Title
CATALYTIC GASIFICATION OF GRAPHITE OR CARBON Annual Report, Oct. 1, 1984-Sept. 30, 1985.

Author
Heinanann, H.

Publication Date
1985-09-01

LBL-20325
UC-90d

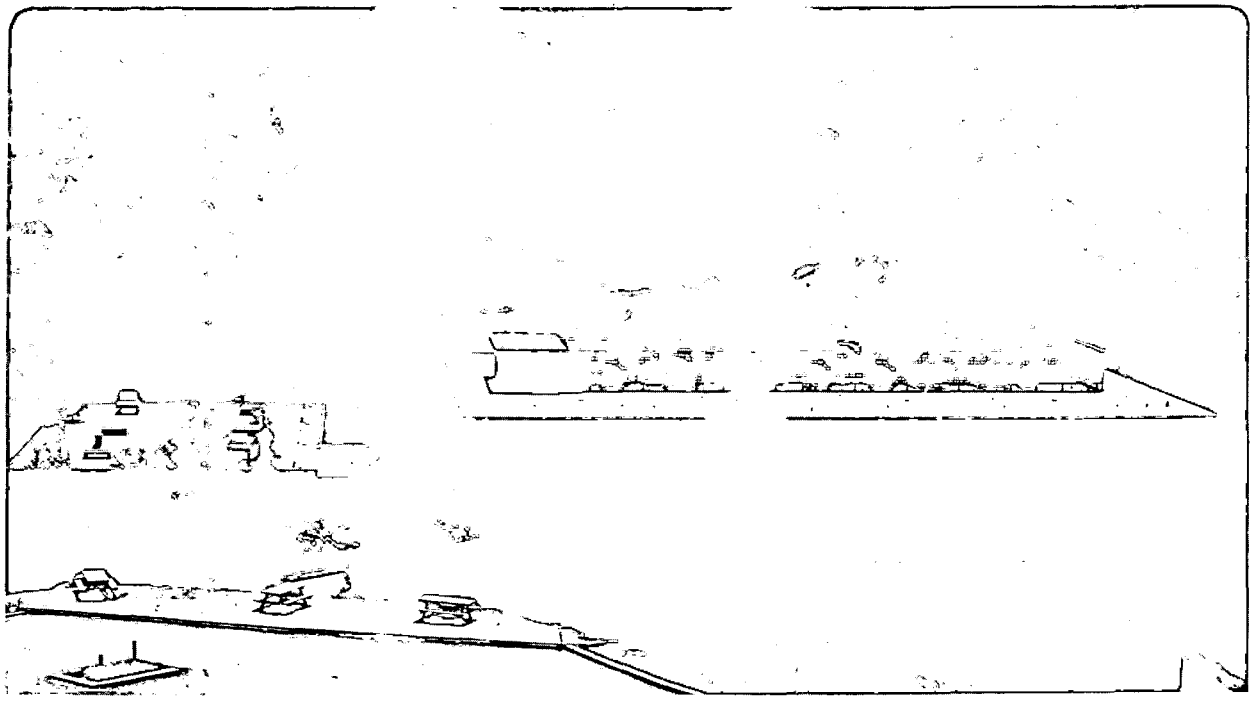
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON
Annual Report, October 1, 1984-September 30, 1985

H. Heinemann

September 1985



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL-20325

ANNUAL REPORT

October 1, 1984 - September 30, 1985

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

Principal Investigator: Heinz Heinemann

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

This work was supported by the Assistant Secretary of Fossil Energy, Office of Management, Planning and Technical Coordination, Technical Coordination Division of the U. S. Department of Energy under Contract Number DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, W. Va. 26505.

TABLE OF CONTENTS

I. INTRODUCTION

This report presents results obtained in the fourth quarter of fiscal year 1985 and also summarizes some information which has been previously reported in greater detail in the three proceeding quarterly reports (October 1, 1984-December 31, 1984; January 1-March 30, 1985; April 1-June 30, 1985).

Part of the work reported in fiscal 1985 has been written up in an article which has been accepted for publication in the Journal of Catalysis during calendar year 1985.

II. TASK DESCRIPTION FOR FY 1985

This program is designed to look at the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Much of the work is being carried out with graphite as a carbon source to insure that hydrogen in hydrocarbons is derived from water. Relatively low temperatures are being used to favor the equilibrium $C+2H_2O \rightarrow CH_4+CO_2$, which is almost thermally neutral. Our earlier work has shown that, in the presence of KOH as catalyst, higher hydrocarbons up to C_6 can be formed. This raises the question whether hydrocarbons are a primary product and syngas a secondary one formed by steam reforming. The formation of hydrocarbons is a stoichiometric reaction in which each H_2 in water reacts to form a phenolate and a hydrocarbon: $5C+4KOH \rightarrow 4COK+CH_4$. We have shown the presence of phenolate by surface spectroscopy and have found that it can be decomposed over metal oxides

to make the reaction truly catalytic: $4COK \xrightarrow{MeOx} 2K_2O+2C+2CO$; $2K_2O+2H_2O \rightarrow 4KOH$. Future work is directed toward combining flow reactor studies with ultrahigh vacuum surface studies to follow the mechanism, to find the best catlysts for phenolate decomposition, to measure and improve kinetics, and to study the effect of added gases, such as CO or CO_2.

III. HIGHLIGHTS

* In the gasification of graphite over KOH/NiO catalysts at 860K (567°C) more hydrogen and less CO and methane are observed than corresponds to equilibrium. CO_2 is a major product along with hydrogen.

* A char derived form Illinois #6 coal was gasified after impregnation with KOH-NiO. The gasification with steam resulted in almost identical results with those obtained from graphite. Gaseous products were hydrogen and CO_2 in ratio of about 2:1. The char gave larger amounts of methane (about 1% of gas products) than graphite at gasification temperatures of up to 900K.

* Nickel is a good gasification catalyst, but it is rapidly poisoned in graphite gasification. Nickel oxide alone is <u>not</u> a catalyst for gasification but mixtures of NiO and KOH are and are greatly superior to either KOH or Ni alone. XPS work shows that at tempertures below 923K a compound such as K_xNi_yO is formed which appears to be catalytically active and which is more temperature stable than either KOH or NiO. KOH volatilizes at >823K and NiO is reduced to Ni metal >823K by graphitic carbon while K_xNi_yO is stable up to 923K.

* The gasification rate of both graphite and char in the presence of KOH/NiO appears to be independent of steam partial pressure in the range tested (up to 60 psig steam).

* To determine whether methane is a major primary product which is then decomposed by steam reforming, methane was added to the steam feed. The vast majority (95+%) of the added methane was recovered in the product, showing that steam reforming plays at most a minor role. However, in the presence of added methane the gasification rate declined. While the reasons for this are not yet clear, they must

lie in a surface poisoning by some decomposition product of the small amounts of methane disappearance. Addition of hydrogen to the steam feed caused about a 25% decrease in the rate of gas production as did the addition of CO_2 instead of hydrogen.

* Addition of CO to the steam feed to KOH-NiO impregnated graphite resulted in a 25% increase in the rate of gasification. The gaseous products were hydrogen and CO_2 in a ratio of 2:1, the same as in the absence of CO from the feed. The data show that formation of H_2 and CO_2 in a ratio OC 2:1 is <u>not</u> due to a water gas shift reaction.

* Adsorption-desorption experiments on graphite using labelled CO, CO_2 and H_2O have been carried out. If CO is adsorbed at room temperature most of it is desorbed at relatively low temperature (450K). However, about 10% is desorbed as CO_2 at 400K indicating the presence of a CO disproportionation reaction.

After adsorption of water on graphite at room temperature, desorption of CO and H_2 is observed at 1200K and methane is desorbed at four temperatures, most strongly at 600K. The CH_4/H_2 ratio is less than 0.3.

IV. PROGRESS OF STUDIES

(1) Flow Reactor Studies

During the present fiscal year a new flow reactor system has been designed and built. A detailed description of the system is given in the April-June Quarterly Report. The advantages of this new system are the following:

(a) capability for higher steam partial pressure reactions (~60 psig);
(b) more reproducible and controllable flow of steam;
(c) more homogenous mixing of inlet gases with steam;
(d) more reproducible gas analysis system.

After the reactor was built, the dependence of the reaction rate of the gasification of graphite was studied for a mixture of KOH and NiO. Figure 1 shows that the rate is independent of the steam pressure up to 60 psig. Similar results are being carried out using char from Illinois #6 coal instead of graphite.

