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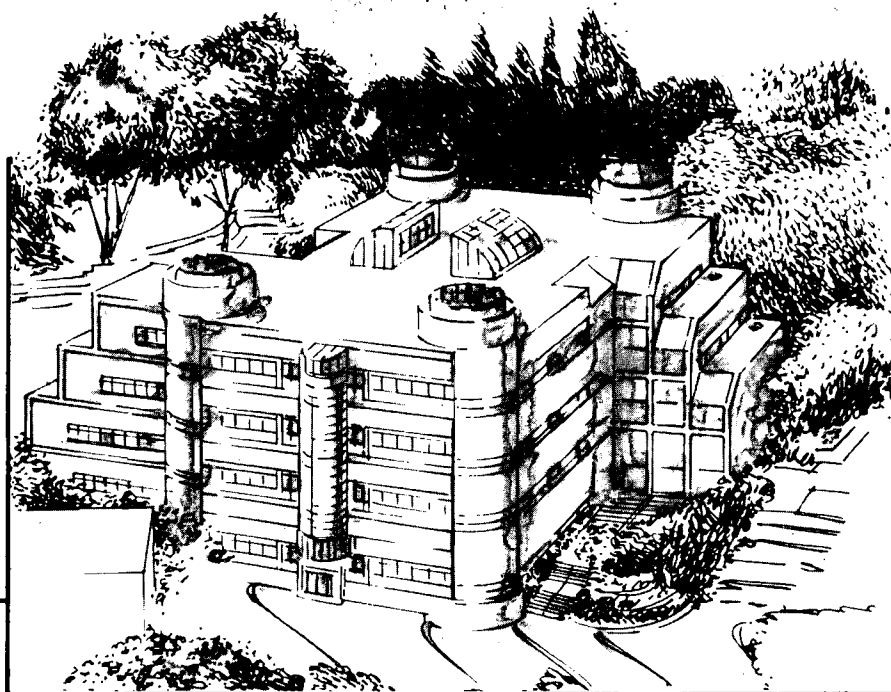
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**Steam Gasification of Carbon Solids Catalyzed
by a Nickel-Potassium Mixed Oxide: Kinetic
and Surface Characterization Studies**

J. Carrazza Duca
(Ph.D. Thesis)

October 1987



Materials and Chemical Sciences Division

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Steam Gasification Of Carbon Solids Catalyzed
By A Nickel-Potassium Mixed Oxide:
Kinetic and Surface Characterization Studies

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**Steam Gasification Of Carbon Solids Catalyzed
By A Nickel-Potassium Mixed Oxide:
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José Carrazza Duca

Abstract

The main goal of this thesis is to evaluate and understand the catalytic properties of a nickel-potassium mixture for steam gasification of carbon solids. This goal pursued by carrying out kinetic and surface characterization studies, using both graphite and a coal-char as carbon substrates.

The kinetic study on graphite gasification shows that the nickel-potassium mixture has distinct catalytic properties for this reaction, when compared with potassium-alone and nickel-alone catalysts. The mixture is active at relatively low temperatures (800 K) compared with the potassium-alone catalyst, and does not deactivate with time, contrary to the case of nickel alone. These properties are attributed to a cooperative effect between nickel and potassium.

The surface characterization studies were focused on the relation between the catalytic characteristics of the mixture, and its morphological and surface-chemistry properties. The morphology study was based on controlled atmosphere electron microscopy results. It shows that the mixture is very mobile under reaction conditions. It spreads over the edge planes of graphite, and favors the steam attack by edge recession in the $[11\bar{2}0]$ crystallographic direction. The surface-chemistry study, based on X-ray photoelectron spectroscopy, shows that the nickel-potassium interaction stabilizes NiO and KOH on the graphite surface, under reaction conditions. It is proposed that the formation of a nickel-potassium mixed oxide is responsible for the distinct properties of this catalyst. This species

is either directly involved in the gasification process, or becomes a support for an active nickel metal species, increasing its mobility and preventing its deactivation.

The performance of the nickel-potassium catalyst in a process of technological interest, such as the steam gasification of coal-chars, was also investigated. The results indicate that the mixture is a better catalyst for steam gasification of low ash chars, than both nickel-alone and potassium-alone catalysts. If the ash content is high (~ 50 wt.% of nonvolatile components in the char), however, the interaction of both nickel and potassium with the minerals present decreases substantially its activity toward steam gasification.

A temperature programmed desorption and X-ray photoelectron spectroscopy study on the adsorption of O_2 , H_2O , CO and CO_2 on clean graphite is also presented. It is proposed that all four gases form the same type of oxygen containing surface species, after chemisorption. The most abundant surface species desorbs as CO between 1000 and 1300 K, and has been assigned to a semi-quinone functional group. This CO precursor can react with the adsorbing gas, and form a second species, that desorbs as CO_2 between 500 and 900 K. A surface lactone has been proposed as the CO_2 surface precursor.

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*To the memory of Carlos Stea,
for all the dreams and good times we shared.*

Chapter 1

Introduction

The reaction between carbon solids and steam is an important route for production of H_2 , CO_2 , CO and CH_4 . These gases can then be used as feedstocks for a variety of chemical processes. For example, the hydrogenation of CO and CO_2 to form gasolines and alcohols has been extensively studied, and several industrial processes based on this technology are currently in operation. Also, the activation of CH_4 to produce olefins and alcohols has recently generated great interest, both in the academic and industrial communities.

These examples show it is feasible to convert substances as abundant as carbon and water into materials of industrial value. All these processes, however, require further research to solve immediate problems. This is specially true for the catalyzed gasification of carbon solids with steam. For this reaction, even though there are several compounds reported to have catalytic activity, all of them present inconveniences that have limited the scaling of the process to an industrial level. The search of a new catalyst that would overcome these difficulties is thus of great importance, and it is considered an important part of this research project.

In this chapter, background information relating to the problem in question

will be presented. First, thermodynamic considerations on the reaction between carbon and H_2O vapor will be described. A brief summary of the main advances on the catalytic gasification of carbon solids with steam will follow, and then a discussion on how these advances led to the study of a potassium-nickel oxide mixture as an alternative catalyst will be presented.

1.1 Thermodynamics

The reaction between H_2O vapor and graphite can be considered as a closed system with six intensive variables: the temperature, and the fractions of H_2O , H_2 , CH_4 , CO , and CO_2 in equilibrium. The activity of graphite is always equal to 1.0, because it is a bulk solid.

The interconversion of these gases can be represented by several equilibria, (see table 1.1), but because of the hydrogen and oxygen mass balances, (equations 1.8 and 1.9), only three of the equilibrium constant equations are linearly independent.

Since the primary concern of the thesis is the reaction between H_2O vapor and graphite, equilibria 1.1 to 1.3 in table 1.1 were chosen to describe the system. The equilibrium constants for these three reactions are given by equations 1.10 to 1.12.

$$(P_{H_2O})_{initial} = P_{H_2O} + P_{H_2} + 2P_{CH_4} \quad (1.8)$$

$$(P_{H_2O})_{initial} = P_{H_2O} + P_{CO} + 2P_{CO_2} \quad (1.9)$$

$$K_1 = \frac{(P_{CH_4})^{1/2} (P_{CO_2})^{1/2}}{P_{H_2O}} \quad (1.10)$$

$$K_2 = \frac{(P_{H_2})^2 P_{CO_2}}{(P_{H_2O})^2} \quad (1.11)$$

$$K_3 = \frac{P_{H_2} P_{CO}}{P_{H_2O}} \quad (1.12)$$

Table 1.1: Reactions involved in the steam gasification of graphite.

Equation	Reaction	ΔG_{298} kcal/mol-C
	Gasification	
1.1	$C + H_2O_{(g)} \rightleftharpoons 1/2 CH_{4(g)} + 1/2 CO_{2(g)}$	1.44
1.2	$C + 2 H_2O_{(g)} \rightleftharpoons 2 H_{2(g)} + CO_{2(g)}$	15.01
1.3	$C + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{(g)}$	22.06
	Water-gas shift	
1.4	$CO_g + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$	-6.84
	Steam reforming	
1.5	$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons 3 H_{2(g)} + CO_{(g)}$	33.98
1.6	$CH_{4(g)} + 2 H_2O_{(g)} \rightleftharpoons 4 H_{2(g)} + CO_{2(g)}$	27.15
	Boudouard equilibrium	
1.7	$CO_{(g)} \rightleftharpoons 1/2 C + 1/2 CO_{2(g)}$	-14.35

Table 1.2: Parameters used in the evaluation of equation 1.14.

i	$(\Delta H_{298})_i$ kcal/mol-C	$(\Delta S_{298})_i$ cal/(mol-C K)	$(\Delta C_p)_i$ cal/(mol-C K)
1	1.83	1.31	-4.35
2	21.54	21.91	4.57
3	31.38	31.29	3.89

where $(p_{H_2O})_{initial}$ is the pressure of H_2O vapor in the initial conditions, and p_i is the pressure of gas i in equilibrium.

A general expression for the dependence of the equilibrium constant on temperature is given by equations 1.13 and 1.14, and the parameters necessary to evaluate each particular one are summarized in table 1.2.

$$K_i = \exp\left(-\frac{(\Delta G_T)_i}{RT}\right) \quad (1.13)$$

$$(\Delta G_T)_i = (\Delta H_{298})_i + (\Delta C_p)_i(T-298) - T(\Delta S_{298})_i - (\Delta C_p)_i T \ln(T/298) \quad (1.14)$$

The equilibrium partial pressures of H_2O , H_2 , CH_4 , CO , and CO_2 at a given temperature, can be calculated by solving the equations 1.8 to 1.12.

Figure 1.1 shows, as an example, the results obtained for a $(p_{H_2O})_{initial}$ equal to 1.0 atm. The partial pressure of H_2O in equilibrium decreases with temperature, and above 1300 K total conversion is achieved. Below 500 K, CH_4 and CO_2 are the main steam gasification products, as represented by equation 1.1. As the

temperature raises above 500 K, the amount of CH_4 in equilibrium decreases, and the main gas products are now H_2 and CO_2 (equation 1.2). This is the case up to 900 K. Above this temperature, the amount of CO_2 in equilibrium starts to decrease, and H_2 and CO become the main gas components in the system (equation 1.3).

1.2 Catalysts For The Carbon-Steam Reaction

Though thermodynamic considerations presented in the previous section indicate that the steam gasification of graphite is feasible even at room temperature, when steam is passed over a clean graphite sample, no significant gas evolution occurs until temperatures above 1400 K are reached [1], indicating that the reaction is kinetically controlled.

It has been known for many years, however, that the addition of mineral salts to carbon solids enhances their reactivity toward reaction with steam. Though during gasification these inorganic materials may be modified, they are not consumed. Their role in the reaction, thus, has been considered to be catalytic.

There is a large number of publications concerning the catalytic effect of several inorganic salts in the steam gasification of carbon solids. Various excellent reviews have surveyed this information, and summarized the most important findings [2-4].

Alkaline and alkaline earth compounds have been the catalysts more widely studied. Hydroxides, oxides and carbonates are reported to be the most active catalysts [5]. Other salts like nitrates, sulfates, and in some instances halides, also show catalytic activity, but only after pretreatments in which the salt decomposes, and the oxide is formed [6]. Several authors have reported that an excellent contact between these catalysts and the carbon substrate is achieved under reac-

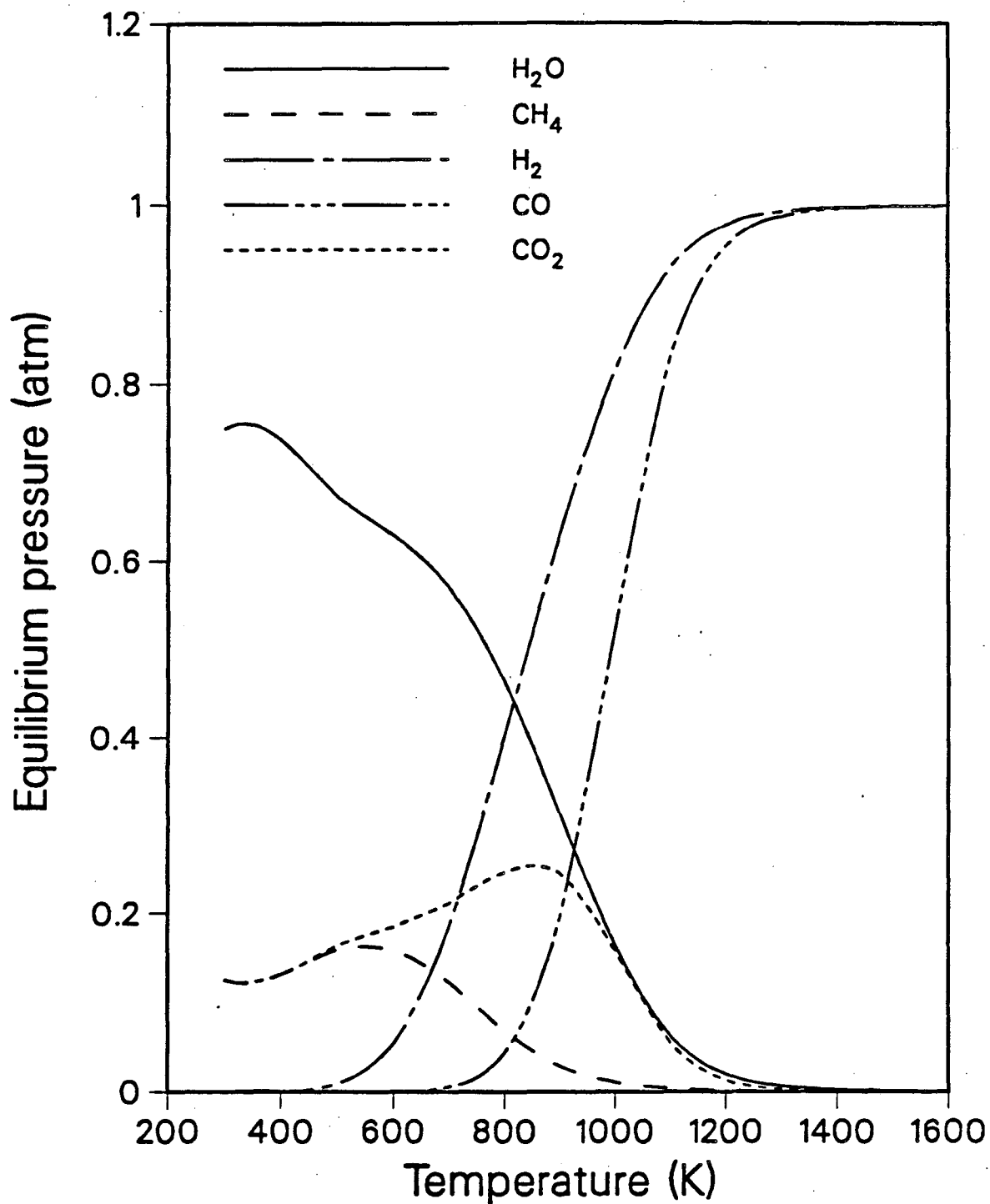


Figure 1.1: Dependence on temperature of the equilibrium partial pressures of H_2O vapor, and the products of the steam gasification of graphite. The initial pressure of H_2O vapor is equal to 1.0 atm.

tion conditions, and that the chemical attack occurs at the carbon atoms in the periphery of aromatic structures (edge planes) [7,8].

The precise state of the alkali under reaction conditions is not clear. It has been suggested that a surface anionic complex, such as an alkali metal phenolate, is formed under reaction conditions, and becomes an intermediate in the gasification reaction [9]. Other authors suggest that the active catalyst forms a separate phase, in liquid state, that is oxygen deficient (metal rich) [10,11].

Whatever the precise nature of the catalyst, there is a broad agreement that it favors the dissociation of H_2O , and supplies oxygen to the carbon. Most authors invoke a redox cycle, in which the catalyst is reduced by carbon, and reoxidized by steam [12,13].

The use of alkali and alkaline earth salts presents some inconveniences. These compounds are only active for steam gasification of graphite above 1000 K [14]. Also, catalyst deactivation and recovery due to vaporization in the case of graphite gasification, and interaction with aluminosilicates in the case of char are important technological problems [6].

Transition metals, particularly iron and nickel, have also been studied as catalyst for steam gasification of carbon solids. In general, these catalysts show a much higher activity for steam gasification of graphite, and at lower temperatures than alkali or alkaline earth salts [15]. Several authors indicate that the catalyst activity of both nickel and iron is associated with the presence of the metal [15,16,17]. There is, however, no consensus over the mechanism promoted by the transition metal. Some authors propose an oxygen transfer mechanism, similar to the case of the alkali metal catalyzed process [15,18,19]. Others propose an electron transfer mechanism [20]. In this case, the metal withdraws electron density from the car-

bon, and weakens the carbon-carbon bonding, facilitating the formation of CO. In some articles it has been proposed that the electron transfer is such that the catalyst breaks carbon-carbon bonds, and the formation of a carbide [21], or the diffusion of carbon through the bulk of the catalyst [22], become steps in the gasification process.

The use of transition metals as catalysts for steam gasification of carbon solids also presents inconveniences. In the case of graphite gasification, several authors have reported that the catalyst deactivates before total carbon conversion [23,24], and cannot be regenerated. Also, in the case of char gasification, the catalyst is poisoned by reaction with sulfur, which is present in significant amounts in many chars.

1.3 Scope of the thesis

The properties of an ideal catalyst for gasification of carbon solids with steam must include a high activity and good contact with carbon. Also, it should be easy to recover, and should not deactivate with time. From the discussion in the previous section, it is clear that alkali and transition metal salts, the two most common type of catalysts studied, present only some of these properties. It is interesting, however, that their properties complement each others. The transition metal catalysts show high activity, but deactivates very easily, while total carbon conversion can be achieved with alkali catalysts, but only at high temperatures.

This observation motivated the study of combinations of alkali and transition metal salts as catalysts for steam gasification of carbon solids. The hope was to produce a novel catalyst that would combine the good contact properties of the alkali metal, with the activity at low temperatures typical of transition metals.

Initial studies show that these alkali-transition metal mixtures indeed have distinct properties for steam gasification of graphite, when compared to the two components loaded by themselves. A detail characterization, from both kinetic and surface science perspectives, became then the main scope of this thesis. Also, since the nickel-potassium mixture showed the best catalytic properties among all the cases evaluated, studies were focused on this particular catalyst. In chapter 3, a detailed kinetic study of the nickel-potassium mixture for steam gasification of graphite is presented. This study showed that the properties of the mixture are due to a cooperative effect between the alkali and the transition metal. Surface characterization studies were then carried out to associate the distinct kinetic properties of the nickel-potassium mixture with morphological and chemical properties, as determined respectively by electron microscopy (chapter 4) and XPS (chapter 5). Also the performance of this catalyst in a process of industrial interest, such as the steam gasification of char, was investigated, and the results are presented in chapter 6. The final section of the thesis describes the initial results of an ongoing study on the surface species involved in the carbon-steam reaction. TPD and XPS results on adsorption of various gases on clean graphite are presented, and a general scheme for the adsorption-desorption mechanism of all the gases is discussed.

Each chapter represents a study carried out to address a particular aspect of the thesis scope, containing the results and discussion related to that particular aspect. They have been written as units that, in principle, can be read independently from the others. With this format, reiteration in the discussion of some specific points is difficult to avoid. This, however, is limited to situations in which results from one chapter are particularly useful to understand those of another.

The order of the chapters reflects, more or less, a chronological sequence in the performance of the studies. With this sequence, the author wants to show how the ideas developed over the performance of the thesis, and how the study presented in a particular chapter was motivated by the results discussed in the preceeding ones.

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Chapter 2

Experimental

2.1 Kinetic Studies

2.1.1 Flow Reactor System

The kinetic experiments presented in chapters 3, 5 and 6 were carried out using a fixed bed flow reactor, with an on-line gas chromatograph. (See figures 2.1 and 2.2). The system is operated by flowing steam through a carbon substrate, loaded with the catalyst. The sample is inside a tubular furnace, heated between 800 and 1000 K. The gas products are separated from the unreacted steam by a condenser, their volume measured with a gas buret, and the product distribution is determined by gas chromatography, using a thermal conductivity detector.

Steam is generated by pumping distilled H_2O through a hot Cu coil (~ 800 K). The pump (Liquid Metronics Inc., model 101A), delivers pulses of H_2O every 1 to 5 sec. The H_2O flow must be kept below 2 ml $\text{H}_2\text{O}_{(l)}/\text{min}$, to avoid steam condensation and accumulation in the lines. To dampen the fluctuations in flow, due to the pump pulsations, a stainless steel cylindrical container (2.5 cm wide and 7.5 cm tall) was added to the system just after the heater (labelled as knock-out container in figure 2.2). This container is also effective for separating steam from

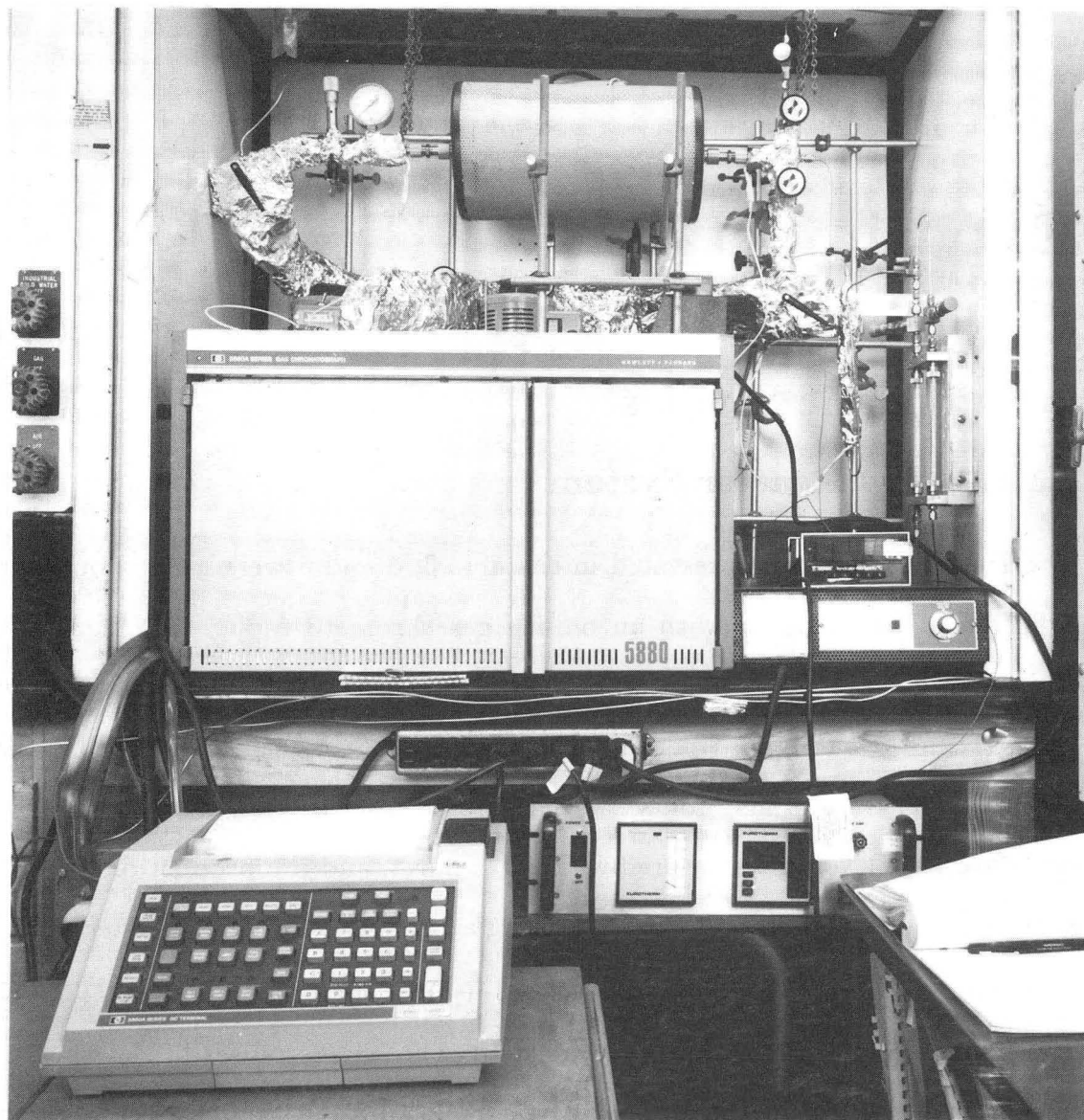


Figure 2.1: Photograph of the flow reactor system used to performed the kinetic studies presented in this thesis.

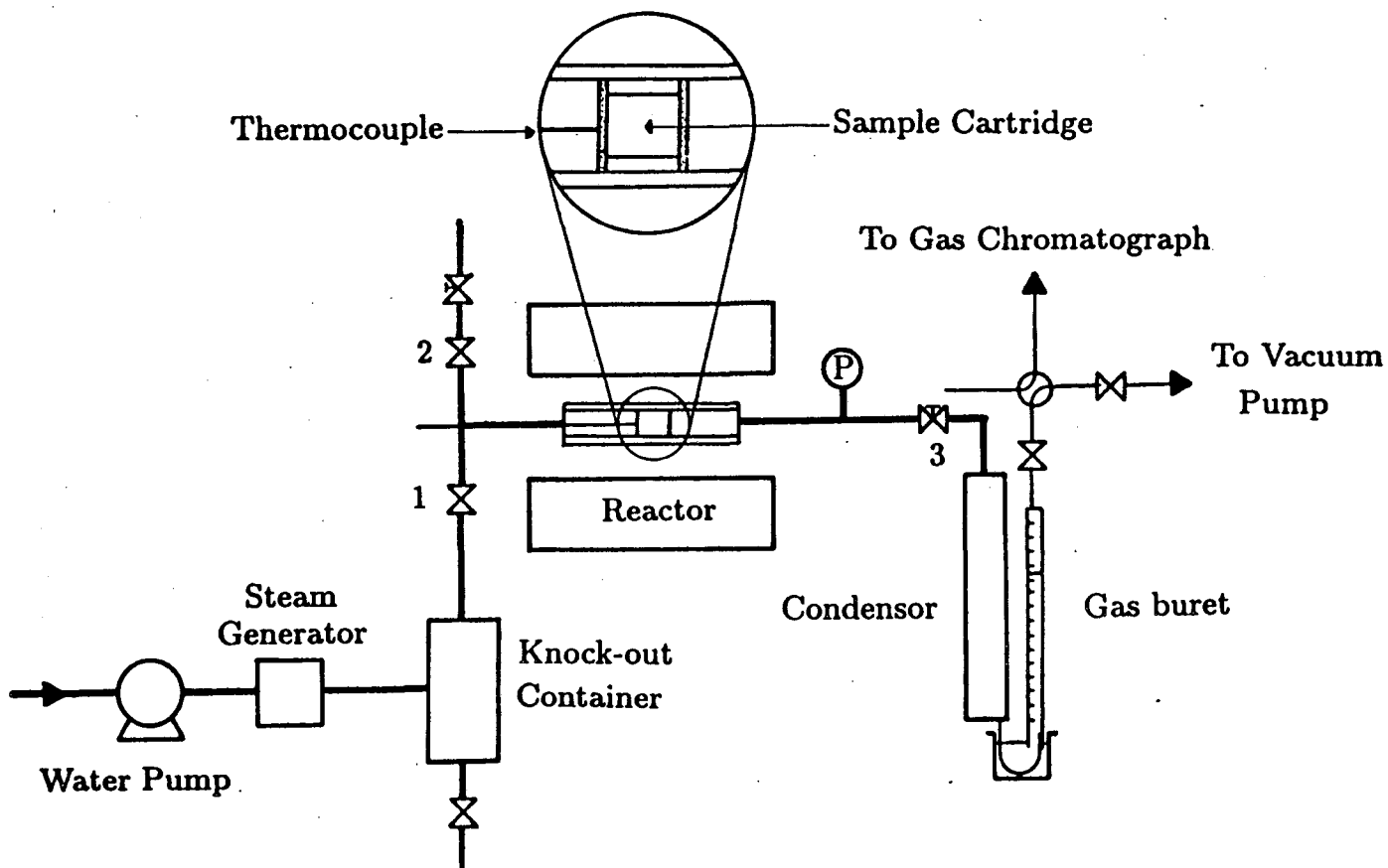


Figure 2.2: Schematic representation of the flow reactor shown in figure 2.1.

condensed H_2O in the lines. Its outlet is connected to the reactor, through valve 1.

The reactor is an 18.5 cm Al_2O_3 tube of 1.25 cm outside diameter, and 0.175 cm wall thickness. This tube is inside a stainless steel jacket, which is needed for mechanical strength. The walls of the jacket are isolated from the steam by viton o-rings. Because of thermal limitations, these seals must be located at least 5 cm from the oven, and kept below 473 K.

The carbon sample, with the catalyst, is loaded into a cartridge, located inside the reactor. This cartridge is also made of Al_2O_3 . Its outside diameter (0.9 cm) is machined to match the inside diameter of the reactor. This assures that steam is forced to flow through the sample. The cartridge walls in the direction of flow are made of a porous ceramic, and constitute the highest restriction to flow in the system. This way, flow conditions are easier to reproduce. Also, the initial packing of the sample is not critical, because during reaction, it is kept compacted against the porous wall of the cartridge by the steam. This also reduces the steam by-pass of the carbon at high conversions.

After loading the sample, the porous walls were glued to the body of the cartridge with a ceramic cement (Aremco 440). The sealed cartridge prevents steam from carrying away part of the sample. It is also convenient for sample handling, in the weight loss determinations.

The cartridge is located in the center of the reactor, and kept in place by spacers. The temperature is measured with a chromel-alumel thermocouple, in contact with the external walls of the cartridge. The temperature output is used as a feedback for an Eurotherm 983 controller, that drives the power output of a Thermolyne F21120 tubular furnace.

The steam pressure at the reactor outlet is controlled by a bellow-type needle valve (Nupro SS-4BMW). Pressures up to 5 atm could be reached. The limiting factor was the performance of the pump.

The outlet gases were cooled to room temperature with the aid of a condenser. Heat is exchanged through a stainless steel coiled tube (723 cm long and 0.31 cm in diameter), using chilled H_2O as a refrigerant. The gas products, once separated from the H_2O , are collected into a gas buret.

The product distribution is determined by gas chromatography. The gas buret is connected to the gas chromatograph (HP 5890A) through an 8 port-2 loop sampling valve (Valco). Gases are detected with a single filament-thermal conductivity detector. The separation is carried out with a Carbosieve SII column (400 cm long and 0.3 cm diameter), operated isothermally at 373 K, and with a He carrier gas flow of 20 ml/min.

The retention times, and relative sensitivities for all the analyzed gases are given in table 2.1. The gas samples usually contained a small amount of H_2O vapor, that under separation conditions remained trapped in the column. After 5 to 10 samples, the column saturates with H_2O , causing the baseline to drift. At this point the column is heated to 498 K for 5 min, to dispose the H_2O . All the peak areas are determined by an HP 3392A integrator, using flat baseline, set before the appearance of each peak.

2.1.2 Sample Preparation

Carbon Substrates

The kinetic studies on steam gasification of graphite (chapters 3 and 5) were carried out on a synthetic material (UCP-1 from Ultra Carbon, lot 10432). Elemental

Table 2.1: Retention time and detector sensitivity of the analyzed gases.

Gas	Retention time (min)	Sensitivity ¹
H ₂	0.85	219.4
Air	1.94	2.73
CO	2.44	1.86
CH ₄	5.0	1.86
CO ₂	11.65	1.00

¹Relative to CO₂.

analysis shows that the substrate is 99.9 wt.% carbon. It contains only 0.1 wt.% of hydrogen and sulfur, and the mineral impurities are below the ppm range. It has a relatively low surface area ($4.1 \text{ m}^2/\text{g}$), and it is nonporous.

In chapter 6, the steam gasification of a lignite char is studied. It was provided by Dr. B. Wood at SRI International (Menlo Park, CA), and it had been prepared by partial steam gasification at 1196 K. A complete description of the elemental analysis, and physical properties of this substrate are given in chapter 6.

Indigenous materials in the char as received were catalytically active toward steam gasification at 893 K. To obtain an inactive support, the char was either treated in steam until no rate of gasification was observed, or demineralized by treatment in HCl and HF. The elemental analysis of the char after these treatments is given in chapter 6.

The procedure for demineralization is as follows. 25 gr of char was first treated with 30 ml washes of 3 F HCl at 333 K, until the calcium, magnesium and iron content of the washes was below 20 ppm, as determined by atomic absorption. (about 35 washes were necessary). In the last wash, the calcium concentration was 0.6 ppm, magnesium 0.15 ppm and iron 6.6 ppm. Temperatures above 333 K were avoided, to prevent carbon oxidation. After the HCl treatment, the remaining solid was treated with 35 ml of 9 F HF solutions, until the silicon concentration in the washes was below 8.0 ppm. (7 washes). The solid was then rinsed with distilled H_2O until no more chloride or fluoride ions were detected in the washes (about 60 times).

Catalyst Loading

The kinetic experiments carried out in this thesis were focused mainly on evaluating and understanding the catalytic properties of nickel and potassium, mixed or by themselves, for steam gasification of carbon solids. The catalysts were loaded onto the carbon substrate by incipient wetness, using KOH (Mallinckrodt lot WHBY and Fisher lot 864497A), and $\text{Ni}(\text{NO}_3)_2$ solutions (Mallinckrodt lot KPBT).

The reaction rates did not vary with the order the salts were loaded. In general, nickel was loaded first, mixed with the carbon substrate, and then potassium was added. After loading the catalyst, the sample was dried in air at 373 K for 15 min, ground with an agate mortar, and introduced into the cartridge.

The cartridge was then treated in Ar, inside the reactor, to condition the ceramic cement used to glue its walls, and to decompose the $\text{Ni}(\text{NO}_3)_2$ in the carbon sample. The treatment involved intervals of 30 min at 363, 393, 643 and 723 K. After this treatment, the sample was cooled in Ar, and the initial weight of the cartridge measured.

The catalytic activity of other transition metal-alkali mixtures was also evaluated. All the samples were prepared using a procedure similar to the one just described. Iron, copper, cobalt and chromium nitrate, zinc and manganese sulfate, ammonium metavanadate, and ammonium molybdate were used to deposit the respective transition metals. Calcium and magnesium nitrates, and sodium hydroxide were used to load the respective alkaline-earth and alkali catalysts.

2.1.3 Experimental Procedure And Data Analysis

The sample is introduced in the reactor, and air is purged with Ar at room temperature for 15 min. The temperature is then raised to 723 K in Ar. The Ar flow is stopped by closing valve 2 in figure 2.2, and steam is introduced by opening valve 1. The temperature is kept at 723 K until no more Ar is collected in the gas buret (~ 10 min), and then it is raised to the reaction value (between 800 and 1000 K). Total production rates are determined by measuring the volume of the gas collected in a given time interval. The product distribution is determined every 15 min, by gas chromatography. The fraction of each gas in the sample is given by equation (2.1),

$$\chi_i = \frac{N_i/S_i}{\sum_i N_i/S_i} \quad (2.1)$$

where, χ_i is the fraction of gas i in the sample

N_i is the number of counts in the gas chromatogram, corresponding to gas i and, S_i is the sensitivity factor for gas i (see table 2.1).

The rate of gas production for each gas (rate_i) is given by,

$$\text{rate}_i = \chi_i \times \text{rate}_{\text{total}} \quad (2.2)$$

where, $\text{rate}_{\text{total}}$ is the global rate of gas production.

The reaction between carbon and steam can be expressed by equations 2.3 to 2.5.



From mass balance considerations,

$$\text{rate}_{H_2} + 2 \text{rate}_{CH_4} = \text{rate}_{CO} + 2 \text{rate}_{CO_2} \quad (2.6)$$

From the observed rates of gas production, however, equation 2.6 is not satisfied. This is probably due to the dissolution of a fraction of the CO_2 produced, since table 2.2 shows that the solubility of CO_2 in H_2O is rather large, compared to those of H_2 , CH_4 and CO . To correct for this deviation, the rate of CO_2 production is calculated, assuming that a mass balance is reached. From equation 2.6, then,

$$(\text{rate}_{CO_2})_{calc} = \frac{1}{2} \text{rate}_{H_2} + \text{rate}_{CH_4} - \frac{1}{2} \text{rate}_{CO} \quad (2.7)$$

and the total rate of carbon consumption is given by

$$(\text{rate}_C)_{consumed} = \text{rate}_{CO} + \text{rate}_{CH_4} + (\text{rate}_{CO_2})_{calc} \quad (2.8)$$

$$(\text{rate}_C)_{consumed} = \frac{1}{2} \text{rate}_{CO} + 2 \text{rate}_{CH_4} + \frac{1}{2} \text{rate}_{H_2} \quad (2.9)$$

By integrating the rate of carbon consumption as a function of time, the total carbon conversion can be obtained. This value agrees, within 10%, with carbon conversions determined by weight loss measurements.

2.2 Morphology Studies

2.2.1 Controlled Atmosphere Electron Microscopy

Electron microscopy studies have proven to be very useful in determining topographical properties of catalytic systems. A major application of this technique has been to determine particle size distribution, and dispersion of supported metals on oxides. These studies, however, have been carried out in high vacuum environments, by analysis of samples before and after reaction.

Table 2.2: Solubilities of gas products in H_2O . Taken from [1]

Gas	Solubility at 298 K (gr gas/100 gr H_2O)
H_2	1.535×10^{-4}
CO	2.603×10^{-3}
CH_4	2.091×10^{-3}
CO_2	1.449×10^{-2}

In the sixties, Hashimoto *et al.* [2] developed an environmental cell, located inside an electron microscope, that allowed to follow morphological changes in samples, as a function of a controlled gas environment, and temperature. Baker *et al.* [3] have successfully used this technique to study the gasification of graphite by steam, O_2 and H_2 , catalyzed by a large variety of materials. These studies have provided both qualitative and quantitative information on the mobility, dispersion, and gas mode of attack favored by these catalysts.

The morphology study presented in chapter 4 was carried out in collaboration with Dr. R. T. K. Baker. An exhaustive explanation of the system is therefore not necessary, since there are several publications in the literature dedicated to this purpose [4,3]. It is felt, however, that a brief description of the apparatus and sample preparation procedures are in order.

2.2.2 Apparatus

The system is a conventional electron microscope (JEOL JEM 7A), shown in figure 2.3, that has been modified, to incorporate a gas reaction cell with heating capabilities (JEOL JEM AGI), shown in figure 2.4. Figure 2.5 presents a schematic representation of the system. The environmental cell is introduced in the specimen chamber (area enclosed by broken lines in figure 2.5). Inside the cell, the sample can be heated up to 1600 K, in the presence of up to 400 Torr pressure of gas. To prevent gas leakage from the cell to the optical stages of the microscope, the specimen chamber is evacuated with a diffusion pump, independent of the normal pumping system of the microscope. An electron beam is passed through the sample, under reaction conditions, and focused into a viewing screen (C). A 2 cm diameter hole in the screen allows a fraction of the electrons to hit a secondary screen (D), which is part of a Phillips Plumbicon TV camera (F). The output of the camera can be monitored and recorded continuously on videotape. An auxiliary shutter (E) can be put on top of the screen (D), and used as a conventional photography plate.

A schematic representation of the gas cell, and holder in the specimen chamber of the microscope, is given in figure 2.6. The holder (A) is permanently fixed to the specimen translational mechanism of the microscope, and the cell (B) can be inserted or removed, as desired. Reactant gas is introduced into the cell, and the gas flow is indicated by arrows. The electron beam hits the sample, located at point C, and it is focused on a phosphorous screen, as previously described.

Figure 2.7 shows the specimen-holder arrangement. It consists of a 2 cm flat mica ring, across which are attached a Pt ribbon and a Pt/Pt-(13%)Rh thermocouple. The Pt ribbon is coated with a SiO_2 film, to prevent possible diffusion of

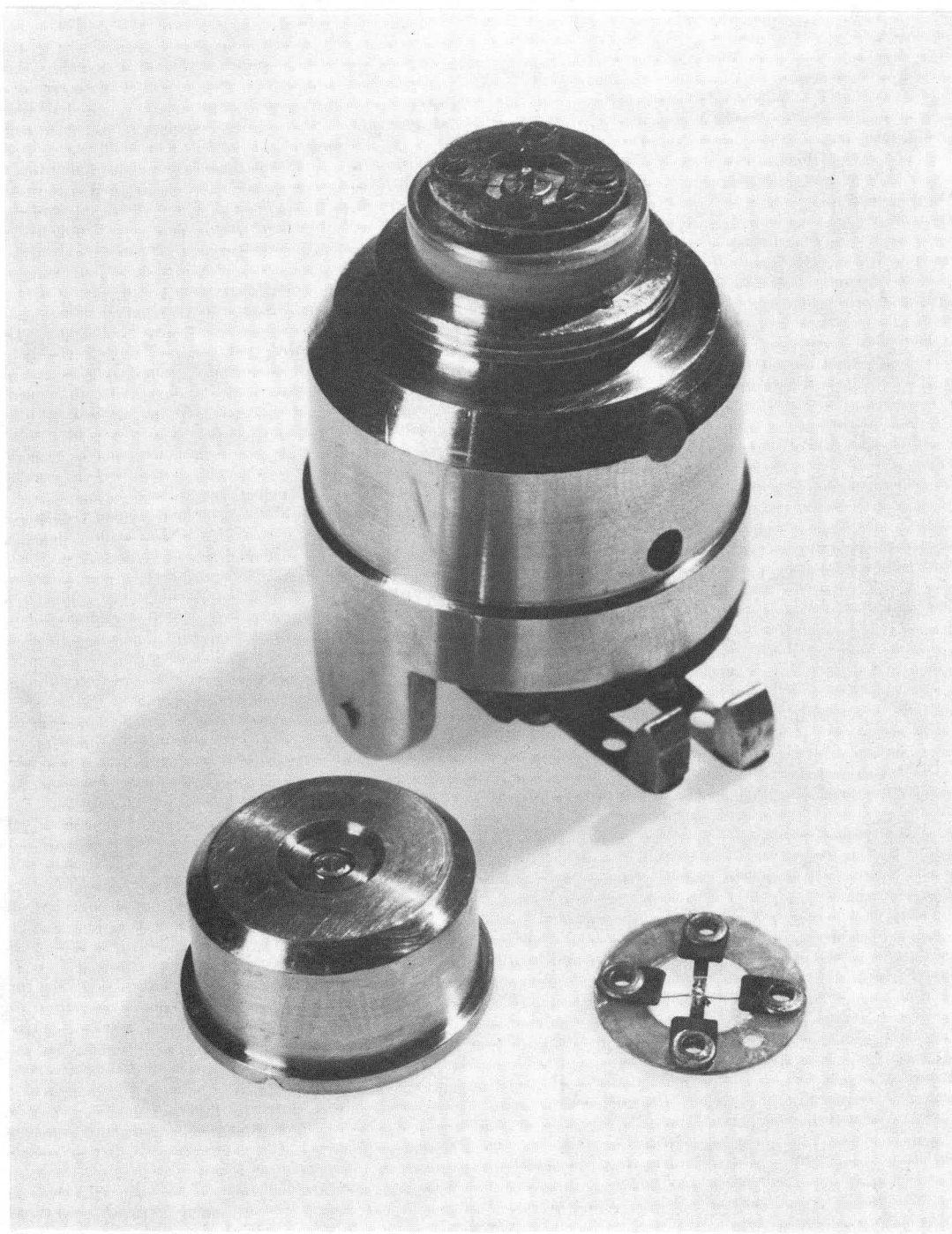


Figure 2.4: Photograph of the environmental cell used inside the controlled atmosphere electron microscope shown in figure 2.3. The sample holder, shown in the lower right is 2cm in diameter.

