories.

At the same time, Dr. Oh devised a mathematical model for this reaction. The model consists of steady-state conservation equations for the surface species, based on the reaction mechanism and the rate expressions for the individual reaction steps determined in Dr. Fisher's UHV studies. Overall reaction rates could then be computed from the surface concentrations satisfying the conservation equations. The reaction rates predicted by this model, which depend only on reactant partial pressures, are shown in Figure 1 (dotted red line).

The kinetics of the NO-CO reaction measured over a rhodium single crystal using realistic reactant partial pressures are shown in Figure 1 (solid red line). The agreement with the model predictions indicates that Drs. Fisher and Oh had correctly identified all of the intermediate reaction steps and confirms that, in this case, nitrogen recombination and desorption (Figure 2f) is the rate-controlling step on Rh(111). The fact that the agreement is so good also indicates that the rates of the elementary reactions measured under UHV conditions are still valid at realistic reactant partial pressures—a pressure extrapolation of more than ten orders of magnitude.

THE KINETICS of the NO-CO reaction measured over the supported rhodium catalyst (Figure 1, blue line), however, were much slower than predicted by the model. In addition, infrared studies have shown that NO is the predominant surface species on the catalyst, suggesting that in this case NO dissociation (Figure 2c) is the rate-controlling step. In fact, if the rate constant for NO dissociation measured under UHV conditions and used in the model is reduced by a factor of 2000, the kinetics of the NO-CO reaction measured over the supported rhodium catalyst are correctly predicted.

The difference between the kinetics of the NO-CO reaction measured over a rhodium single crystal and the kinetics measured over supported rhodium shows that this reaction depends on the environment of the rhodium in the catalyst. The reaction model strongly suggests that the NO dissociation reaction is the reaction step most sensitive to the rhodium environment.

"While our reaction model cannot tell us why NO dissociation is slower on supported rhodium," observes Dr. Oh, "it can help identify the kinds of studies necessary to clarify the origins of such sensitivity." Comparative kinetic studies can also provide useful insights for developing improved NO reduction catalysts. "Our studies have already told us," adds Dr. Fisher, "that one possible path to improving automobile catalysts is to make modifications that increase the NO dissociation rate."

General Motors

THE MEN BEHIND THE WORK

Dr. Galen B. Fisher (left) and Dr. Se H. Oh are both Group Leaders in the Physical Chemistry Department at the General Motors Research Laboratories.

Dr. Fisher holds the title of Senior Staff Research Scientist, and heads the Surface Chemistry and Corrosion Science Group. He attended Pomona College as an undergraduate and received his graduate degrees from Stanford University in Applied Physics. Before coming to General Motors in 1978, he did post-doctoral studies at Brown University and worked at the National Bureau of Standards. Since then, his research has been involved with surface science studies of various catalytic reactions.

Dr. Oh is a Senior Staff Research Engineer, heading the Catalytic Kinetics Group. He received his undergraduate degree from Seoul National University and holds a doctorate in Chemical Engineering from the University of Illinois. Dr. Oh did post-doctoral work at the University of Toronto prior to joining GM in 1976. Since then, he has been involved in measuring and modeling the kinetics of catalytic reactions.