Previously it was reported (January-March report) that the NiO/KOH catalyst was as active for the gasification of Illinois #6 char as it was for graphite (see figure 2). Preliminary results show that as in the case of graphite, the rate of gasification of char from Illinois #6 coal is independent of the steam pressure up to 60 psig. The scatter on the data is, however, larger and more experiments are needed to reach a final conclusion.

Also during the present fiscal year, the effect of adding several gases to the inlet stream on the total activity of a mixture of KOH/NiO for gasification of graphite was studied (see October-December and January-March quarterly reports). It was observed that addition of CH_4, H_2, CO and CO_2 did not affect the product distribution obtained. The rate of reaction, on the other hand, depended on the inlet stream composition. Addition of H_2, CH_4 and CO_2 decreased the rate of gasification, while presence of CO increased the rate.

Figure 1

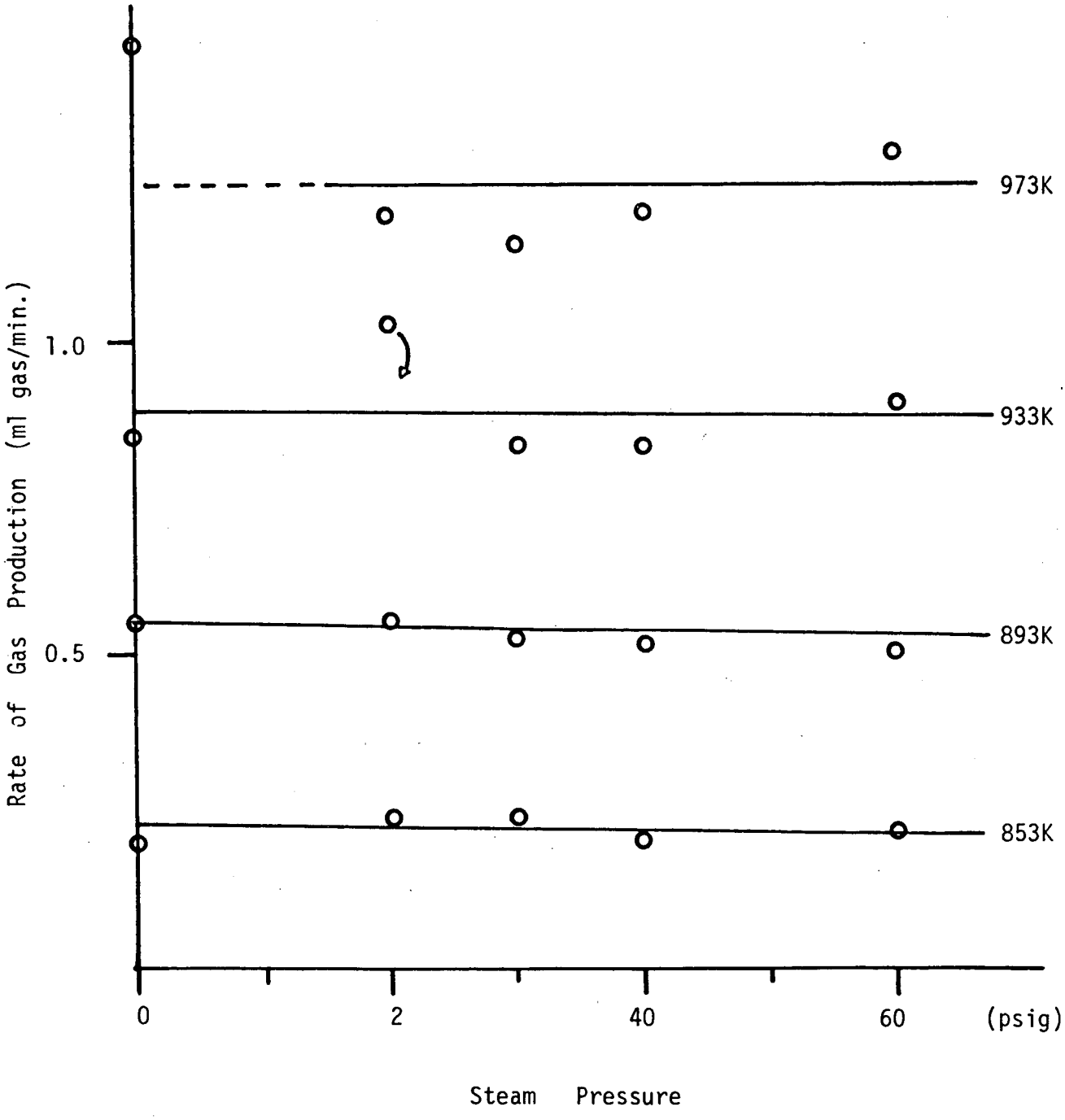
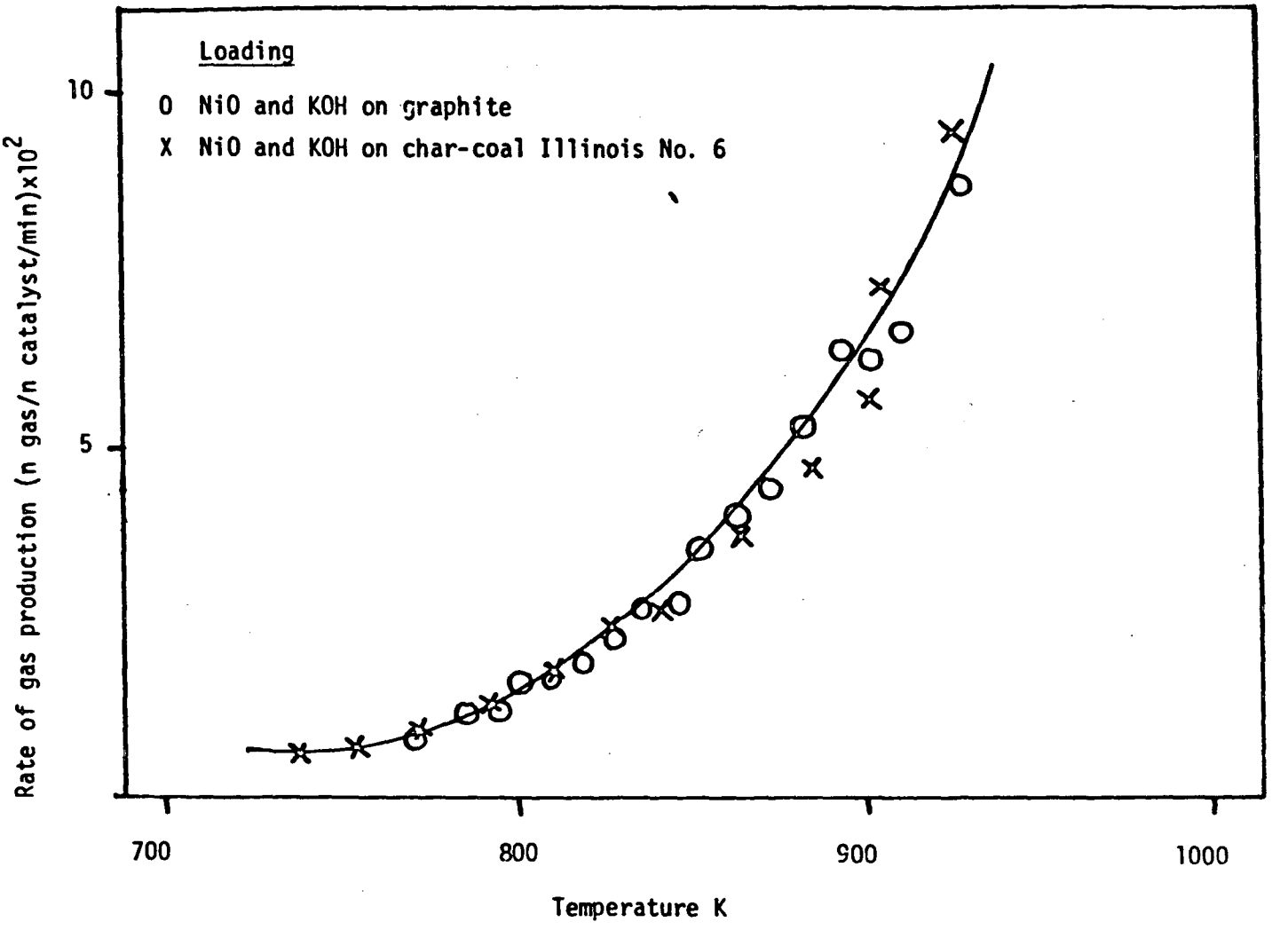

Rate of Gas Production (ml gas/min.)
1.0
0.5
973K
933K
893K
853K
0
2
40
60
(psig)
Steam Pressure

Figure 2


Loading
O NiO and KOH on graphite
X NiO and KOH on char-coal Illinois No. 6
10
5
Rate of gas production (n gas/n catalyst/min)x10^2
700
800
900
1000
Temperature K

Future Work

As mentioned before, the dependence of steam partial pressure on the gasification of char from Illinois #6 coal is being investigated when KOH/NiO is used as catalyst.