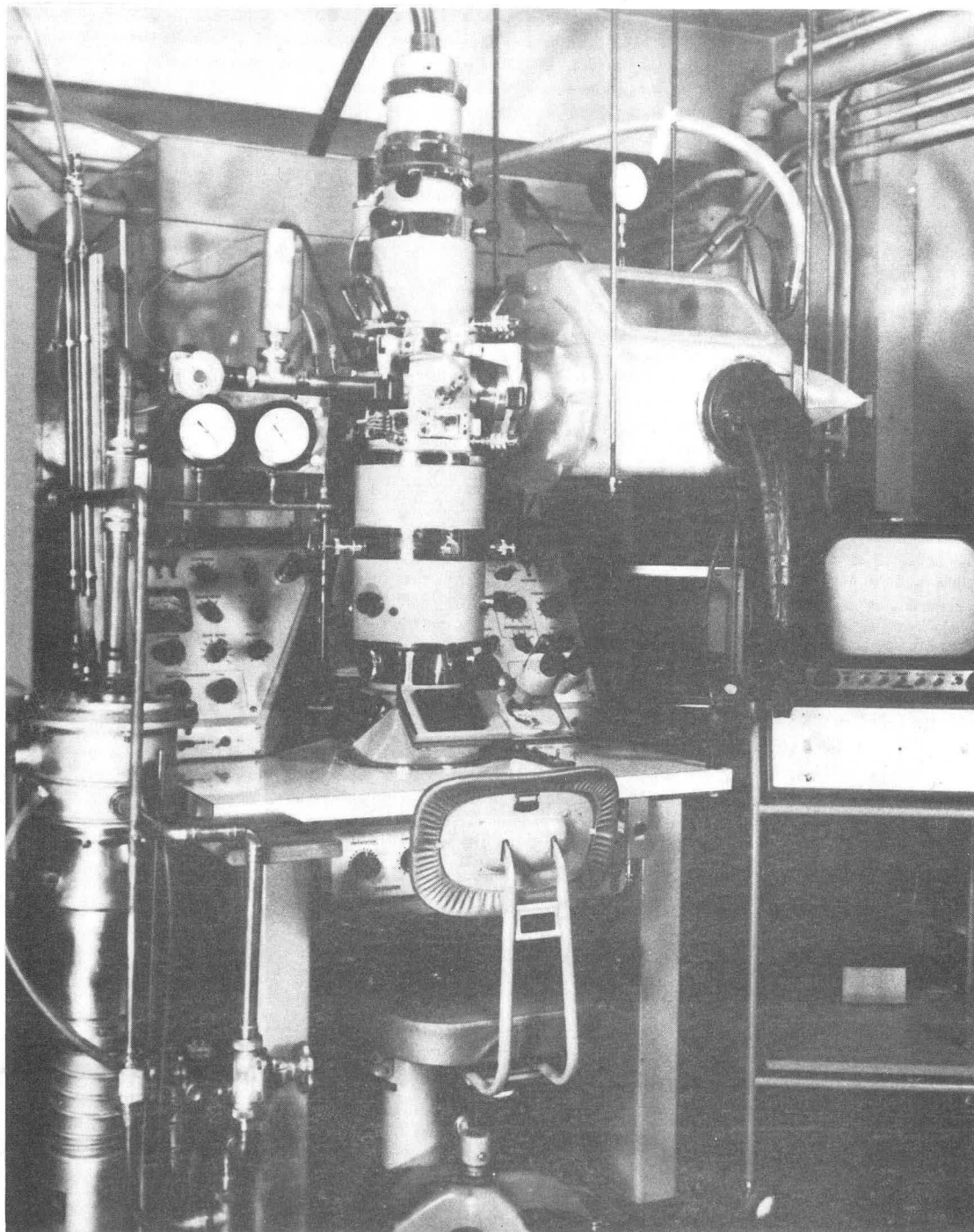


Figure 2.3: Photograph of the electron microscope used to perform the morphology study presented in chapter 4.

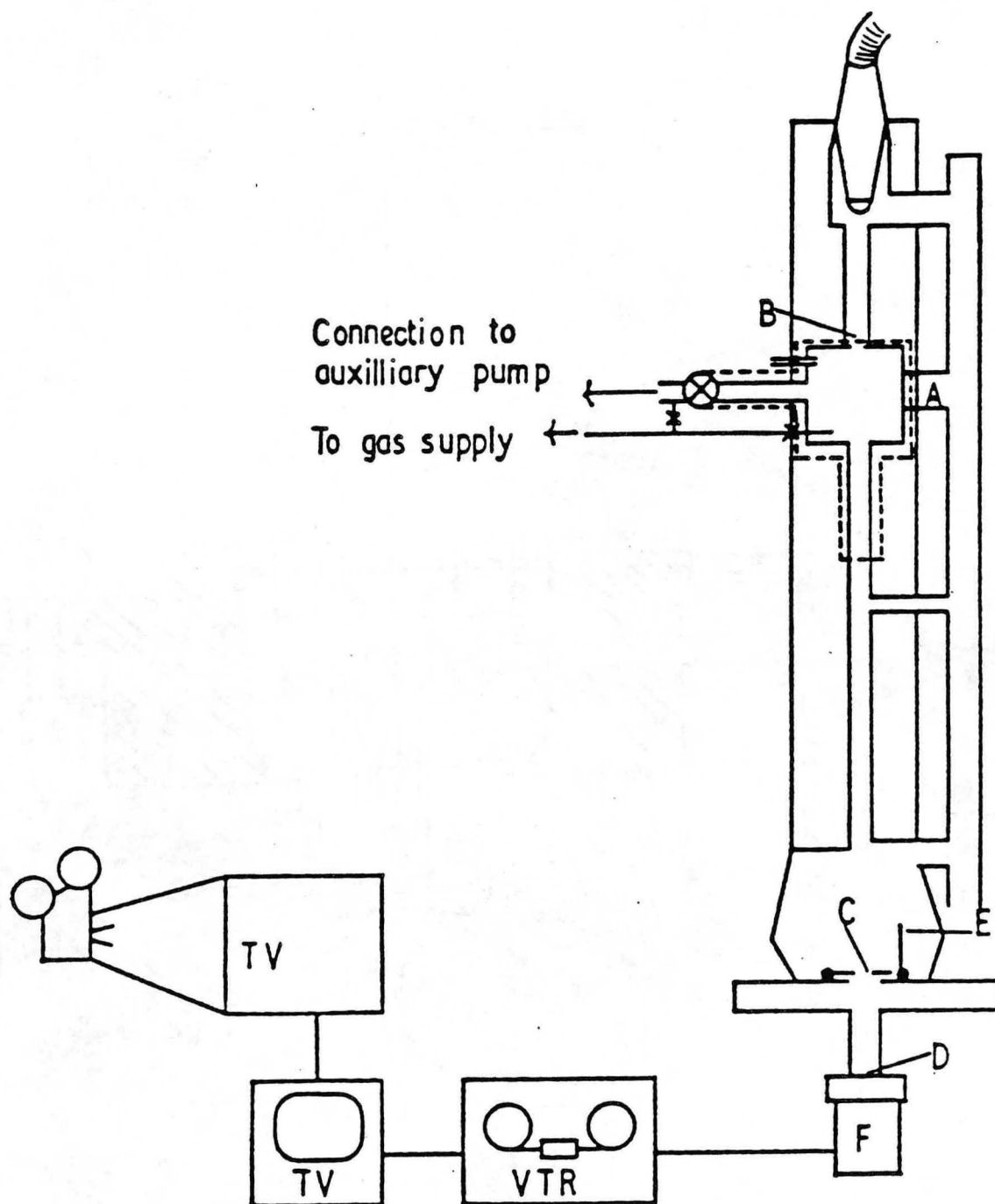


Figure 2.5: Schematic representation of the microscope shown in figure 2.3.

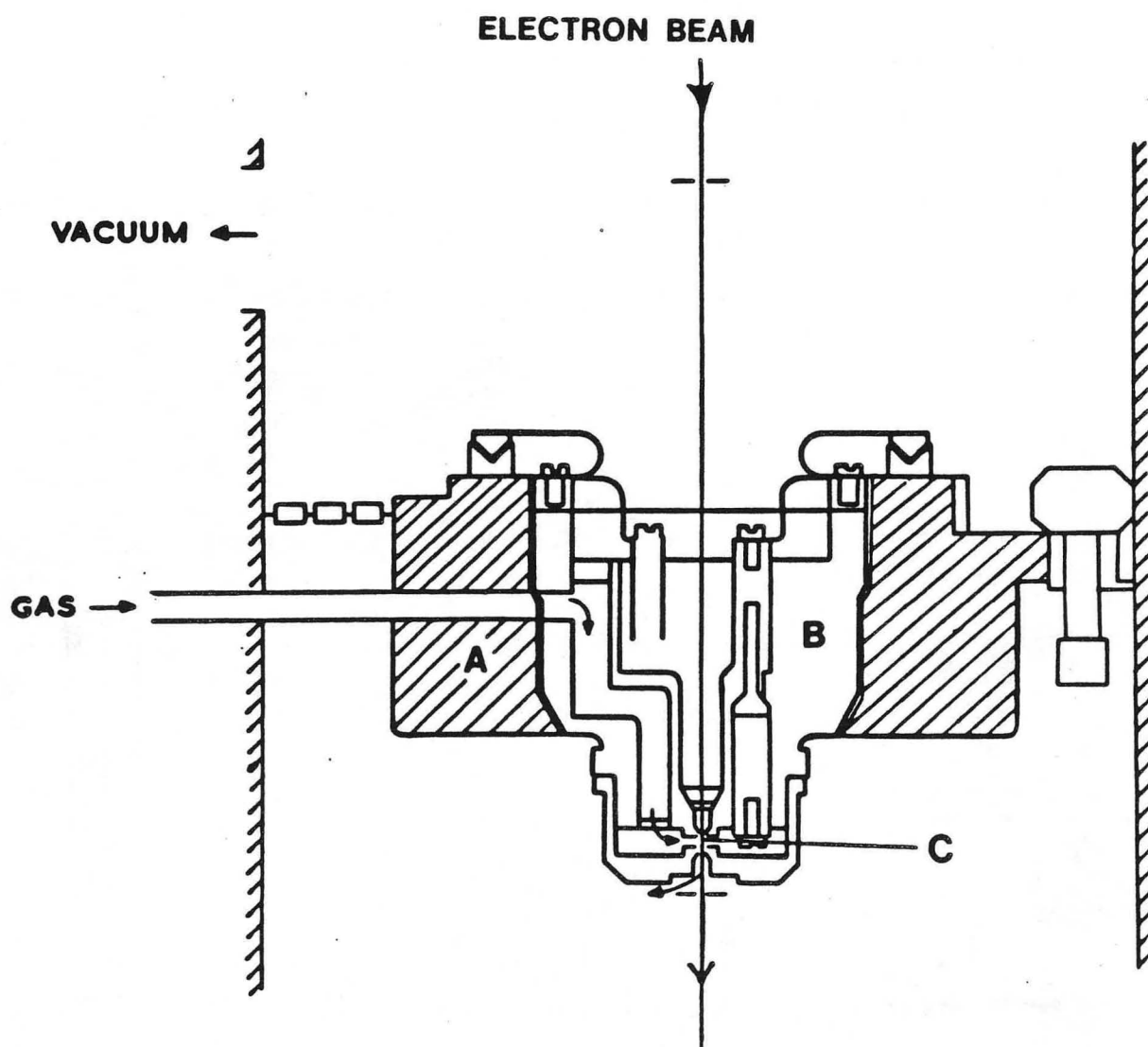


Figure 2.6: Schematic diagram showing the environmental cell and stage.

extraneous metals onto the graphite specimen, during reaction. The thermocouple is spot-welded very close to a 0.3 mm diameter hole, where the specimen is placed. The specimen can be heated up to 1600 K, by passing current through the Pt ribbon.

The instrumental resolution of the apparatus in vacuum is 0.4 nm. Because of the environmental cell, and the resolution of the TV camera, however, the resolution under experimental conditions was limited to approximately 2.5 nm.

2.2.3 Sample Preparation

The carbon substrate used in this study is a natural single crystal graphite, obtained from a mine near Ticonderoga (NY). The crystals are separated from the pyroxene mineral in which they were embedded, by heating in HCl and HF, and by flotation. They were first cleaved between glass slides coated with "Durofix" polystyrene cement, and then released and washed with acetone. The crystals were mounted on glass slides with aqueous polyvinylpyrrolidone (PVP) adhesive. The PVP was allowed to dry, and the catalyst further cleaved with scotch tape. Successive layers were removed, until an optically transparent portion of the crystal was obtained. The cleaved crystals were released from the slides onto a clean H₂O surface, and picked up on a sapphire hot plate. They were then heated in vacuum at 1200 K for 20 min, after which they were floated in H₂O, picked up on the specimen microscope holder, and dried.

Both nickel and potassium were loaded on the graphite sample, after being mounted on the holder by atomized sprays of 0.1 wt% solutions of KOH and Ni(NO₃)₂. The samples were then dried in air for 15 min, mounted in the environmental cell, loaded in the microscope, and heat treated in Ar at 723 K for 30 min.

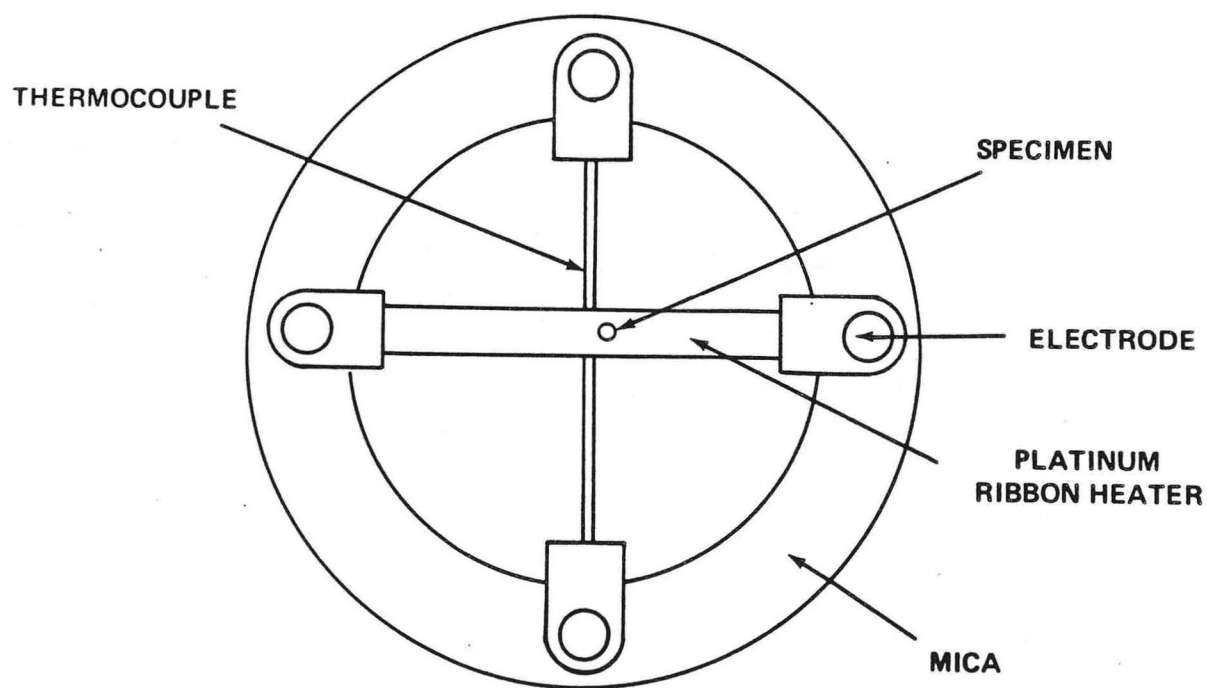


Figure 2.7: Specimen-holder arrangement for the electron microscope.

After this treatment, the sample is observed with the microscope, to check if good particle nucleation has been achieved.

After the pretreatment in Ar, the environmental cell is evacuated, and 2 Torr of either Ar, H₂, or O₂ saturated with H₂O (40:1 gas to H₂O) are introduced in the cell at 723 K. At this point, two people are required, in order to operate the microscope. The first person controls the sample temperature, and decides, by watching at the video, the information to be collected. The second person maintains the sample in focus, and controls the translation mechanism of the microscope, to search for areas of interest in the sample. In a typical experiment, the sample is ramped from 750 to 1400 K, with 10 K steps. At each temperature, more than one area in the carbon substrate is scanned, for a time period long enough to visually appreciate its consumption due to reaction with the gas. Special attention is also taken to record information about the mobility and dispersion of the catalyst .

Selected sections of the video record are transferred onto 16 mm cinematography film. Quantitative analysis is carried out by measuring frame by frame the position of the catalyst and carbon edge, with respect to a fixed reference point in the picture. These references points were usually twin bands in the graphite, which are also useful to determine the direction of gas attack, since they are always present in the (10 $\bar{1}$ 0) direction.

2.3 Surface Analysis Studies

2.3.1 X-ray Photoelectron Spectroscopy

In recent years, X-ray photoelectron spectroscopy has become a very common technique for surface analysis of a variety of systems. Its principle is based on the creation of a free electron and an ionized atom, by the interaction of a soft X-ray

photon with the electronic core level of an atom (See figure 2.8).

From energy conservation principles, the kinetic energy of the free electron (E_k) is equal to the difference of the energy of the soft X-ray photon ($h\nu$) minus the energy of the ionized core level in the atom, also known as binding energy (E_b).

$$E_k = h\nu - E_b \quad (2.10)$$

The surface sensitivity of the technique arises from the mean free path of the photoelectrons. In figure 2.9, it is shown that for electrons of kinetic energy between 300 and 1200 eV, the typical range for XPS, the mean free path of electrons is between 5 and 20 Å, which indicates that the technique is sensitive to the composition of the 3 to 10 topmost layers.

With the aid of an electron energy analyzer, the kinetic energy and flux of the generated electrons can be determined. The kinetic energy is associated with a particular core level in a given element, and its flux is proportional to the number of excited atoms of this particular element. Therefore, from an XPS spectrum, information regarding the identity and concentration of the elements present on the surface can be obtained.

By analytical standards, however, the sensitivity of this technique is not excellent. For a typical analyzer and X-ray source, a surface concentration between 1 and 10% is sometimes required to obtain an XPS spectrum in a reasonable time frame (2 hours).

Beside being used as an analytical technique, XPS also provides information about the chemical environment of the surface atoms. One of the earliest observed, and most widely studied effects of XPS in solids is a shift in the binding energy of the detected electrons, due to factors like formal oxidation state, molecular

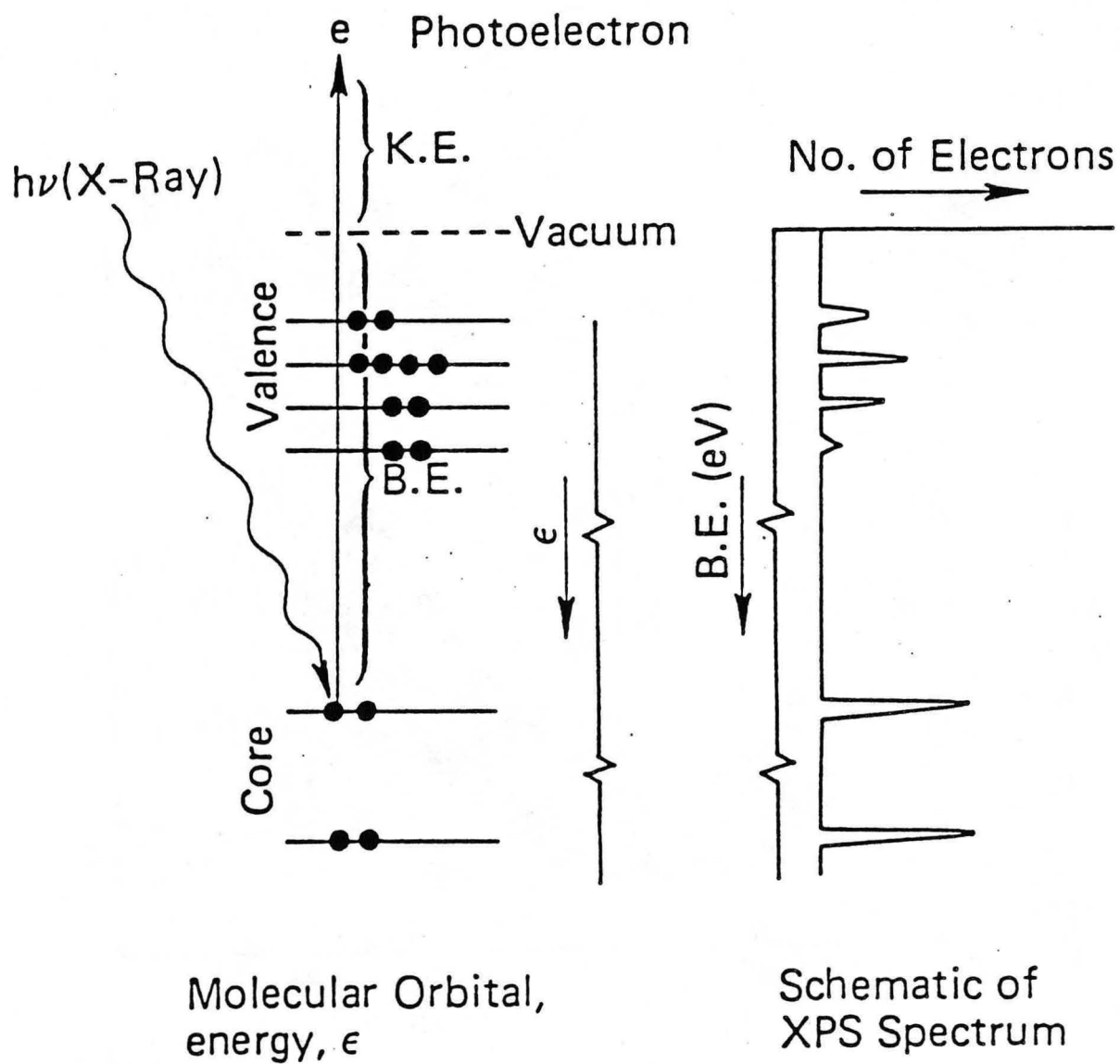


Figure 2.8: Scheme of the photoemission process.

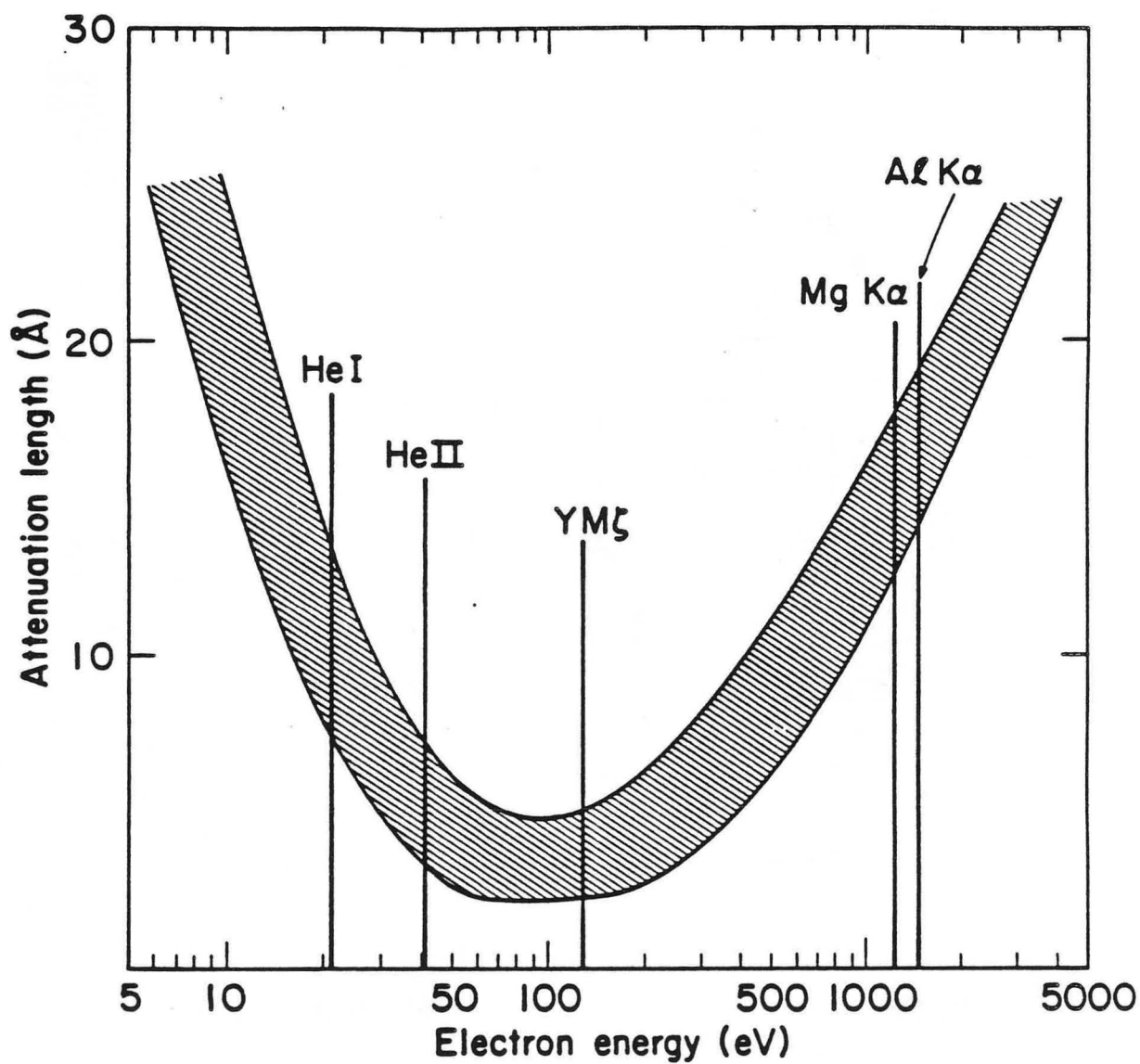


Figure 2.9: Universal curve for condensed phases, showing the dependence of the inelastic-electron mean free path (attenuation length) as a function of kinetic energy.

environment, or lattice site [5]. This shift is also known as the "chemical shift", by analogy with NMR. Figure 2.10 shows the Ni $2p_{3/2}$ -XPS signal of Ni metal and NiO. Notice that the binding energy of the most intense peak in the NiO is 2.1 eV higher than that of Ni metal. This shift is attribute to an increase in the binding energy of all the electronic levels in the oxide, due to the higher effective charge in the electronic part of the potential. For nickel compounds, these shifts in binding energy have also been correlated with changes in ligand electronegativities, delocalization of charge on the ligand, and stereochemistry [6].

Another clear difference in the XPS spectra of Ni metal and NiO is the presence of a second peak in the oxide spectrum. There are rigorous explanations for the existence and intensity of these peaks [7], but they are beyond the scope of this section. Qualitatively, they are associated with final state configurations in the ionized atom, where beside the emission of the primary core level electron, a valance electron is promoted to an unoccupied level. The energy involved in this transition, of course, is not available for the primary XPS electron. Therefore, these electrons are detected at lower kinetic energies (*i. e.* higher binding energies) than the electrons associated with the process described in figure 2.8.

The higher intensity of the high binding energy peak in NiO, compared to Ni metal, is due to the selection rules controlling the process. The promotion of the second electron can be thought as an internal rearrangement in the configuration of the final state, without any new source of momentum. Therefore, the total, angular, and spin momenta of the final state cannot vary with this rearrangement. In the case of Ni metal, which is diamagnetic, these rearrangements are prohibited, because all the valance electrons are paired, whereas in the case of NiO, which is paramagnetic, they are allowed. A similar case is observed for nickel(II) complexes.

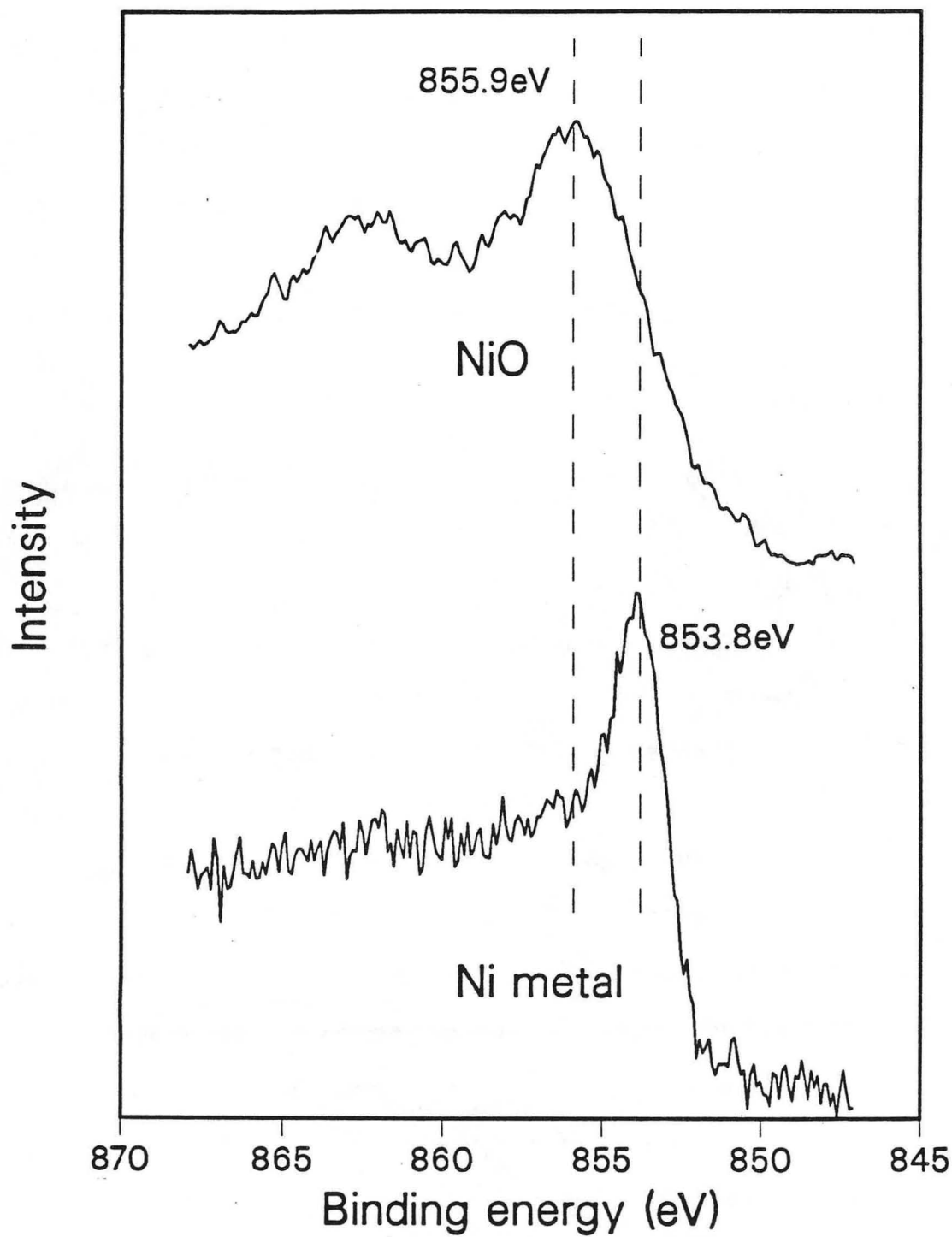


Figure 2.10: XPS of the Ni 2p_{3/2} signal for Ni metal and NiO, collected at a 40 eV analyzer pass energy.

Tetrahedral nickel(II) (high spin and paramagnetic) gives satellites, while planar square nickel(II) (low spin and diamagnetic) does not [6].

A third important feature of an XPS signal is the asymmetry of the peak. Both the Ni metal, and NiO spectra show a tail at high binding energies, due to photoelectrons inelastically scattered. The intensity of this background level has been associated, by several authors, with the particle size of metal supported catalysts [8,9].

2.3.2 Apparatus

The apparatus used for the XPS study presented in chapters 5 and 7 is shown in figures 2.11 and 2.12. It consists of a stainless steel bell-jar, evacuated to pressures below 5×10^{-9} Torr by a Varian VHS6 diffusion pump, backed by a rotary pump.

X-rays of 1253.6 eV energy and 0.7 eV FWHM, are directed toward the sample, at a glancing angle. They are generated by an X-ray gun, equipped with a Mg anode (Physical-electronics, model 04-151). The emitted photoelectrons are detected by a cylindrical mirror analyzer (CMA), located 90 degrees with respect to the X-ray source (Physical-electronics, model 15-2556).

The diagram of a CMA is shown in figure 2.13. By changing the potential at the outer and inner cylinder of the analyzer, electrons of different energy can be focused, first into a small aperture in the initial stage of the analyzer, and then into a channeltron (Detector Technology, model 309), which for each electron detected, generates a pulse of 1 ns width and 2 to 20 mV height (measured with a 50Ω resistance). These signals are sent to a pulse discriminator, which generates a 3.5V high-500 ns wide signal (measured with a 50Ω resistance), for each pulse received above a set voltage threshold. These pulses are sent to the analog/digital

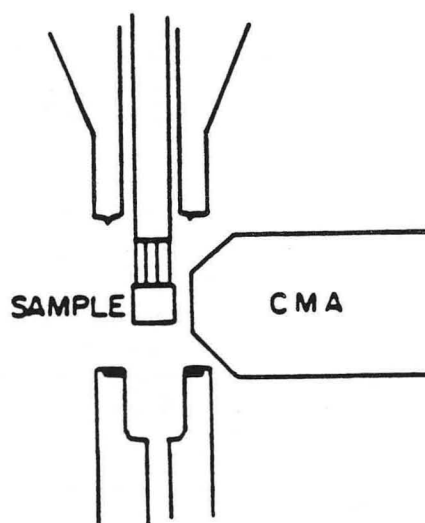
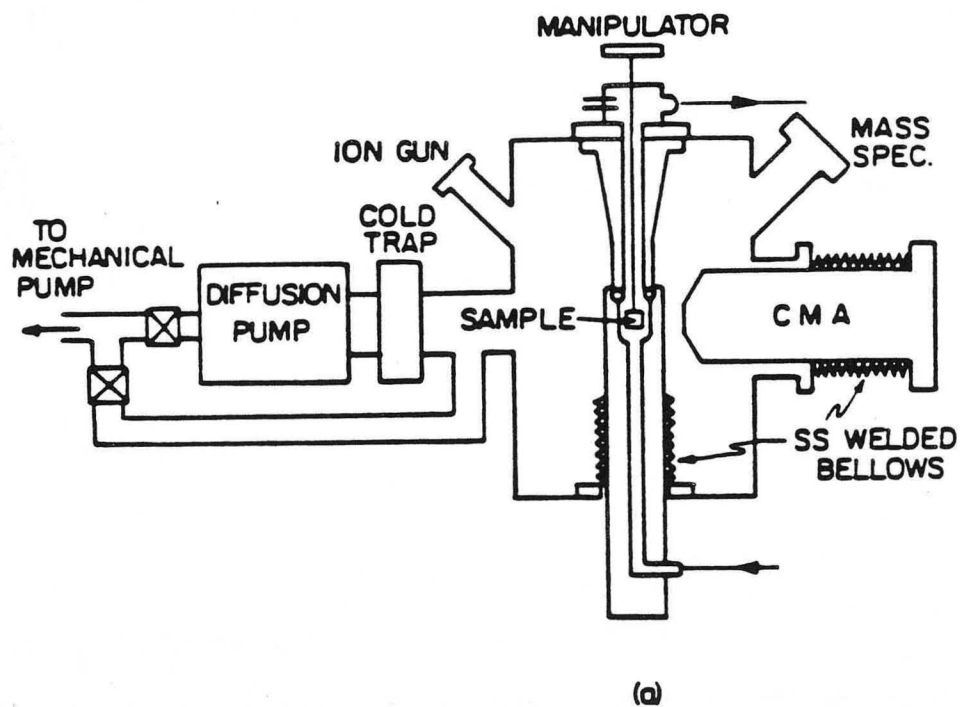


Figure 2.11: Schematic of the ultra-high vacuum/high pressure apparatus used for surface analysis studies.

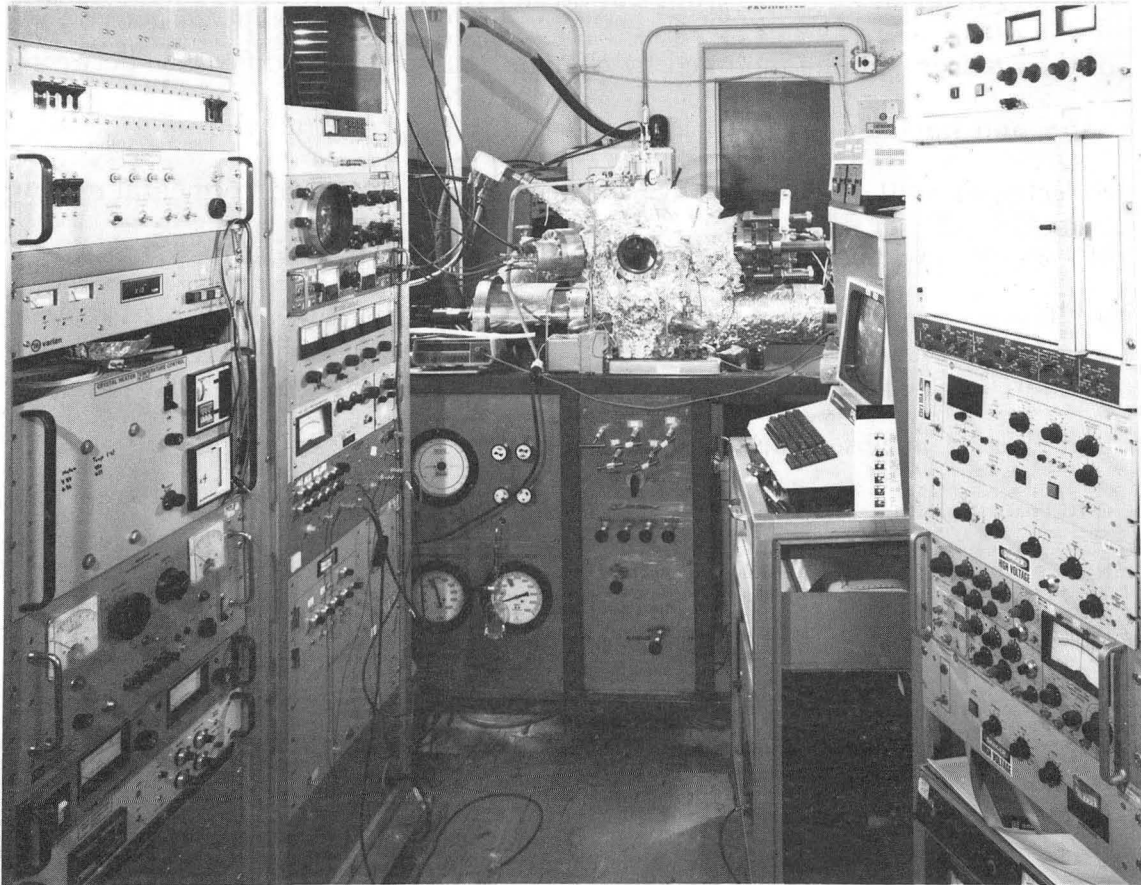


Figure 2.12: Photograph of the apparatus shown schematically in figure 2.11.

interface of a PET 4032 computer. The interface counts and stores the number of pulses received in a given time period, during which the analyzer is set at a particular energy. By repeating this procedure at various energy values, in a desired range, an XPS spectrum can be generated. The resolution and sensitivity of the analyzer can be modified by changing the potential difference between the outer and inner cylinders (pass energy). In this study, all the information was collected at a 40 eV pass energy. This corresponds to an instrumental resolution of 1.38 eV, as determined from the width of the Au 4f_{7/2} peak.

The sample holder is part of a high pressure cell, shown in figure 2.11. When it is open, the cell exposes the sample to ultra-high vacuum (UHV), for XPS analysis, and when it is closed, becomes part of a reactor, used for sample treatments. A diagram of the sample holder is shown in figure 2.14. It consists of a 50 μ m Au foil, spot-welded to 2 mm Au supports, through 0.5 mm Pt wires. The sample is pressed against a stainless steel Au coated mesh, and it is in intimate contact with a chromel-alumel thermocouple. The mesh is then held against the foil by two lateral flaps. By passing current through the foil, the sample can be heated to the desired temperature.

2.3.3 Experimental Procedure And Data Analysis

The sample used for the XPS study presented in chapter 5, is the same as those used for the catalytic study on steam gasification of graphite (chapter 3). Its characteristics, and preparation procedure are given in a previous section of this chapter.

The purpose of the XPS study in chapter 5 is to correlate catalytic properties of nickel and potassium, with changes in their surface concentration and oxidation

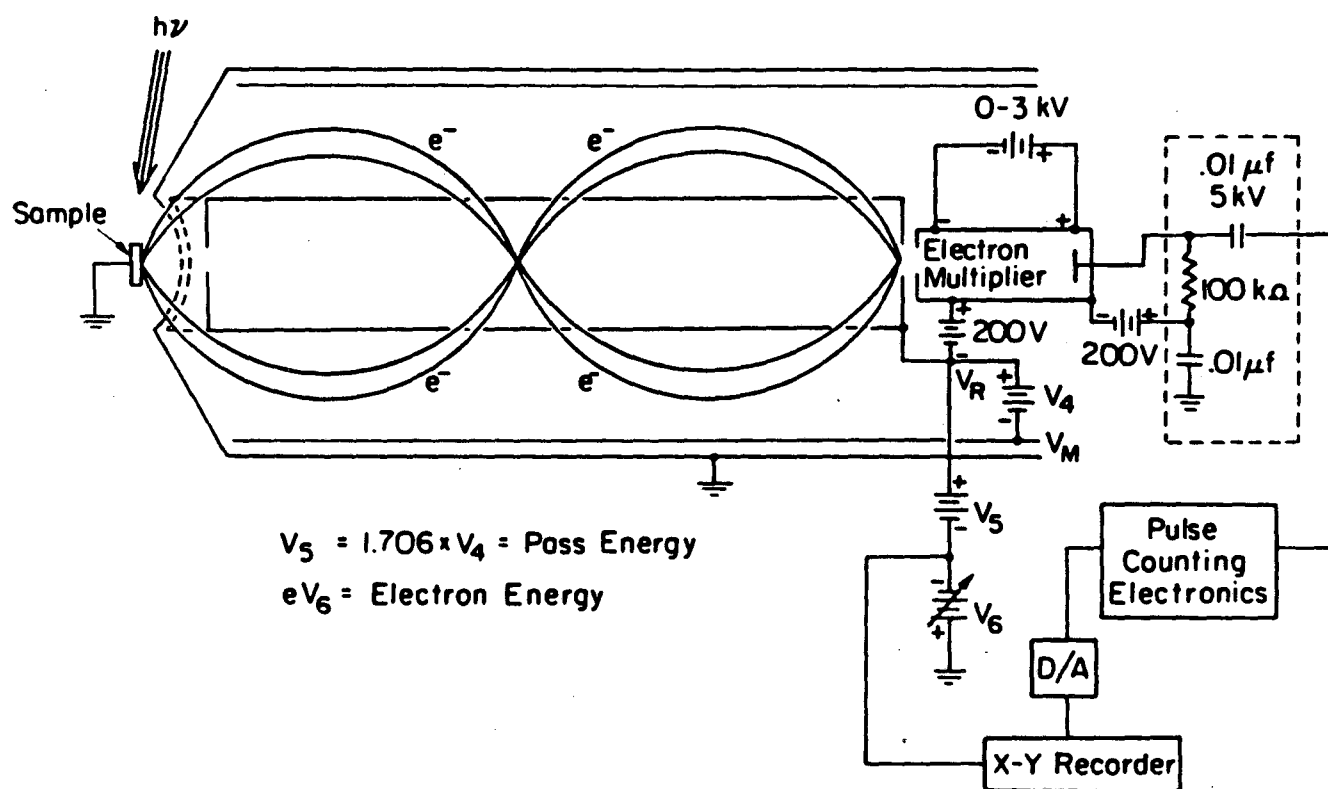


Figure 2.13: Schematic diagram of the double pass cylindrical mirror analyzer for X-ray photoelectron spectroscopy.