The catalytic activity of this catalyst for the gasification of other types of char will be investigated and compared with the results obtained so far.

The dependence of the rate of reaction and resistance to poisoning as a function of the KOH to NiO ratio will be investigated. So far, there is no evidence that a ratio of one is the optimum for this type of catalysts. Results will be correlated with XPS studies in the Ultra High Vacuum equipment.

Finally, the effect of adding small amounts of H_2S to the inlet stream will be studied. It is known that for several catalysts, the presence of sulfur reduces their catalytic activity for steam gasification of carbon solids. Such a study is not available for the NiO/KOH catalyst.

(2) XPS Studies

We have reported that mixtures of KOH and a variety of transition metal oxides are excellent catalysts for the gasification of carbon solids with steam. It was shown that there was a cooperative effect between KOH and the transition metal oxide. This effect may be the reason for the high resistance to poisoning shown by these catalysts. In order to understand the nature of this effect, X-ray Photoelectron Spectroscopy (XPS) studies on this type of catalysts have been done as a function of temperature.

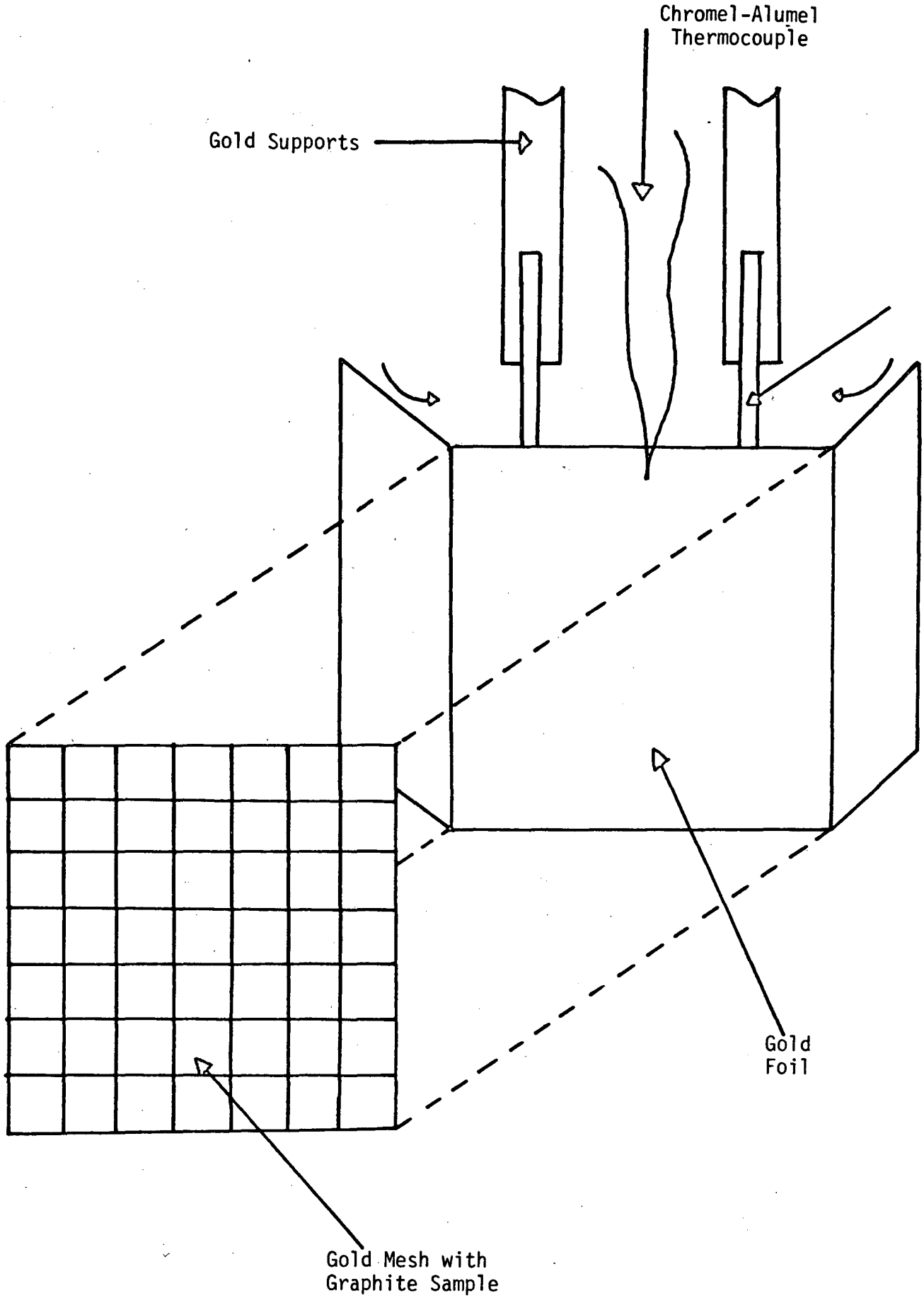
The mixture of KOH and NiO had shown the highest activity among those studied. For this reason, it was chosen for the XPS study. Nickel and KOH were adsorbed on graphite by impregnation to incipient wetness of soluble salts. The samples were prepared and/or XPS studies were carried out by exactly the same procedure as those used in the previously described kinetic studies.

The graphite sample was pressed into a gold mesh and held against a gold foil. The foil was spotwelded to a 0.020" platinum wire. The whole ensemble was then spotwelded to gold supports (see figure 3). The sample was heated by passing current through the gold foil. A chromel-alumel thermocouple was spotwelded between the gold foil and the mesh to monitor and control the temperature.

The XPS studies were carried out in an Ultra High Vacuum chamber (UHV) with a base pressure of 5.0×10^{-10} torr. The chamber is equipped with a high pressure cell. This system allowed us to treat the sample under a controlled atmosphere and then transfer it to UHV conditions without exposure to air. For these studies a Mg $K\alpha_1,\alpha_2$ X-ray source (1253.6 eV) and a Double Pass Cylindrical Mirror Analyzer with 40 eV pass energy were used.

Three different catalysts were studied. The first sample was loaded with both KOH and nickel. The initial ratio of potassium to nickel was 1.0 and the ratio of nickel to carbon was 0.04. The second sample was loaded only with KOH in a ratio of potassium to carbon equal to 0.04. The third

Figure 3


Chromel-Alumel
Thermocouple
Gold Supports
Gold
Foil
Gold Mesh with
Graphite Sample

sample contained nickel alone with a ratio of nickel to carbon equal to 0.04.

All three samples were treated under the same conditions used in the earlier reported kinetic experiments. XPS spectra of the Ni 2p, K2p, C1s and O1s signals were taken before and after every step in the treatment. A diagram of all the steps studied is given in figure 4.

In this report, the discussion will be centered on two main points; (a) the oxidation state of nickel, and (b) the ratio of potassium to carbon on the surface. Both characteristics were studied as a function of temperature under a water vapour atmosphere (as discussed in (c)).

(a) Oxidation State of Nickel

Figures 5a and 5b show the XPS spectrum of the NiO and Ni metal adsorbed on graphite. Three main differences can be observed between these two spectra. First, the Ni 2p 3/2 energy shifts from 856.6 eV (binding energy) in the case of NiO to 854.5 eV in the case of Ni metal. Second, the difference in energy between the Ni 2p 3/2 and Ni 2p 1/2 levels changes from 17.8 eV in the NiO case to 17.2 in the Ni metal. Third, the NiO sample shows two satellite peaks at 864.3 and 881.0 eV binding energy that were not present in the case of Ni metal. These three differences allow us to determine the oxidation state of nickel on the catalysts studied in this report.

In figure 6, the position of the Ni 2p 3/2 peak is plotted as a function of treatment conditions for the NiO/KOH on graphite catalyst and for Ni alone deposited on graphite.

When nickel is deposited alone on the graphite surface, the oxide state is stable up to 723K in the presence of steam. At 823K some reduction, according to the following equation is already taking place.

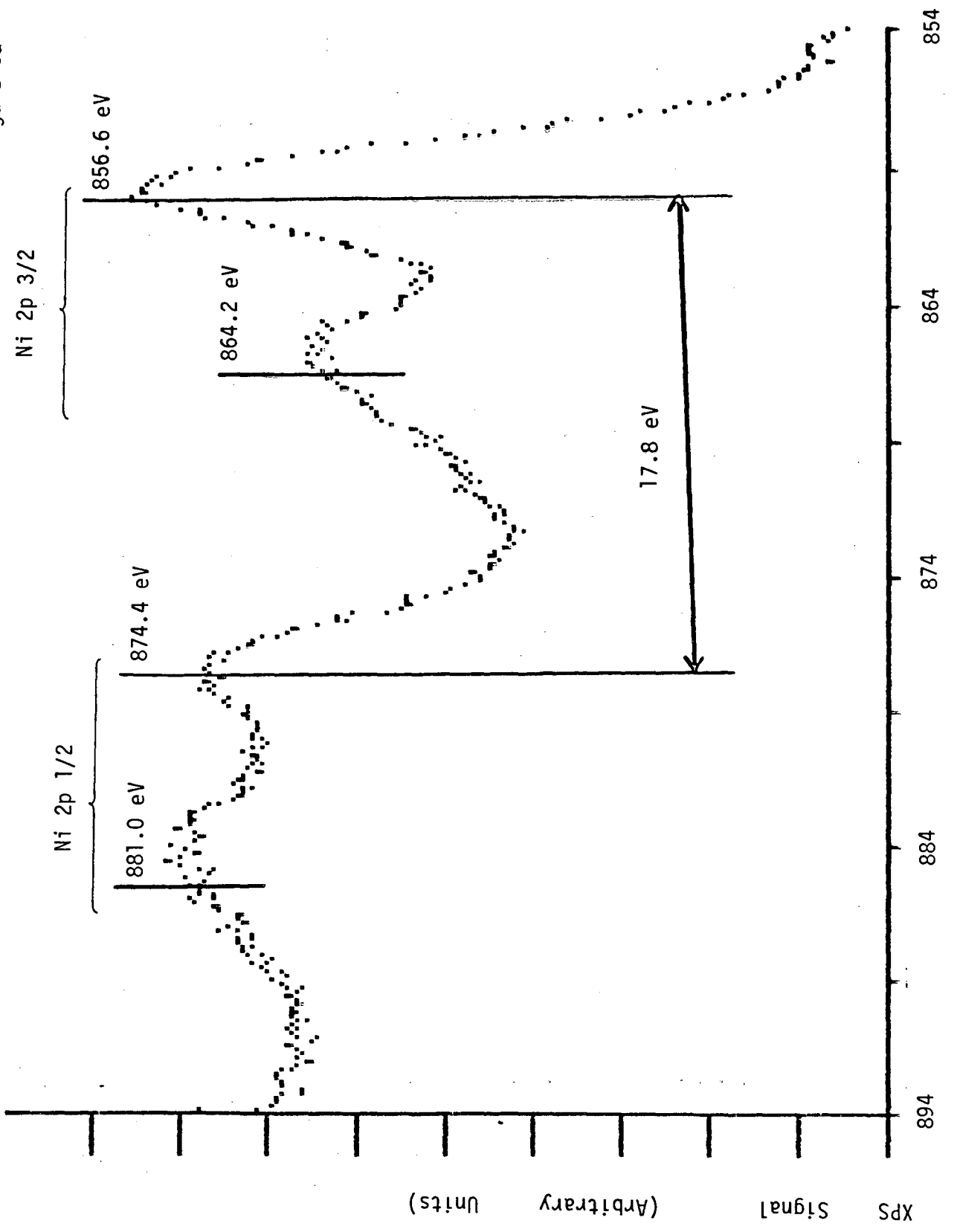
$$NiO + C \rightarrow Ni + CO$$

Description of the treatment given to graphite samples loaded with various catalysts for steam gasification. XPS spectra was taken after each step.

Step	Description
1	Loading of the catalyst by incipient wetness method.
2	Formation of the oxide by heating the to 723K under Ar.
3	Heating the sample to 723K under 24 torr of water vapour for 15 min.
4	Heating the sample to 823K under 24 torr of water vapour for 15 min.
5	Heating the sample to 923K under 24 torr of water vapour for 15 min.
6	Heating the sample to 1023K under 24 torr of water vapour for 15 min.

(Figure 4)

Figure 5a


856.6 eV
Ni 2p 3/2
864.2 eV
17.8 eV
874.4 eV
Ni 2p 1/2
881.0 eV
894
884
874
864
854
Binding Energy (eV)
XPS Signal (Arbitrary Units)