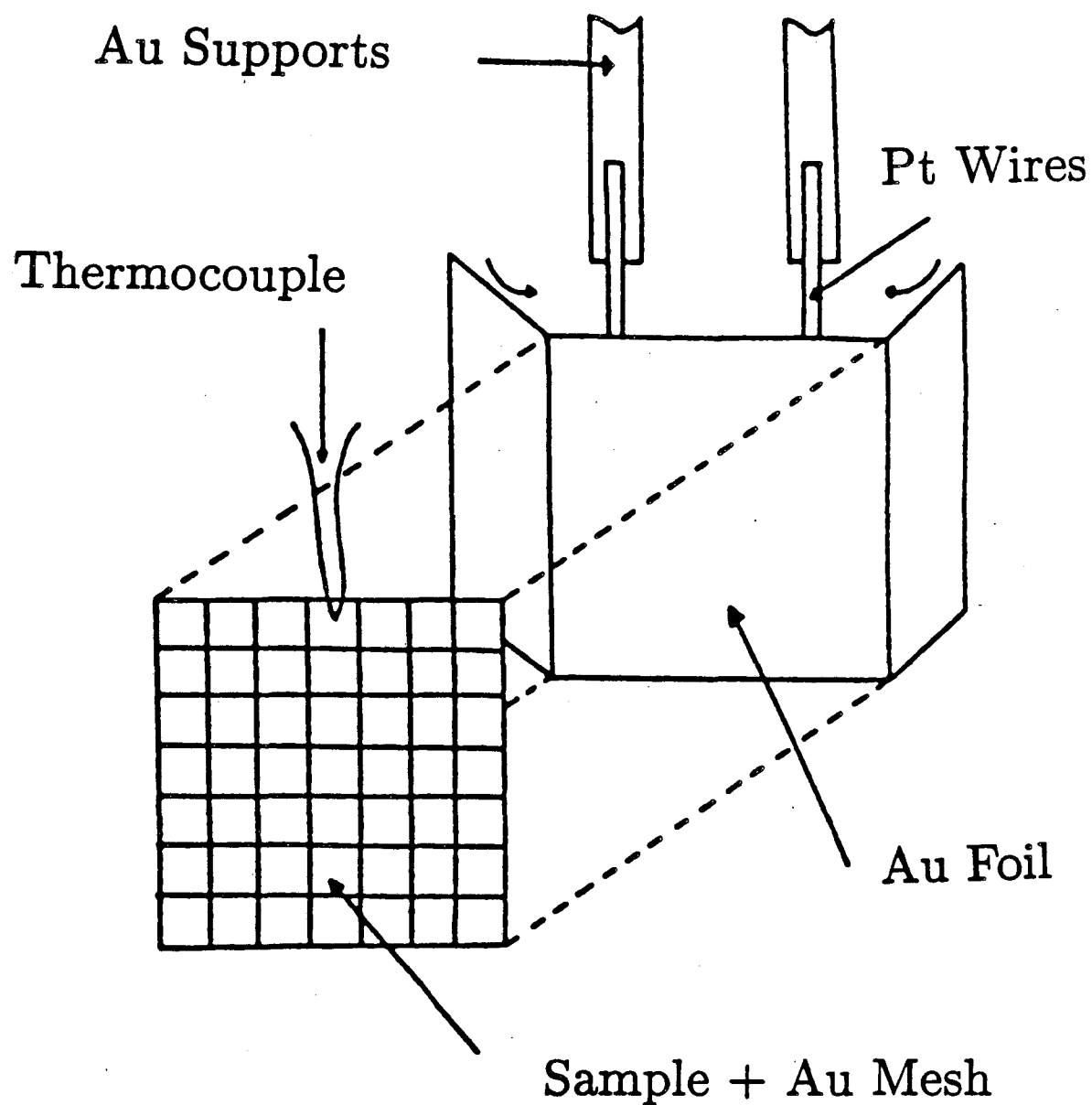


Figure 2.14: Representation of the sample holder used for surface analysis studies.

state. Therefore, the conditions for sample treatment in the XPS study were as similar as possible to those in the kinetic study.

Before exposing the sample to H_2O vapor, the sample was treated at 723 K for 15 min, in either vacuum or Ar, to decompose the $\text{Ni}(\text{NO}_3)_2$. This step is analogous to the heat treatment step in the kinetic study. The procedure for sample treatment in H_2O vapor is as follows. The sample is heated to 723 K in vacuum, before closing the high pressure cell. A continuous 10 Torr flow of H_2O vapor is introduced in the cell, while maintaining the sample at 723 K. The sample temperature is then raised to 893 K, and kept at this value for up to 135 min. After this treatment, the H_2O flow, and the current through the Au foil in the sample holder, are stopped at the same time. The H_2O pressure in the loop decreases from 10 to 0.1 Torr in less than 20 sec, and the temperature drops from 893 to 300 K in less than 40 sec.

There are two important points about this procedure. First, the H_2O vapor should not be circulated in the loop, because accumulation of reaction products from the gasification reaction (in particular H_2) and change the oxidation state of the catalyst, and give misleading results. A continuous flow of "fresh" H_2O vapor should be used instead. Second, it is important to stop the H_2O vapor flow and sample heating at the same time. If the sample is cooled in the presence of H_2O vapor, sample oxidation can occur, and if the sample is kept at 893 K in the absence of H_2O vapor, reduction of nickel by graphite can take place.

For the XPS data analysis, two standards were used to calibrate the positions of the peaks: the C 1s signal from graphite (284.3 eV), and the Au 4f_{7/2} peak (84.0 eV) from the Au support foil in the back of the sample. The calibration of one standard with respect to the other was always better than 0.3 eV accurate.

The XPS signal of both standards, and those of Ni 2p_{3/2}, O 1s, and K 2p, were collected after each experiment.

2.3.4 Temperature Programmed Desorption (TPD)

The temperature programmed desorption (TPD) study presented in chapter 7 was aimed at elucidating the type and stability of the various surface species formed after adsorption of O₂, CO₂, H₂, and H₂O on graphite.

Experimentally, the graphite surface is dosed with a known exposure of a gas, and then heated, under UHV conditions, with a constant heating rate. A mass spectrometer monitors the gas evolution of a given mass, and a plot of the signal intensity versus temperature is generated.

A typical TPD spectrum is shown in figure 2.15. In this case, ¹³CO₂ is adsorbed on a graphite (¹²C) surface, and the evolution of ¹²CO (mass 28 amu), ¹³CO (mass 29 amu), ¹²CO₂ (mass 44 amu), and ¹³CO₂ (mass 45 amu) are followed as a function of temperature. The peak position and intensity of the various peaks provides information about chemical interactions between the adsorbate, and the substrate. In addition, the activation energy for desorption of the species formed can be obtained from the different desorption temperatures observed.

There are various methods to determine the activation energy for desorption, from the peak maximum, and the width of a TPD signal [10,11,12]. The one chosen in this study has been formulated by Redhead [13]. He proposes that the rate of desorption per unit area is given by

$$-d\theta/dt = \nu_n \theta^n \exp(-E/RT) \quad (2.11)$$

where, n is the order of the desorption reaction,

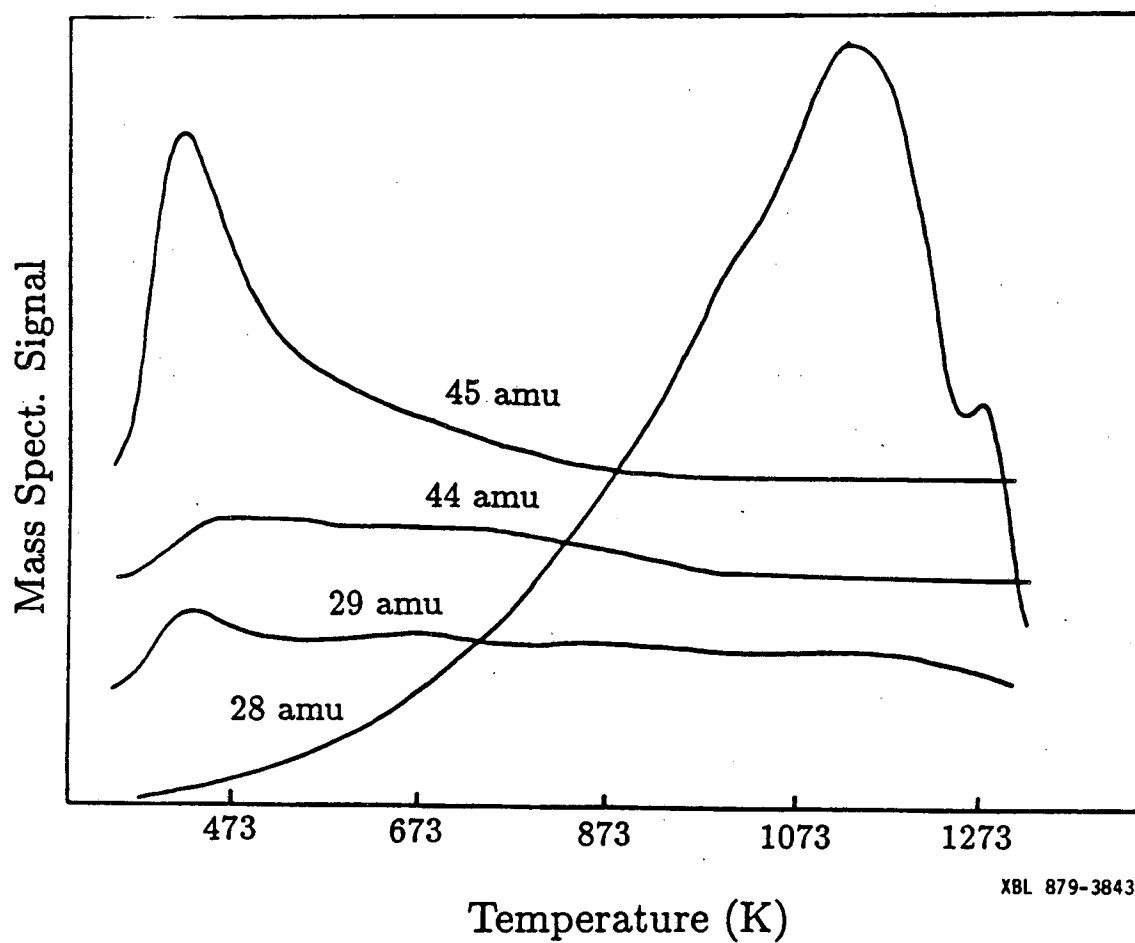


Figure 2.15: Example of a TPD spectrum. In this case, the desorption products after adsorption of $^{13}\text{CO}_2$ on graphite are shown.

θ is the surface coverage,

ν_n is the rate constant,

and E is the activation energy of desorption.

For a linear heating ramp, $T=T_o+\beta T$, and assuming that E is independent of coverage, equation (2.11) can be solved to find T_p , the temperature at which the desorption rate is maximum.

$$E/RT_p^2 = (\nu_1/\beta)\exp(-E/RT_p) \quad \text{for } n=1 \quad (2.12)$$

$$= \left(\frac{\theta_o \nu_2}{\beta}\right)\exp(-E/RT_p) \quad \text{for } n=2 \quad (2.13)$$

When the desorption process is of first order ($n=1$), E can be calculated from the measurement of T_p , provided a value of ν_1 is assumed.

2.3.5 Sample Preparation And Experimental Procedure

The adsorption of O_2 , H_2O , CO and CO_2 occurs only in the edge planes of graphite. In order to maximize the number of these sites in our samples, three kinds of finely dispersed polycrystalline graphite were used: two of them were commercial suspensions, one in isopropyl alcohol (Electrodag), and the other in H_2O (Aquadag). The third sample was composed of sintered mechanical graphite, finely ground, and dispersed in hexane.

None of the samples is expected to be of maximum purity, since all of them contain a small amount of binder. In most cases, however, the binder is organic, and very dilute. It is therefore likely to decompose at high temperatures.

All the gases used were of standard purity (99.99%), and provided by the Lawrence Berkeley Laboratory (LBL). The ^{13}C and ^{18}O compounds were 98% enriched, and were provided by Cambridge Isotope Laboratories.

The suspensions were deposited as thin films on a Ta foil. Ta was chosen for its high melting point (3269 K), low vapor pressure, good mechanical properties, and because it is coated with an inert passivating oxide layer. Blank TPD experiments were carried out on the Ta foil, without graphite, and no significant amount of CO or CO₂ adsorbed on the foil.

The carbon-coated Ta foil was mounted on a X-Y-Z- Θ manipulator, and heated resistively. A linear ramp in the whole temperature range (300–1400 K) is indispensable to obtain reproducible TPD results. In this case, a linear heating rate of 50 K/min was achieved by using a power supply, whose output is controlled by a sample-temperature feedback (LBL, model 7S3173). The temperature was measured with a chromel-alumel thermocouple in intimate contact with the Ta foil. The experiments were performed in a stainless steel UHV chamber, similar to the one described in the XPS section. A base pressure of 5×10^{-10} Torr was obtained after bakeout. Repeated adsorption-desorption cycles, however, led to working base pressures of 2×10^{-9} Torr. An UTI 100C mass spectrometer was used for gas analysis. A coaxial high pressure reactor was incorporated into the chamber, so that the sample could be exposed to high pressures (up to 1 atm) of H₂O, CO and CO₂. It was found indispensable to bake out the loop for a least one hour before any gas introduction, to avoid contamination by residual H₂O and O₂.

In chapter 7, TPD spectra after graphite wetting by H₂O are presented. The sample was prepared as follows. It is first degassed under UHV, brought to air, wet first with ethanol, and then with H₂O, dried with a heat gun, and brought back into the the UHV chamber, via the high pressure cell. The wetting of the clean sample directly with H₂O could not be achieved, because of its high hydrophobicity. No significant ethanol adsorption occurs when the sample is only wetted with ethanol,

and then dried, as checked by XPS.

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Chapter 3

Kinetic Study Of The Steam Gasification Of Graphite Catalyzed By A Nickel-Potassium Mixture

3.1 Introduction

As described in the introductory chapter, even though thermodynamic considerations suggest that the gasification of graphite with steam is feasible at temperatures as low as 300 K, the reaction is kinetically controlled, and the presence of a catalyst is necessary to carry out this process below 1000 K.

The catalytic properties of alkali metals and transition metals for steam gasification of carbon solids have been extensively studied when they are loaded by themselves [1,2]. There is little information, however, on the properties of catalysts derived from their mixture. The goal of this chapter is to demonstrate that these mixtures exhibit distinct catalytic properties when compared with the components used alone, due to a strong interaction between the alkali and the transition metal.

Graphite has been chosen as the carbon source for this study. Its use as a model substrate for gasification reactions is generally considered as a valid ap-

proach [2]. In addition, graphite has various advantages for fundamental studies, when compared with other carbon substrates, such as activated carbons, chars or cokes. First, since graphite does not contain appreciable amounts of hydrogen and oxygen, the gas products come certainly from the reaction between graphite and steam. Second, the interaction between the catalyst and carbon can be studied without interference of other components in the solid, such as mineral, nitrogen and sulfur compounds, which are usually present in chars and cokes. Third, graphite has no microporosity, therefore the kinetic study is not complicated by factors like changes in surface area, and mass transport limitations.

3.2 Results

The catalytic activities for steam gasification of graphite of nine different potassium-transition metal mixtures have been evaluated. Figure 3.1 shows the rates of carbon consumption at 1000 K and activation energies of all the cases studied. Even though all of them show catalytic properties, the activity varies from system to system, the nickel-potassium and iron-potassium mixtures being the most active.

The rate of steam gasification of graphite also varies with the alkali or alkaline earth combined with nickel. Figure 3.2 shows that the mixtures of sodium and potassium salts with nickel were more active and showed lower activation energy than analogous mixtures with calcium and magnesium. For the potassium-nickel system, the catalytic properties were the same, regardless if the salt used to load the potassium was KOH, K_2CO_3 or KNO_3 .

Since the nickel-potassium mixture showed the lowest activation energy, and therefore the highest activity at low temperatures (below 900 K), it was studied in greater detail. Our results indicate that the catalytic properties of the mixtures

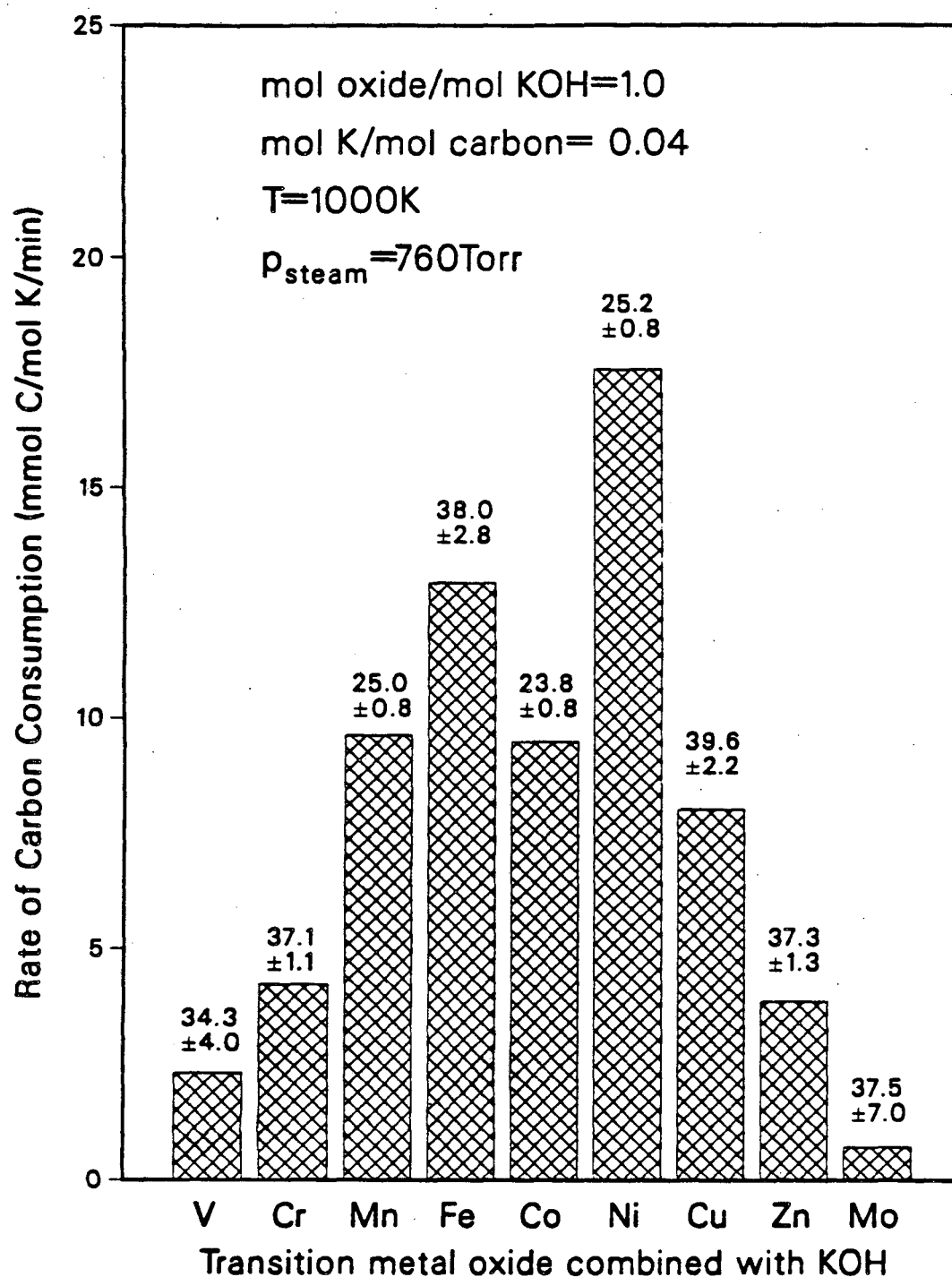


Figure 3.1: Rate of gas production at 900 K for the nine transition metal-potassium catalysts studied. The number above each bar is the activation energy in kcal/mol.

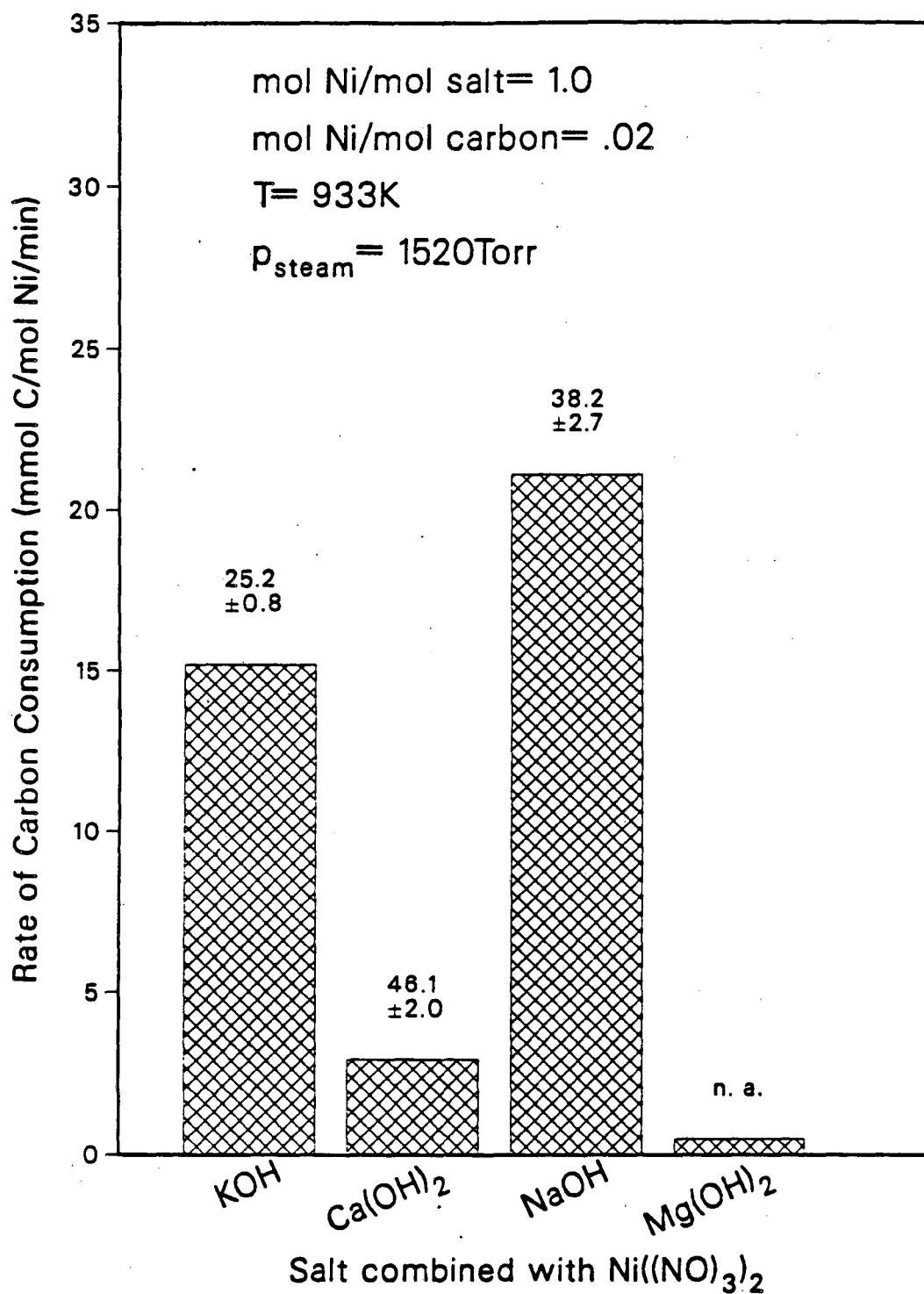


Figure 3.2: Rate of gas production at 1000 K obtained for the four mixtures of nickel and an alkali or alkaline earth hydroxide studied. the number above each bar is the activation energy is kcal/mol.

are due to a synergistic effect between the components. As shown in figure 3.3, the properties of the nickel-potassium mixture are different from those of nickel and potassium loaded by themselves. In this figure it is presented the dependence of the rate of gas production on temperature, for samples loaded with KOH, NiO and their mixture. In all cases the sample is heated in Ar at 723 K previous to the introduction of steam. This treatment is carried out to decompose the nickel salt and form the oxide. After this pretreatment the mixture has a higher activity than the components loaded alone. Curve A shows that for the mixture the rate of gas production increases steadily with time. No initial gas burst was observed, in contrast with the case of the catalyst derived from KOH alone (curve B). In this case, below 900 K the reaction stops after 0.5 (mol H₂/mol K) are produced, as also observed by Dellanay *et al.* [3]. When heating is continued above 900 K, a catalytic rate of gas production is observed, but with lower rates than in the case of the nickel-potassium mixture. Curve C shows that the rate of gas production was very low in the case of NiO.

The activation energies reported in figure 3.1 were calculated from the rates of gas production obtained in temperature programmed experiments. Arrhenius type plots for the nickel-potassium mixture and KOH alone are presented in figure 3.4. This figure shows that when the reaction is catalyzed by the mixture, the rates are higher and the activation energy lower (25 ± 0.8 kcal/mol) than when it is catalyzed by KOH alone (40.7 ± 1.3 kcal/mol). This figure also includes results obtained when the reaction is promoted by the catalyst derived from Ni(NO₃)₂ alone after reduction in H₂ at 723 K (labelled as Ni metal). These results will be described in detail later in this section.

For the nickel-potassium mixture, isothermal experiments at 893 K (figure 3.5)

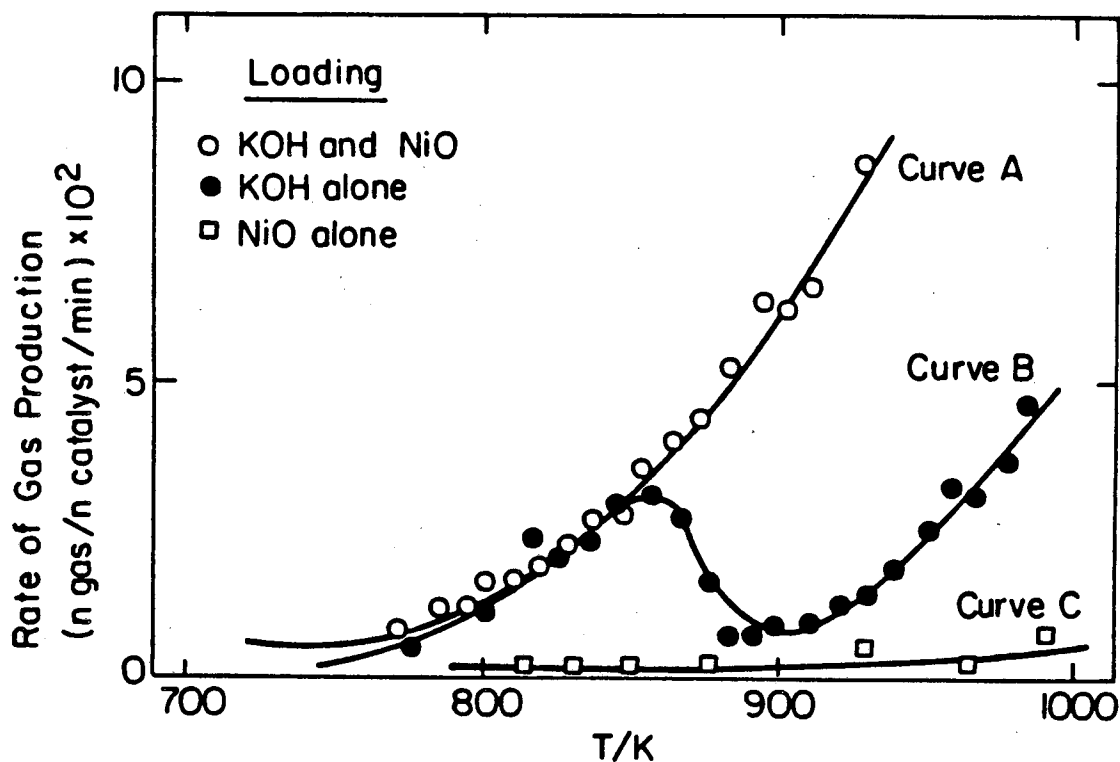


Figure 3.3: Plot of the temperature dependence of the gas production rate during a temperature programmed experiment at a heating rate of 5 K/min. The open circles (curve A) correspond to NiO and KOH codeposited on graphite, the black dots (curve B) to KOH deposited alone, and the open squares (curve C) to NiO deposited alone. In curves A and B the K/C molar ratio is 0.04. In curves A and C the Ni/C molar ratio is 0.04.

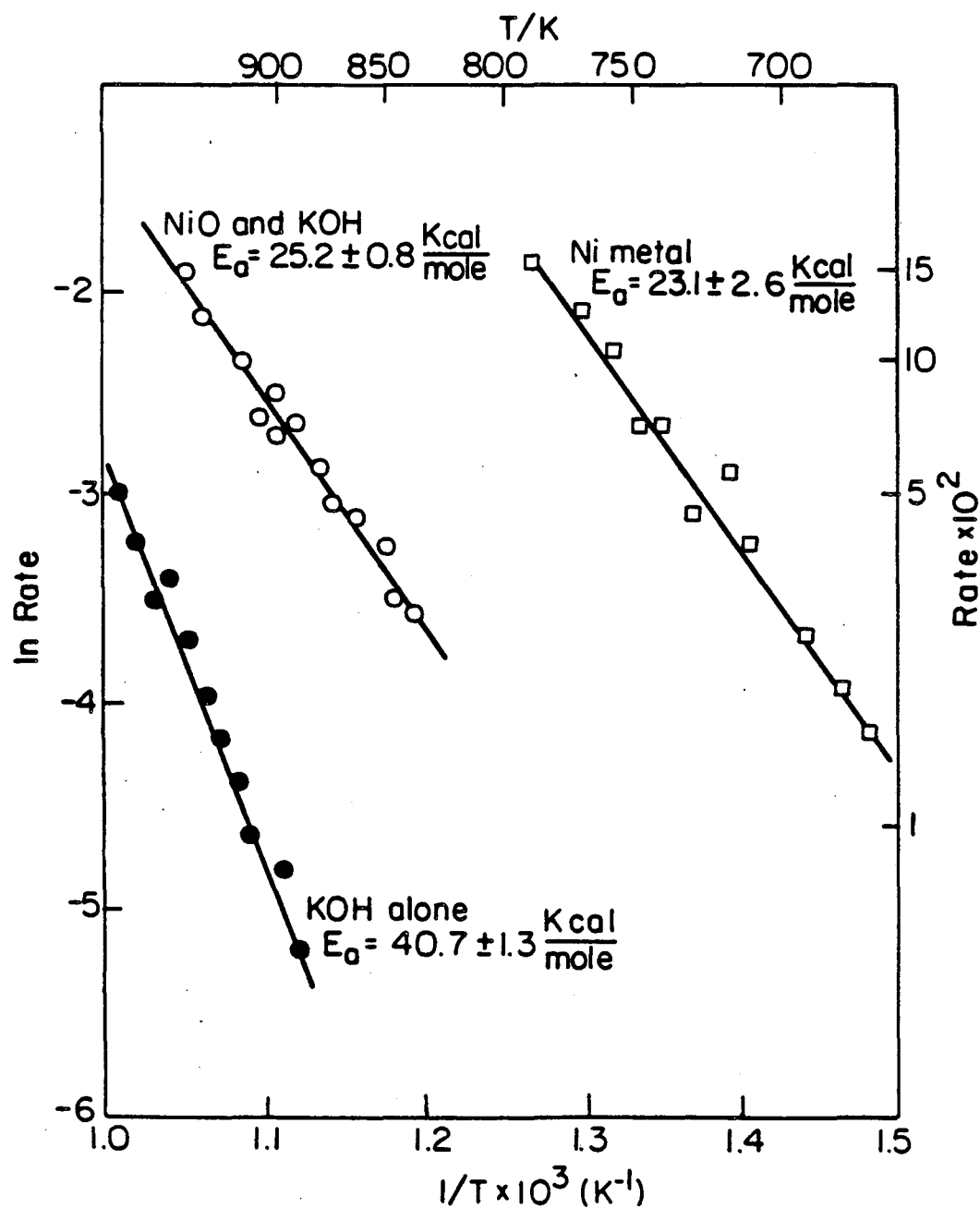


Figure 3.4: Arrhenius plots of the temperature dependence of the catalyzed gas production by the calcined nickel-potassium mixture (open circles), KOH alone (black dots) and Ni metal (open circles).

indicate that the catalytic activity and product distribution for steam gasification of graphite do not vary significantly with time. Figure 3.5 also shows that H_2 and CO_2 are the main reaction products. A small rate of CO production is also determined ($p_{CO}/p_{CO_2} \sim 4 \times 10^{-3}$), and the amount of CH_4 collected is within the detection limits of the apparatus. (less than 0.1% in the products).

The dependence of the rate on the catalyst loading, and on the ratio of nickel to potassium have also been determined. Figure 3.6 shows that, at a constant Ni/K molar ratio equal to 1.0, the rate of carbon consumption is proportional to the catalyst loading, up to a value of Ni/C molar ratio of 2×10^{-2} , with a slight decrease at higher loadings. Figure 3.7 shows a large scatter in the results collected to determine the dependence of the rate on the ratio of nickel to potassium. This is probably due to the low nickel loading chosen for these experiments ($\text{mol Ni/mol C} = 5 \times 10^{-3}$). Such a low loading, however, was necessary to ensure that the experiments were performed in a region where the rate depended on the catalyst concentration. Despite the scatter, there seems to be a maximum in the rate of carbon consumption at potassium fractions in the catalyst between 0.2 and 0.5, corresponding to K/Ni molar ratios between 0.2 and 1.0.

When the reaction is catalyzed by the nickel-potassium mixture no clear dependence of the gas production rate with steam pressure is observed in the ranged studied (760 to 4000 Torr), as shown in figure 3.8.

Even though the catalyst derived from $Ni(NO_3)_2$ alone is inactive for steam gasification of graphite when it is pretreated in Ar, a very high catalytic activity is observed when the pretreatment is carried out in H_2 . Figure 3.4 shows that this catalyst (Ni metal) has a much higher initial activity than the nickel-potassium mixture after Ar pretreatment. This is also observed by comparing the initial rates

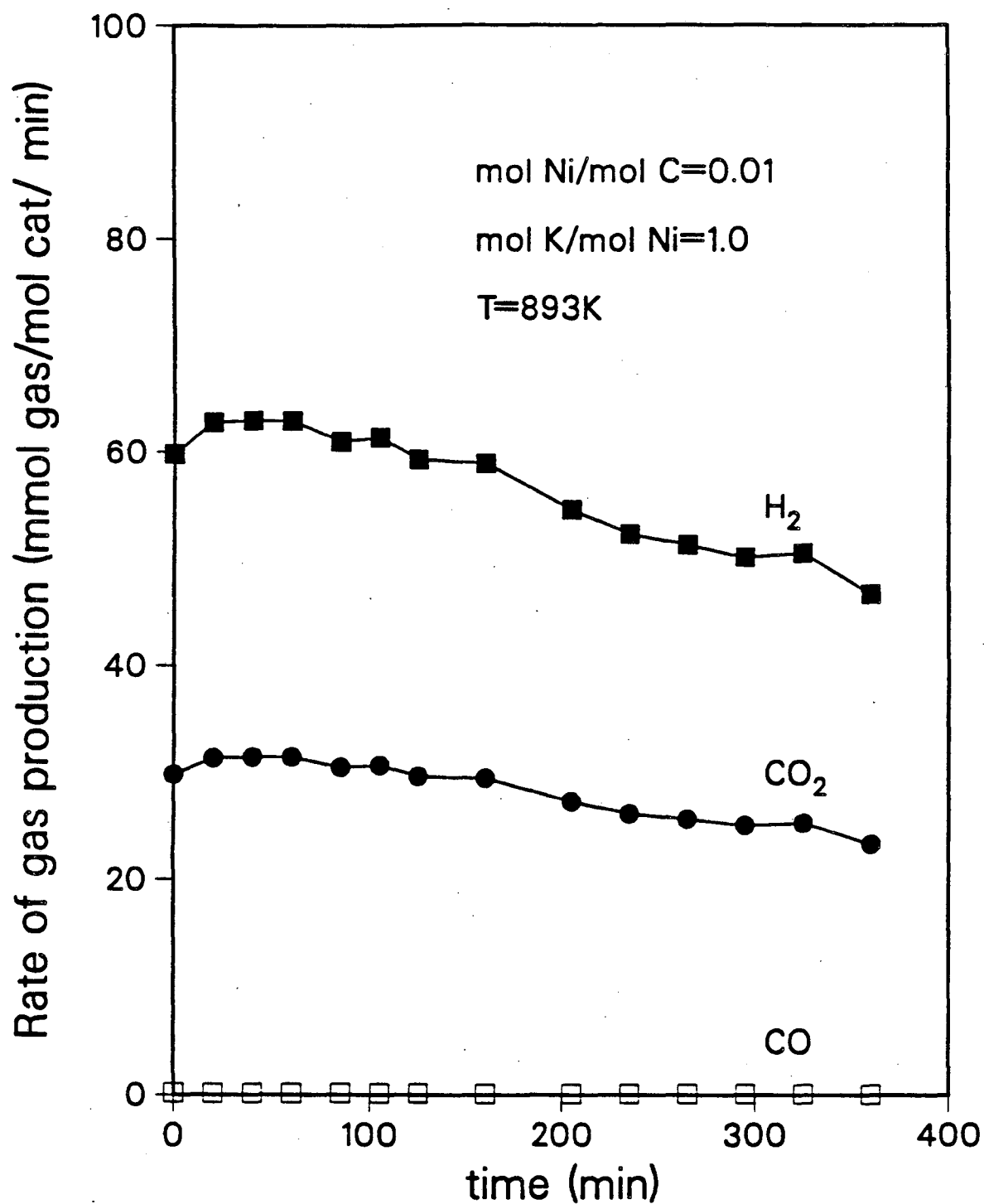


Figure 3.5: Rate of gas production at 893 K as a function of time from the steam gasification of graphite catalyzed by the calcined nickel-potassium mixture

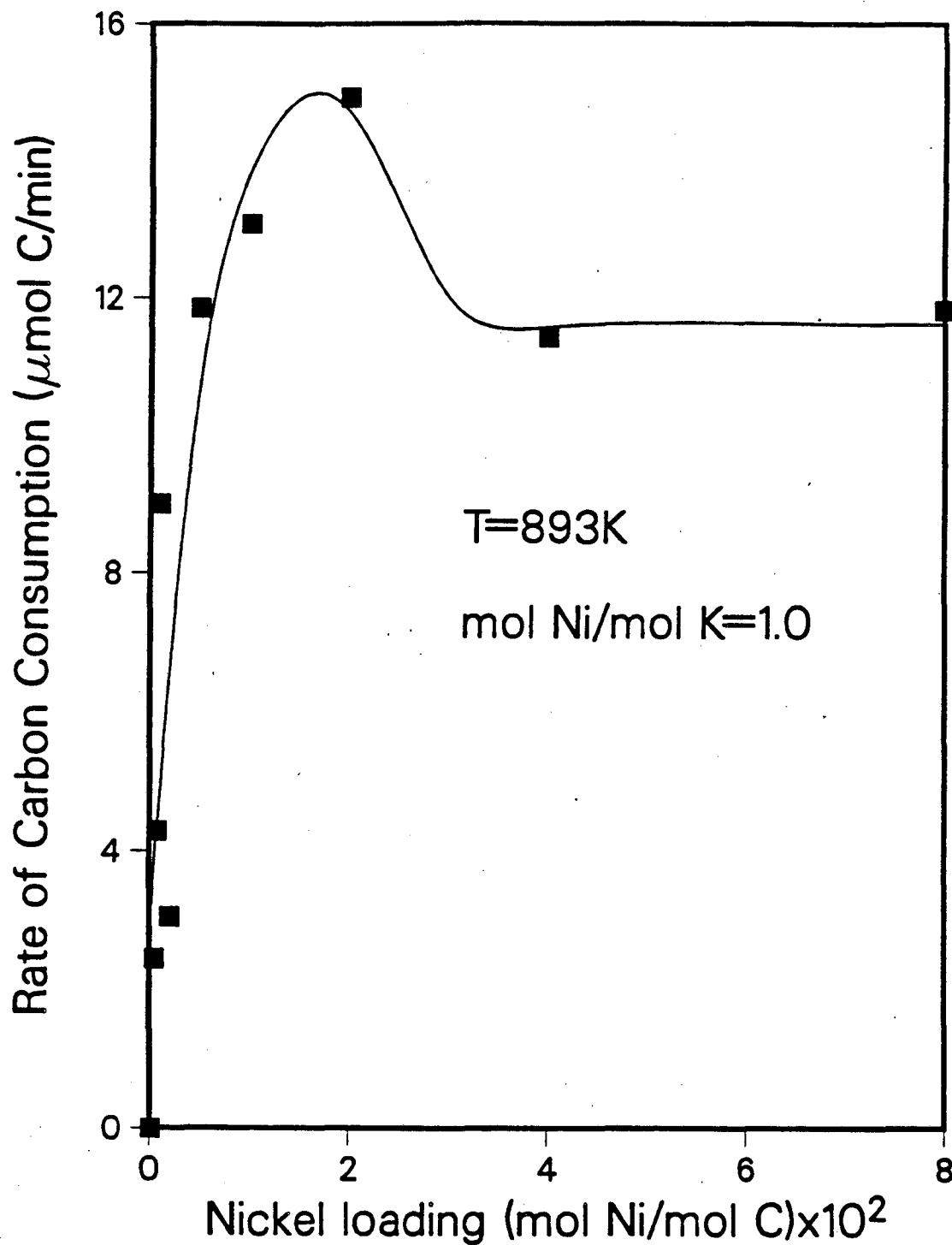


Figure 3.6: Dependence of the rate of carbon consumption at 893 K on the catalyst loading for the calcined nickel-potassium mixture. For all the points the molar ratio of Ni to K is equal to 1.0.

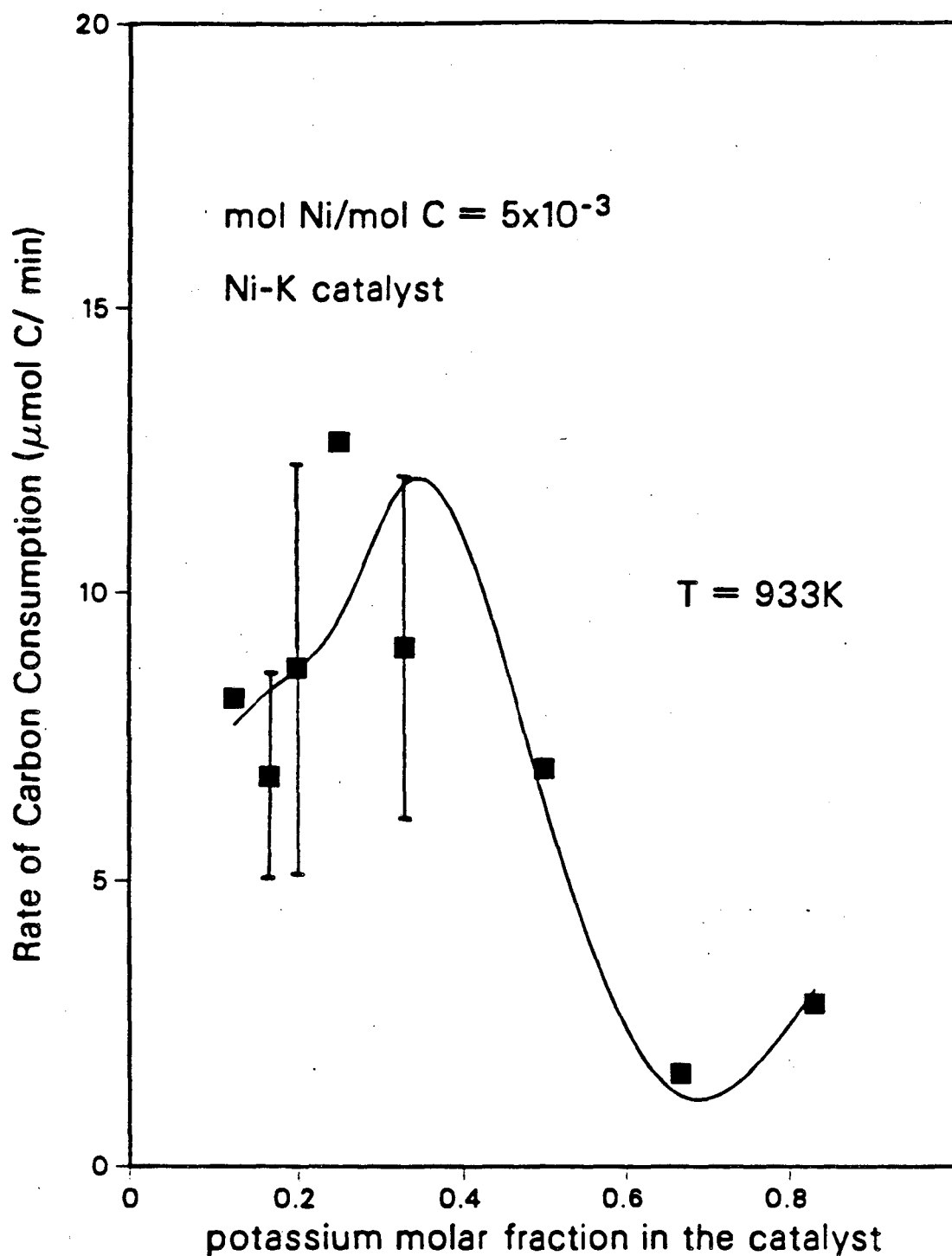


Figure 3.7: Dependence of the rate of carbon consumption at 933 K on the fraction of potassium in the calcined potassium-nickel catalyst. For all the points the molar ratio of Ni to C is equal to 5×10^{-3} .