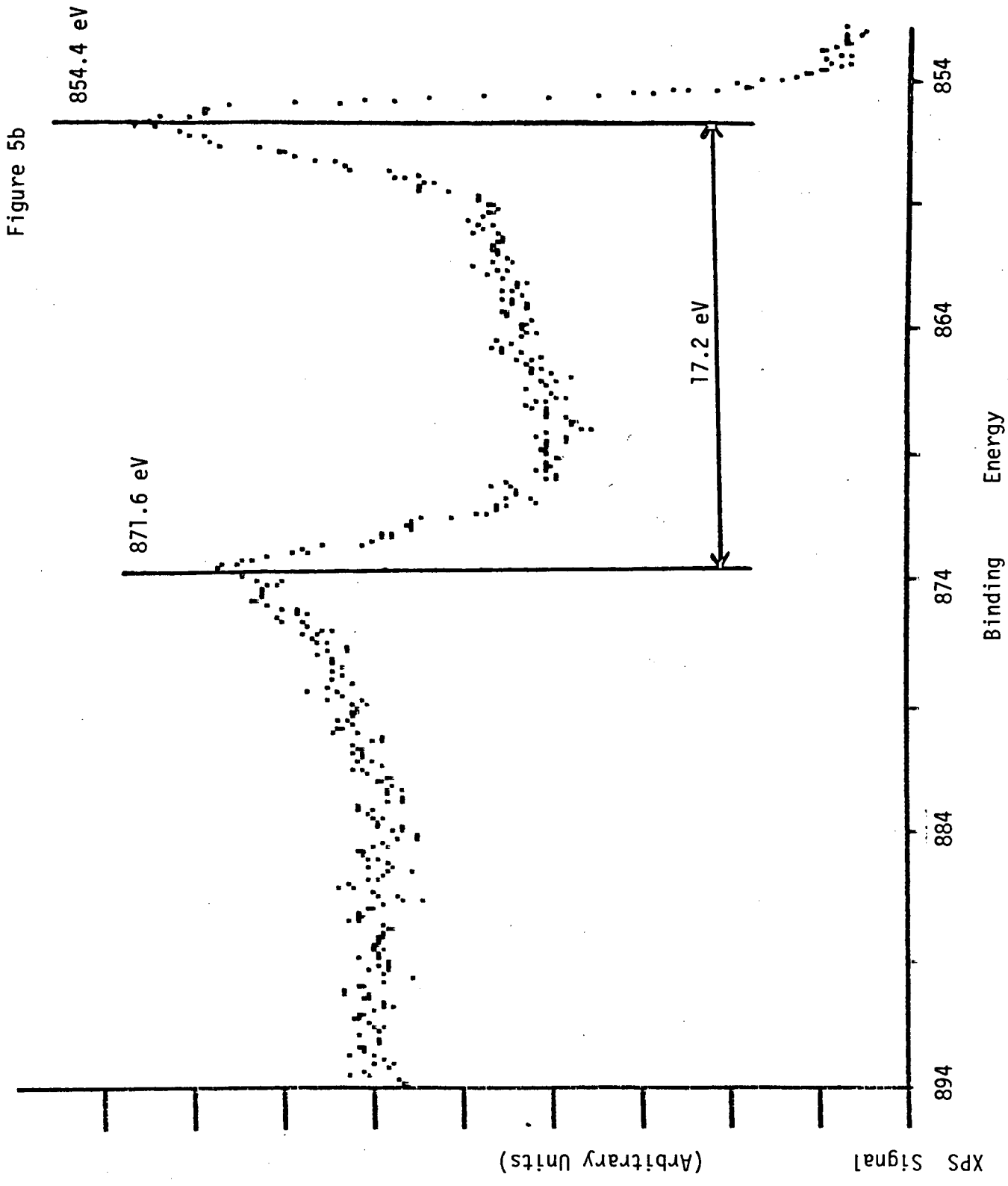
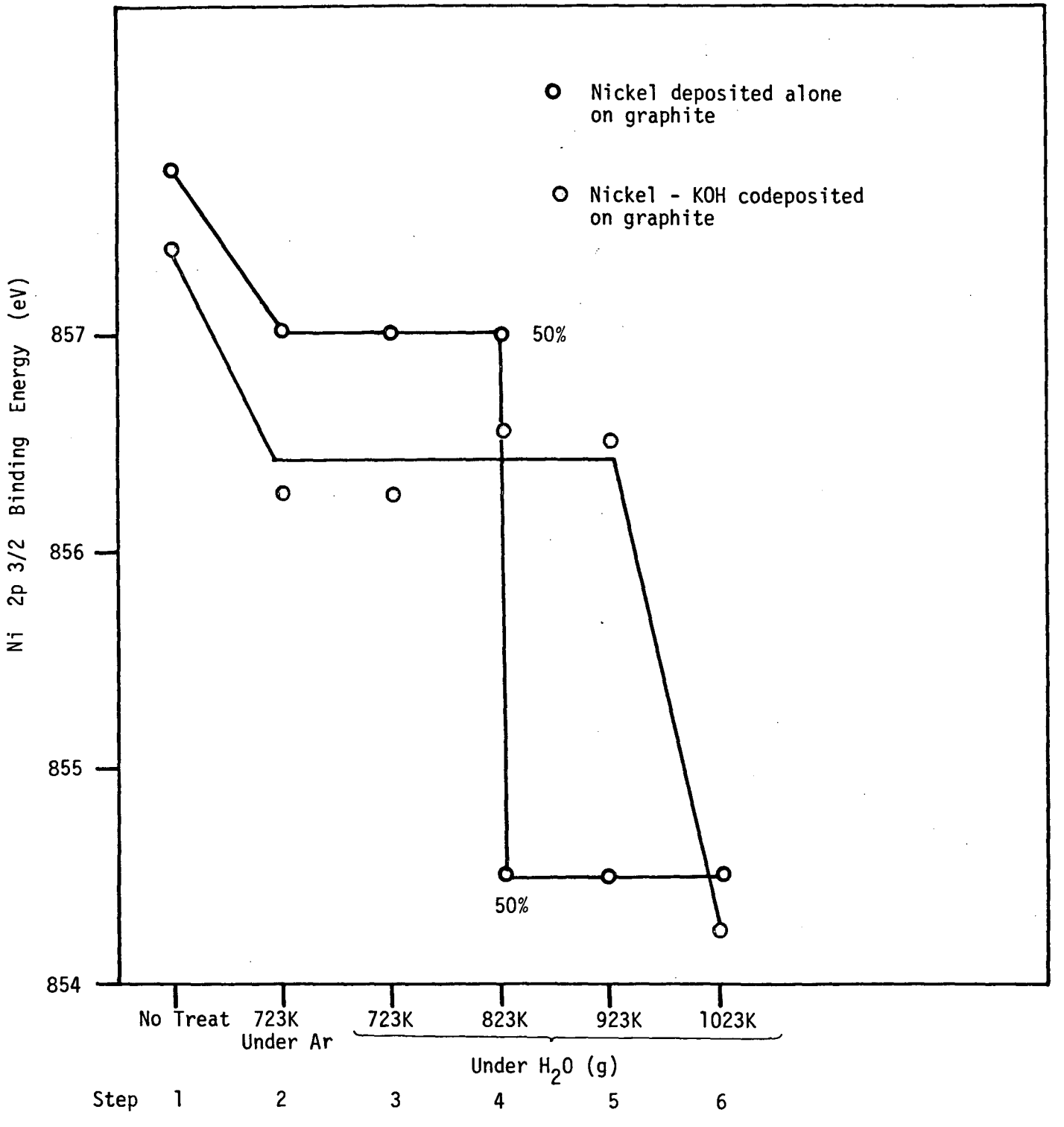

854.4 eV
871.6 eV
17.2 eV
854
864
874
884
894
Binding Energy
XPS Signal
(Arbitrary Units)

Figure 5b

Figure 6


Nickel deposited alone on graphite
Nickel - KOH codeposited on graphite
Ni 2p 3/2 Binding Energy (eV)
857
856
855
854
50%
50%
No Treat
723K Under Ar
723K
823K
923K
1023K
Under H_2O (g)
Step 1 2 3 4 5 6

At 923K the nickel is completely reduced. When nickel is adsorbed with KOH on the surface, it remains in the oxide state at temperatures up to 923K.

(b) Ratio of Potassium to Carbon

In figure 7 the XPS spectrum of a KOH loaded graphite sample is shown. The C1s peak of graphite appears always at 284 eV binding energy and can be used to calibrate the position of all the other peaks in the spectrum. The K2p signal is a doublet at 293.5 (K2p 3/2) and 296.2 eV (K2p 1/2). In order to get a relative value of the amount of potassium on the surface as a function of temperature, the ratio of intensities of K2p 3/2 to C1s was obtained. The results are shown in figure 8. For both samples KOH adsorbed alone and KOH coadsorbed with NiO, the amount of potassium on the surface increases as a function of temperature up to 823K. This is expected, since the increase in temperature favors the diffusion of KOH to the surface of the catalyst. When KOH is adsorbed alone on graphite, the amount of potassium on the surface suddenly drops at temperatures above 823K. This is probably due to a desorption process. When KOH is codeposited with NiO, there is still a considerable amount of potassium on the surface at 923K. In the presence of nickel the desorption process only becomes important at temperatures above 1023K. It should be remembered that only above 923K is nickel reduced to the metallic state when it is codeposited with KOH.

(c) Discussion

The XPS results presented in this report indicate that when KOH and NiO are codeposited on graphite, both the temperature at which the NiO is reduced by carbon and the temperature at which the potassium desorbs from the surface increase by more than 100K. This is shown schematically in figure 9. These results can be explained if KOH and NiO form a compound on the surface

Figure 7

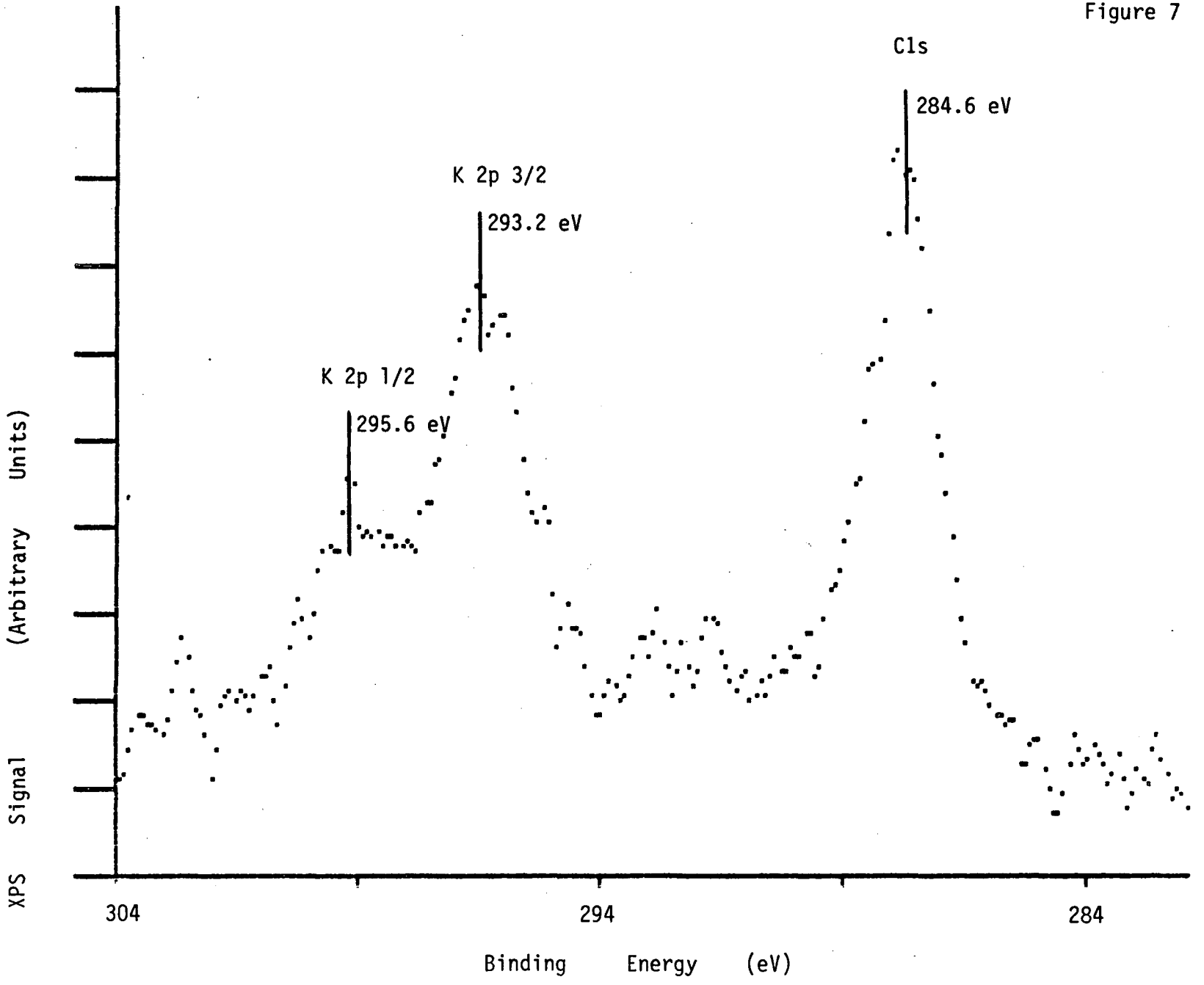
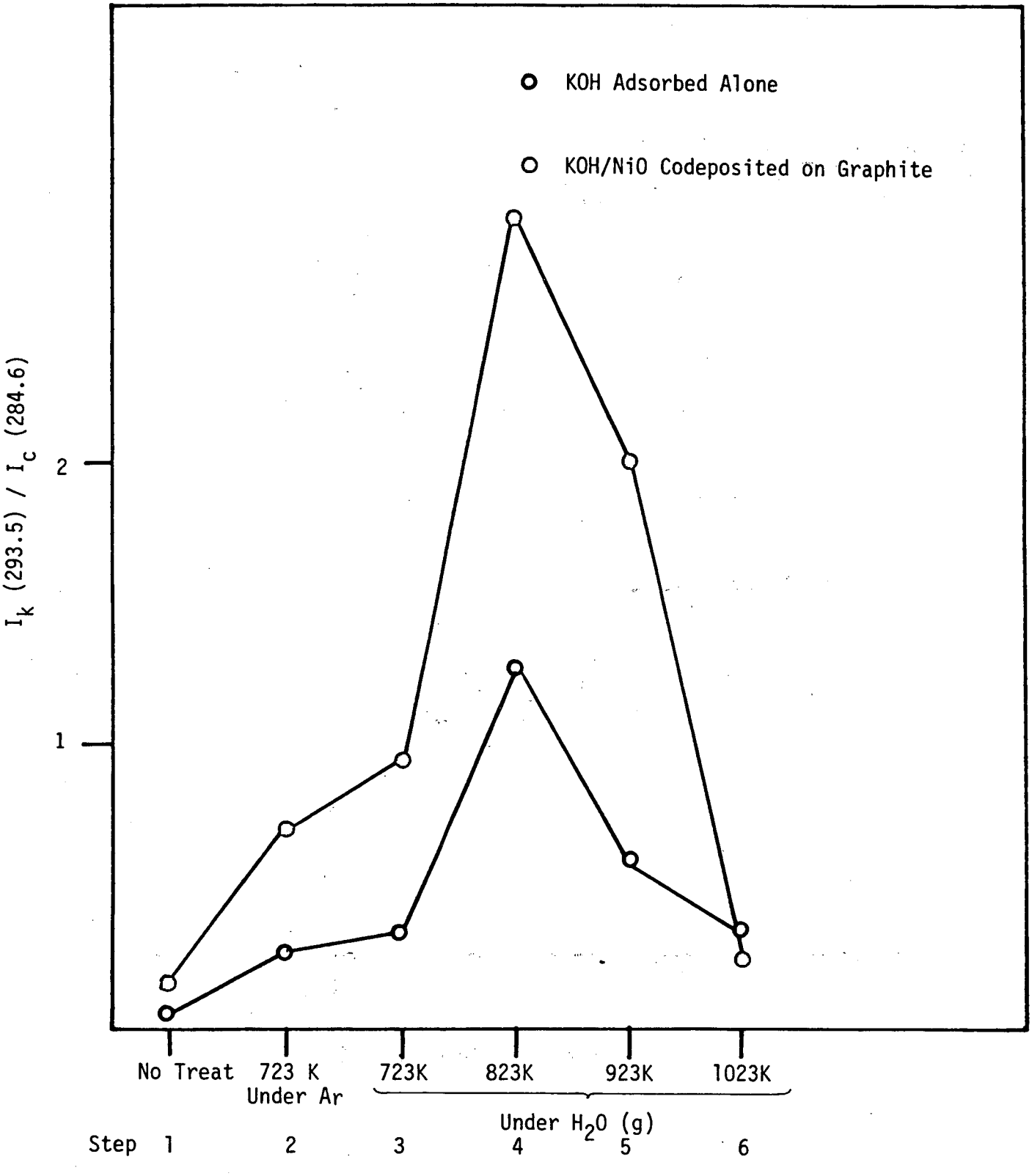
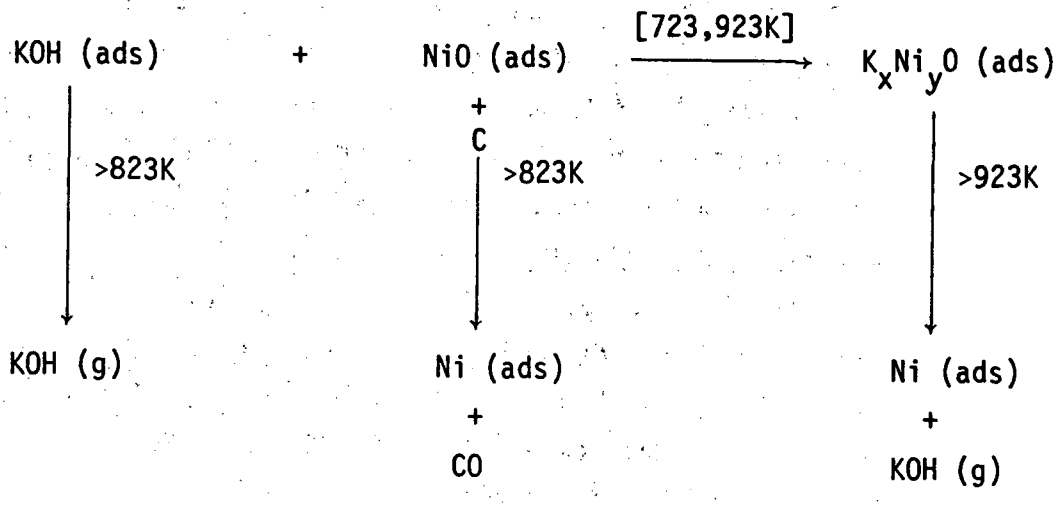

C1s
284.6 eV
K 2p 3/2
293.2 eV
K 2p 1/2
295.6 eV
XPS Signal (Arbitrary Units)
304
294
284
Binding Energy (eV)

Figure 8


KOH Adsorbed Alone
KOH/NiO Codeposited on Graphite
I_k (293.5) / I_c (284.6)
2
1
No Treat
723 K Under Ar
723K
823K
923K
1023K
Under H_2O (g)
Step 1
2
3
4
5
6

that decomposes only at temperatures above 923K. When this temperature is reached the nickel oxide is liberated and immediately reduced to the nickel metallic state, while the potassium desorbs from the surface. At temperatures below 923K, the stability of the compound inhibits the two processes. Since we have previously shown that the mixture of KOH and NiO is a good catalyst for the gasification of graphite with steam at temperatures as low as 853K, we conclude that the cooperative effect observed is due to the formation of a potassium nickelate compound (K_x Ni_y O) that has catalytic activity for the gasification of carbon solids with steam.