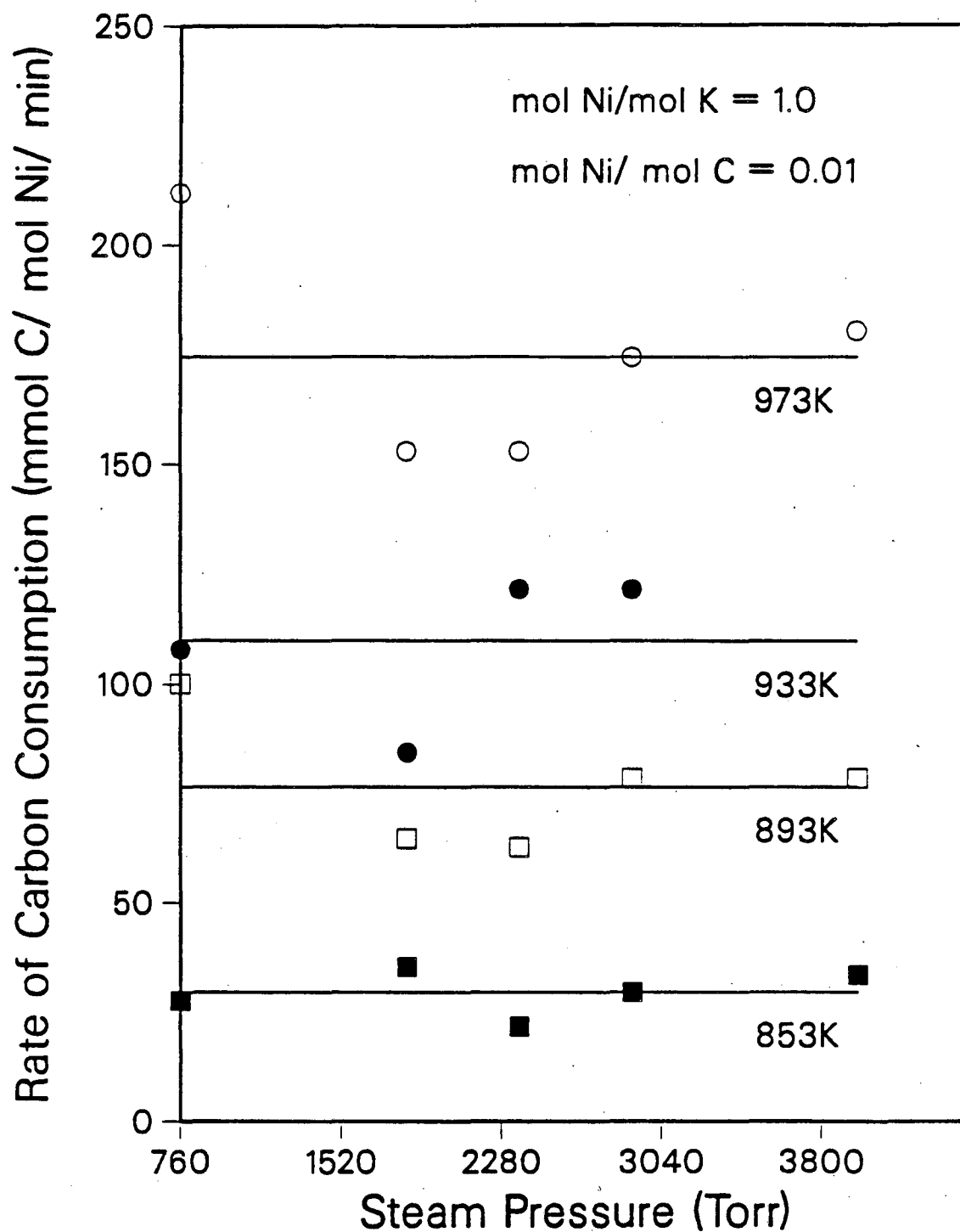


Figure 3.8: Dependence of the rate of carbon consumption on the pressure of steam at various temperatures, for the steam gasification of graphite catalyzed by the calcined nickel-potassium mixture.

at 893 K obtained for the Ni metal catalyst (figure 3.9), and the nickel-potassium mixture (figure 3.5). At this temperature the rate of H_2 production in the case of Ni metal (6000 mmol H_2 /mol Ni/min) is 100 times higher than in the case of the mixture (60 mmol H_2 /mol Ni/min).

The activity of the Ni metal catalyst, however, decreases very fast with time as observed in figure 3.9, and complete deactivation occurs before total carbon conversion. Once the catalyst deactivates, its activity cannot be recovered by treatments in either reducing conditions (723 K in H_2), or combinations of oxidizing and reducing conditions (723 K in O_2 followed by 723 K in H_2).

Figure 3.9 also shows that, as in the case of the nickel-potassium mixture, H_2 and CO_2 are the main products when the reaction is catalyzed by Ni metal. In the case of the latter catalyst, however, the rate of CO production is higher. As observed in figure 3.10, the CO to CO_2 ratio obtained with Ni metal is one order of magnitude higher than that obtained with the nickel-potassium mixture. Also, while the ratio remains constant with time in the case of the mixture, it decreases by a factor of 2.5 in one hour in the case of the Ni metal catalyst.

The rates of steam gasification of graphite at 893 K obtained after reduction of the nickel-potassium mixture are presented in figure 3.11. The initial rate of gas production is similar to that obtained with Ni metal. A decrease in rate with time is observed after 10 min, and the reaction rate levels at the value obtained for the mixture after pretreatment in Ar at 723 K (figure 3.5). After 1000 min under reaction condition, the steam flow was stopped, and the reduction step was repeated. (Dotted line in figure 3.11). This second reducing treatment was not able to recover the high reaction rates observed at the beginning of the experiment. The rates of gasification observed after reintroduction of steam were the same as

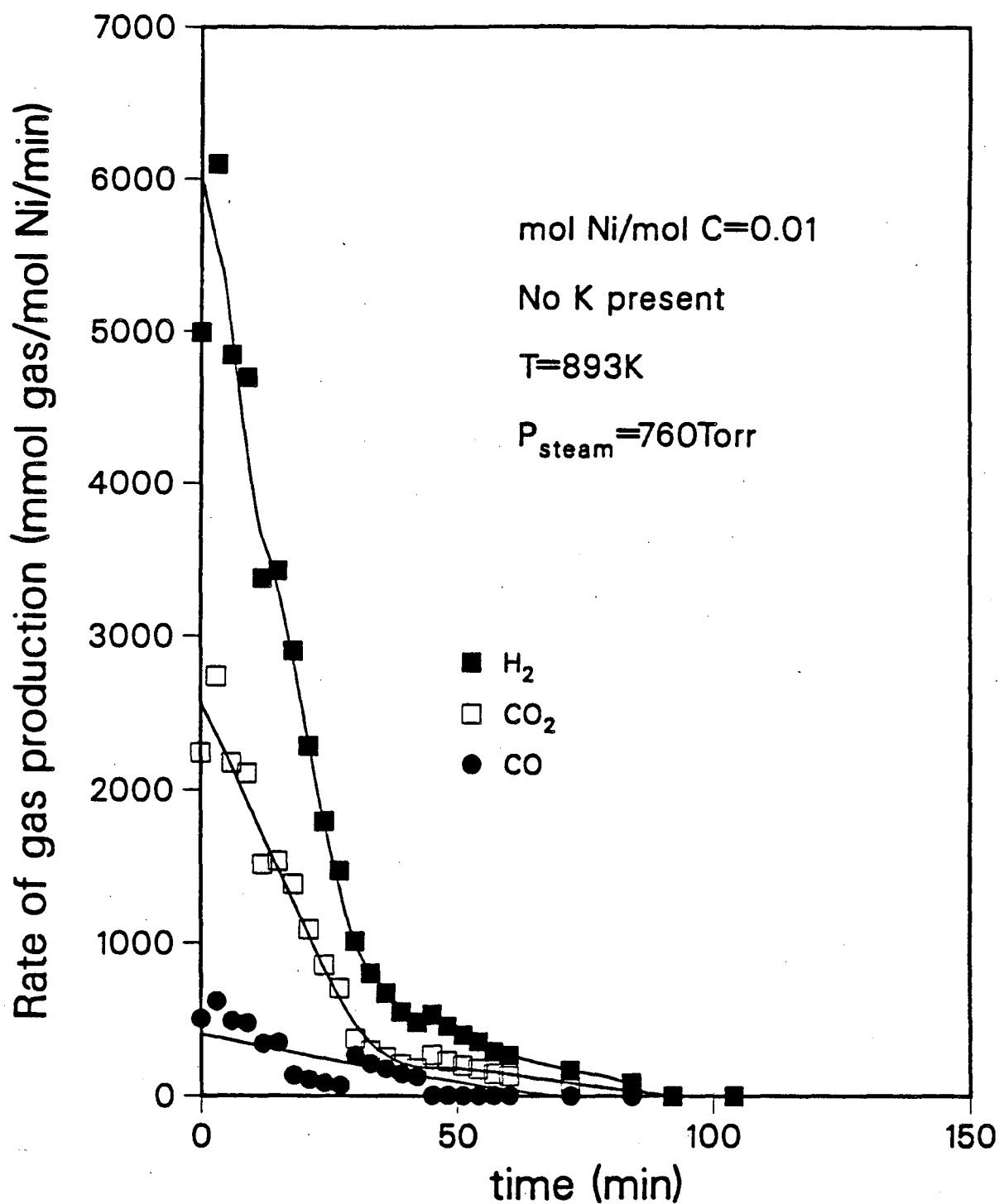


Figure 3.9: Rate of gas production at 893 K as a function of time from the steam gasification of graphite promoted by the prerduced nickel alone catalyst.

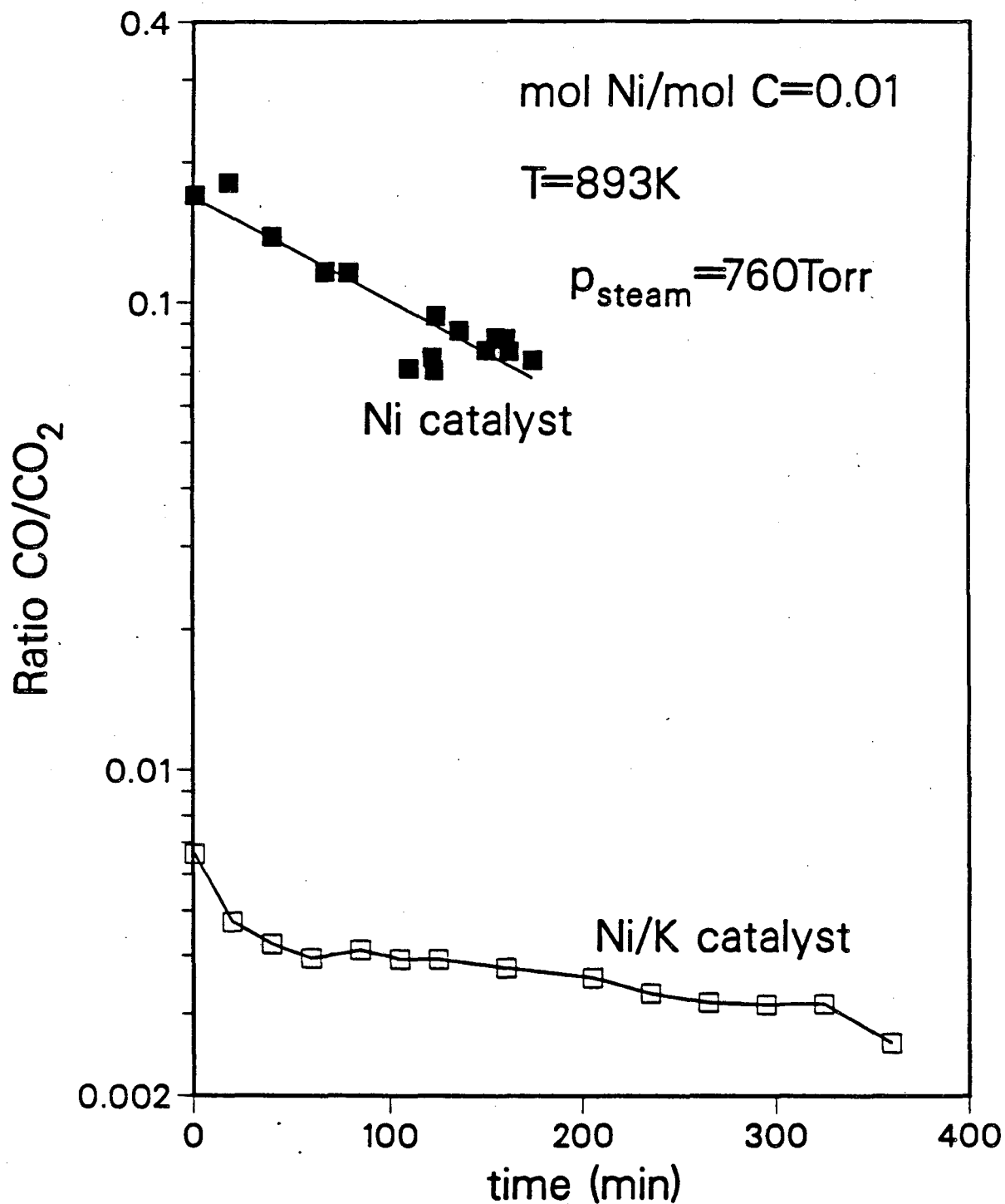


Figure 3.10: Ratio of CO to CO₂ produced as a function of time for the steam gasification of graphite promoted by the reduced Ni alone catalyst (black squares) and the calcined nickel-potassium mixture (open squares).

before stopping its flow.

The conditions required to obtain this initial high activity with the nickel-potassium catalyst were stronger than those required for nickel alone. In the case of the mixture, activation was only possible after exposure to H_2 at 923 K for 30 min, while in the case of nickel alone reduction was achieved after treatment in H_2 at 723 K or in Ar at 923 K, in which case carbon becomes the reducing agent.

In the case of the nickel-potassium prereduced catalyst, as shown in figure 3.12, H_2 and CO_2 are the main gas products, and the ratio of CO to CO_2 varies as a function of time. The initial ratio (0.2 to 0.5) is similar to that obtained with Ni metal. After 50 min the ratio decreases to the range reported for the mixture after pretreatment in Ar ($\sim 5 \times 10^{-3}$), and remains constant at this value for the remainder of the experiment (up to 1400 min).

The rate of carbon gasification as a function of total conversion are plotted in figure 3.13 for the Ni metal catalyst, and for the nickel-potassium mixture after both calcination and prereduction. This figure summarizes most of the kinetic properties described for these catalysts. The initial activity of nickel alone is high but suddenly stops before total carbon conversion. A carbon conversion of $65 \pm 12\%$ was obtained before total deactivation, as determined both by sample weight loss and integration of the gas production curves in figure 3.9. The nickel-potassium catalyst that has only been calcined previous to introduction of steam shows an initial carbon consumption rate lower than that of Ni metal, but no significant loss of activity is observed in the monitored time. Since the rate is rather low, however, only carbon conversions up to 10% were reached with this catalyst. When the nickel-potassium catalyst is prereduced, the initial gasification rates are comparable to those of Ni metal, but after 10% carbon conversion the

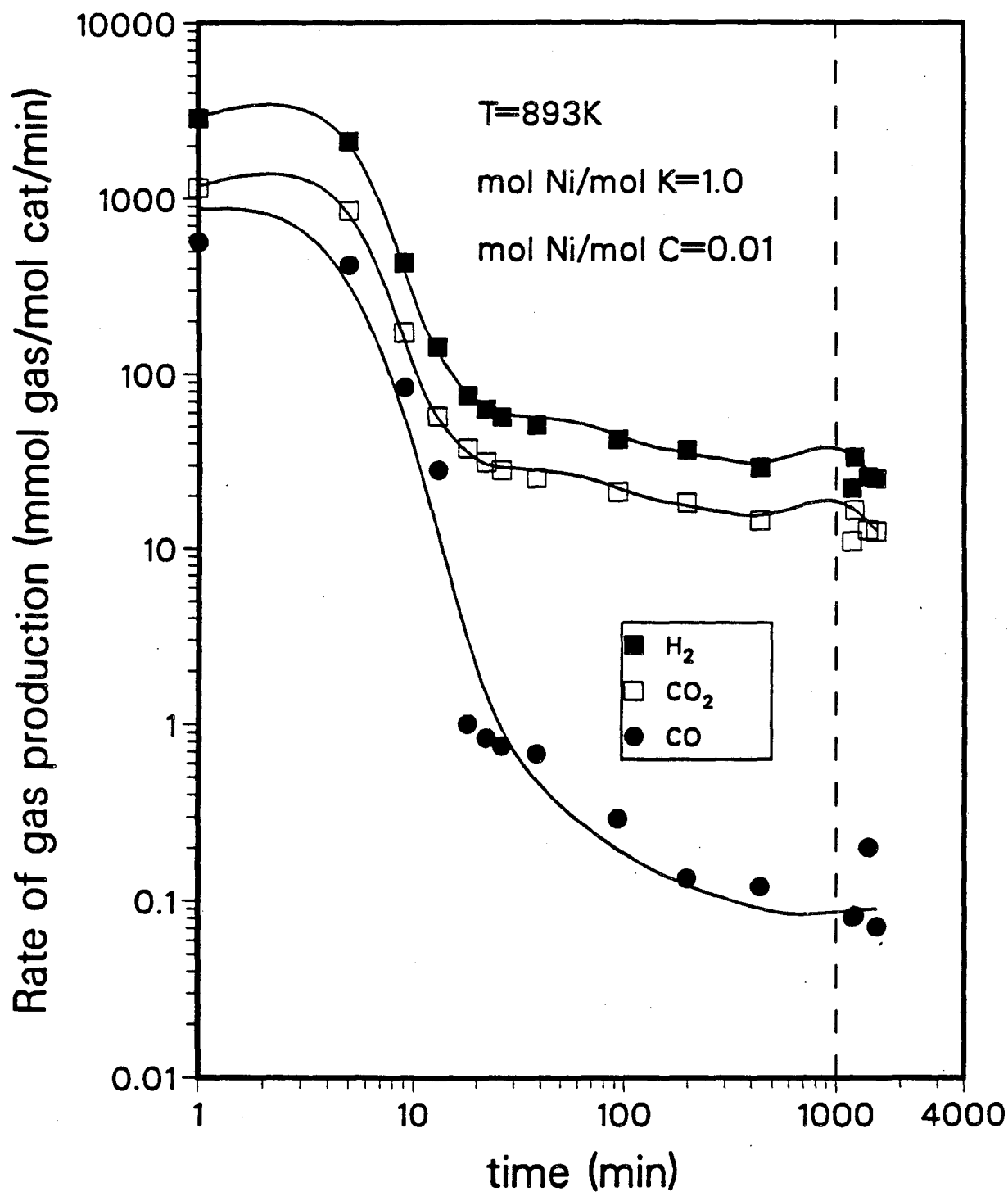


Figure 3.11: Rate of gas production at 893 K as a function of time from the steam gasification of graphite catalyzed by the reduced nickel-potassium mixture

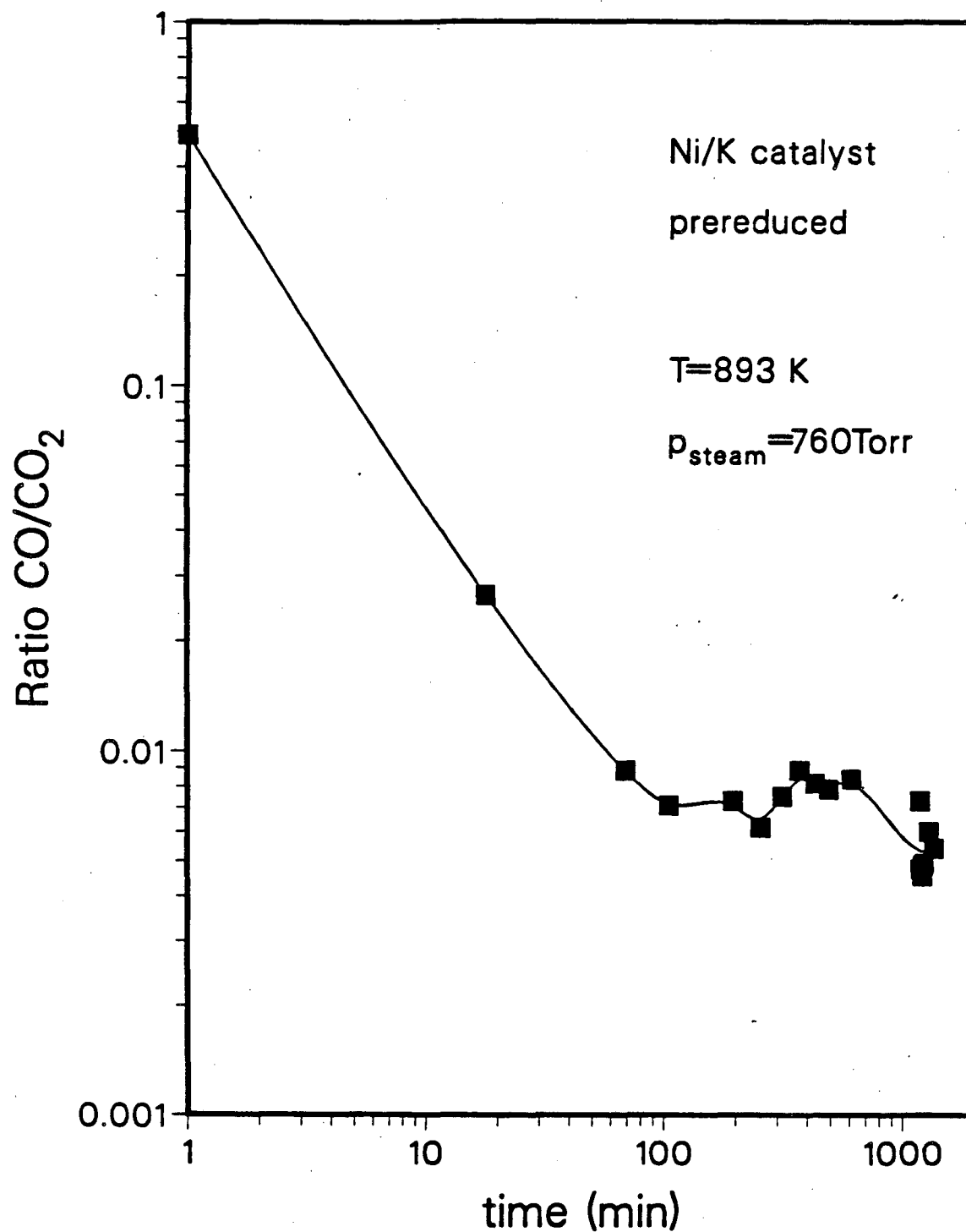


Figure 3.12: Ratio of CO to CO₂ produced as a function of time for the steam gasification of graphite promoted by the prereduced nickel-potassium catalyst.

rates decreases to that of the calcined mixture, and remained at this level during the rest of the experiment. A final conversion of 50% after 16 hours was determined in this case by both sample weight loss and total gas production.

The turnover number has been defined as the moles of carbon consumed per mole of catalyst loaded. In the case of the alkali-transition metal mixture one mole of catalyst is considered as one mole of alkali plus one mole of transition metal, since both components are necessary to obtain an active species. This definition of one turnover gives a lower limit for the efficiency of the catalyst, since it considers that all the molecules deposited are active, which is not necessarily the case. Even so, the results in figure 3.13 show that both the Ni metal and the nickel-potassium mixture are indeed catalysts for the steam gasification of graphite. In the case of Ni metal 65 turnovers are obtained before deactivation, and for the nickel-potassium mixture, 50 turnovers in 1000 min are obtained when the catalyst is prereduced, and 10 turnovers in 400 min when it is calcined.

Blank experiments were carried out adsorbing a mixture of KOH and $\text{Ni}(\text{NO}_3)_2$ on silica, followed by a treatment in Ar at 723 K. No gas products were detected up to 1273 K when a steam flow was passed through the sample.

3.3 Discussion

The results presented in this chapter show that catalysts derived from mixtures of an alkali salt and a transition metal salt are able to catalyze the steam gasification of graphite at temperatures as low as 860 K. The activity and activation energy for this reaction varies with both the transition metal and alkali present. The nickel-potassium mixture is the most active catalyst at 900 K found so far, although mixtures of other transition metals (specially iron), and other alkalis (like

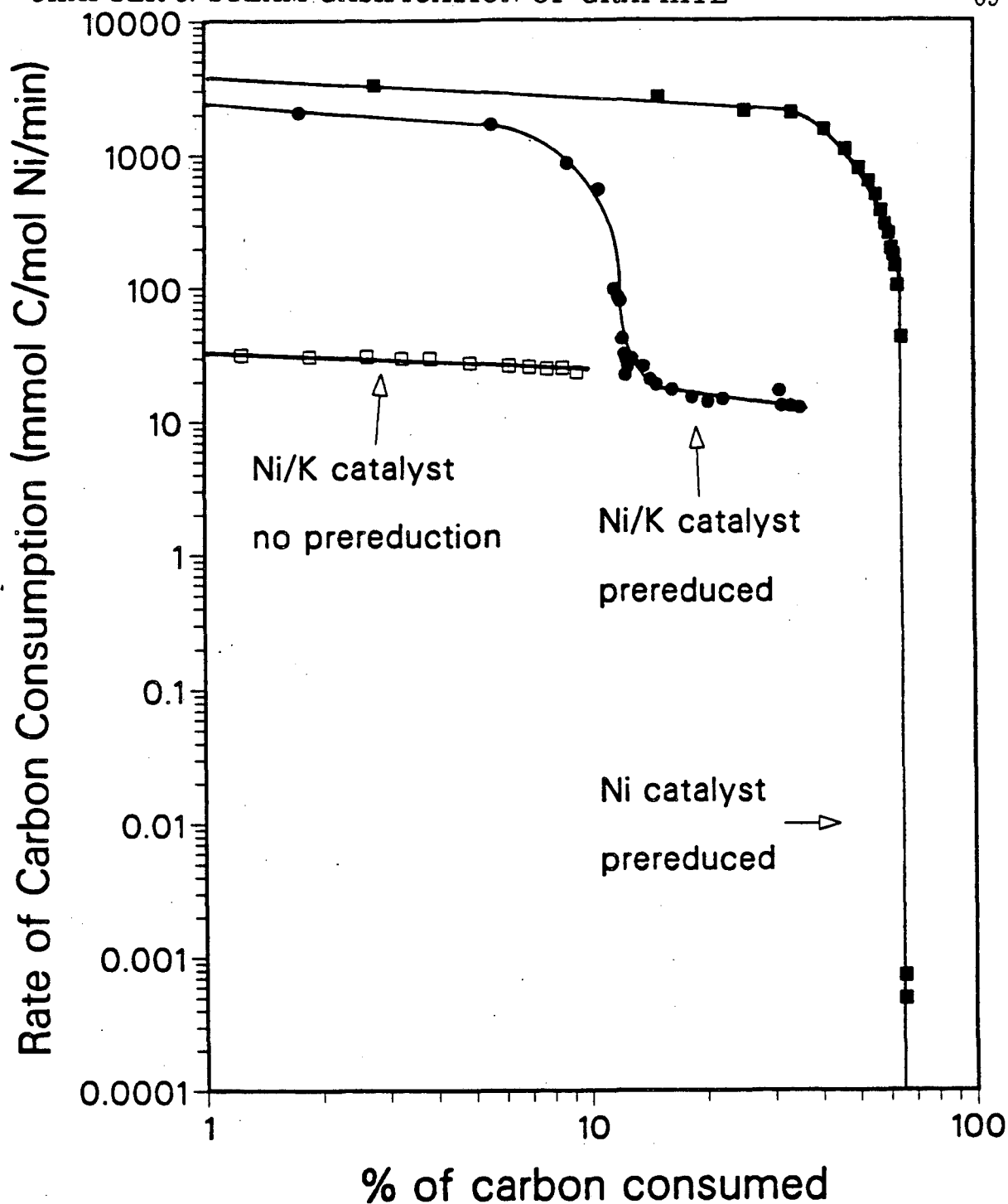


Figure 3.13: Rate of carbon consumption at 893 K as a function of carbon conversion for the steam gasification of graphite promoted by the calcined nickel-potassium catalyst (open squares), the reduced nickel-potassium catalyst (black dots), and the reduced Ni alone catalyst (black squares). In all cases, the nickel loading is equal to 1.0×10^{-2} mol Ni/mol C. For the nickel-potassium catalyst, the nickel to potassium molar ratio is equal to 1.0.

sodium) are also effective. The activity of these mixtures cannot be attributed to an additive effect, but rather to a cooperative effect between the alkali and the transition metal. This is best shown when the catalysts are only calcined previous to the introduction of steam. While the mixture is catalytically active below 900 K, KOH adsorbed alone behaves as a reactant at this temperature, and the transition metal oxide adsorbed alone is inactive.

The most important catalytic property of the nickel-potassium mixture is its resistance to deactivation. Figure 3.9 shows that this mixture conserved its initial activity even after 400 min under reaction conditions. On the contrary, figure 3.9 shows that the Ni metal catalyst completely deactivates after 90 min, and its activity cannot be recovered by treatments in either reducing or oxidizing conditions. In the case of the KOH catalyst, several authors have reported loss of activity with time, due to vaporization under reaction conditions [4,5].

Evidence for the interaction between alkalis and transition metals in the catalytic steam gasification of carbon solids has also been reported by other authors. Adler *et al.* [6,7] have studied the properties of catalysts derived from mixtures of K_2SO_4 and $FeSO_4$ for gasification of PCV model coke in H_2/H_2O atmospheres. They report that this mixture has improved activity under "steady state" conditions of gasification compared with pure potassium or pure iron, including improved CH_4 selectivity. They also report that the rate depends on the ratio of potassium to iron in the mixture, with a maximum at an Fe/K molar ratio of 0.2. Sukuzi *et al.* [8] report that catalysts derived from mixtures of sodium and iron salts have better kinetic properties than the one derived from Na_2CO_3 for steam gasification of Yallourn coal. Also Ohtsuka *et al.* [9,10] report that the presence of potassium increases markedly the catalytic activity of both iron and nickel for

steam and hydrogen gasification of brown coal, while calcium decreases it. All of these studies are in good agreement with results presented in this chapter. On the other hand, Wigmans and Moulijn [11] did not find any evidence for interaction between K_2CO_3 and Ni metal for the gasification of carbon with steam at 1075 K. All these suggest that the interaction between the alkali and the transition metal components in the catalyst depends on the reaction conditions. The work presented in chapters 4 and 5, and carried out using surface characterization techniques (electron microscopy and X-ray photoelectron spectroscopy) is aimed at studying this dependence.

In the case of nickel deposited alone on graphite, our results show that even though the oxide is inactive for steam gasification of graphite, the metal is an excellent catalyst. The same conclusion has been reached by other authors. McKee [12] reports that iron is effective for gasification of graphite with steam, only when it is present as a metal. Walker *et al.* [13] found the same behavior for iron in the case of CO_2 gasification, and Yamada *et al.* [14] reported that the activity of nickel compounds in the gasification of char was related to their facility to decompose and form metallic nickel.

The results presented in this chapter indicate that there are several differences in the catalytic properties of the nickel-potassium mixture and the Ni metal catalyst. The most important is that the catalyst derived from $Ni(NO_3)_2$ requires a prereduction step to be activated, while the one derived from the $Ni(NO_3)_2/KOH$ mixture does not. Furthermore, our results suggest that the interaction between nickel and potassium is stabilizing the presence of a large fraction of the nickel as an oxide under reaction conditions. First, the pretreatment conditions required to activate nickel in the presence of potassium (923 K in H_2) were more drastic

than those necessary to do it in its absence (723 K in H_2). Also, in figure 3.13 it is observed that when the mixture is reduced, even though the initial activity is similar to that of Ni metal, after 10% carbon conversion (10 min under reaction condition) the rate decreases to the value observed with the mixture after calcination. The stabilization of a large fraction of NiO in the presence of potassium is confirmed by XPS results presented in chapter 5. Our results also show that in the presence of potassium, once a fraction of the nickel is reduced to the metal, its catalytic behavior is the same as that observed for Ni metal alone. This suggests that the potassium in the mixture does not interact with the metal but rather with the oxide. It also implies that the presence of potassium has no effect in the product distribution obtained with the Ni-metal catalyst, and its deactivation process.

Another important difference between the Ni metal catalyst and the nickel-potassium catalyst is the product distribution as a function of time. Even though in both cases H_2 and CO_2 are the main products, in the Ni metal catalyzed reaction the amount of CO evolved is larger than in the case of the mixture. Also, while the ratio of CO to CO_2 remains constant when the reaction is catalyzed by the nickel-potassium mixture, its value decreases with time in the case of nickel alone. For Ni metal, it has been proposed that CO is the primary product of the gasification reaction, and that CO_2 is formed by the water gas shift reaction ($H_2O + CO \rightarrow H_2 + CO_2$), which is also catalyzed by Ni metal [12,15]. The decrease in the CO to CO_2 ratio can be explained in terms of the extent of the water gas shift [16]. Initially the gasification rate is fast, and the contact time of the products is not enough to convert all the CO. As the total rate of gasification decreases, less CO is present, and since neither its contact time nor the water gas shift activity change,

a larger fraction of CO should react with steam, thus decreasing the ratio of CO to CO₂.

In the nickel-potassium catalyzed reaction, the ratio of CO to CO₂ (4×10^{-3}) is much lower than in the case of Ni metal. This is the case, even when the Ni metal activity for steam gasification is similar to that of the nickel-potassium catalyst. Two possibilities can justify this difference. The first is that the catalytic activity of the nickel-potassium catalyst for water gas shift is higher than that of Ni metal, and therefore the amount of CO converted to CO₂ is higher. The second possibility is that the nickel-potassium mixture favors the formation of CO₂ directly from the gasification reaction, as also proposed for the K₂CO₃ catalyzed steam gasification of carbon [17].

For graphite gasification, Ni metal is more active than the nickel-potassium mixture. Ni metal deactivates before total graphite conversion, and in the case of char gasification it is immediately poisoned when small amounts of sulfur or clays are present (less than 1 wt.%). The results obtained with the nickel-potassium mixture show that there is a strong interaction between the components. This interaction prevents the catalyst deactivation in the case of graphite gasification, and as discussed in chapter 6, makes the mixture resistant to the attack of sulfur and minerals in the substrate, when their concentration is low (less than 4 wt.%).

There is no consensus on the reasons for the interaction between the alkali and the transition metal in the combined catalyst. Hüttinger *et al.* [7,18] propose that the transition metal catalyses the reduction of the alkali salt to the metal at around 1100 K, and the latter then becomes the main catalytically active species for gasification. At 933 K, however, the fraction of K metal expected from ther-

modynamic considerations is not high enough to account for the activity observed for the nickel-potassium mixture [19]. Suzuki *et al.* [8] suggest the opposite situation. They propose that the alkali salt favors the reduction of the transition metal, which then becomes the active catalyst. The differences presented in this chapter between the Ni metal and nickel-potassium catalyst, however, tend to indicate that this is not the case.

The present work suggests that the catalytic properties of the mixture cannot be explained by the promotion of the catalytic properties of one component by the presence of the other. It is then proposed that the potassium and nickel precursors form a compound, which is involved in the gasification process. Following chapters include supporting results for this model, and a more detailed discussion of it.

3.4 Summary

The results presented in this chapter show that catalysts derived from mixtures of a transition metal and an alkali metal salts are able to catalyze the steam gasification of graphite. This is due to a strong interaction between the two components. Their most distinctive property is their resistance to deactivation at low temperatures (below 1000 K). Mixtures of nickel and iron oxides with alkali hydroxides (KOH or NaOH) are the most active catalysts under our conditions of preparation.

The kinetic properties of the nickel-potassium mixture are different from those of nickel alone, whereas potassium alone is inactive at the temperature chosen for this study (893 K). This suggests that different active species and/or mechanisms are involved in the steam gasification of graphite, when catalyzed by these compounds.

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Chapter 4

Controlled Atmosphere Electron Microscopy Study Of The Graphite Gasification By Water Vapor, Hydrogen And Oxygen Catalyzed By A Nickel-Potassium Mixture

4.1 Introduction

This chapter presents a study using controlled atmosphere electron microscopy (CAEM) to characterize the morphological properties of the nickel-potassium catalyst. The interaction between the nickel-potassium catalyst and graphite surfaces is studied in three gas environments; H_2O vapor, $\text{H}_2/\text{H}_2\text{O}$, and $\text{O}_2/\text{H}_2\text{O}$. This technique is an excellent tool to study the surface mobility and wetting properties of the catalyst. It also allows the determination of the mode of attack of the gaseous reactants to the graphite lattice promoted by the catalyst, and the intrinsic rates of carbon consumption. This characteristic is very important because comparisons of the activities of various catalysts can be made without the interference of

geometric effects, such as surface area or number of active sites.

The goal of this chapter is to show that the nickel-potassium catalyst has distinctive morphological and kinetic properties for carbon gasification. These properties will be discussed in the three gas environments studied, and then compared to those reported by other authors for KOH or Ni metal deposited alone [1–4]. The distinctive properties observed for the nickel-potassium mixture are further evidence of the cooperative effect between nickel and potassium in the promotion of carbon gasification.

4.2 Results

4.2.1 The nickel-potassium/graphite-water vapor system

After treating graphite samples loaded with KOH and $\text{Ni}(\text{NO}_3)_2$ at 723 K in Ar, particle nucleation was observed on both the basal and edge planes. After this treatment, the sample was treated in a H_2O vapor environment (2 Torr, Ar: H_2O 40:1), from 723 to 1400 K. In this gas environment, particles located on the graphite edge region underwent a transformation from non-wetting condition to wetting condition between 745 and 800 K. They spread over the whole edge area, and formed a very thin film that became very difficult to observe. This suggests that the film width is of the order of the apparatus resolution (2.5nm).

On continued heating to 830 K these regions started to erode, giving a ragged appearance to the initially uniform edges. The carbon erosion developed into a more ordered edge recession as the temperature approached 950 K. Figure 4.1 shows a two picture sequence illustrating this mode of attack at 1173 K.

The edge recession involved the whole area, and the various fronts of attack were separated by 60 degree angles, in orientations corresponding to the $[11\bar{2}0]$

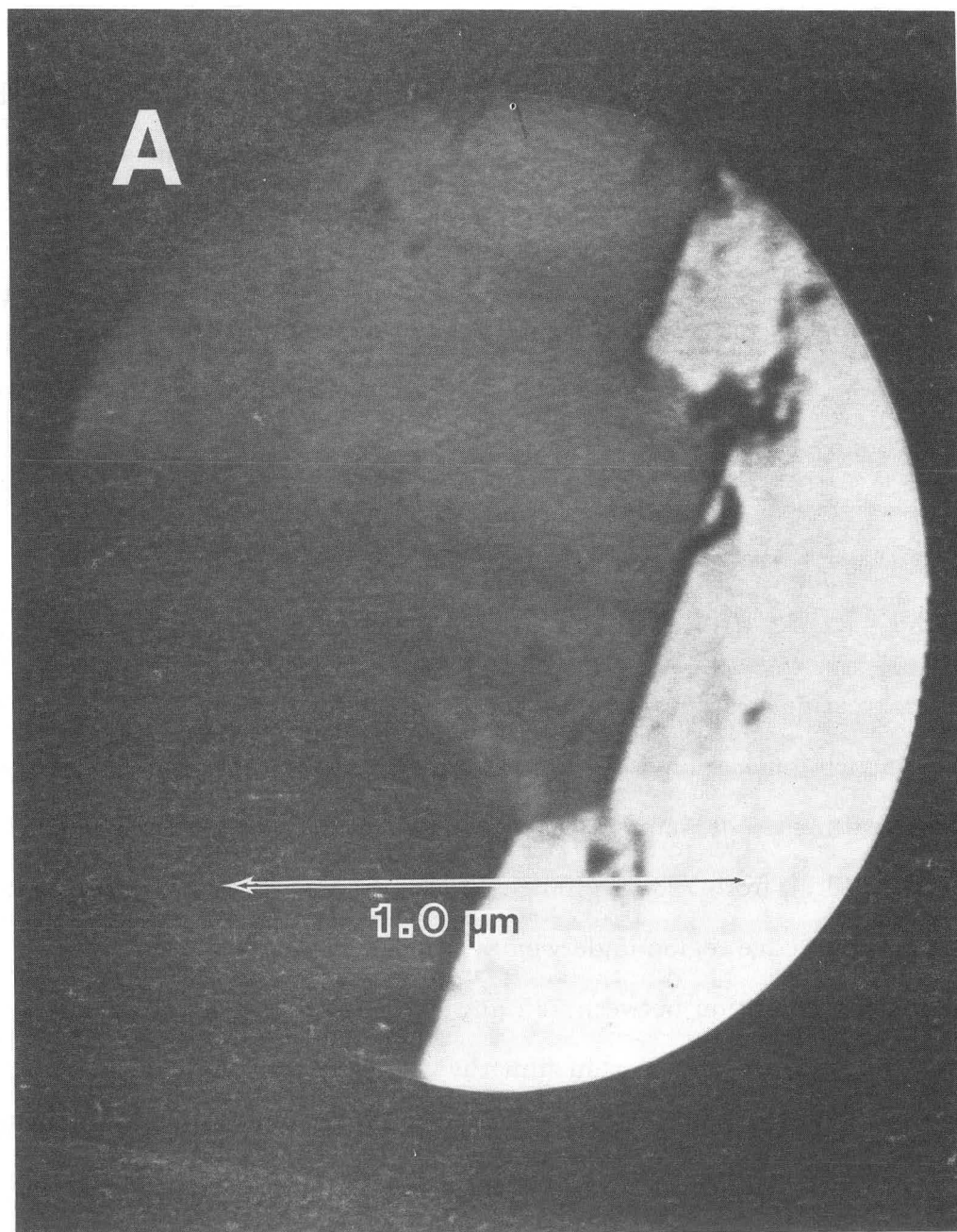


Figure 4.1: Sequence of CAEM photographs showing the edge recession mode of carbon attack by H_2O vapor at 1173 K, promoted by a nickel-potassium catalyst. The time between photographs is 3s.