Figure 9


KOH (ads)
+
NiO (ads)
[723,923K]
K_xNi_yO (ads)
>823K
+
C
>823K
>923K
KOH (g)
Ni (ads)
+
CO
Ni (ads)
+
KOH (g)

(3) Thermal Desorption Studies

In the last quarterly report (April-June 1985) the TDS experiments done on graphite after exposing the sample to several torrs of CO, CO_2 and some of their isotopic derivatives (labelled with ^{13}C and ^{18}O) have shown evidence of gas contamination by oxygen or water in the high pressure loop. In particular, a significant amount of $C\ ^{18}O\ ^{16}O$ desorbed after exposing the graphite to pure $C\ ^{18}O_2$. In order to determine the cause of this contamination, we carried out extensive TDS studies on polycrystalline graphite coated on a tantalum foil. This was found to give reproducible results. It has also the advantage of avoiding "bulk effects" such as molecular diffusion into a thick porous material. No interaction of graphite with tantalum was observed as Auger spectra of the graphite surface after several TDS experiments did not show any tantalum peaks. The loop and the whole high pressure cell system was free of air leaks and the introduction of gases into it was done after at least one hour of pumping down with a sorption pump.

(a) CO Interaction with Graphite

Figure 10 shows the TDS spectra at masses 28 amu (CO) and 44 amu (CO_2) from the graphite surface after exposure to 760 torr of CO for 30 seconds. This pressure was chosen in order to minimize any possible leak from outside the loop. The same results were obtained after exposure times in the range of 10 seconds to 5 minutes, indicating that saturation coverage was reached.

Surprisingly, no high temperature peaks are observed in the desorption spectra of CO or CO_2. CO shows a sharp and intense desorption peak at around 450K and a broader and smaller one at 650K. CO_2 desorption is smaller than CO desorption by a factor of ten and shows similar features at 400 and 650K. This shows clearly

Figure 10: TDS spectra after exposing graphite to 760 torr of CO for 30 sec. at room temperature.

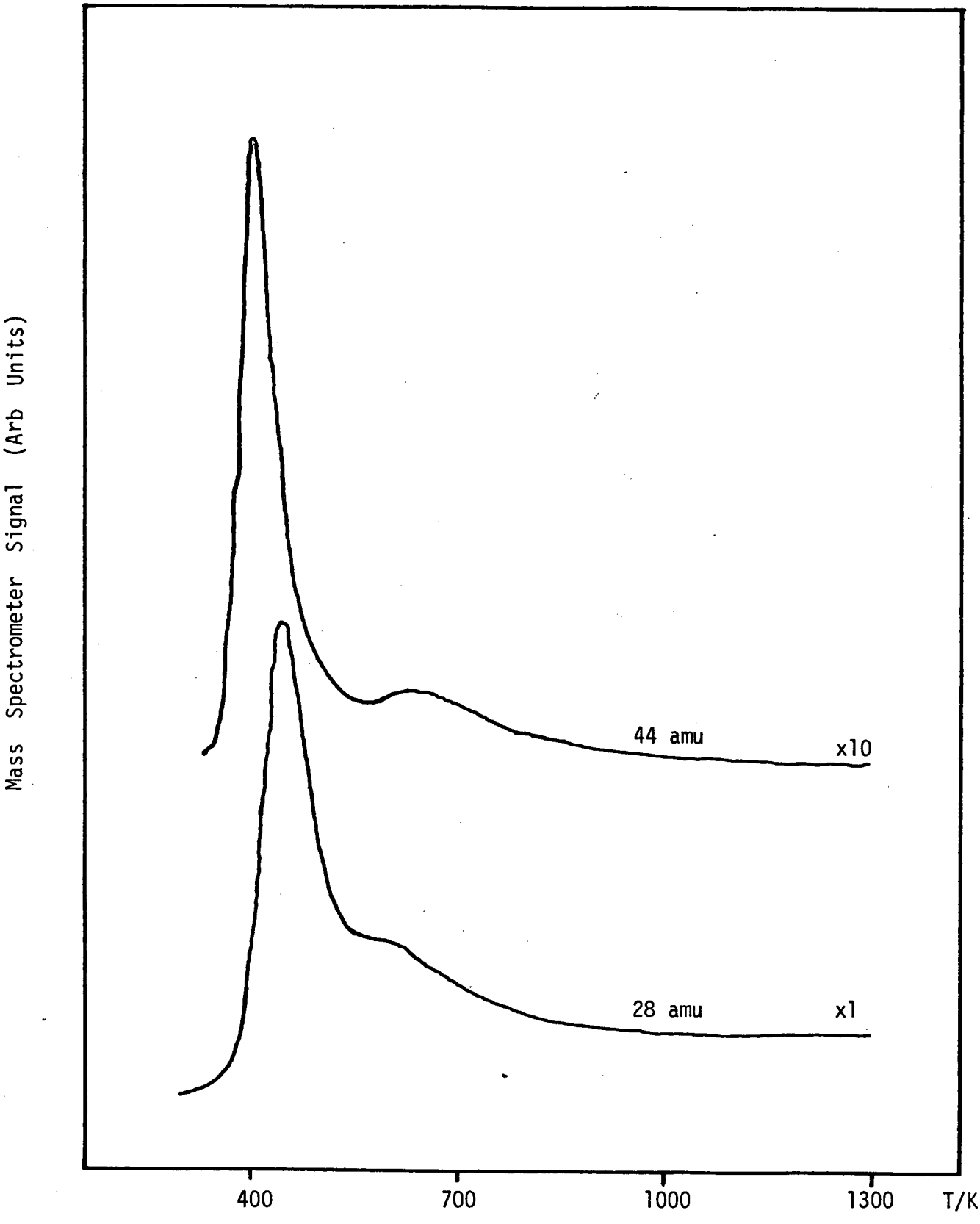
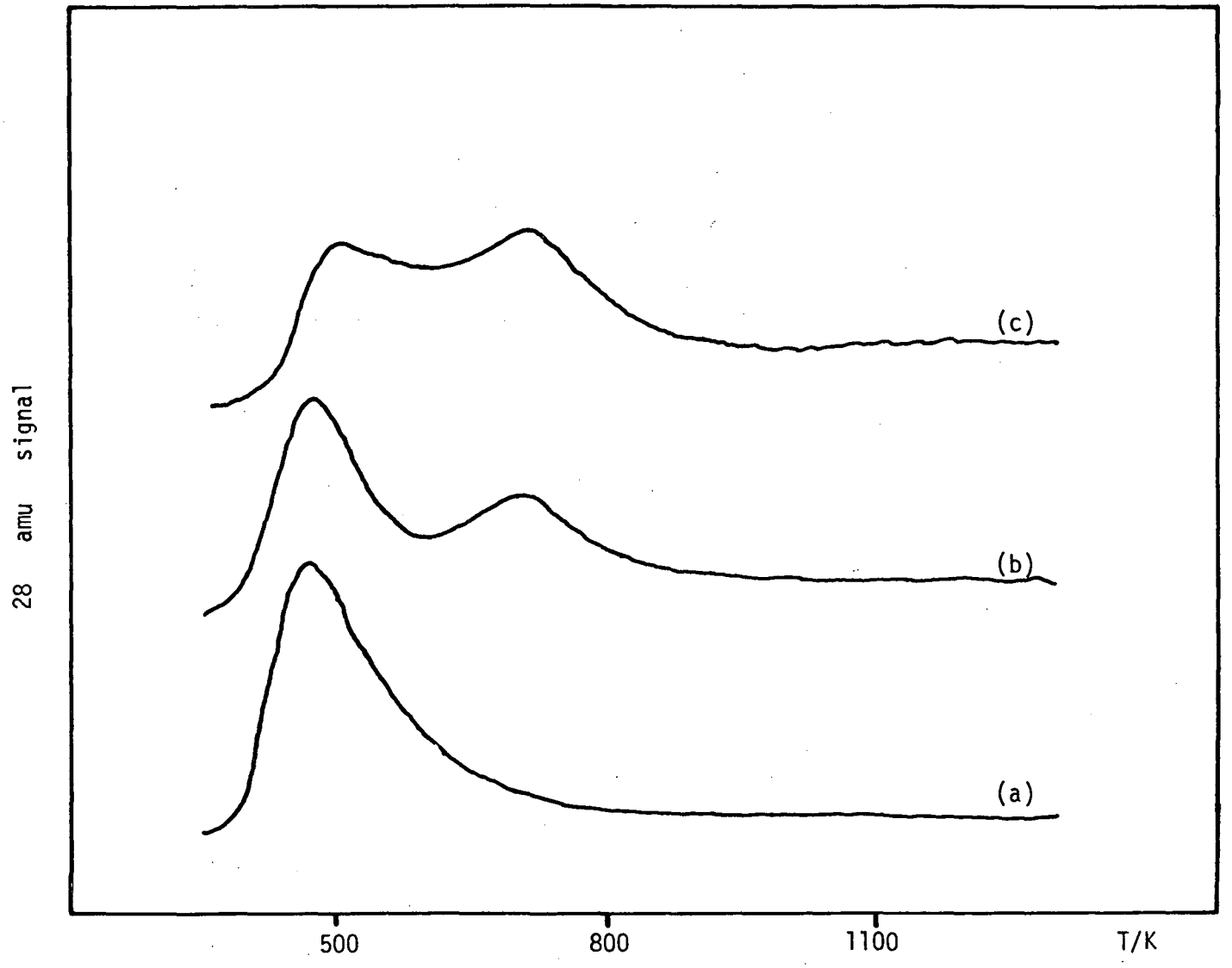


Figure 11: TDS spectra (mass 28 amu) obtained after exposing the graphite surface to 760 torr of CO at

(a) 300K

(b) 470K

(c) 520K



that the high temperature desorption peaks we observed before were due to contamination by air leaks.