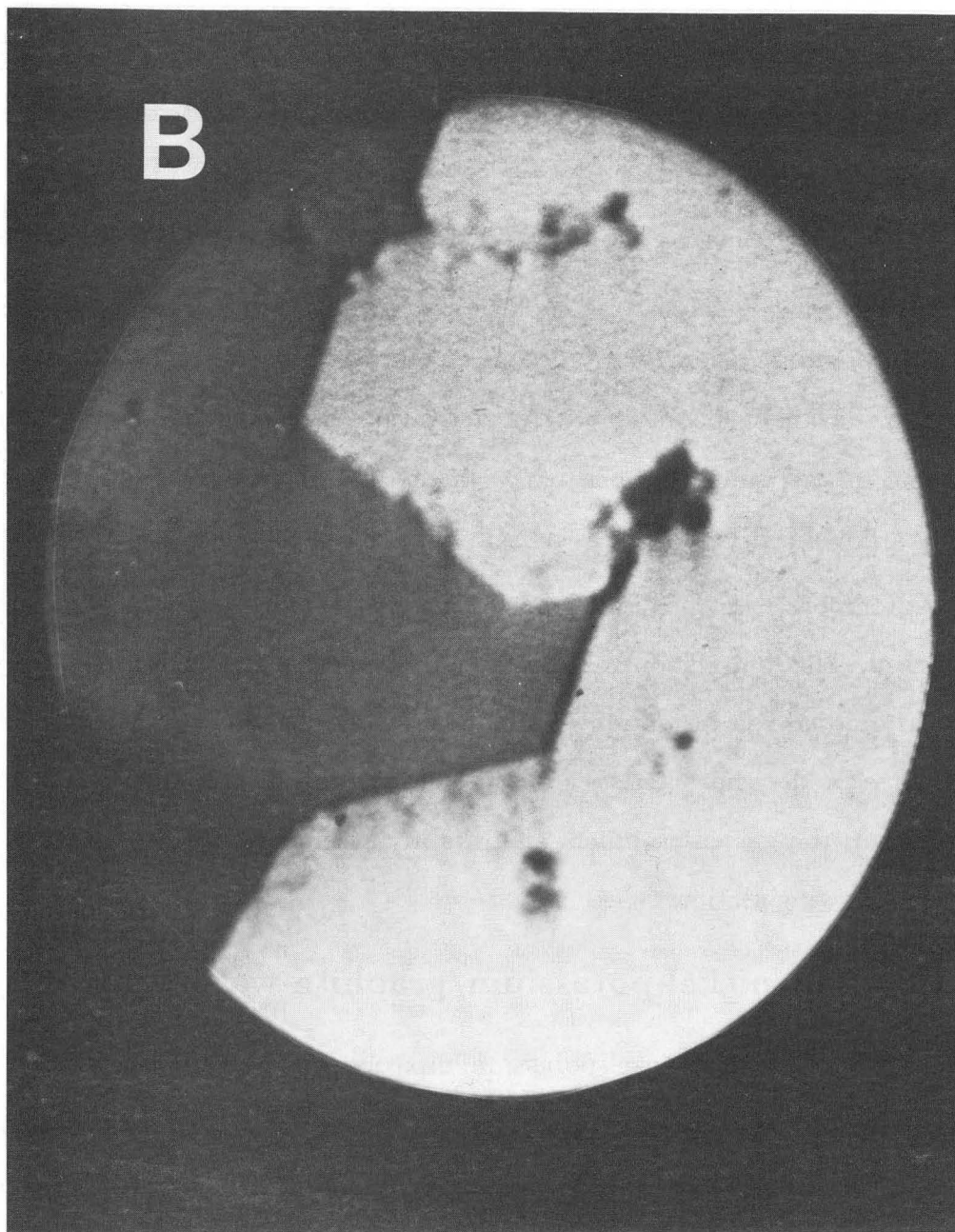


Figure 4.1b

crystallographic direction of the graphite structure. (See figure 4.1). The orientation was determined by referring the position of the fronts of attack to that of twin bands, which are always present in graphite in the $[10\bar{1}0]$ direction.

The rate of edge recession increased continuously when the temperature was raised from 950 to 1370 K, and no evidence of deactivation was observed. The rates of edge recession as a function of temperature are shown in figure 4.2 in the form of an Arrhenius plot. An activation energy of 30.8 ± 0.9 kcal/mol was obtained. This value is consistent with the one determined from kinetic studies using a flow reactor system, as presented in chapter 3.

At temperatures above 1230 K, a change in the mode of attack was occasionally observed. The film responsible for the edge recession sintered into small particles that promoted the formation of channels. This phenomenon may be caused by a change in the characteristics of the catalyst, brought about by a build of H_2 product in the gas environment. This is in agreement with the results described in the following section.

4.2.2 The nickel-potassium/graphite-wet hydrogen system

The catalytic effect of nickel-potassium mixtures on the gasification of graphite in a $H_2:H_2O$ 40:1 atmosphere was studied on samples that had been either gasified in H_2O vapor at 1273 K or heat treated in Ar at 723 K. The results in both cases were identical, and they will be described without making reference to the sample pretreatment.

The first signs of catalytic attack occurred at 820 K. It took the form of relatively straight channels, which were created by catalyst particles that had nucleated along the edges of graphite.

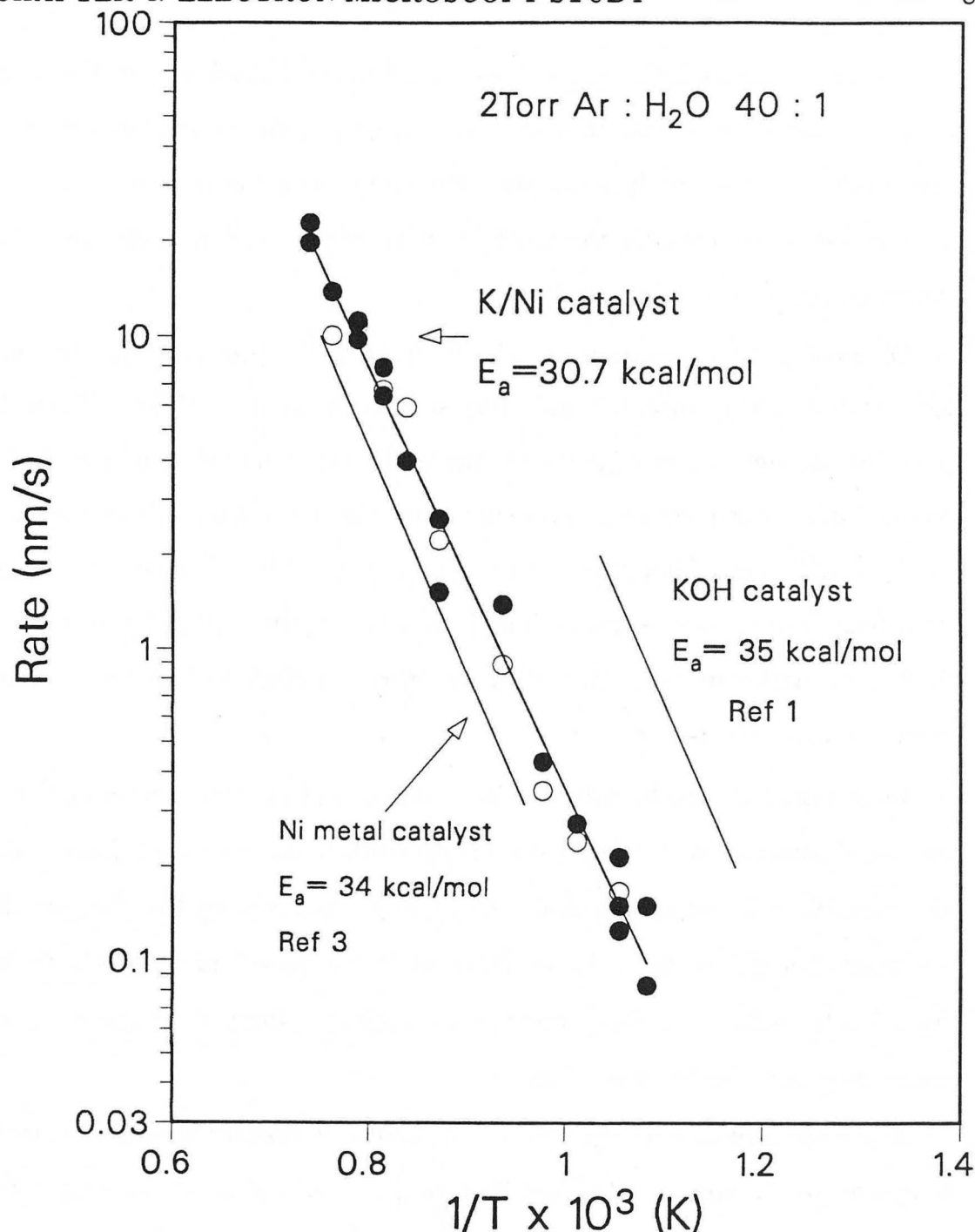


Figure 4.2: Arrhenius plot of nickel-potassium catalyzed edge recession rates of graphite in 2 Torr of wet Ar. The black dots correspond to the results obtained after heat treating the sample in Ar for 30 min at 723 K, and the open circles to those obtained after treating the sample in 2 Torr of wet H₂ at 1373 K. Results previously reported for the KOH and Ni metal catalyzed reactions are included for comparison purposes. The length of the curves indicates the temperature range studied.

When first formed, the channels remained parallel-sided, and as the temperature was raised to 840 K, they started to acquire a fluted appearance. This is the result of active catalyst particles spreading along the channel walls, which then proceeded to catalyze the reaction by an edge recession mode. (See region indicated by arrows in figure 4.3)

On raising the temperature to 950 K many of the previously inactive particles located on the graphite basal plane started to exhibit mobility. When these particles encountered an edge they underwent a rapid spreading action, and this resulted in a subsequent removal of carbon by edge recession in directions parallel to the $[11\bar{2}0]$ crystallographic orientation. The variation in edge recession rate with temperature was determined, and the data is presented in figure 4.4 in the form of an Arrhenius plot. An activation energy of 30 ± 2 kcal/mol was obtained from the slope of this line.

Both modes of attack, edge recession and channeling, were occurring simultaneously during the whole temperature range studied (850 - 1400 K). Below 1173 K the channels were very short, and were usually taken over by the progress of the recession of neighbor edges. As the temperature was raised up to 1373 K, the edge recession tended to slow down, and in some regions it stopped completely, leaving channeling as the only mode of attack.

The edge recession activity in wet H_2 could be regenerated by the reaction temperature. In addition, the wet H_2 treatment did not affect the properties of the nickel-potassium mixture for promotion of the edge recession mode of attack of steam. Figure 4.2 shows that the rates of edge recession obtained in wet Ar after a H_2/H_2O treatment (open circles) are identical to those obtained after a heat treatment in Ar (black dots).

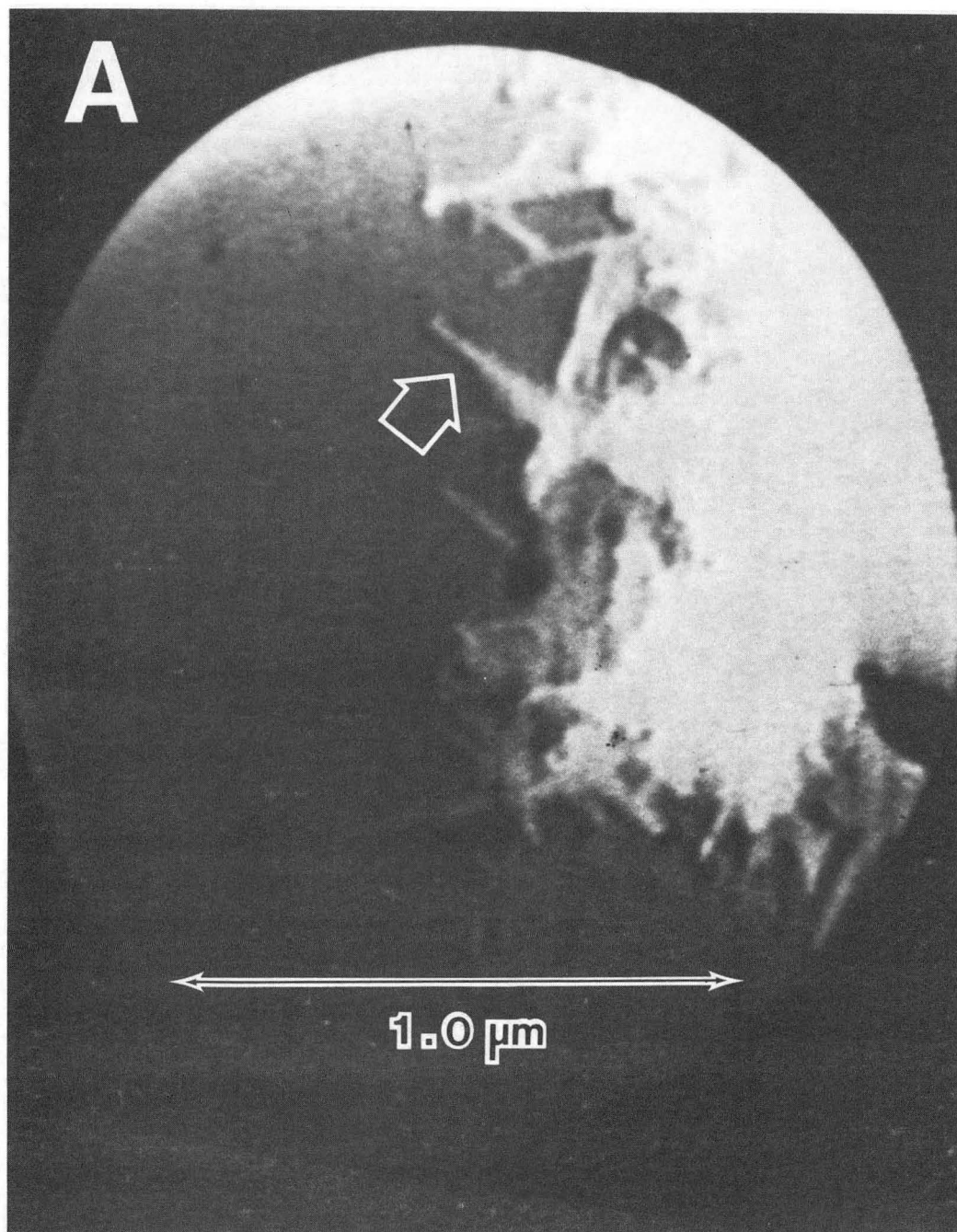


Figure 4.3: Sequence of CAEM photographs showing the modes of carbon attack promoted by the nickel-potassium mixture in 2 Torr wet H_2 at 1173 K. The region indicated by arrows shows the recession of channels, as described in the text. Also notice the simultaneous carbon attack by edge recession and channeling in the lower part of the photographs. The time between photographs is 1s.

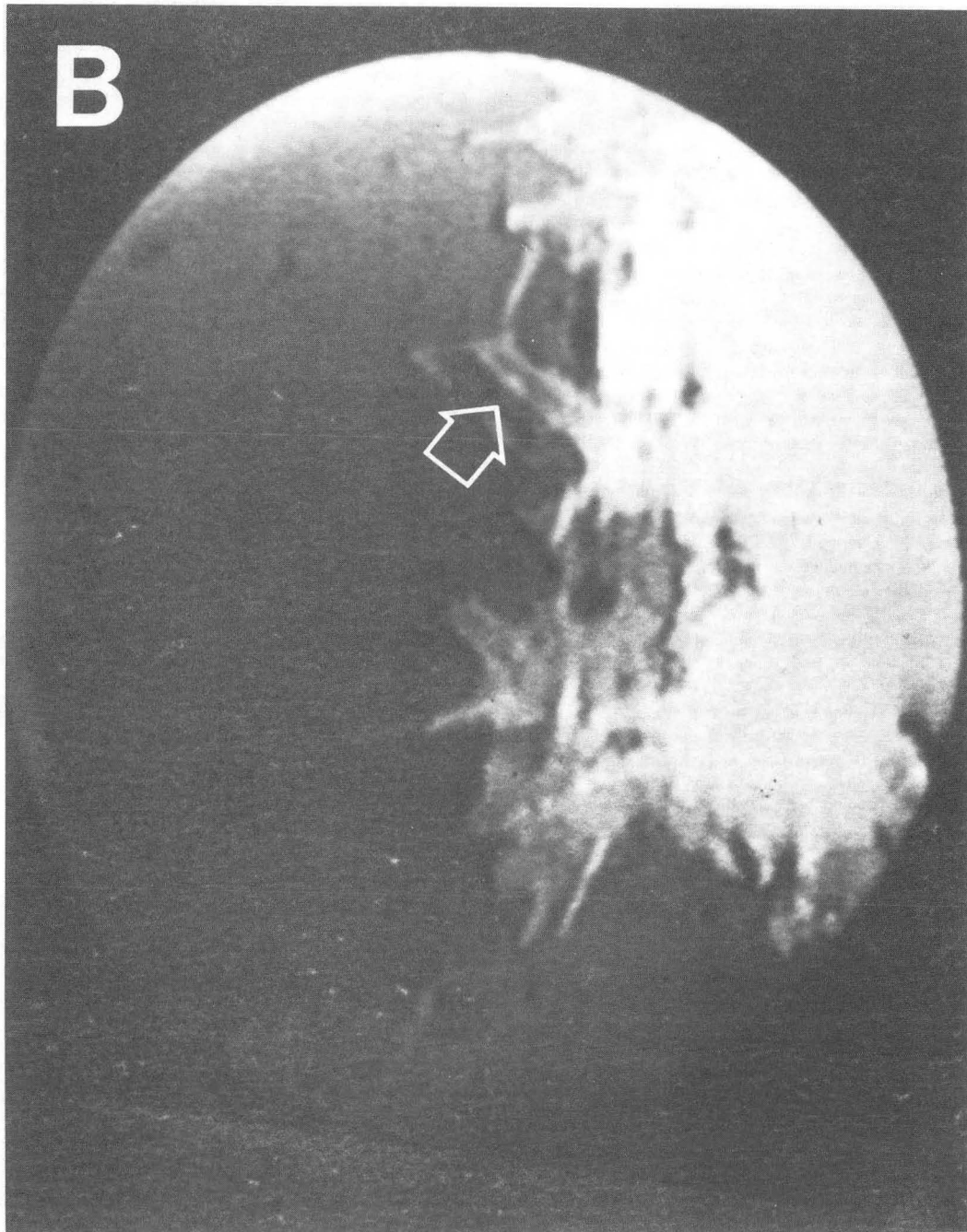


Figure 4.3b

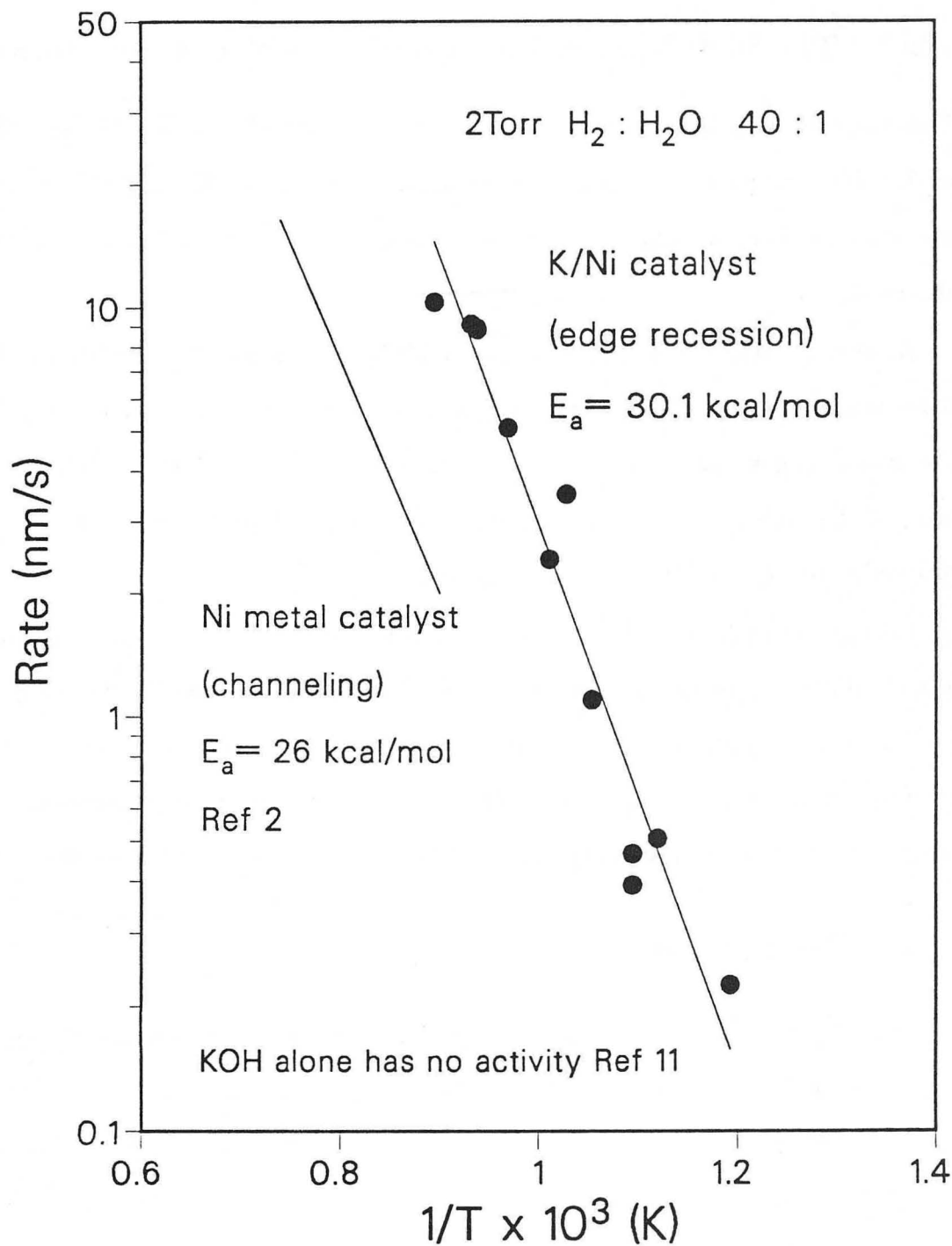


Figure 4.4: Arrhenius plot of the nickel-potassium catalyzed edge recession rates of graphite in 2 Torr of wet H_2 . The reported results for the channeling mode of attack promoted by Ni metal are included for comparison. The length of the curves indicate the temperature range studied.

4.2.3 The nickel-potassium/graphite-wet oxygen system

Treatment of nickel/potassium specimens in 2.0 Torr of wet O_2 ($O_2:H_2O$ 40:1) at 878 K resulted in the formation of shallow channels. During this stage of the reaction channels followed random pathways, and no erosion of the walls was observed.

As the temperature was raised above 940 K particle mobility increased. Particles that came into contact with edges immediately underwent spreading, and the coated edges started to recess. At the same time, catalyst particles at the head of channels previously formed gradually spread along the walls, which then proceeded to expand laterally. (See figure 4.5)

In contrast with the behavior observed in wet H_2 and wet Ar, the recession in wet O_2 did not appear to follow any preferred direction. Also, in this case, the catalyst attack continued up to 1290 K, with no evidence for deactivation of the gasifying edges. From an Arrhenius plot of the variation of the edge recession with temperature an activation energy of 25 ± 3 kcal/mol was obtained. (See figure 4.6)

4.3 Discussion

The nickel-potassium mixture catalyses the gasification of graphite both in reducing and oxidizing environments. The carbon consumption in all cases occurs at the catalyst/carbon interface and the gas mode of attack is affected by the morphology of the mixture on the surface. In wet Ar and wet O_2 , the catalyst spreads and promotes the carbon attack by an edge recession mode. In wet H_2 , the catalyst is present both in a wetting and a spreading condition, and the gasification occurs simultaneously by channeling and edge recession.

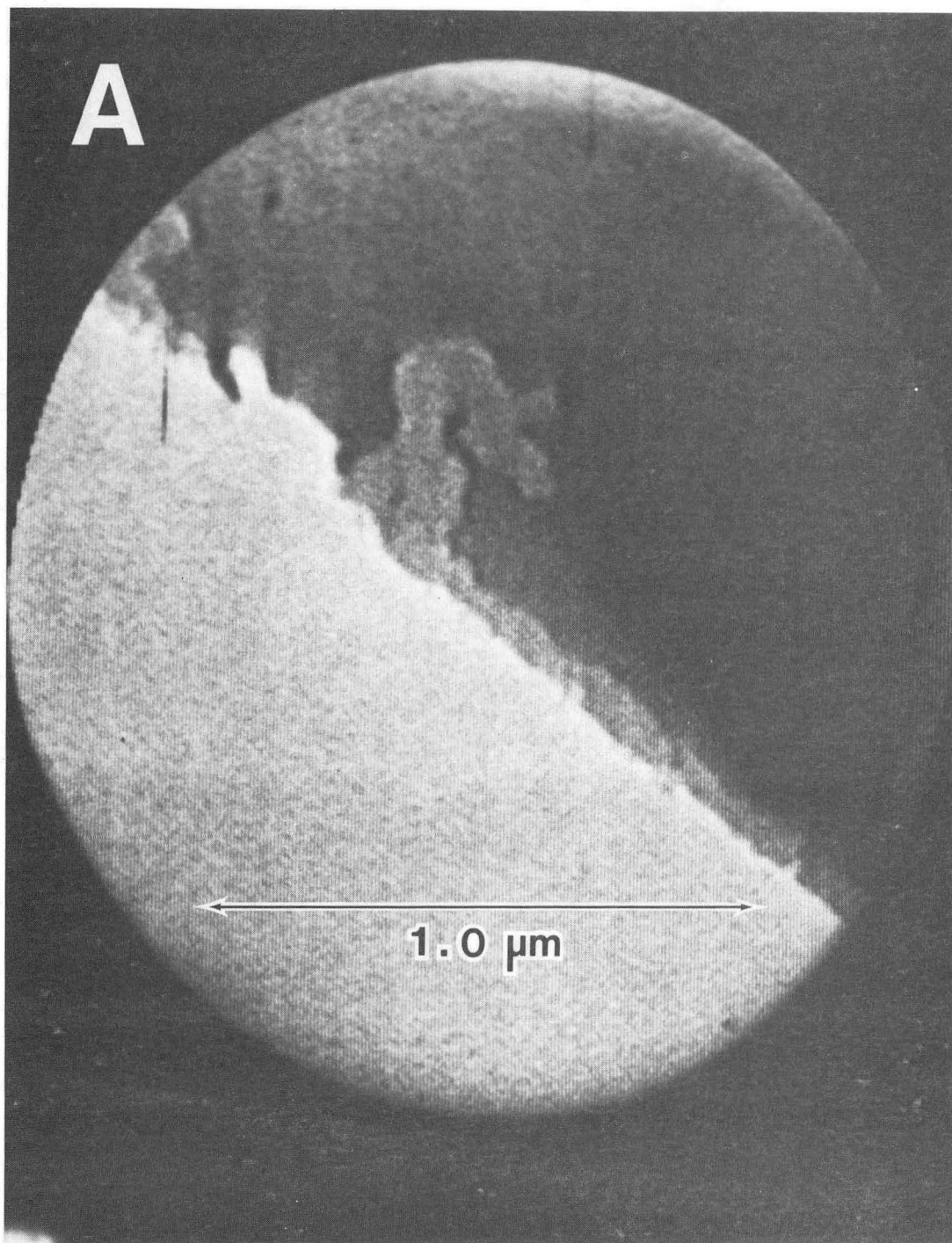


Figure 4.5: CAEM sequence of photographs of the carbon attack promoted by the nickel-potassium mixture at 923 K in wet O_2 , showing the irregular channels formed before catalyst spreading. Notice also the erosion of the edges, which is the first indication of edge recession attack. The time between photographs is 10s.

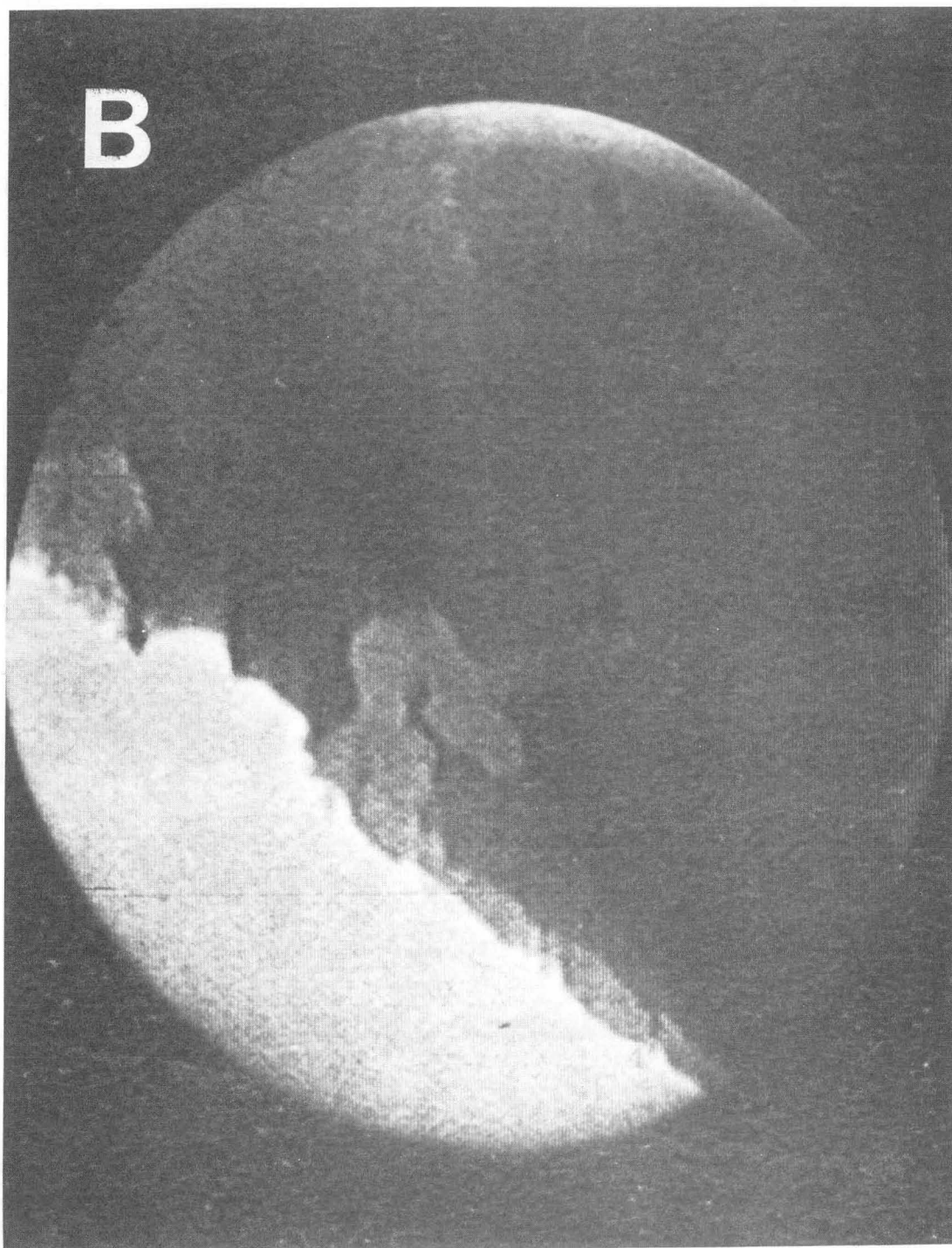


Figure 4.5b

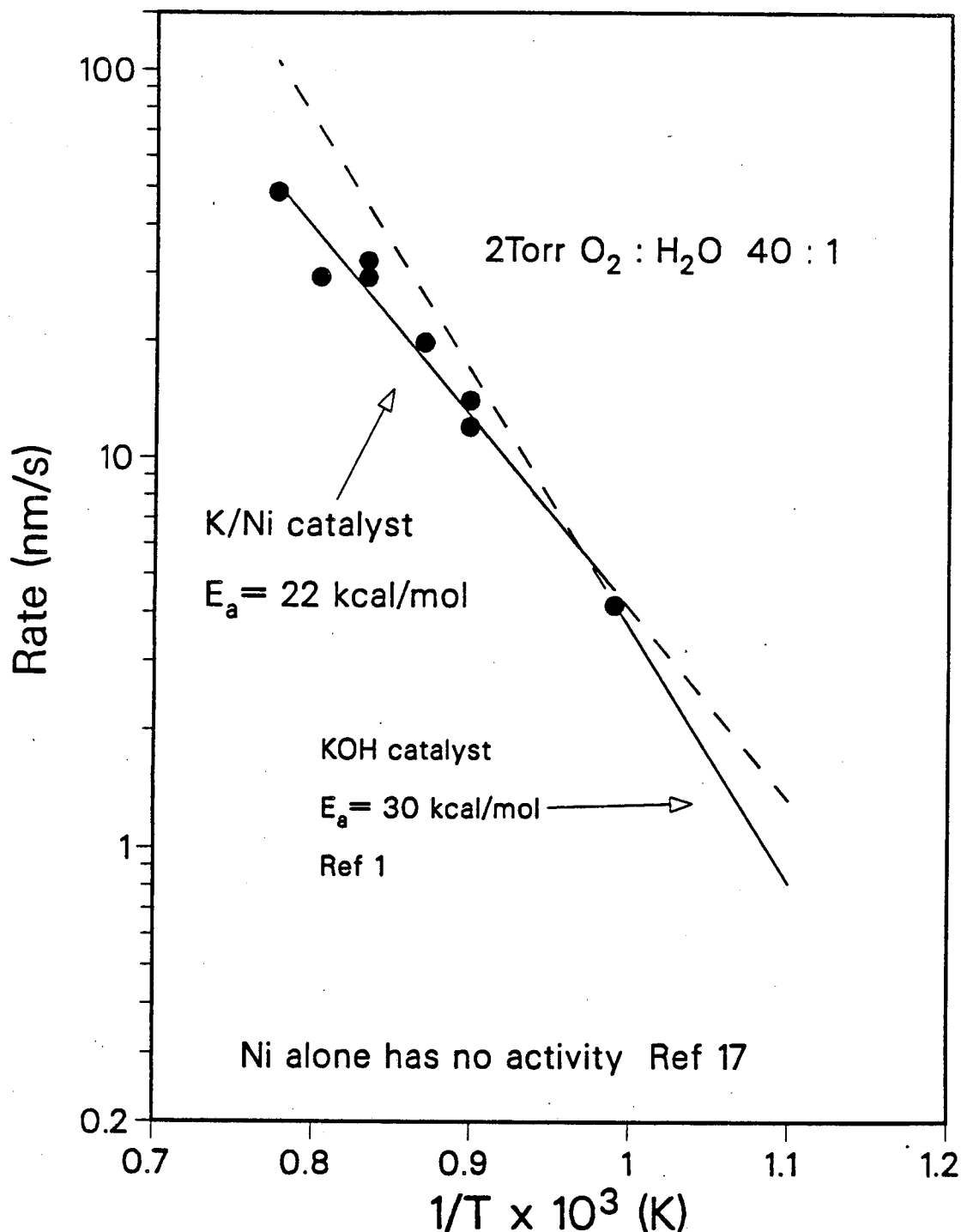


Figure 4.6: Arrhenius plot of the nickel-potassium catalyzed edge recession rates of graphite consumption in 2 Torr of wet O₂. The results previously reported for KOH alone are also presented. The length of the curves indicates the temperature range studied. The dotted lines are extensions of the curves, included to facilitate the comparison.

The surface tension forces between the carbon substrate (solid), the catalyst (liquid) and the gas environment control the wetting properties of the catalyst, and are responsible for the different modes of attack observed. The catalyst spreads over the carbon surface, and favors edge recession, because the sum of the surface tensions at the catalyst-substrate (γ_{sl}) plus catalyst-gas (γ_{lg}) interfaces is lower than the surface tension at the gas-substrate interface (γ_{sg}).

$$\gamma_{sg} > \gamma_{lg} + \gamma_{sl} \quad (4.1)$$

This is the case in H_2O vapor and $\text{O}_2/\text{H}_2\text{O}$ environments. There are, however, differences in catalyst behavior in these two environments. In wet O_2 at 770 K, the catalyst forms particles that only wet the carbon surface, and as the temperature raises above 920 K these particles spread over the edge planes. In wet Ar the opposite behavior is observed. The catalyst spreads at temperatures as low as 770 K, and as the temperature approaches 1250 K particle nucleation takes place.

Changes in the interface interactions due to chemisorbed species on the carbon surface, and/or oxidation state of the catalyst can be responsible for this difference. In wet O_2 the edge surfaces of graphite are covered with oxygen containing species [5,6]. This lowers the gas-solid surface tension (γ_{sg}) to such an extent that equation 4.1 is no longer satisfied, and particle nucleation is favored. These species desorb from the surface between 850 and 920K [5,6], and since the surface free energy of clean edge planes of graphite is much higher than that of the catalyst [7,8], spreading becomes now favored. In H_2O vapor, below 923 K the catalyst interacts with a larger fraction of clean edges than in the O_2 case because the sticking coefficient of H_2O on graphite is much smaller than that of O_2 [5]. For this reason, in the wet Ar case the catalyst spreading over the edge surfaces is observed as soon

as the nickel-potassium mixture becomes mobile. As the temperature approaches 1250 K, H_2 formed in the graphite- H_2O vapor reaction builds up in the cell. This changes the wetting properties of the catalyst, and favors particle nucleation.

A second difference between these two cases is the direction of the edge recession attack. In wet O_2 the edge recession does not follow a particular orientation, while in wet Ar this mode of attack occurs only parallel to the $[11\bar{2}0]$ crystallographic direction. A preferred orientation for the gasification of graphite in various gas environments has been reported for many catalysts [8]. At this point the reasons for this preferential direction are not well understood. Several suggestions have been made in the literature, but they do not explain all the cases studied. It has been suggested [9] that because H_2O vapor adsorbs preferentially at "arm chair" sites [10], the graphite gasification is favored in a $[11\bar{2}0]$ direction. This, however, is not always the case, since several transition metals catalyze the H_2O attack of graphite in the $[10\bar{1}0]$ direction. It has also been suggested [8] that the affinity of the catalyst to a particular edge face is the driving force for the gasification in that direction, but our observations indicate that the catalyst spreads over the whole edge, and carbon attack is only promoted in a particular direction.

In wet H_2 between 850 and 1250 K, both edge recession and channeling modes of attack are observed simultaneously, since a fraction of the catalyst spreads upon the edges, while the rest only wets them. The channelling attack is probably due to Ni metal, since the characteristics observed in our study are very similar to those reported previously when nickel was deposited alone on graphite [2]. The edge recession, on the other hand, can only be explained as the result of the interaction between nickel and potassium, because nickel deposited alone does not show any evidence for this mode of attack in wet H_2 [2] and potassium salts are not active

for carbon gasification in reducing environments [11]. Furthermore, this mode of attack has not been previously reported in reducing environments.

The nickel-potassium interaction in wet H_2 is suppressed above 1250 K, but can be recovered by lowering the temperature. This indicates that the suppression is due to the decomposition of the active species, rather than its deactivation. In chapter 5, based on an XPS study, it is suggested that the activity of the nickel-potassium mixture is due to the formation of a mixed oxide. This oxide can be reduced by H_2 above 1250 K, suppressing the edge recession activity. When the temperature is decreased, the mixed oxide is formed again, and the activity recovered. In chapter 3, it is concluded that potassium only interacts with NiO, and does not affect the properties of Ni metal. This is in agreement with the fact that the channeling activity observed for the nickel-potassium catalyst is the same as that of Ni alone.

The catalytic properties of the nickel-potassium mixture for carbon gasification are different, and in some cases superior, than those of nickel or potassium alone. In the reaction between H_2O vapor and graphite the clearest advantage of the nickel-potassium mixture is its resistance to deactivation. CAEM [1,3] and flow reactor [12,13] studies show that both potassium and nickel deactivate when used as catalysts for steam gasification of graphite below 1000 K. On the contrary, this study shows that the nickel-potassium mixture does not show any sign of deactivation in wet Ar up to 1370 K. This result is in agreement with flow reactor studies reported in chapter 3. In wet H_2 , the intrinsic activity of the nickel-potassium mixture is two times higher than the one reported for nickel alone, while potassium salts are inactive. Furthermore, the nickel-potassium mixture favors an edge recession mode of attack and nickel alone promotes channeling, therefore the

difference in total rate of carbon consumption should be even higher. In wet O_2 , the rates of edge recession for potassium alone and nickel-potassium are similar and neither of them deactivate. There are differences, however, between these two systems. The activation energy in the nickel-potassium case (22 kcal/mol) is lower than the one reported for potassium alone (30 kcal/mol), and even though both promote an edge recession mode of attack for the reaction between O_2 and graphite, in the nickel-potassium case there is no preferential direction of attack, while in the case of potassium alone the carbon consumption occurs parallel to the $[10\bar{1}0]$ direction.

The distinct catalytic properties of the nickel-potassium system are due to a cooperative effect between the components. This effect increases the surface mobility of the mixed catalyst, and allows its spreading over the edge planes of graphite. The excellent contact between catalyst and substrate, even at high temperatures (~ 1300 K) is probably the reason why the nickel-potassium mixture does not deactivate. It has been reported, for example, that the Ni metal catalyst deactivates because it loses contact with the active planes of graphite [13].

The nickel-potassium interaction also stabilizes potassium on the surface. No loss of catalyst was observed in any of the experimental conditions studied in this chapter. On the contrary, in the case of KOH alone, it was reported that the experiments had to be carried out below 900 K to prevent potassium vaporization [1]. A similar conclusion was reached in chapter 5, based on XPS results.

This cooperative effect has also been observed in other systems. In H_2O vapor, CAEM studies of platinum-barium catalysts [14] indicate that this mixture is more resistant to deactivation than the components used independently. In wet H_2 , mixtures of K_2SO_4 and $FeSO_4$ form a molten phase at 923 K and this phase

has a higher steady state activity and an improved CH_4 selectivity than the components used alone [15]. A CAEM study of the catalytic activity of nickel-calcium mixtures for graphite gasification in wet Ar has been reported [3]. This catalyst shows several similarities with the nickel-potassium catalyst for the H_2O vapor-graphite reaction. The catalytic properties of the nickel-calcium mixture, as in the case of nickel-potassium, can only be explained by the interaction between the components. Both systems spread over the edge surfaces of carbon between 770 and 870 K, and they both promote an edge recession mode of attack in the $[11\bar{2}0]$ orientation. Also, both systems maintain their activity at high temperatures and no sign of deactivation was observed. The nickel-potassium mixture, however, is more active and shows a lower activation energy than the nickel-calcium one. The same result was presented in chapter 3, based on a flow reactor study, and has also been reported by other authors [16].

4.4 Summary

The catalytic properties of nickel-potassium mixtures in H_2O , $\text{H}_2/\text{H}_2\text{O}$ and $\text{O}_2/\text{H}_2\text{O}$ atmospheres have been studied by controlled atmosphere electron microscopy. In H_2O and $\text{O}_2/\text{H}_2\text{O}$ environments an edge recession mode of attack is favored, and no sign of deactivation was observed. In $\text{H}_2/\text{H}_2\text{O}$, both edge recession and channeling occur simultaneously and the catalyst deactivates above 1273 K. This is the first reported system to favor carbon attack by edge recession mode in reducing environments. The distinct morphological properties of the nickel-potassium mixture are further proof of cooperative effect between the components on the promotion of graphite gasification.

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Chapter 5

X-ray Photoelectron Spectroscopy Study Of The Nickel-Alone, Potassium-Alone And Nickel-Potassium Catalysts For Steam Gasification Of Graphite

5.1 Introduction

In previous chapters it has been concluded that the catalyst derived from a mixture of $\text{Ni}(\text{NO}_3)_2$ and KOH shows properties for steam gasification of carbon solids that indicate a very strong interaction between nickel and potassium.

Kinetic experiments (chapter 3) show that the potassium-nickel catalyst is active under conditions in which the components alone are inactive. Furthermore, the mixture remained active for long periods of time (up to 400 hours), under reaction conditions.

The electron microscopy study presented in chapter 4 indicates that the mixture is very mobile under reaction conditions. It spreads over the edge planes of graphite, even under reducing environments, and favors the steam gasification of carbon by edge recession in the $[11\bar{2}0]$ direction.

In chapter 3 it is also shown that the catalyst derived from $\text{Ni}(\text{NO}_3)_2$ alone is active when it is prereduced previous to the introduction of steam. Its initial activity is higher than that of the nickel-potassium catalyst, but it deactivates before total carbon conversion.

This chapter presents an XPS study performed on catalysts derived from $\text{Ni}(\text{NO}_3)_2$ and KOH, deposited either together or by themselves. The purpose of this study is to correlate the catalytic results described in chapter 3 with surface properties of nickel and potassium. First kinetic results obtained with the three catalyst studied will be presented. Their purpose is to define a set of experimental conditions in which the kinetic differences between the various catalysts studied is clear. Then XPS studies performed under these conditions are presented. They were carried out on identical samples to those used for kinetic experiments. These experiments should establish a correlation between changes in the kinetic behavior of these catalyst with oxidation state and surface concentration of nickel and potassium.

5.2 Results

5.2.1 Kinetic Results

Nickel-Alone Catalyst

When $\text{Ni}(\text{NO}_3)_2$ deposited alone on graphite is only pretreated in Ar at 723 K, no steam gasification activity is observed at 893 K for up to 2 hours. The catalyst is only active when it is pretreated under reducing environments. (H_2 at 723 K, or Ar at 923 K in which case carbon is the reducing agent). In this case the initial carbon consumption rate is equal to 1.3 (mol C/mol Ni)/min with a ratio of CO/CO_2 equal to 0.22. The initial rate of carbon consumption is maintained

for the first ten minutes, and it then decreases very rapidly (see figure 5.1). After 80 to 200 min, depending on the sample, the catalyst has completely deactivated. At this point a graphite conversion of $62 \pm 15\%$ has been reached, as determined by both carbon weight loss and total gas production. (See chapter 2 and 3).