If CO_2 is desorbed after CO adsorption, some carbon must be deposited on the surface, following the desproportionation reaction.

$$2\ CO \rightarrow CO_2 + C$$

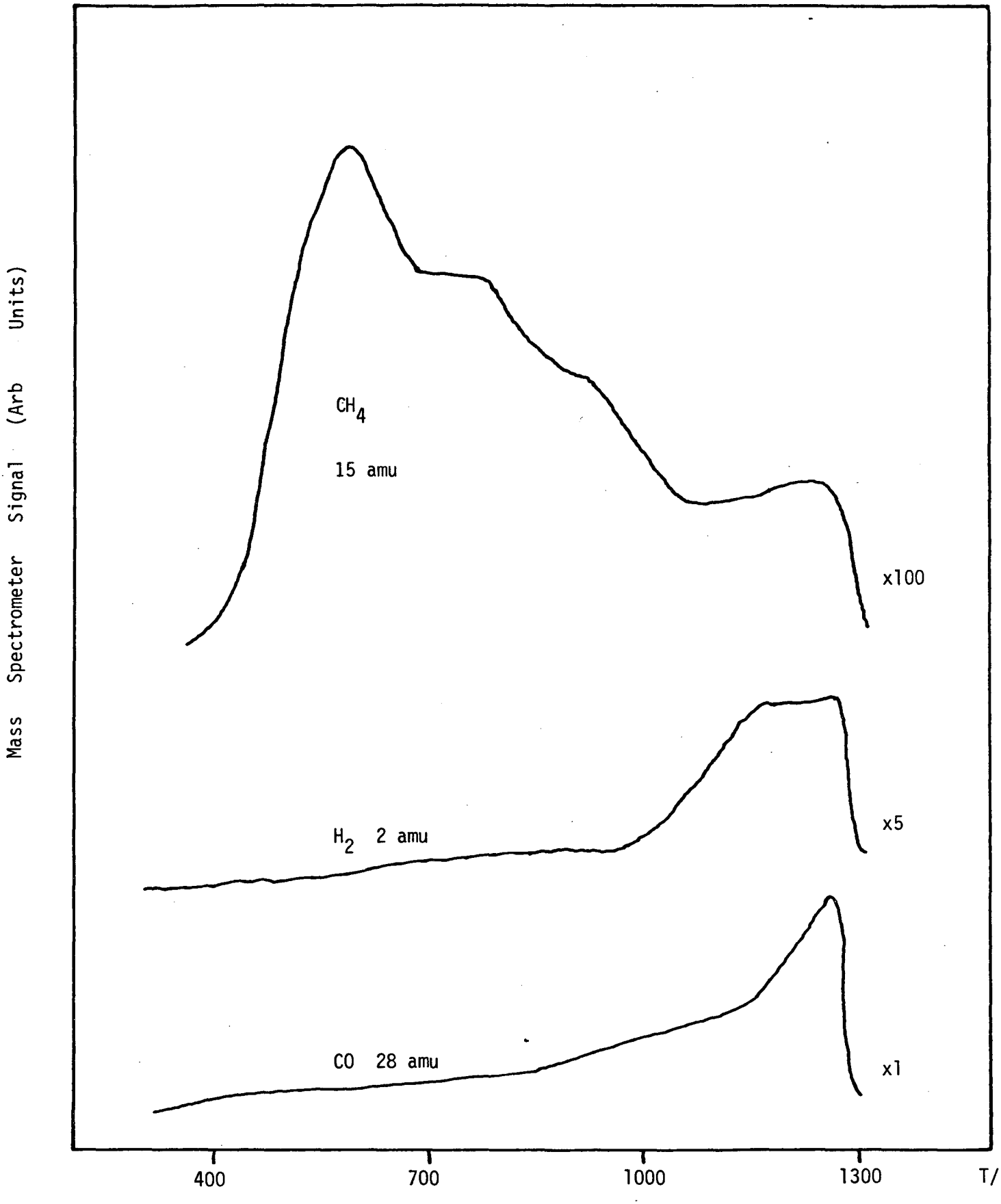
After several CO exposure desorption cycles, no changes in the spectra are observed, showing that the carbon formed is not much different from the one existing on the surface of the graphite.

Figure 11 shows the TDS spectra (mass 28 amu) after CO adsorption at 300 (a), 470 (b) and 520K (c). As the temperature is increased, a new desorption peak appears at 700K whereas the intensity of the 500K peak decreases. It seems then that different sites on the graphite surface can be activated by increasing the temperature of adsorption. Further experiments are in progress to determine the nature of these sites.

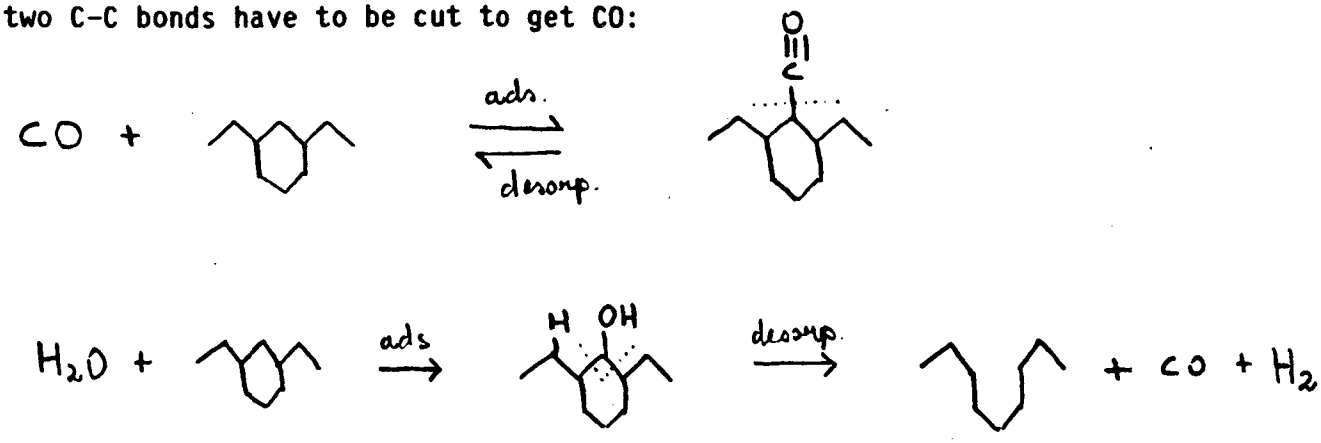
(b) Water Interaction with Graphite

In the graphite gasification process the interaction of water molecules with the graphite surface is of major importance. Figure 12 depicts TDS spectra after exposing the nonactivated graphite surface to water vapor pressure for 30 seconds. In spectrum (a) it is shown that CO desorbs at very high temperature (1250K) and this can account for the peak observed earlier, after contaminated CO adsorption. The difference in the CO desorption temperatures after CO or H_2O adsorption can be related to the fact that in one case one

Figure 12: TDS spectra after exposing the non-activated graphite to H_2O vapor pressure for 30 sec. at room temperature.



must break only one C-C bond, whereas after H_2O adsorption, at least two C-C bonds have to be cut to get CO:



Hydrogen desorption (Figure 12 Spectrum (b)) gives a broad peak around 1200K. A small amount of methane was also detected (Spectrum (c)). Methane was monitored using the mass 15 amu signal. The mass 16 amu signal cannot be used, even though it is the most intense ($I_{16}/I_{15}=1.20$), since it also contains contributions from the cracking patterns of CO, CO_2 and H_2O. The integrated intensity for the desorption of methane represents less than one third of the production of hydrogen.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720