After the catalyst has completely deactivated, its activity cannot be recovered by either treatments in reducing conditions (923 K in Ar or 723 K in H_2) or by a combination of oxidizing and reducing conditions (723 K in O_2 and then 923 K in Ar).

Potassium-Alone Catalyst

No steady state gasification rate at 893 K is observed when KOH is deposited alone on graphite. The same result is obtained when KNO_3 is used instead of KOH. If the sample is heated to 1073 K, a rate of carbon consumption equal to $0.18(\text{mol C/mol K})/\text{min}$ is observed, with a ratio of CO/CO_2 in the gas products equal to 0.15. Treatment in an O_2 atmosphere at 723 K prior to the introduction of steam did not change these results.

Nickel-Potassium Catalyst

When the catalyst derived from a 1:1 molar mixture of KOH and $Ni(NO_3)_2$ loaded on graphite is treated in Ar at 723 K, and then exposed to H_2O at 893 K, an initial carbon consumption rate of $1.3 \times 10^{-2}(\text{mol C/mol Ni})/\text{min}$ is observed, with a CO/CO_2 ratio of 0.08 (figure 5.1). Over a period of 24 hours, the product distribution remains constant, and the reaction rate decreases by only 10 %.

When the nickel-potassium catalyst is reduced in H_2 , previous to the introduction of steam, an initial high carbon consumption rate of $0.75(\text{mol C/mol Ni})/\text{min}$

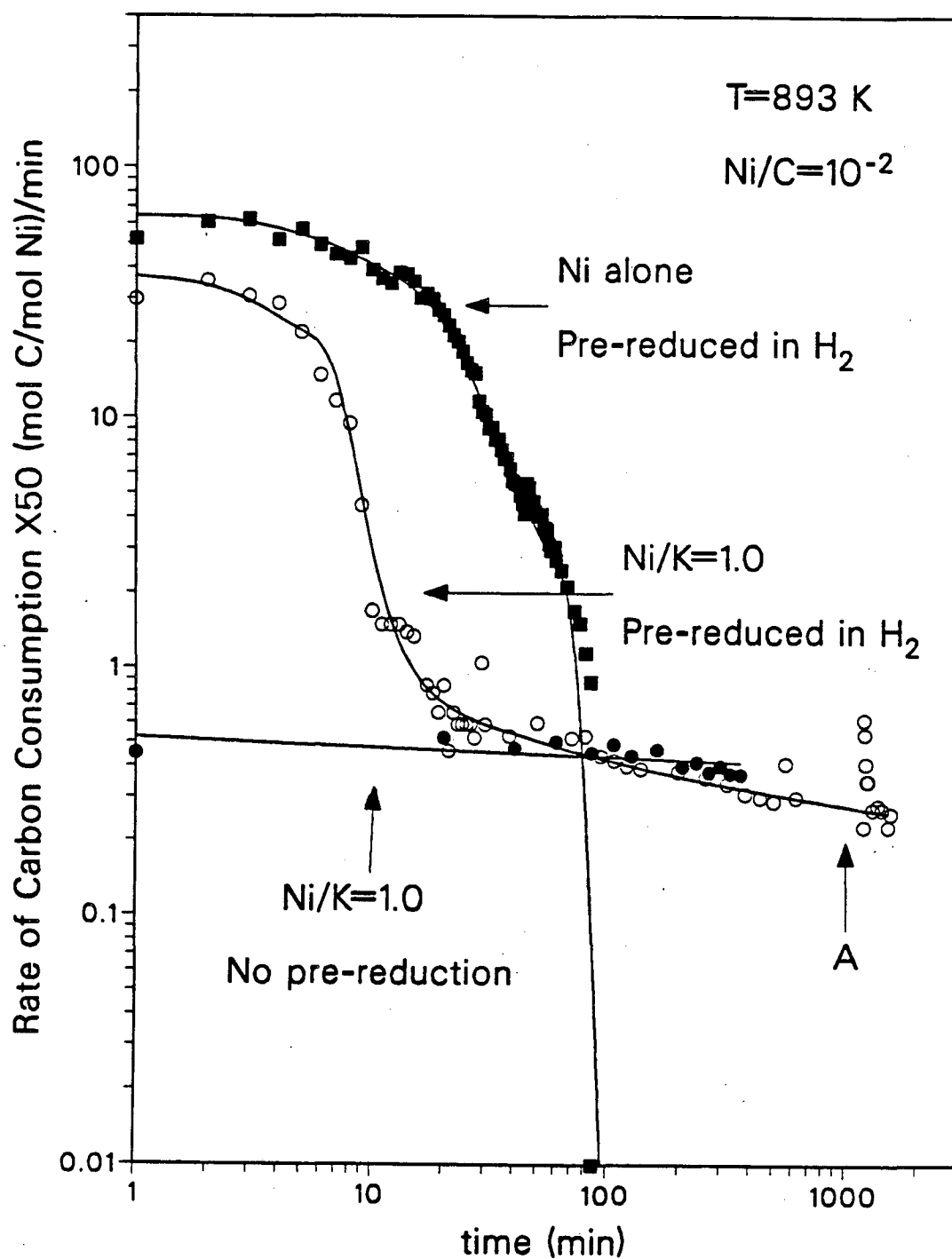


Figure 5.1: Rate of carbon consumption, as a function of time, for steam gasification of graphite at 893 K, promoted by catalysts derived from $\text{Ni}(\text{NO}_3)_2$ alone and mixed with KOH. In all cases the ratio of Ni/C is equal to 10^{-2} and the H_2O mass flow was equal to $5.6 \times 10^{-2} \text{ mol/min}$ at 760 Torr. Experiments were carried out after prereduction in H_2 at 723 K, or heat treatment in Ar at 723 K.

is observed, with a CO/CO_2 ratio equal to 0.33. Even though this rate is lower than that obtained with nickel alone, the nickel-potassium catalyst prereduced in H_2 does not deactivate completely. (See figure 5.1). After 20 min, the reaction rate is similar to that obtained when the catalyst has not been pre-reduced, and from there on both cases show the same kinetic behavior. If the catalyst is treated again in H_2 at 943 K after 10 hours in H_2O at 893 K (point A in figure 5.1), no noticeable increase in the rate of carbon consumption is observed after the re-introduction of H_2O at 893 K.

5.2.2 XPS Results

Nickel-Alone Catalyst

Bulk NiO is formed at 723 K in vacuum, when $\text{Ni}(\text{NO}_3)_2$ is deposited alone on graphite. Curve A in figure 5.2 shows that after this treatment the $\text{Ni } 2p_{3/2}$ adiabatic peak has a binding energy of 855.2 eV, which is 1.4 eV higher than that observed for Ni foil, and a satellite at 862.2 eV, both typical of NiO . The adiabatic peak has a tail at higher binding energies, with an intensity due to the contributions of the multiplet splitting signal, typical of high spin Ni(II) species, and some surface $\text{Ni}(\text{OH})_2$ [1]. The $\text{O } 1s$ signal shows a peak at 530 eV, typical of transition metal oxides, and a shoulder at 532 eV, due to the presence of surface OH^- groups [2] (figure 5.3). Graphite is not able to reduce NiO at 893 K in the presence of 10 Torr H_2O for 10 min (see figure 5.2 curve B). Longer exposures under the same conditions (up to 135 min) do not alter this result.

NiO deposited on graphite is partially reduced to the metallic state, when it is heat treated in vacuum at 923 K. A comparison of curve A in figures 5.2 and 5.4 shows that the position of the $\text{Ni } 2p_{3/2}$ adiabatic peak has shifted to a

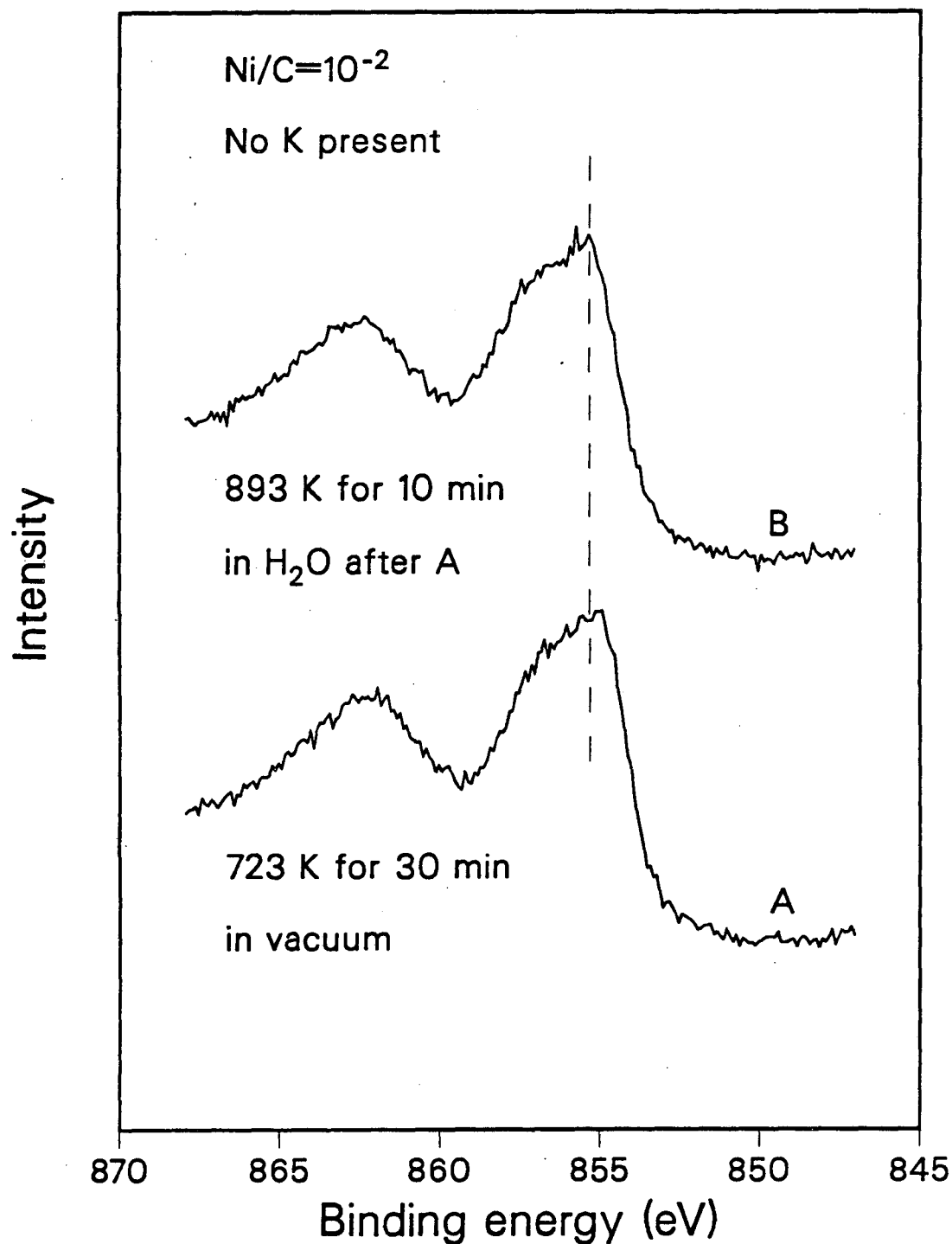


Figure 5.2: Ni 2p_{3/2} XPS signal of the catalyst derived from Ni(NO₃)₂ alone after (a) heat treatment in vacuum at 923 K, and (b) further exposure to H₂O vapor at 893 K.

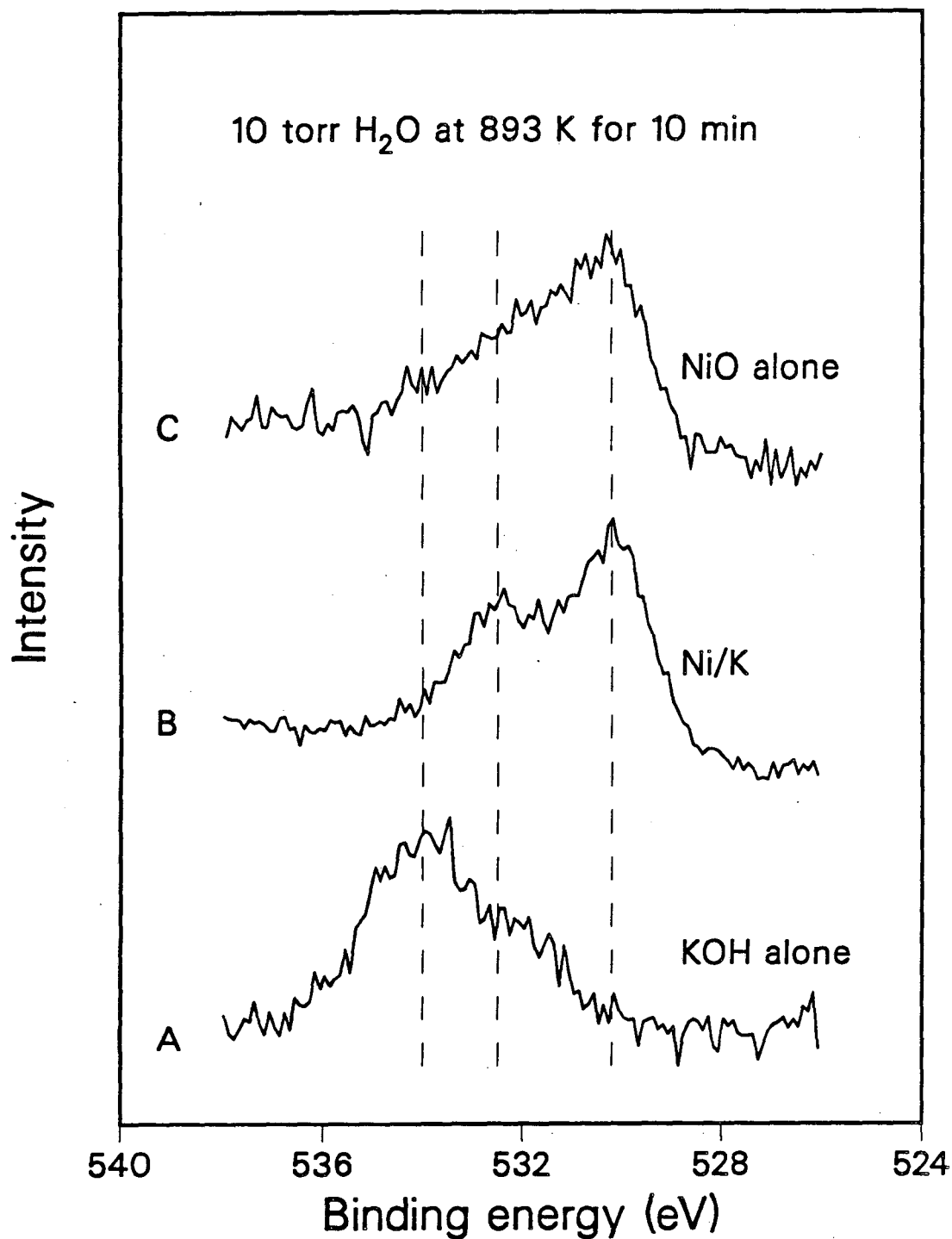


Figure 5.3: O 1s XPS signal obtained for (a) KOH alone on graphite after 10 min in H₂O at 893 K, (b) the catalyst derived from a KOH/Ni(NO₃)₂ mixture after 135 min in H₂O at 893 K, and (c) NiO after 10 min in H₂O at 893 K.

lower binding energy (854.7 eV), and the intensity of the multiplet and satellite peaks has decreased considerably after the heat treatment at 923 K. There is also a decrease in intensity of the O 1s peak at 530 eV, corresponding to a reduction of 60% of the NiO to the metallic state. Further treatment of the sample at 923 K in vacuum did not increase the percentage of metallic Ni in the sample, as observed by XPS.

When the sample just described (after the heat treatment at 923 K in vacuum) is treated in a 10 Torr flow of H₂O at 893 K for 10 min, an almost complete reduction of the NiO is observed (see figure 5.4 curve B). The binding energy of the Ni 2p_{3/2} peak (853.8 eV) is very close to that obtained for Ni foil, and the O 1s signal is very small. However, a H₂O treatment at 893 K for 80 more minutes, reoxidizes the metal to NiO as shown in figure 5.4 curve C. The binding shift of the Ni 2p_{3/2} peak to 855.4 eV, and the reappearance of the O 1s signal at 530 eV are evidence of the oxidation process.

After NiO is formed during the H₂O vapor treatment, it cannot be reduced back to the metallic state by heat treatment in vacuum at 923 K, as shown in figure 5.5 curve A. Reduction of the NiO is possible by treatment in H₂ at 723 K (figure 5.5 curve B), but exposure to H₂O vapor at 893 K for 5 min after this treatment is enough to completely reoxidize the metal (curve C in figure 5.5).

Potassium-Alone Catalyst

When a graphite sample loaded with KOH is heated at 723 K in vacuum, surface enrichment by potassium is observed. The binding energy of the K 2p_{3/2} peak (294 eV) is close to that reported for bulk KOH [3]. From the ratio of intensities of the K 2p_{3/2} and C 1s signals, a surface ratio of potassium to carbon equal to 0.2

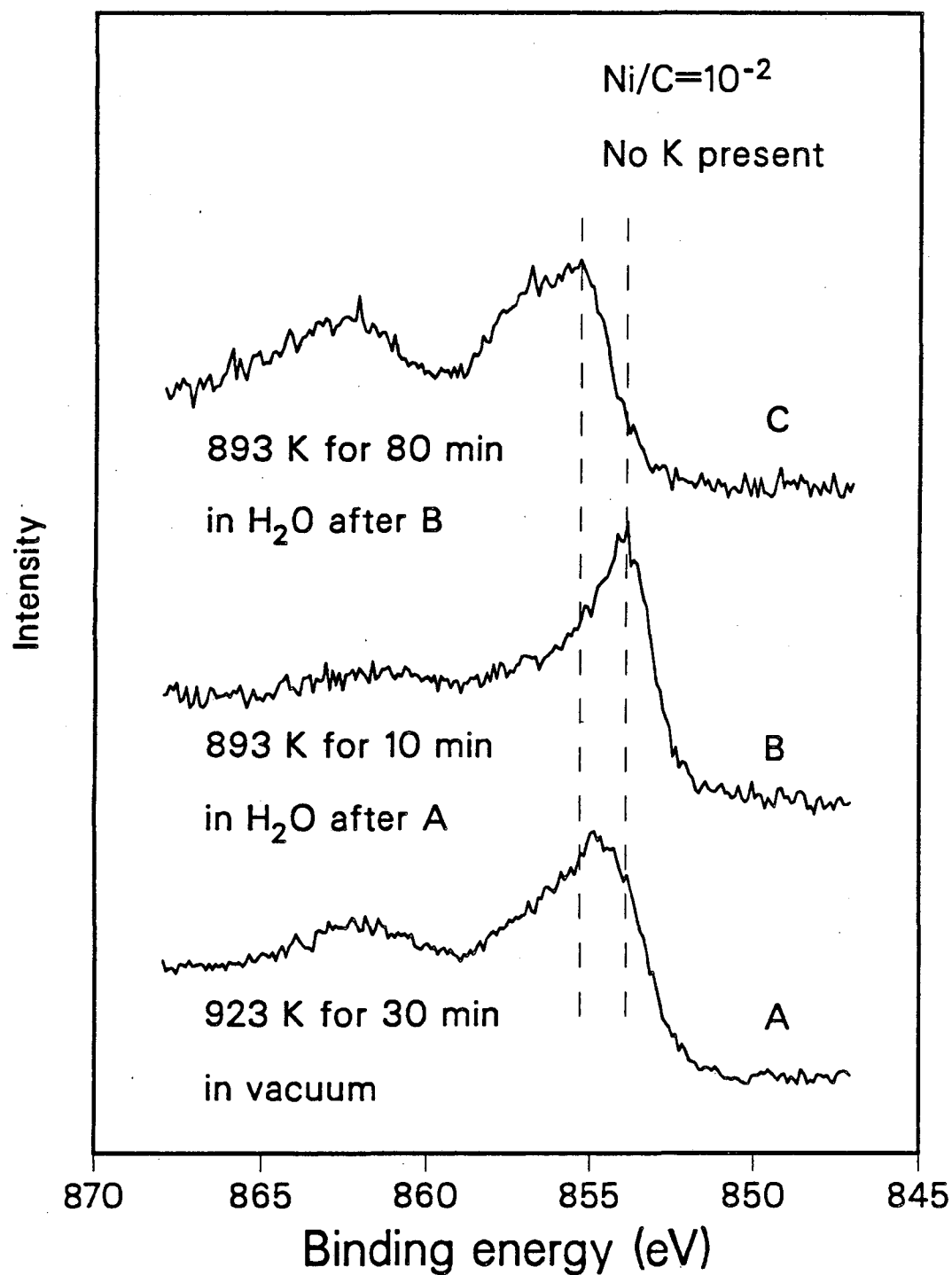


Figure 5.4: Ni 2p_{3/2} XPS signal of the catalyst derived from Ni(NO₃)₂ alone after (a) treatment in vacuum at 923 K, and further exposure to H₂O vapor at 893 K for (b) 10 min and (c) 90 min.

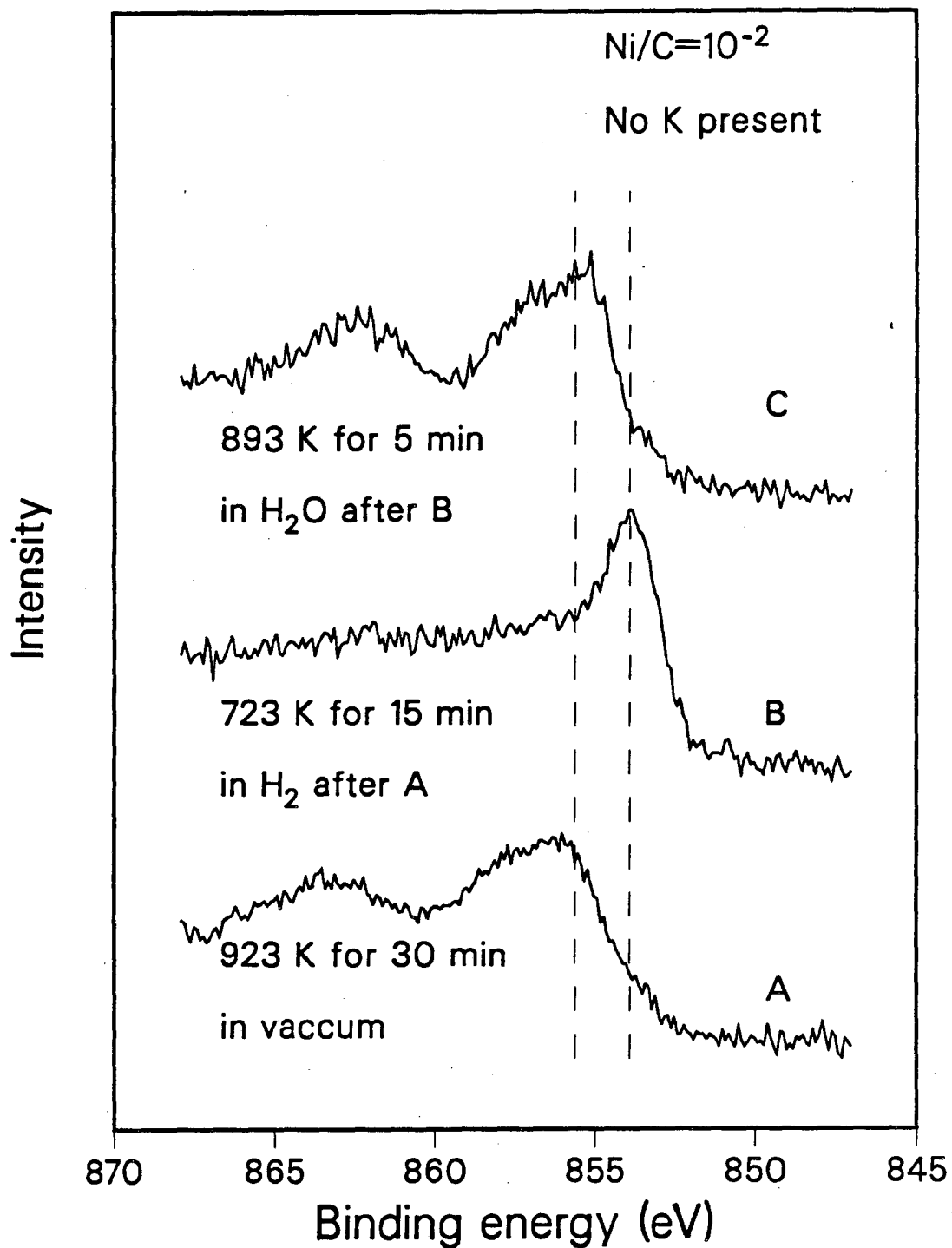


Figure 5.5: Ni 2p_{3/2} XPS signal after various treatments performed on a catalyst derived from Ni(NO₃)₂, and previously exposed to H₂O at 893 K for 90 min.

is determined, which is higher than the initial bulk concentration (K/C equal to 10^{-2}). The O 1s binding energy at 532 eV, typical of a hydroxyl group, and the ratio of potassium to oxygen equal to 0.9, suggest the presence of multilayers of KOH on the graphite surface.

After treating this sample in 10 Torr of H_2O at 893 K for 10 min (figure 5.6 curve A), the potassium signal decreases drastically and the binding energy of the K $2p_{3/2}$ peak shifts to higher values, compared with bulk KOH. The peak position varies from sample to sample, and an average of 295.0 ± 1.0 eV was determined. The O 1s signal also decreases and shows a peak at 534 eV with a shoulder at 532 eV.

If the sample is treated for 60 more minutes in H_2O the K 2p signal completely disappears (see figure 5.6 curve B). Very similar results are obtained if KNO_3 is deposited on graphite instead of KOH.

Nickel-Potassium Catalyst

Heat treatment at 723 K in vacuum of a mixture of KOH and $Ni(NO_3)_2$ deposited on graphite favors the formation of NiO. The binding energy and lineshape of the Ni $2p_{3/2}$ signal obtained after this treatment for the $Ni(NO_3)_2/KOH$ mixture is the same as that obtained after treatment of $Ni(NO_3)_2$ alone. The O 1s signal shows two peaks at 530 and 532 eV. The peak at 530 eV is associated with the presence of NiO, and the one at 532 eV with the presence of multilayers of KOH on the carbon surface. This treatment also favors the diffusion of potassium to the graphite surface. The K $2p_{3/2}$ binding energy is 293.8 eV and the ratio of potassium to carbon is equal to 0.12, much higher than the initial bulk ratio (K/C equal to 10^{-2}).

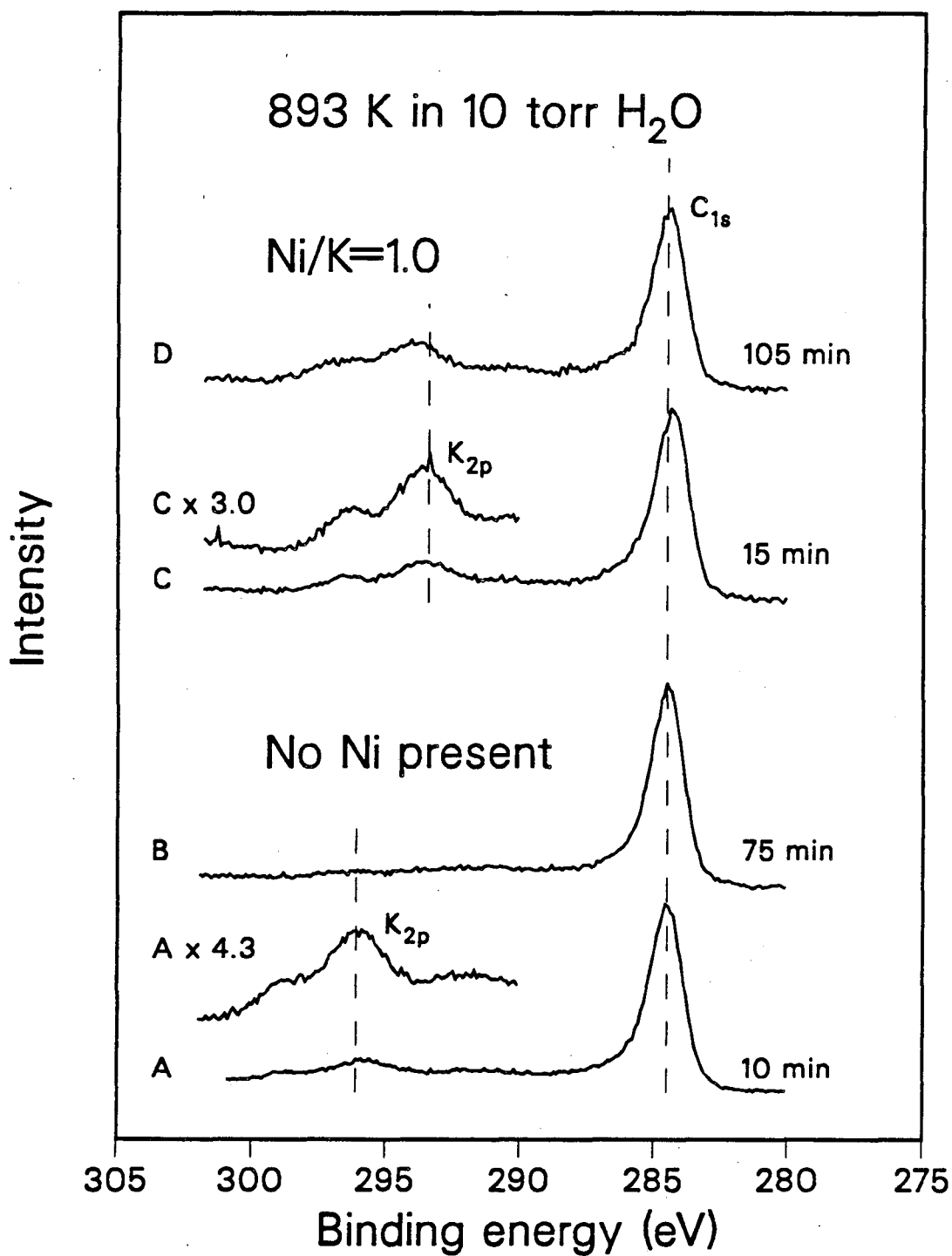


Figure 5.6: C 1s and K 2p XPS signals of catalysts derived from KOH alone and mixed with Ni(NO₃)₂ after various exposure-times to H₂O at 893 K.

After exposing the vacuum treated sample to a 10 Torr flow of H_2O at 893 K for 15 min, the amount of potassium on the surface decreases substantially (curve C in figure 5.6). The K $2p_{3/2}$ binding energy in the case of the mixture remains at 294 eV, in contrast to the shift to higher binding energy observed for the potassium-alone catalyst (compare curves A and C in figure 5.6). In the case of the nickel-potassium mixture, the O 1s signal still shows two peaks at 530 and 532 eV. The intensity of the 532 eV peak decreases to a value such that the atomic ratio of potassium to oxygen remains equal to 1.0. The intensity of the 530 eV peak remains constant, indicating that NiO is still present. This is corroborated by the Ni $2p_{3/2}$ lineshape and binding energy (855.2 eV) (see figure 5.7 curve A). Exposure of this sample to H_2O vapor for 120 more minutes did not change either the oxidation state of nickel or the surface concentration of potassium. As mentioned previously, a similar treatment in the case of KOH deposited was enough to suppress completely potassium from the carbon surface (compare curves B and D in figure 5.6).

When a fresh nickel-potassium catalyst is treated in H_2 at 723 K, formation of Ni metal, and surface diffusion of potassium are observed, as is the case when two components are loaded by alone on graphite. When the mixture is then treated in H_2O vapor at 893 K for 5 min, partial oxidation of the Ni metal is observed (figure 5.7 curve B), and a 10 min treatment is enough for a complete oxidation. This result is the opposite to that observed for the nickel catalyst, where after 10 min treatment in H_2O , only Ni metal is present (compare curve C in figure 5.7 with curve B in figure 5.4). After 10 min in H_2O vapor at 893 K, the surface concentration of potassium and binding energy of the K $2p_{3/2}$ peak is the same, regardless of if the sample has been pre-reduced or not.

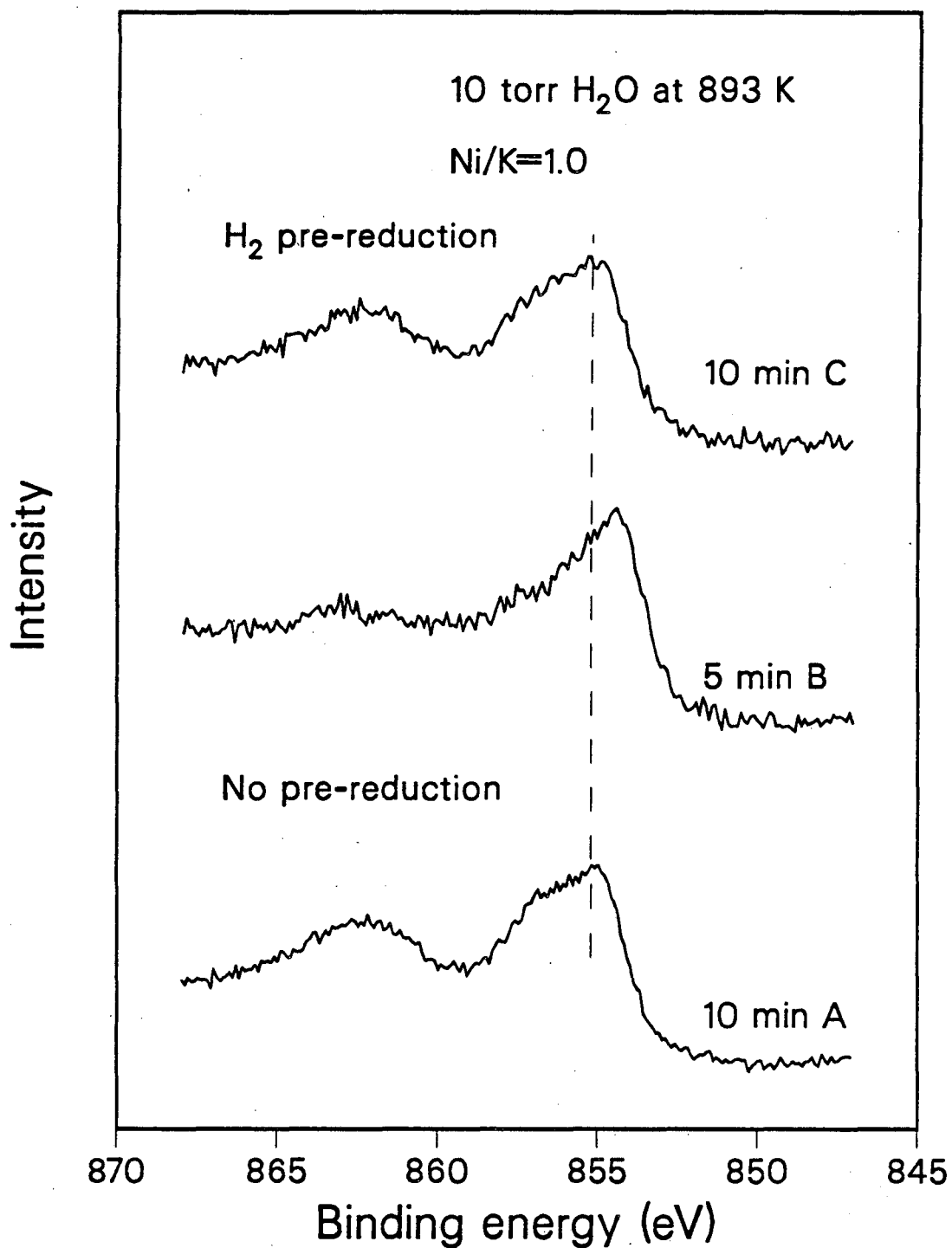


Figure 5.7: Ni 2p_{3/2} XPS signal after various treatments performed on a catalyst derived from a mixture of KOH and Ni(NO₃)₂.

5.3 Discussion

5.3.1 Nickel-Alone Catalyst

The results obtained for the catalyst derived from $\text{Ni}(\text{NO}_3)_2$ alone are summarized in figure 5.8. These results show, as also indicated by McKee [?], that the activity of the nickel catalyst for graphite steam gasification can be associated with the presence of the metal under reaction conditions. After 10 min exposure to H_2O at 893 K, figure 5.1 show that the catalyst is active, and figure 5.4 curve B shows that metallic nickel is present, whereas after 90 min, the catalyst has completely deactivated, and figure 5.4 curve C shows that NiO has been formed. The results also show that if the steam gasification reaction is carried out below 900 K, a pre-reduction step is necessary in order to activate the nickel. That is, if metallic nickel is initially present (curve A in figure 5.4), the catalyst is active because it can be stabilized under reaction conditions by its interaction with graphite (curve B in figure 5.4). If the pretreatment is such that NiO is formed instead (curve A in figure 5.2), then graphite is not able to reduce the oxide (curve B figure 5.2), and the catalyst shows no activity.

A mechanism for steam gasification of graphite by transition metals to form H_2 and CO_2 is described in equations (5.1) to (5.3), as proposed by several authors [?,?].



In this mechanism, below 900 K, equation 5.2 cannot involve the direct reaction between NiO and graphite, as indicated by our XPS results. In addition, if this

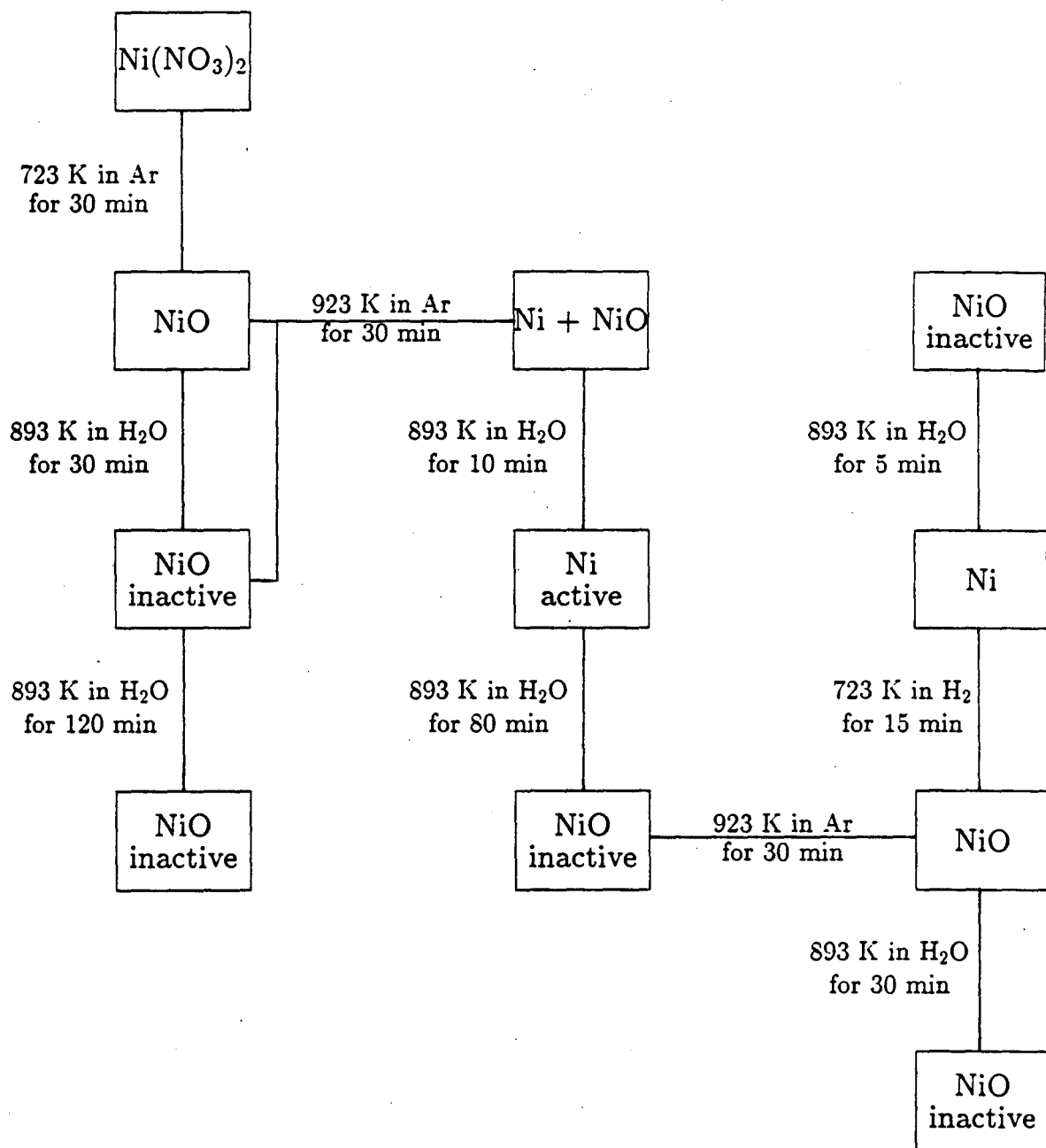


Figure 5.8: Summary of results obtained with the catalyst derived from $\text{Ni}(\text{NO}_3)_2$ alone

reaction were possible, the pre-reduction step just described should not be necessary, since the reaction represented by equation 5.2 would occur first, and then the metallic nickel would be oxidized by water, completing the cycle.

In order to justify the need of the preactivation step, equation 5.2 must involve the reaction of either surface carbon or surface oxygen on the nickel. Holstein and Boudart [5] suggest that a surface carbide is involved in the gasification reaction. This species can be formed at the nickel metal-graphite interface, followed by diffusion through the metal surface, and subsequent removal reaction with oxygen formed from the dissociative chemisorption of H_2O . Various surface science studies indicate the feasibility of these steps at 900 K (steam gasification reaction temperature) [6,7]. In the case of the nickel catalyst, magnetic studies have suggested that a bulk carbide is not being formed during the gasification reaction [8]. These results, however, do not discard the formation of a surface compound, since the technique used is only bulk sensitive.

Another possibility for the step represented by equation 5.2 is the reaction between oxygen chemisorbed on nickel metal, and graphite [9]. In this case, Ni metal serves as a site for dissociation of H_2O , and for recombination of H_2 . The chemisorbed oxygen left on the surface after dissociation of H_2O diffuses toward the nickel-carbon interface, and reacts with graphite to form CO. Production of H_2 and CO_2 are due to the reaction between CO and H_2O (water gas shift reaction).

These two models share a common point. In both cases Ni metal is the site for dissociation of H_2O , and it is required for the formation of an activated species. This species, then, has to diffuse across the nickel-carbon interface to form the oxygenated gas product.

Even though the presence of the metal correlates with the properties of the

nickel catalyst, the formation of NiO cannot be considered as the cause of the loss of activity, but rather as another consequence of the deactivating process. The results in figure 5.5 show that once the catalyst has deactivated, and NiO formed, Ni metal can be recovered by heating in H_2 at 723 K. This treatment, however, does not regenerate the catalyst, and figure 5.5 curve C shows that exposure to H_2O vapor at 893K for 5 min is enough to completely reoxidize the metal. This is contrary to a fresh sample, where Ni metal is maintained after H_2O exposure at 893 K for 10 min (see figure 5.4 curve B).

Our results indicate that, in the steam gasification of graphite, deactivation occurs when carbon is no longer able to stabilize Ni metal under reaction conditions. It is proposed, in agreement with Wigmans *et al.* [10,11], that this occurs because there is a loss of contact between nickel and the edge planes of carbon, hindering the diffusion of either surface oxygen or surface carbon species. This then prevents the removal of oxygen from the chemisorption of H_2O , and allows the formation of NiO. The fact that graphite cannot reduce NiO at 973 K in Ar in the case of the deactivated sample (figure 5.2 curve A), whereas this treatment is as effective as the H_2 treatment in the case of the fresh sample, indicates that there is no intimate contact between the deactivated catalyst and the active planes of carbon.

A combination of several processes may be responsible for this total loss of carbon-nickel contact. Sintering of the nickel particles is certainly taking place under our reaction conditions (893 K in H_2O) [8,12]. This process reduces the contact area between carbon and nickel, but does not explain, by itself, the total loss of contact. It has been suggested that in addition to the sintering phenomenon, the presence of surface oxygen or surface carbon can decrease the wetting proper-

ties of nickel on carbon, and cause the complete separation of the nickel particles from the carbon edges [11,12].

The reasons for the deactivation of the nickel catalyst varies with the nature of the carbon substrate being gasified, as indicated by Lund [12]. For the case of graphite gasification, he suggests that deactivation is caused by sintering, in agreement with our conclusion, and in the case of an amorphous carbon (spherocarb), encapsulation of the metal particles by a graphitic layer is the cause of deactivation. XPS studies are an excellent way to distinguish between these two possible modes of deactivation, because of its sensitivity to oxidation state and surface concentration of the catalyst. When catalyst encapsulation takes place, dissociative chemisorption of H_2O is hindered, and therefore metallic Ni should remain on the surface, once the catalyst deactivates. This is the reverse of the situation described in this work for the case of graphite gasification, where NiO is formed on the surface when the catalyst deactivates, due to the loss of catalyst-carbon contact.

5.3.2 Potassium-Alone Catalyst

Under our reaction conditions (below 900 K), KOH deposited alone is inactive for catalytic steam gasification of graphite. This result was also observed by Dellanay *et al.* [13] on the same carbon substrate (graphite UCP-2). They suggested that KOH interacts with oxygen containing species formed from the dissociation of H_2O on the carbon surface, to form a compound that could only be thermally decomposed above 950 K. These surface species have also been proposed by other authors. Mims *et al.* [14] suggested the formation of a "phenoxide" on the surface based on solid state NMR results, and Kelemen *et al.* [15] reported the formation of

a potassium surface compound at submonolayer coverages, based on UPS results.

Our XPS results also suggest the interaction of potassium ions with oxygenated carbon surface species. This interaction is able to stabilize a small fraction of potassium on the surface, under conditions in which bulk KOH would not be present. After treatment in 10 Torr of H₂O at 893 K for 10 min, a K 2p_{3/2} binding energy of 295±1 eV was obtained. This value is higher than that observed for multilayers of KOH on graphite, even considering that its precision is not as good as those obtained for all the other cases. The higher potassium binding energy suggests that the potassium-oxygen bound has a larger ionic character than in KOH. This assumption is in agreement with the formation of a C-O^{-δ}K^{+δ} species, where the stabilization of the negative charge by the resonant π -system in graphite can be larger than by hydroxyl groups.

A probable reason for the low precision in the potassium-binding energy measurements is the low intensity signal. After a 10 min H₂O treatment at 893 K, a potassium to carbon atomic ratio equal to 10⁻² was obtained. Even though this is only a lower bound limit for the potassium surface concentration, due to the mean free path of the photoelectrons involved (15Å at 1000 eV), it is safe to assume that it corresponds to a sub-monolayer coverage of potassium.

After treatment in H₂O at 893 K, the O 1s XPS signal shows a peak at 534 eV, with a shoulder at 532 eV (figure 5.3 curve C). The 532 eV shoulder can be associated with hydroxyl groups, and the 534 eV peak with carbon-oxygen surface groups [15]. From the intensities of the K 2p and O 1s at 532 eV signals, a potassium to carbon atomic ratio higher than one would be obtained. This suggests either the formation of some metallic potassium, as proposed by McKee [16], or the interaction of a fraction of the potassium ions with oxygenated species in the

graphite surface, which is also concluded from the K 2p analysis.

Figure 5.6 curve B shows that after a treatment in H_2O vapor for 75 min, no potassium is present on the surface. Our kinetic experiments, however, indicate that a catalytic rate of steam gasification is observed at 1073 K with the potassium-alone catalyst, suggesting that some potassium is present. The reason for this discrepancy might reside on the different H_2O pressures used in these experiments. In the XPS study, a continuous flow of 10 Torr of H_2O vapor was used, while in the kinetic study, the H_2O vapor pressure was above 760 Torr. Since the H_2O sticking coefficient on carbon is extremely small [17,18], the concentration of oxygenated surface species under the kinetic conditions is higher than under the XPS conditions. In the former case, thus, a higher concentration of potassium ions can be stabilized, making possible the high temperature catalytic activity of KOH alone. Kelemen *et al.* [15] have reported, based on AES results, that a much higher concentration of potassium ions can be stabilized on the surface of glassy carbon, when the substrate is oxidized previous to the potassium deposition.

5.3.3 Nickel-Potassium Catalyst

A summary of the results obtained with the catalyst derived from a mixture of KOH and $\text{Ni}(\text{NO}_3)_2$ is given in figure 5.9. These results indicate that the properties of the mixture are different from those of the components alone. In the case of the mixture, XPS results indicate that KOH and NiO are stabilized on the surface under reaction conditions. On the contrary, nickel is reduced to the metal when it deposited alone, and the potassium signal on XPS vanishes in the case of the potassium catalyst. Differences between the mixed catalyst, and the components alone have also been observed in other chapters, based on CAEM results (chapter

4) and on kinetic results on both graphite (chapter 3) and char gasification (chapter 6). Other authors have also reported similar situations for this [19], and other transition metal-alkali mixtures such as nickel-calcium [20], iron-sodium [21] and iron-potassium [22,23,24].

As reported in this and previous chapters, the catalytic property of the nickel-potassium mixture is the maintenance of its initial activity for long periods of time. This is certainly related to the fact that the catalyst remains in contact with the active planes of graphite, as observed in the CAEM study described in chapter 4. The CAEM study also shows that the catalyst activity is uniform among all the active areas in the carbon, indicating that nickel and potassium are uniformly distributed within the mixture. This study also shows that the catalyst mobility is high. The use of alkali metal salts to decrease the melting point of high temperature oxides is a very common procedure [25]. It is suggested, then, that the interaction between potassium and nickel can lower the high melting point of NiO by formation of a compound, which is either the active catalyst, or becomes a precursor for its formation. The formation of such a compound can also explain the stability of potassium ion on the surface under conditions at which KOH is not present. Our results suggest that potassium is stabilized by interaction with nickel, and not by its interaction with oxygenated groups in the carbon surface. If the latter were the case, a shift in the K 2p XPS signal to higher binding energies, and a higher intensity O 1s peak at 534 eV would be expected, as in the case of KOH alone. Neither result is observed. Also, the high catalyst mobility of the nickel-potassium mixture suggests that the mixture is not "anchored" to the carbon surface by interaction with oxygenated surface groups.

An important difference between the catalyst derived from $\text{Ni}(\text{NO}_3)_2$ alone, and

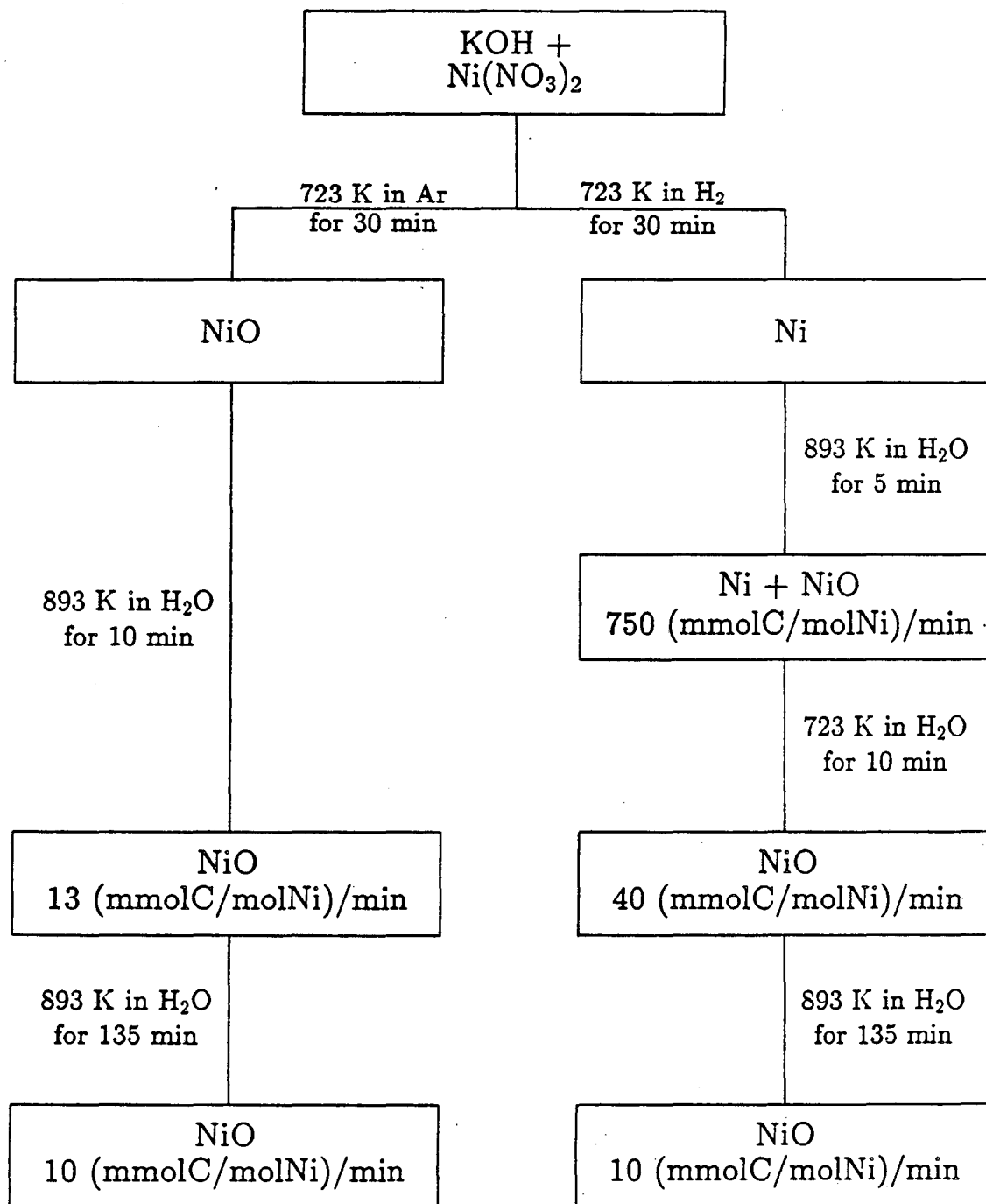


Figure 5.9: Summary of the results obtained with the catalyst derived from a mixture of KOH and Ni(NO₃)₂.

the one derived from the $\text{Ni}(\text{NO}_3)_2/\text{KOH}$ mixture is that the former is only active when the metal is present, while the latter is active in conditions where nickel in the +2 oxidation state is the major species. Furthermore, when both catalysts are present at the same time, the gasification rates obtained can be accounted for by the addition of the activities of the two catalysts. Figure 5.1 shows that when a catalyst derived from a $\text{Ni}(\text{NO}_3)_2/\text{KOH}$ mixture is prereduced in H_2 , the gasification activity observed can be ascribed to a combination of an initial high rate that stops after 10 min, which is due to the fraction of free nickel, and a lower but more stable one, which is due to the nickel-potassium mixture. Again the formation of a mixed oxide between potassium and a fraction of the total nickel, may be responsible for the different catalytic behavior, when compared with the nickel alone catalyst.

An important point to be discussed is whether the nickel-potassium activity is due to a small fraction of nickel present in the metallic state, which is kept active by the presence of potassium, or if the nickel in the +2 state is directly involved in the gasification reaction. Our results cannot clearly distinguish between these two possibilities, but we would like to summarize the arguments in favor of each case.

The first possibility is that the active catalyst is a small amount of metallic Ni. The kinetic results presented in chapter 3 show that the product distribution and activation energies observed with the nickel-potassium mixture are very similar to those obtained with nickel alone, even though the gas production rates obtained with the mixture are lower. The CAEM study (chapter 4) shows that the intrinsic activity of the nickel-potassium mixture is similar to that reported for Ni metal [26], but figure 5.1 shows that the initial bulk activity of the mixture is 50

times lower than that obtained with Ni alone. All these results can be justified by the formation of a very small amount of metallic Ni ($\sim 2\%$), that remains active due to the presence of potassium. Such a small amount of Ni metal cannot be discerned by XPS in the presence of the oxide, and therefore its presence cannot be excluded. As previously discussed, potassium can be stabilized by its interaction with NiO, but the species formed is not the active one, but rather a support for the active Ni metal. This support can increase the mobility of the Ni metal, and prevent the loss of contact with the carbon, which is the reason described for deactivation of Ni alone.

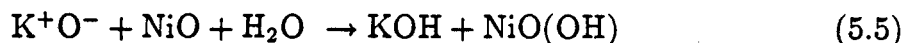
An important question that develops from this model is why the prereduc-tion step is not necessary, if the active species is Ni metal. A possible reason is that potassium, beside stabilizing NiO, also interacts with graphite. It has been reported [27], based on UPS results, that potassium ions can donate electron density to the valence levels of carbon, increasing its reducing power. This is also implied by our XPS results, as previously discussed. The effects of potassium and carbon on nickel are opposite, since potassium would stabilize NiO and carbon favors the formation of Ni metal. This might explain why only a small fraction of the nickel is stable as a metal. It has been reported in chapter 3 that mixtures of NiO and various alkali salts are more efficient than analogous mixtures with alkaline earth salts. This trend has also been reported by Ohtsuka *et al.* [19], and can be explained by the larger electron donation effects of alkalis, compared with alkaline earths.

An explanation for the catalytic properties of the nickel-potassium mixture, without involving Ni metal as an active species, is also possible. NiO by itself is not active for steam gasification of carbon because it is not able to dissociate H_2O ,

but the interaction of NiO with KOH can create an active species for dissociation of H_2O , without involving the metal. It has been reported that alkali metal salts are able to stabilize O^- species [28]. This species, as described in the literature [29], can be created by reaction of two adjacent KOH groups, according to equation 5.4.

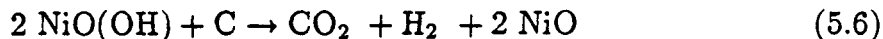


The K^+O^- species could induce the dissociation of H_2O , by abstraction of a hydrogen atom. The hydroxyl group could then attach to the nickel atom, leading to the formation of a formal $\text{Ni}(3+)$ species, according to equation 5.5.



It has been reported that $\text{NiO}(\text{OH})$ can be formed under oxidizing environments, in the presence of alkali metal salts [30], and electrochemical studies show that the potential for oxidation of $\text{Ni}(2+)$ to $\text{Ni}(3+)$ depends on the concentration and kind of alkali metal hydroxide present [31,32].

This formal $\text{Ni}(3+)$ species has a strong oxidizing power, and can react with carbon (equation 5.6) to produce CO_2 and regenerate the $\text{Ni}(2+)$ species, completing the cycle.



Even though the two mechanisms are quite different, they have common points. In both cases the interaction between nickel and potassium creates a new species which gives the system catalytic properties that are not present with either component alone. In the first mechanism described, this species is not the active one, but maintains Ni metal active, whereas in the second case, this species is the actual

active site for dissociation of H_2O . It is clear that more evidence is necessary to support or reject either mechanism, but the idea that should be emphasized at this point is that the mixtures of a transition metal and an alkali metal can generate catalysts with particular properties for steam gasification of carbon solids, that are superior to those of the components alone.

5.4 Summary

The activity of the nickel alone catalyst can be associated with the presence of Ni metal under reaction conditions. It is suggested that the reaction pathway for steam gasification of carbon involves the reaction of either a surface carbon or surface oxygen species on the nickel surface. Deactivation of the catalyst occurs when carbon is not able to maintain nickel in the metallic state, possibly due to a loss of catalyst-substrate contact.

The formation of a K-O-C surface compound is proposed to be formed under reaction conditions, when KOH is deposited alone on graphite. This compound is able to stabilize potassium on the carbon surface under conditions in which bulk KOH would not be present.

In the catalyst derived from a mixture of KOH and $\text{Ni}(\text{NO}_3)_2$, the interaction between nickel and potassium stabilizes NiO and KOH on the carbon surface under reaction conditions. It is proposed that a nickel-potassium mixed oxide is formed, and it is responsible for the unique properties of the mixture. This species is either directly involved in the gasification process, or it becomes a support for the active Ni metal catalyst, increasing its mobility and preventing its deactivation.

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Chapter 6

Kinetic Study Of The Steam Gasification Of Char Catalyzed By A Nickel-Potassium Mixture

6.1 Introduction

In previous chapters, it has been demonstrated that potassium-nickel mixtures have distinct properties for steam gasification of graphite. A common conclusion in all these studies is that a cooperative effect between the components is responsible for these properties. In chapter 3, it is shown that the mixture has higher activity than potassium alone, and it is more resistant to deactivation than nickel alone. Electron microscopy studies, presented in chapter 4, highlight the excellent dispersion and mobility of the catalyst. In addition, the X-ray photoelectron spectroscopy study described in chapter 5, shows that the nickel-potassium interaction stabilizes potassium on the surface, and favors the presence of nickel as an oxide.

These results indicate that the nickel-potassium system is a promising new type of catalyst for steam gasification of graphite. Its industrial application, however, requires that these properties can be expanded to gasification of other carbon solids, like chars and cokes, derived from coals and petroleum oil. For the gasifica-

tion of these carbon sources, it is important to evaluate the stability of the catalyst toward problems such as sulfur poisoning, inclusion in micropores, reaction with mineral content, and sintering.

These points are addressed in this chapter, by presenting a kinetic study on the catalytic properties of the nickel-potassium mixture for gasification of a coal-derived char, and by comparing the results with those obtained with potassium-alone and nickel-alone catalysts.

6.2 Results

6.2.1 Steam Gasification Of The Char, As Received

The parent coal of the char chosen for this study is a lignite from North Dakota. The char, as received, had been prepared by partial steam gasification at 1196 K. Its elemental analysis is given in table 6.1. The organic content of the char is composed mainly of carbon, oxygen and hydrogen ($H/C_{at.ratio}=0.18$ and $O/C_{at.ratio}=0.07$). The inorganic content is very high (24.95 wt.%), and the ash analysis indicates the presence of mainly Al_2O_3 , SiO_2 , CaO and Fe_2O_3 .

The indigenous materials in this char have catalytic activity for steam gasification of carbon. Figure 6.1 shows that the char, as received, without addition of any salt, is active toward reaction with steam at 893 K. The rate of steam gasification of the raw char, however, decreases with carbon conversion and time. For the particular experiment presented in this figure, the reaction rate is almost zero after 30% carbon conversion (reached after 10 hours in steam). The total conversion achieved before deactivation varies from sample to sample, and ranges from 30 to 60% of the initial carbon present.

For the steam gasification of the raw char at 893 K, H_2 and CO_2 are the main

Table 6.1: Compositional data for the North Dakota-lignite char, as received.

Proximate Analysis wt. %	^a Ultimate Analysis wt. %	^b Ash Analysis wt. %
Moisture 3.32		
Loss on ignition ^c 71.76	C 89.63 H 1.33 N 0.51 S 0.0 Cl 0.1 O 8.42	
Ash 24.95		SiO ₂ 26.06 Al ₂ O ₃ 13.71 TiO ₂ 0.62 Fe ₂ O ₃ 6.55 CaO 22.40 MgO 8.14 K ₂ O 0.59 Na ₂ O 1.82 SO ₃ 18.10 P ₂ O ₅ 0.23 SrO 0.56 BaO 0.36 Mn ₃ O ₄ 0.13 total 99.27

^aOxygen by difference.^bMineral results are reported on an ignited basis.^cLoss after ignition at 1023 K.

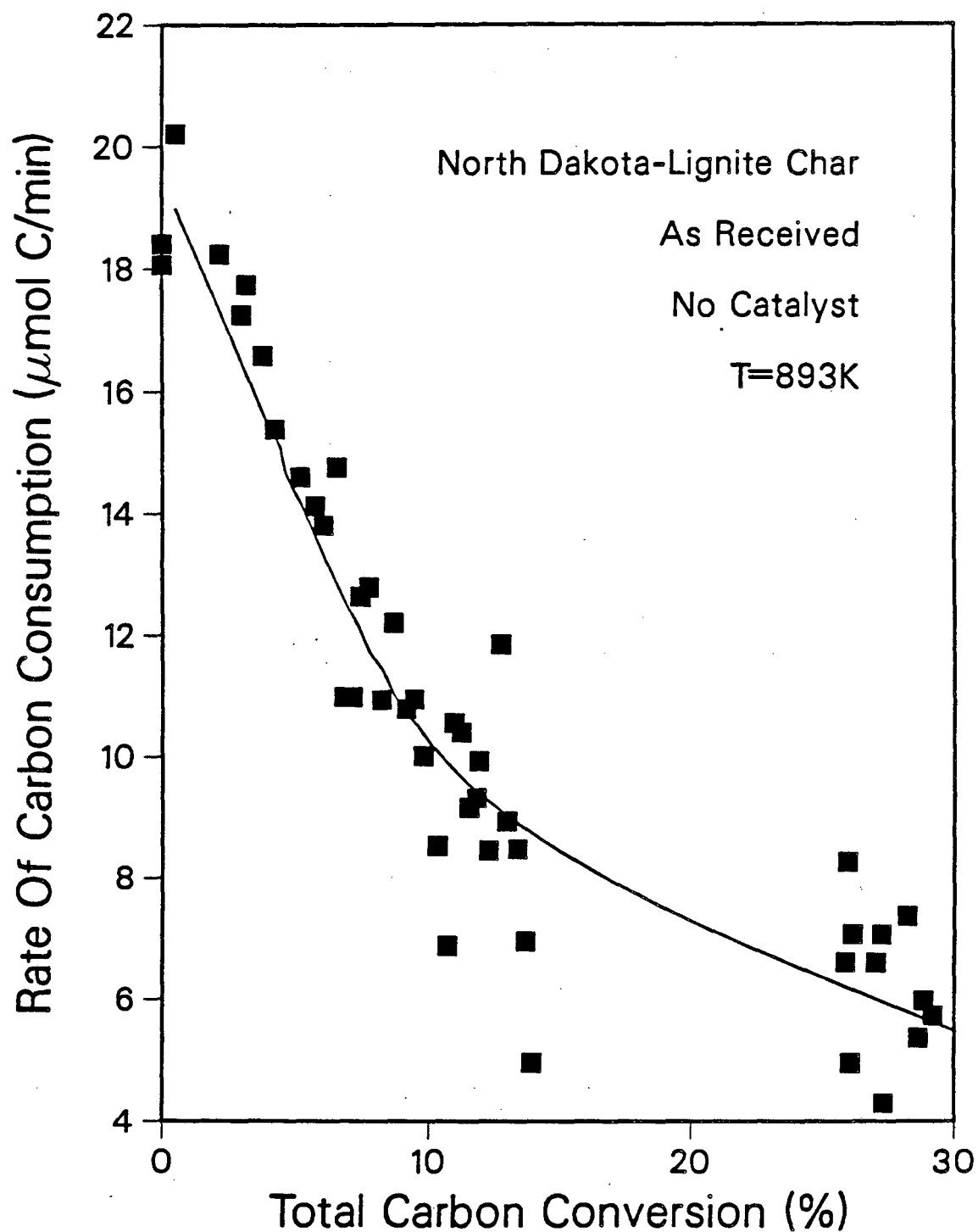


Figure 6.1: Variations of the rate of carbon gasification by steam at 893 K, with total carbon conversion, for North Dakota-lignite char, as received, without addition of any catalyst.

gas products, plus a small amount of CO ($p_{CO}/p_{CO_2}=0.04$). The ratio of CH_4 to H_2 in the collected gases is only slightly above the detection limit of the apparatus ($p_{CH_4}/p_{H_2} < 2 \times 10^{-3}$).

In figure 6.2, it is shown that the rates of steam gasification of the char as received, after addition of potassium and/or nickel salts, are comparable to those observed with the char alone. From these experiments, however, it is difficult to determine the catalytic properties of these compounds. Fluctuations in the total rate observed, possibly due to inhomogeneity in the char composition, could mask changes in the gasification rate, due to the addition of nickel and/or potassium salts. Notice for example, that for the char as received, without addition of any catalyst, the rate of steam gasification reported in figure 6.2 is three times higher than the one shown in figure 6.1.

6.2.2 Steam Gasification Of The Deactivated Char

In order to minimize the catalytic contribution of the indigenous materials to the steam gasification rate, the raw char was treated in steam at 933 K, until no more gas products were evolved. The properties of the potassium and nickel salts, codeposited or by themselves, were then studied for the steam gasification of the remaining solid at 893 K. This way, gasification rates observed after addition of the salts, are certainly due to the presence of nickel and/or potassium.

The elemental analysis of the deactivated char is given in table 6.2. The decrease in the percentage of the organic fraction in the char, from 71.76wt.% to 50.11wt.%, agrees with the 48% weight loss determined after the steam gasification process. The composition of the organic and inorganic fractions in the char do not change significantly after the steam treatment, with the noticeable excep-

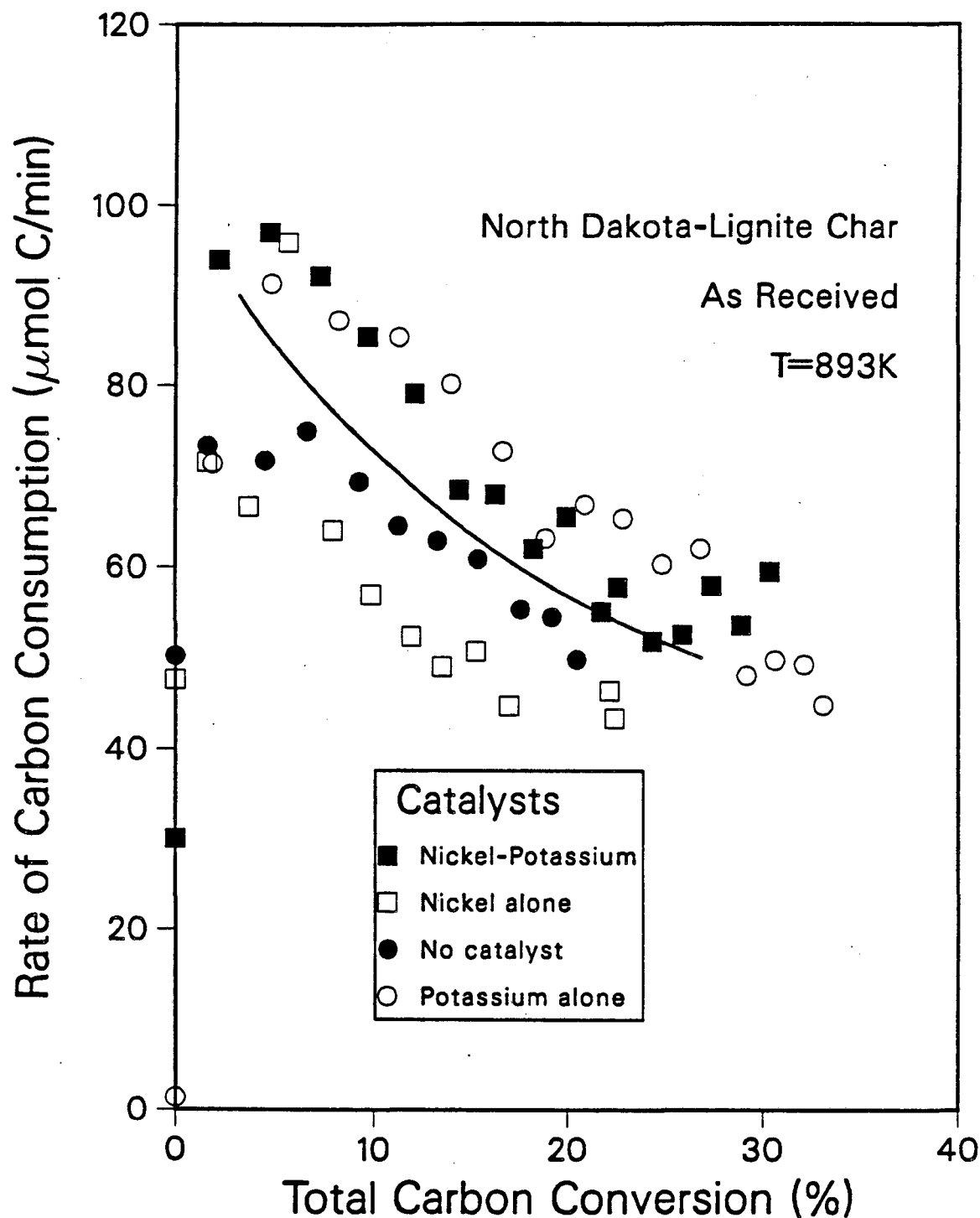


Figure 6.2: Variation of the rate of carbon gasification by steam at 893 K, with total carbon conversion, for North Dakota-lignite char, as received, after addition of either nickel, potassium, or their mixture. When present, the nickel and potassium loadings were 0.83 mmol cation/ g char.

tion of the amount of sulfur in the ashes, which decreases from 18.10 wt.% before treatment, to 2.16 wt.% after.

The catalytic activity of the nickel-potassium mixture for steam gasification of the deactivated char at 893 K is shown in figure 6.3. The rates of gas production remain constant with total carbon consumption, up to 35% conversion; reached after 120 min under reaction conditions. At low carbon conversions, a small increase in the rates of gas production was observed, but this was not always reproducible. The product distribution is very similar to that obtained for the gasification of the char as received. H_2 and CO_2 are the main products. CO is also produced ($p_{CO}/p_{CO_2}=0.13$), and the amount of CH_4 in the gas collected is within the sensitivity limits of the system.

The rates of gas production are proportional to the amount of nickel and potassium present. For this reason, the reaction rates reported in figure 6.3 have been normalized, with respect to the catalyst loading. In the case of the nickel-potassium mixture, one mole of catalyst is considered to be mole of nickel plus one mole of potassium. In the particular experiment shown in figure 6.3, the catalyst loading was equal to 1.04×10^{-3} moles. The absolute rate of carbon consumption is equal, then, to $41 \mu\text{mol C/min}$, which is the same order of magnitude as the initial rates observed for the char as received. This rate, however, is certainly due to the catalytic effect of the nickel-potassium mixture, since in this case the char by itself is inactive.

The results obtained for nickel and potassium loaded by themselves are qualitatively similar to those obtained for their mixture. A summary of the rate of carbon consumption and ratio of CO to CO_2 obtained for these three catalysts is given in table 6.3. The initial rates of carbon consumption, catalyzed by the potassium

Table 6.2: Compositional data for the deactivated North Dakota-lignite char.

Proximate Analysis wt. %	^a Ultimate Analysis wt. %	^b Ash Analysis wt. %
Moisture 1.04		
Loss on ignition ^c 50.11	C 89.55 H 1.05 N 0.41 S 0.0 Cl 0.0 O 8.99	
Ash 49.37		SiO ₂ 29.72 Al ₂ O ₃ 16.48 TiO ₂ 0.75 Fe ₂ O ₃ 7.09 CaO 27.80 MgO 8.14 K ₂ O 0.62 Na ₂ O 2.29 SO ₃ 18.10 P ₂ O ₅ 0.28 SrO 0.68 BaO 0.43 Mn ₃ O ₄ 0.15 total 98.54

^aOxygen by difference.^bMineral results are reported on an ignited basis.^cLoss after ignition at 1023 K.

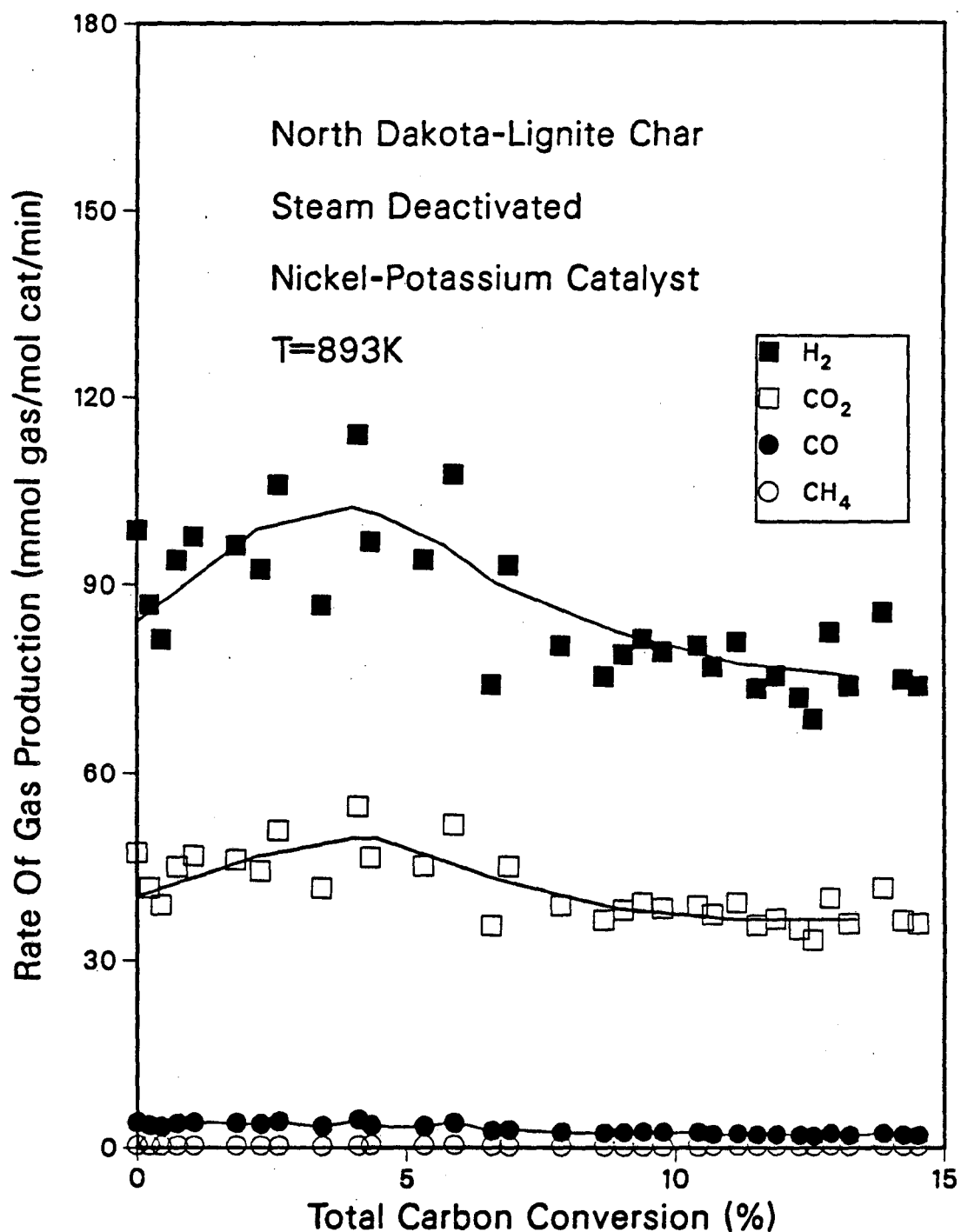


Figure 6.3: Rate of production, as a function of carbon conversion, for all the gases formed on the steam gasification of deactivated char at 893 K, catalyzed by the nickel-potassium mixture. The molar ratio of nickel to potassium was equal to 0.9, and the catalyst loading was equal to 2.0 mmol cat/ g char. The initial weight of char was 0.6 g.

Table 6.3: Rate of carbon consumption and ratio of CO to CO₂ in the gas products, for steam gasification at 893 K of deactivated North Dakota-lignite char.

Catalyst	Rate (mmol C/mol cat/min)		p_{CO}/p_{CO_2}	
	2 % conv.	11 % conv	2 % conv.	11 % conv.
No catalyst	No activity			
Nickel-potassium	38±9	42±13	0.13±0.02	0.12±0.02
Nickel alone	21±13	—	0.04±0.01	—
Potassium alone	47±9	36±15	0.08±0.01	0.06±0.01

alone catalyst, are similar to the one obtained with the nickel-potassium mixture. Also, as in the case of the mixture, no clear sign of deactivation of the potassium catalyst is observed, up to 30% carbon conversion (obtained after 120 min). The activity of the nickel catalyst is lower than those of potassium alone, and nickel-potassium. This is clearly shown by the lower rates of carbon consumption (see table 6.3), and the lower total carbon conversions observed after 120 min (17% conversion).

For graphite gasification, it was reported in chapter 3, that a prereduction

step enhances the activities of the nickel alone and nickel-potassium mixtures. In the case of the steam gasification of lignite char, however, a pretreatment in H_2 at 933 K has no effect on the activity of these catalysts, since similar rates of gasification are observed, with and without the prereduction step.

The total carbon conversions, determined by weight loss measurements, were 10 to 20% higher than those determined by integration of the gas production curves. These differences are probably caused by the dissolution of a small fraction of the products in H_2O , during the gas collection step. (See chapter 2). This implies that the reaction rates presented in this chapter are slightly lower than the real values. It is not likely, however, that these differences would change the main conclusions reached in this study.

6.2.3 Steam Gasification Of The Demineralized Char

The results of the steam gasification of the deactivated char show that the catalytic properties of nickel and potassium, codeposited or by themselves, are different from those observed for steam gasification of graphite. (See chapter 3). This is probably due to the interaction between the ash content in the char, and the nickel and/or potassium.

In order to study this possibility, the raw char was demineralized by extractions in HCl and HF . (See chapter 2). Table 6.4 shows that after these treatments the ash content of the char is reduced from 24.95 wt.% to 3.63 wt.%. The remaining ash is composed mainly of CaO , Al_2O_3 and MgO , with a small amount of iron. In the organic fraction, the oxygen concentration after demineralization is slightly higher ($O/C_{at.ratio}=0.10$), indicating that some oxidation has taken place during the extraction process. Also, a small amount of sulfur and chlorine are

now present ($S/C_{at.ratio}=1.3\times 10^{-5}$ and $Cl/C_{at.ratio}=1.3\times 10^{-5}$). The char, after demineralization treatment, has no activity toward steam gasification.

The initial rates of steam gasification of the demineralized char at 893 K, promoted by the nickel-potassium mixture, are one order of magnitude higher than those observed for the deactivated char. (Compare figures 6.4 and 6.3). The gas products distribution is similar to those reported previously, that is mainly H_2 and CO_2 with small amounts of CO ($p_{CO}/p_{CO_2}=0.14$), and with CH_4 production rates just above the sensitivity threshold of the system.

Figure 6.4 also shows that, for the nickel-potassium catalyzed gasification of the demineralized char, the rates of gas production increase with total carbon consumption, up to 50% conversion. Above this value, the rate starts to decrease, but does not stop until all the carbon initially present has reacted. Pore volume analysis of the demineralized char shows that about 25% of the total surface area is accounted by micropores of less than 20 Å average diameter. This surface area, probably becomes accessible for reaction only after partial gasification, and would explain the increase in reaction rate.

The steam gasification of demineralized char at 893 K, catalyzed by potassium alone, shows qualitatively the same behavior as when the reaction is promoted by the nickel-potassium mixture. The gas products are, again, H_2 and CO_2 plus a small amount of CO ($p_{CO}/p_{CO_2}=0.07$). The rate of gas production increases with the total carbon consumption, up to 50% conversion, and gasification of all the carbon initially present is achieved. The activity of the potassium catalyst, however, is around 50% lower than that of the nickel-potassium mixture. (See table 6.5).

In contrast with the nickel-potassium and potassium alone catalysts, the ac-

Table 6.4: Compositional data for the demineralized North Dakota-lignite char.

Proximate Analysis wt. %	^a Ultimate Analysis wt. %	^b Ash Analysis wt. %
Moisture 4.04		
Loss on ignition ^c 92.33	C 85.85 H 0.91 N 0.68 S 0.4 Cl 0.4 O 11.7	
Ash 3.63		SiO ₂ 2.66 Al ₂ O ₃ 15.25 TiO ₂ 1.94 Fe ₂ O ₃ 3.38 CaO 41.91 MgO 18.27 K ₂ O 0.08 Na ₂ O 0.39 SO ₃ 14.88 P ₂ O ₅ 0.36 SrO 0.44 BaO 0.16 Mn ₃ O ₄ 0.17 total 99.89

^aOxygen by difference.^bMineral results are reported on an ignited basis.^cLoss after ignition at 1023 K.

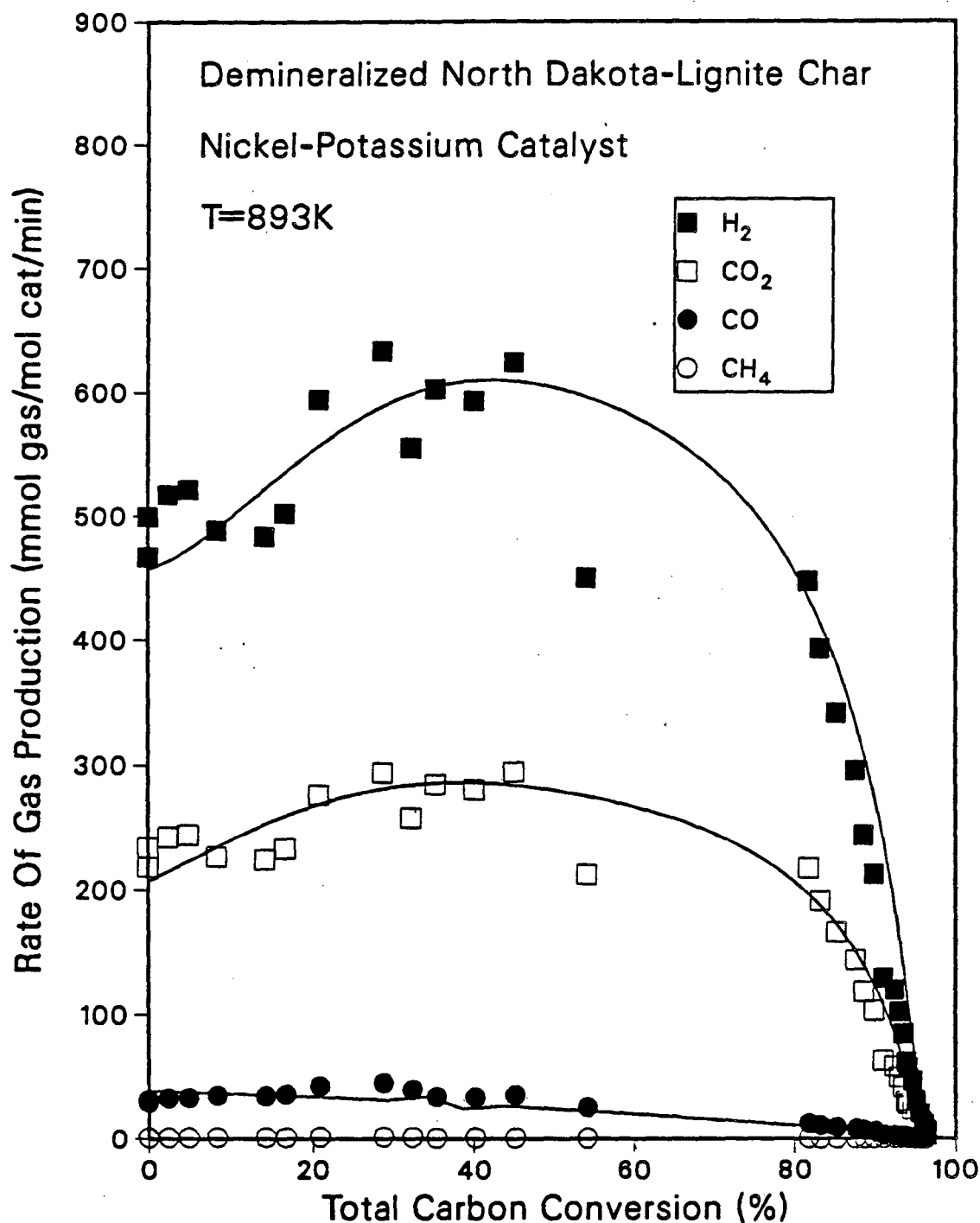


Figure 6.4: Rate of production as a function of carbon conversion, for all the gases formed from the steam gasification of demineralized char at 893 K, catalyzed by the nickel-potassium mixture. The molar ratio of nickel to potassium was equal to 0.9, and the catalyst loading was equal to 2.0 mmol cat/ g char. The initial weight of char was 0.5 g.

Table 6.5: Rate of carbon consumption and ratio of CO to CO₂ in the gas products, for the steam gasification at 893 K of demineralized North Dakota-lignite char.

Catalyst	Rate (mmol C/mol cat/min)		p_{CO}/p_{CO_2}	
	32 % conv.	75 % conv	32 % conv.	75 % conv.
No catalyst	No activity			
Nickel-potassium	348±60	224±64	0.14±0.01	0.14±0.01
Nickel alone	14±6	—	0.17±0.01	—
Potassium alone	233±20	133±40	0.09±0.01	0.05±0.01

tivity of the nickel catalyst for steam gasification of demineralized char at 893 K is similar to that of the deactivated char. Also, as in the case of the deactivated char, prereduction of the nickel alone did not enhance the catalyst activity.

6.3 Discussion

The catalytic properties of nickel and potassium for steam gasification of char, are in some cases different from those of graphite steam gasification. This is the case for both the mixed catalyst, and the two components by themselves. In this section, these differences will be explained by the interaction of nickel and potassium with the mineral content in the char.

Let's first compare the results presented in this chapter for the steam gasification of the demineralized char, with those reported in chapter 3 for the steam gasification of graphite. The demineralized char contains a relatively low amount of ash (4 wt.%), and the volatile fraction is composed mainly of carbon, hydrogen and oxygen. It has a large surface area ($540 \text{ m}^2/\text{g}$), with an average pore volume of $0.41 \text{ cm}^3/\text{g}$, and a microporosity (pores of diameter less than $20 \text{ \AA}$) that accounts for 25 to 30% of the total surface area. The graphite used in the study presented in chapter 3 (UCP-1 from Ultra Carbon) is almost 100% carbon, with no ash. Its surface area is relatively low ($5 \text{ m}^2/\text{g}$), and it has no micropores.

The nickel-potassium mixture shows similar catalytic properties for the steam gasification of graphite and demineralized char. In neither case does the catalyst deactivate with time. The product distribution is similar ($p_{\text{CO}}/p_{\text{CO}_2}$ is equal to 0.12 for the demineralized char, and 0.04 for graphite), and in both cases it remains constant with time. For the steam gasification of the demineralized char, the reaction rate at 893 K ($348 \text{ mmol C/mol cat/min}$), is higher than that for

graphite gasification (18 mmol C/mol cat/min), but so is the surface area of the carbon substrate.

Contrary to the nickel-potassium mixture, the nickel-alone catalyst has different properties for steam gasification of graphite and the demineralized char. It has been reported in this thesis (chapter 3), and by other authors [1,2], that nickel alone is a good catalyst for steam gasification of graphite, despite the fact that it deactivates. In the case of the demineralized char, even though the catalyst does not deactivate, its activity for the steam gasification reaction at 893 K (14 mmol C/mol cat/min) is almost 30 times lower than for graphite (400 mmol C/mol cat/min). In addition, for the char steam gasification, the pre-reduction step does not enhance the catalyst activity, while in the case of graphite gasification it is indispensable.

These differences can be explained by the interaction between nickel and the ash content of the char. Table 6.4 shows that calcium and sulfur are two major components in the ash content of this carbon substrate. In chapter 3, it was reported that nickel-calcium mixtures showed the same qualitative properties for steam gasification of graphite, as the nickel-potassium mixtures, but with much lower activity. In addition, Baker and Chludzinski [3] have reported that the activity of the nickel-calcium mixture for steam gasification of graphite is lower than those of nickel and calcium by themselves. These authors have also shown that despite the low activity, the nickel-calcium catalyst has good mobility. This allows the mixture to remain in contact with the active planes of the substrate, and prevents its deactivation. Ohtsuka *et al.* [4] have also studied the interaction of potassium and calcium with nickel, in the steam and hydrogen gasification of brown coal. They concluded, in agreement with our results, that while the activity

was increased markedly by potassium, it was decreased by the presence of calcium.

The initial concentration of calcium in the demineralized char (271 $\mu\text{mol Ca/g char}$) is almost eight times lower than the amount of nickel catalyst loaded (2.08 mmol Ni/g char). This, however, does not exclude the possibility of an interaction between nickel and calcium, since for the nickel-potassium case, as discussed in chapter 3, the cooperative effect between these two components was observed, even at nickel to potassium atomic ratios as high as ten.

Sulfur is another component in the char that could be responsible for the low activity of nickel. Its concentration in the char is similar to that of calcium (194 $\mu\text{mol S/g char}$) and the sensitivity of nickel catalysts to sulfur content, for a variety of chemical reactions, is very well documented.

The properties of the potassium catalyst for steam gasification of the demineralized char and graphite are also different. Dellanay *et al.* [5], reported that KOH loaded by itself on UCP-1 graphite is only active for steam gasification at temperatures above 1000 K, whereas it is shown in this chapter that KOH loaded alone on the demineralized char is active for steam gasification reaction at 893 K. Furthermore, in the latter case, the catalyst does not deactivate, and total carbon conversion is achieved.

The behavior of the potassium catalyst for steam gasification of the demineralized char can also be explained by its interaction with the ash content in the char. McKee *et al.* [6] have indicated that the degree of promotion of K_2CO_3 for steam gasification of char increases with the rank of the coal char. Wood and Sancier [7], in a review article, suggest that "this dependence on the coal rank is likely a manifestation of the variation of native calcium ion concentration in the coal chars".

Our interpretation for the interaction between potassium and calcium and/or magnesium, is analogous to that discussed in the previous chapter for the nickel-potassium case. It involves the formation of a compound, that improves the mobility of the catalyst, and prevents its deactivation. The advantages of an eutectic mixture of alkali salts or alkali-transition metal salts, as catalysts for steam gasification of carbon solids, has also been suggested by Hüttinger and Minges [8] and by McKee *et al.* [9]. To the knowledge of the author, however, no work on alkali-alkaline earth mixed catalysts has been reported in the literature.

The catalytic activity of the calcium-potassium or magnesium-potassium mixtures, could be due to their ability to extract a hydrogen atom from H_2O vapor, and to enhance its dissociation on the carbon surface. A similar mechanism has been proposed for CH_4 activation by alkali/alkaline earth catalysts [10], which is certainly a more demanding reaction.

Further experiments are necessary to support this model. Preliminary results, obtained on graphite, show that the calcium-potassium mixture is active for steam gasification at 893 K, while both potassium and calcium by themselves are inactive. This result, if confirmed, would support the proposed model, and technologically, would be of great importance because of the natural abundance of both potassium and calcium.

A comparison of the catalytic behavior of the nickel-potassium mixtures for steam gasification of the demineralized char, with those of nickel and potassium by themselves, are further evidence for a cooperative effect being responsible for the distinct properties of the mixture. In this case, the increase of the activity of the mixture at 893 K is higher than that expected from the sum of those of nickel and potassium by themselves. (See table 6.5). These results indicate that the

nickel-potassium interaction is not affected by the presence of micropores, and by small amounts of sulfur and ashes.

For the gasification of the deactivated char, however, the activity of the nickel-potassium mixture is the same, within experimental error, as that of potassium alone. In this case, the nickel-potassium interaction is probably hindered by interactions between the catalyst components and the ash content, which in this case, is much more abundant than in the demineralized char. A similar conclusion was reached by Suzuki *et al.* [11] for a sodium-iron mixture. Nickel, as previously discussed, can interact with calcium and/or sulfur, whose concentrations in the deactivated char (2.5 mmol Ca/ g char and 1.0 mmol S/ g char) are similar to the nickel loadings (1.0 mmol Ni/ g char). This idea is also supported by the fact that the activity of the nickel catalyst for steam gasification of the deactivated char is similar to that observed for the demineralized char. On the other hand, potassium can react with clays and pyrite present in the ash to form catalytically inactive compounds [12]. This could also explain why the activity of potassium alone for gasification of the deactivated char is lower than that of the demineralized char. The ash fraction in the deactivated char, however, is uncommonly high (>50 wt.%), and further work is necessary to determine catalyst tolerance to ash content, for both the nickel-potassium and potassium-alone catalyst.

In the case of the char as received, the catalytic activity of the indigenous materials is probably associated with the presence of calcium. Walker *et al.* [13] have studied the catalytic properties of calcium for steam gasification of lignite chars, and concluded that it is the best *in situ* catalyst for steam gasification of char. Radović *et al.* [14-17] have studied its deactivation, and suggest that it is caused by sintering and loss of contact with the active planes of carbon. The same

conclusion for deactivation of the nickel catalyst have been concluded in chapter 5, and in chapter 4 it is shown that addition of potassium to nickel improves its mobility, and prevents its deactivation. As already suggested, a similar interaction between potassium and calcium is feasible, and further studies should be performed to explore this possibility.

6.4 Summary

The results presented in this chapter indicate that the nickel-potassium mixture is a better catalyst for steam gasification of the demineralized North Dakota-lignite char (low ash) than both the nickel-alone and potassium-alone catalysts. For the char as received (high ash content), however, the interaction of both nickel and potassium with the minerals present, decreases substantially its activity toward steam gasification.

For the potassium-alone catalyst, different catalytic behaviors for gasification of demineralized (low ash) North Dakota-lignite char and graphite are observed. These differences are explained by a cooperative effect between potassium and calcium and/or magnesium, present in the low ash char. This effect is explained by a model similar to that proposed in chapter 5 for the nickel-potassium system.

The nickel-alone catalyst is extremely sensitive to the ash content in the char. It is suggested that the interaction between nickel and either calcium or sulfur, is responsible for the low activity observed for this catalyst.

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Chapter 7

Adsorption Of Carbon Monoxide, Carbon Dioxide, Oxygen And Water On Clean Graphite Surface.

7.1 Introduction

Knowledge of the structure and stability of the various surface species formed after adsorption of CO, CO₂, O₂ and H₂O on graphite is very important for the understanding of graphite chemistry and its connection with processes such as carbon gasification.

No work has been published on the adsorption of CO on graphite, and in the case of CO₂, O₂ and H₂O adsorption, even though numerous studies have been performed, little understanding has yet been achieved, owing to the complexity of the system. The studies reported in the literature have been conducted on various carbonaceous samples such as graphite, carbon black, glassy carbon, coconut char and carbon fibers. Techniques such as gravimetric balances [1-5], reactor beds [6], pH measurements [7,8], Auger electron spectroscopy (AES) [9,10], infrared adsorption [11-14], X-ray photoelectron spectroscopy (XPS) [15-17], ultra-

violet photoelectron spectroscopy (UPS) [18], electron-spin resonance (ESR) [19], transmission electron microscopy (TEM) [20], and temperature programmed desorption (TPD) [21-28] were employed and to light useful information about the nature of the graphite species. In particular, TPD and XPS have proven to be good probes for the study of surface adsorbates, but in the case of carbon-oxygen species, the work has been conducted mostly on raw, or highly oxidized carbon samples under poorly controlled atmospheres, giving broad features, difficult to analyze.

The approach of the work presented in this thesis has been to study species produced by the chemisorption of CO, CO₂, O₂ and H₂O, and their isotopic derivatives onto a clean graphite sample, under ultra high vacuum (UHV) conditions. With this procedure only a small number of the sites on the surface are covered, giving better resolved and more reproducible TPD features. Also, XPS studies have been carried out in order to determine the surface concentration of the adsorbed gases, and to attempt to assign the TPD features to plausible species on the graphite surface.

Experiments have been carried out on graphite samples from three different origins. Kinetic measurements have also been undertaken, to study the interconversion of CO and CO₂ at the graphite surface (Boudouard equilibrium).

7.2 Results

7.2.1 CO Adsorption

The dependence of the CO adsorption on graphite, upon gas exposure is shown in figure 7.1. The amount of chemisorbed CO is monitored by integration of the mass 28 amu signal in TPD experiments, and plotted versus exposure at various

pressures.

The thermal desorption spectra, taken after adsorption of 6×10^{-5} Torr of CO for 30 s at different temperatures, is plotted in figure 7.2. When adsorbed at 323 K, CO desorbs in two overlapping peaks at 393 and 503 K, and when adsorption is carried out at higher temperatures, peaks at 673, 973 and 1093 K are also observed. No ^{12}CO is evolved after adsorption of ^{13}CO , showing that no carbon exchange with the bulk occurs. This allows also to rule out any contamination from O_2 or H_2O , since they would lead to ^{12}CO desorption. Additional experiments performed with C^{18}O confirm this observation.

Some CO_2 (mass 44 amu) is also produced after CO adsorption (figure 7.3). Room temperature adsorption leads to a single peak at 443 K, whereas higher adsorption temperatures lead to more stable species that desorb at 673 and 923 K. In our experimental conditions the amount of CO_2 desorbed after CO adsorption is always less than 10% of the total amount of CO chemisorbed.

7.2.2 CO_2 Adsorption

The TPD spectra for mass 28 (^{12}CO), 29 (^{13}CO), 44 ($^{12}\text{CO}_2$) and 45 amu ($^{13}\text{CO}_2$) after exposure to 8 Torr of $^{13}\text{CO}_2$ for 60 s are reproduced in figure 7.4. Molecular $^{13}\text{CO}_2$ desorbs at 423 K. A large high temperature ^{12}CO TPD peak at 1093 K is observed, with two shoulders at 973 and 1253 K. C^{18}O_2 adsorption results in identical desorption peaks at mass 30 amu (C^{18}O) indicating that these high temperature features are not due to contaminants. Some ^{13}CO (mass 29 amu) is evolved at low temperatures, and a weak mass 44 amu signal ($^{12}\text{CO}_2$) can be ascribed to isotopic impurities.

Adsorption of a 58–42% mixture of C^{16}O_2 and C^{18}O_2 leads to nearly total oxy-

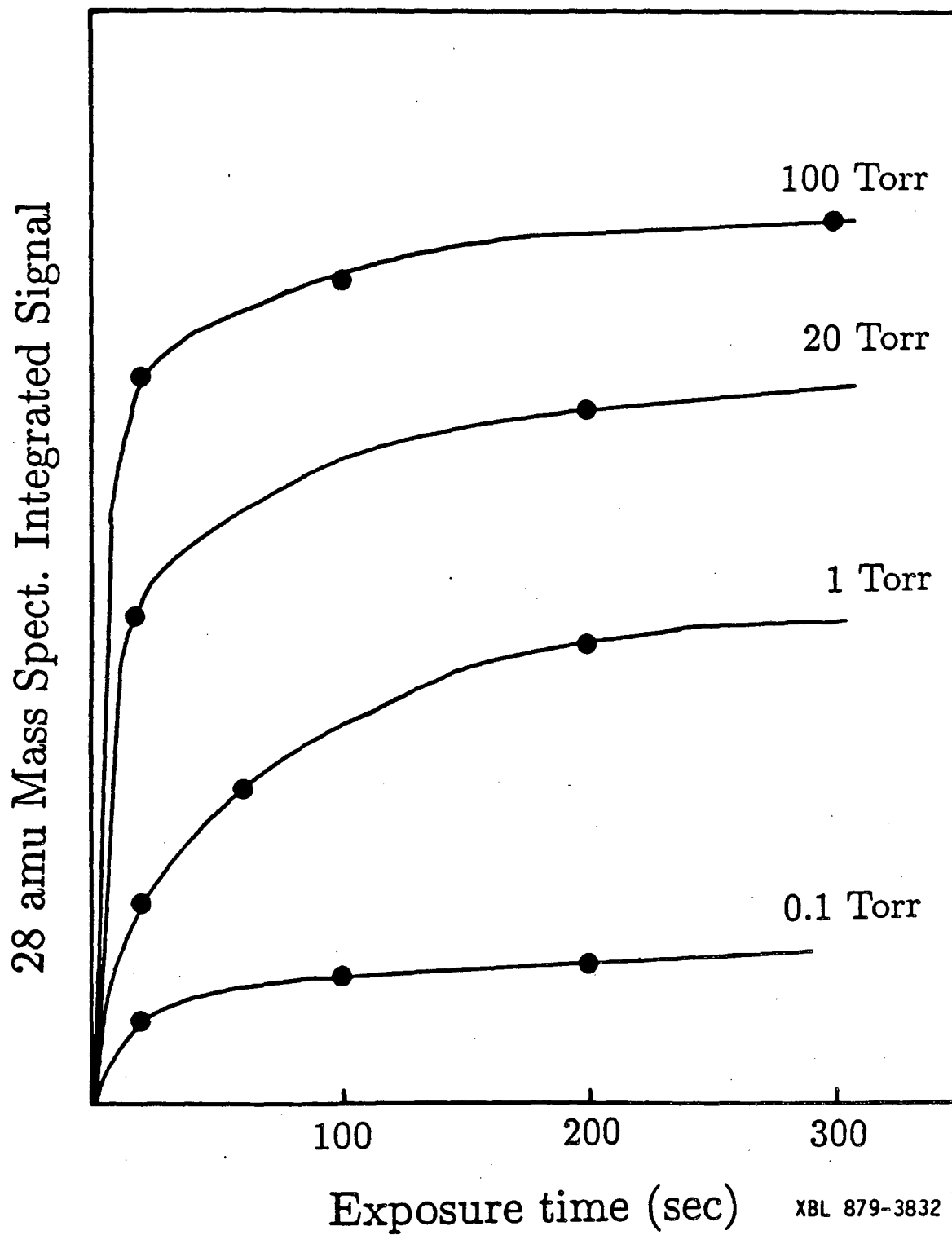


Figure 7.1: Intensity of the 28 amu TPD signal, as a function of CO adsorption time at various pressures.

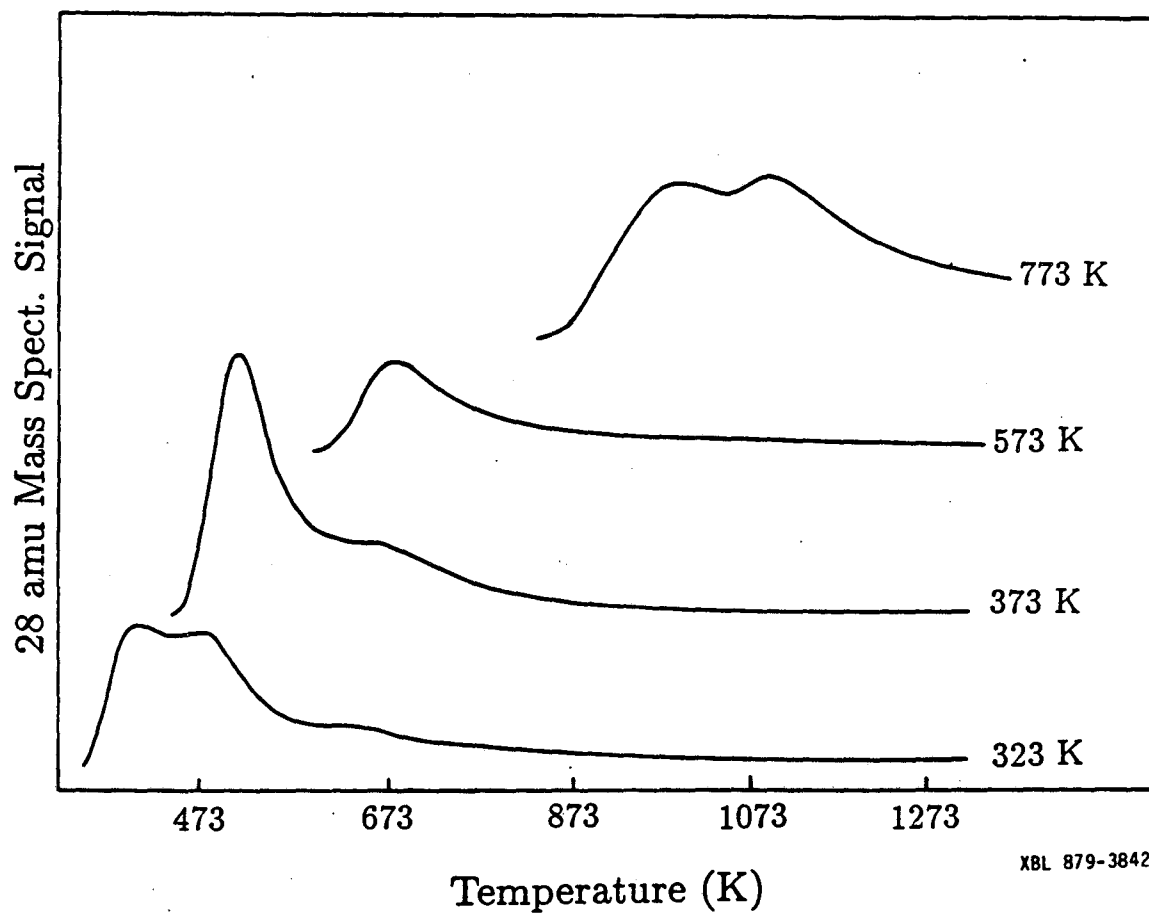


Figure 7.2: Mass-28 amu TPD spectra after 1800 L (6×10^{-5} Torr for 30 s) CO exposure to graphite at various temperatures.

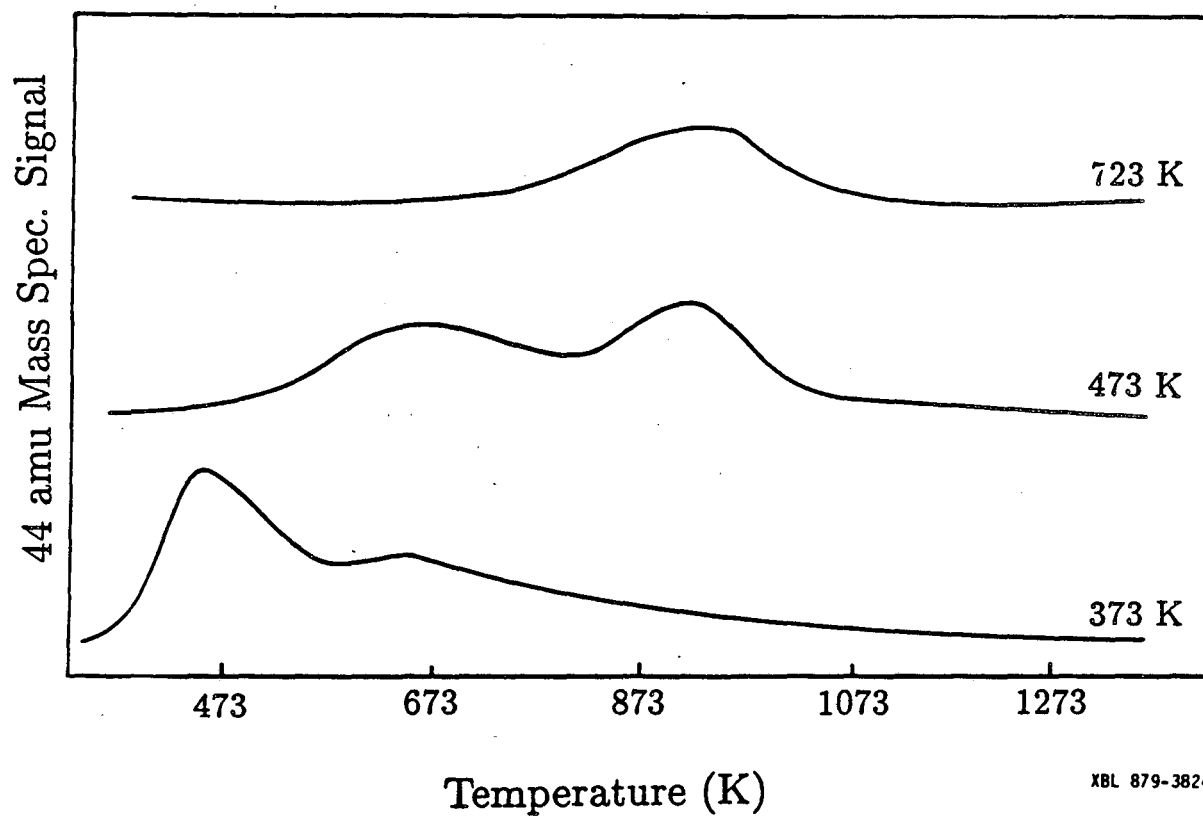


Figure 7.3: Mass-44 amu TPD spectra after 1800 L (6×10^{-5} Torr for 30 s) CO exposure to graphite at various temperatures.

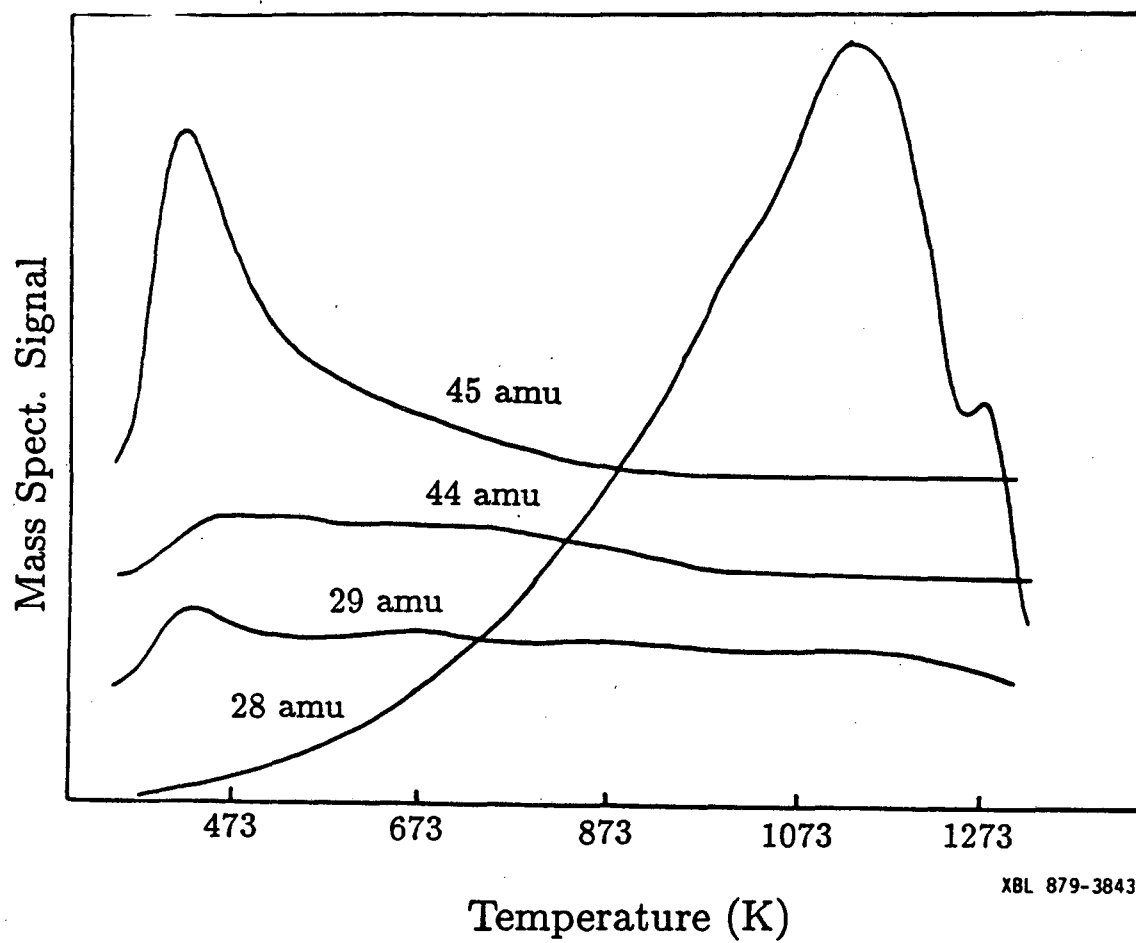


Figure 7.4: TPD spectra after $^{13}\text{CO}_2$ exposure (8 Torr for 60 s) to graphite at room temperature.

gen scrambling of the CO_2 desorbed, as 35% C^{16}O_2 (mass 44 amu), 41% $\text{C}^{16}\text{O}^{18}\text{O}$ (mass 46 amu) and 24% C^{18}O_2 (mass 48 amu) is evolved (figure 7.5). Theoretical proportions for the total scrambling are 34, 48 and 18% respectively.

Under UHV conditions, CO_2 chemisorption leads to the same TPD features as after adsorption at high pressures. Again, the 28 amu TPD signal shows a maximum at 1093 K, which can be enhanced by raising the adsorption temperature (figure 7.6). A shoulder near 1220 K becomes the predominant feature of the spectrum, when adsorption is carried out at 773 K. Finally, the 973 K shoulder observed after high pressure exposure or after O_2 adsorption is hardly detectable.

7.2.3 CO and CO_2 Interconversion. Kinetic Study

Reaction rates for CO and CO_2 reactions with graphite were obtained using the high pressure cell reactor. Data for the $\text{C} + \text{CO}_2 \rightarrow 2 \text{CO}$ reaction as a function of temperature (plotted in Arrhenius form) is shown in figure 7.7. The slope of this line yields an activation energy of 67 ± 3 kcal/mol. This value is in agreement with that reported in flow reactor experiments [29].

Figure 7.8 shows a similar plot for the reverse reaction, $2 \text{CO} \rightarrow \text{C} + \text{CO}_2$. In this case, rates were measured from the accumulation of CO_2 , and the linear portion of the curve yields an activation energy for CO_2 formation of 24 ± 2 kcal/mol.

7.2.4 O_2 Adsorption

Figure 7.9 shows the TPD spectra of mass 28 amu obtained after exposing the clean surface to various doses of O_2 at 523 K. Two maxima at 1093 and 1253 K, and a shoulder at 973 K are observed. High exposures are necessary to get a measurable adsorption signal. O_2 chemisorption can be enhanced by raising the

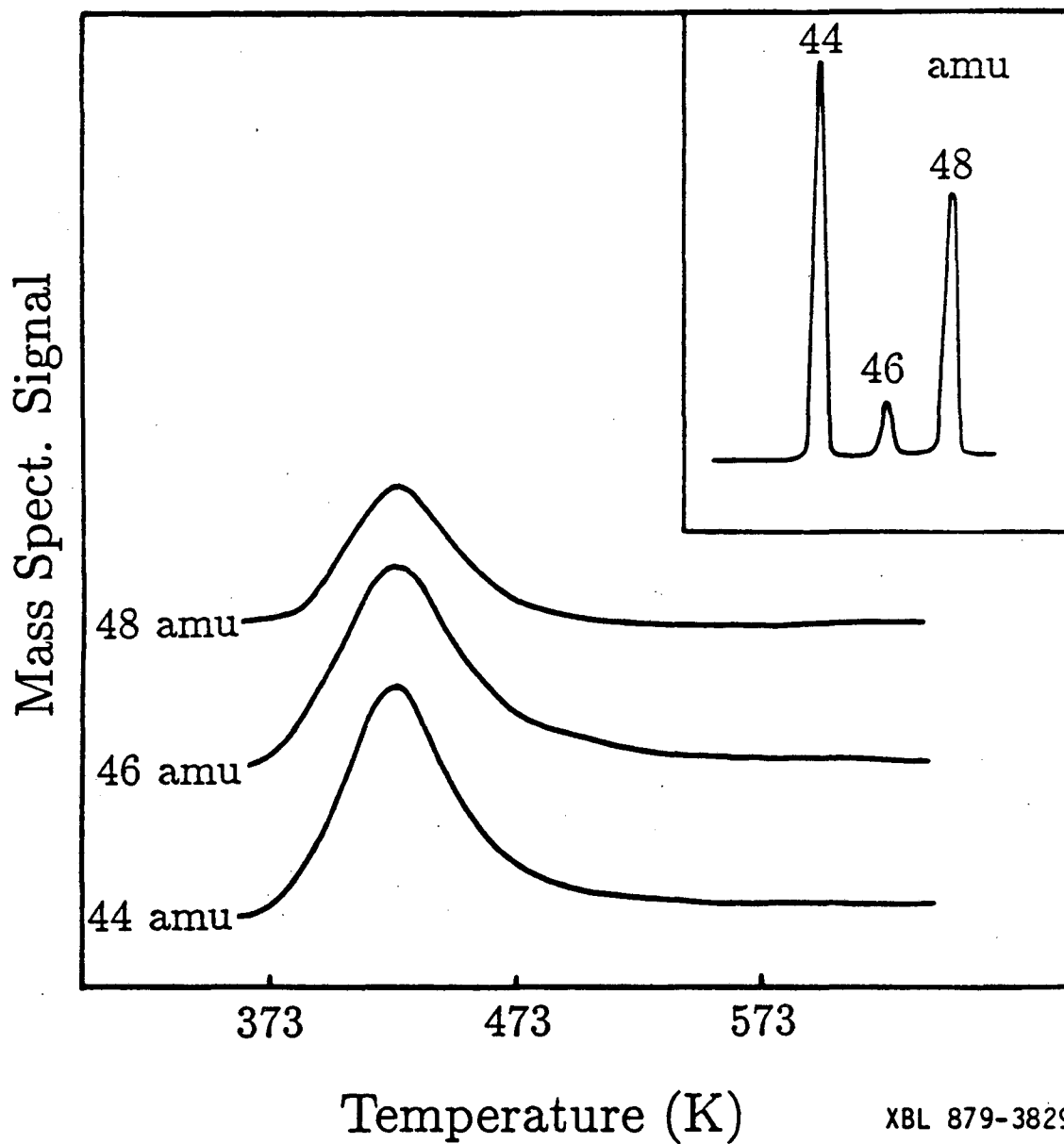


Figure 7.5: (a) TPD spectra after 6000 L exposure (2×10^{-4} Torr for 30 s) of a C^{16}O_2 (58%)– C^{18}O_2 (42%) mixture to graphite at room temperature. (b) Mass spectrum of the mixture used for adsorption. The mass 46 amu peak is ascribed to isotopic impurity.

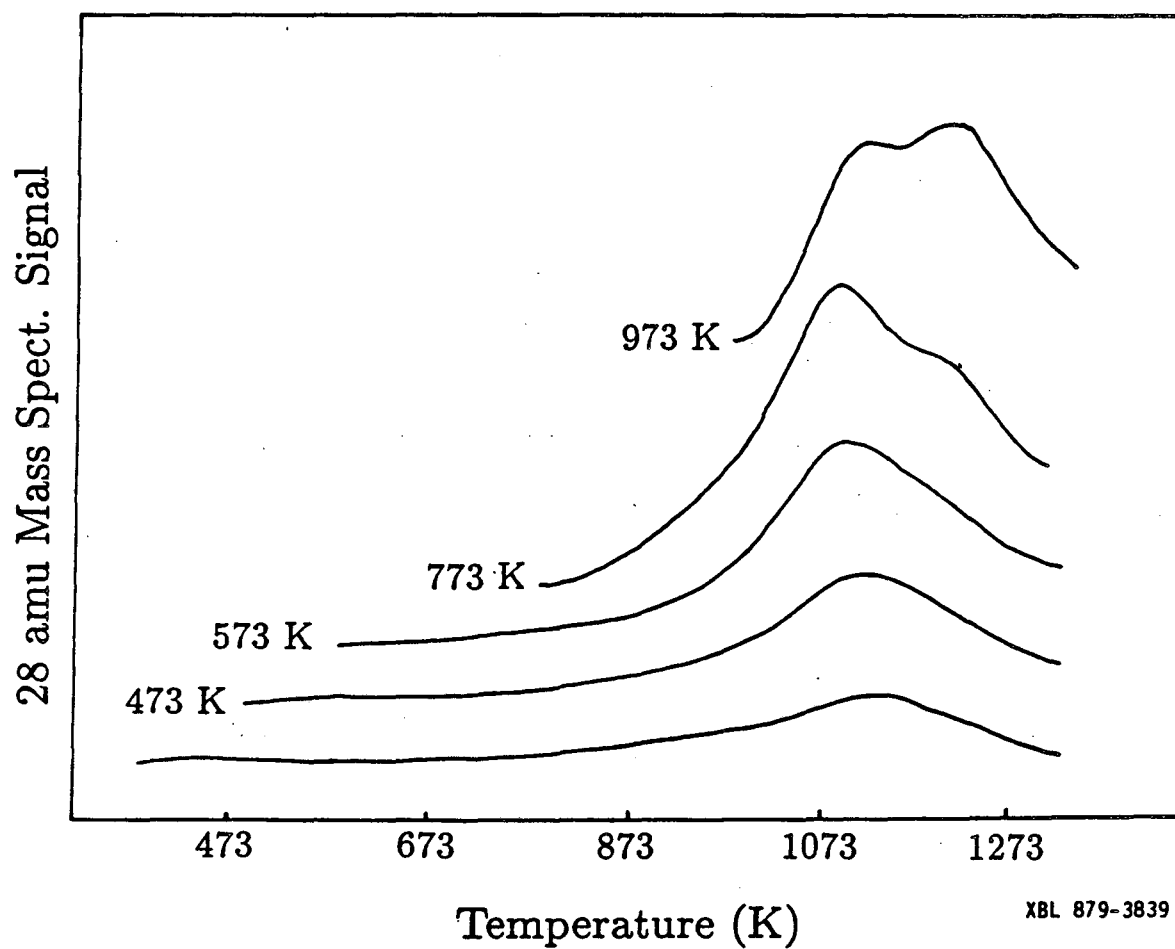
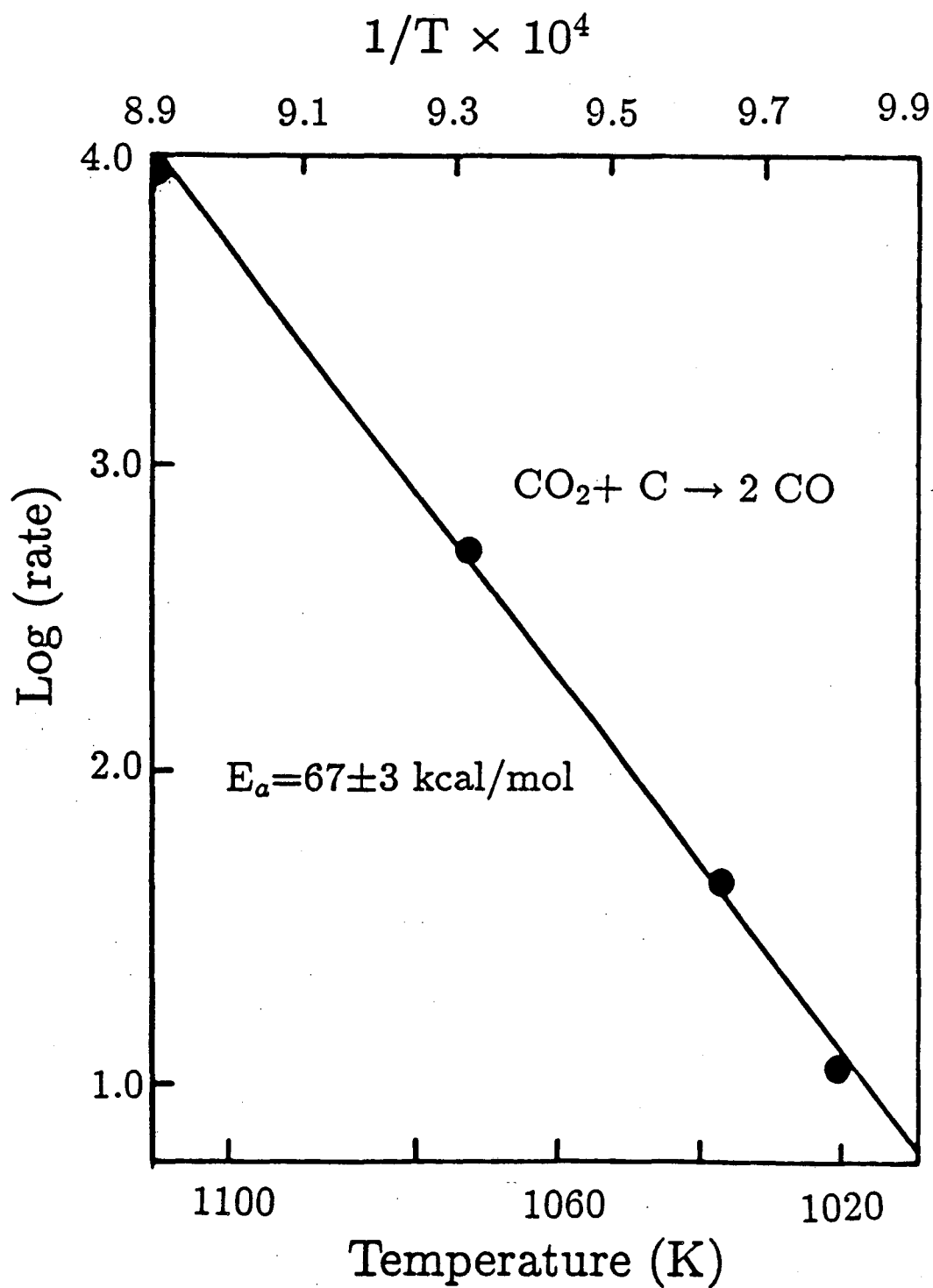


Figure 7.6: Mass-28 amu TPD spectra after 48000 L (8×10^{-4} Torr for 60 s) CO₂ exposure to graphite at various temperatures.

Figure 7.7: Arrhenius plot for the $\text{C} + \text{CO}_2 \rightarrow 2 \text{CO}$ reaction.

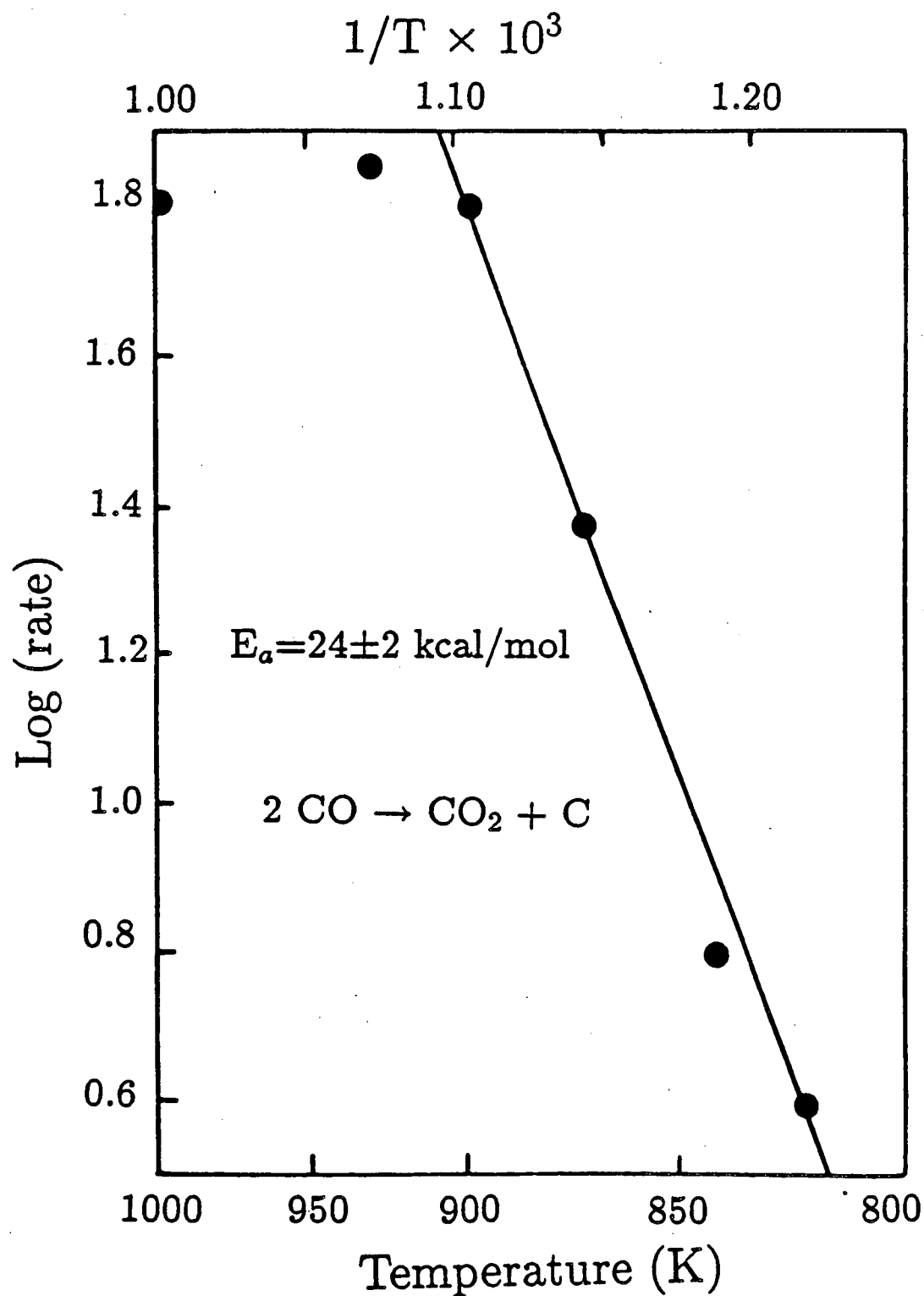


Figure 7.8: Arrhenius plot for the $2 \text{ CO} \rightarrow \text{C} + \text{CO}_2$ reaction.

adsorption temperature (figure 7.10), with the 1093 K TPD peak increasing the most. Some CO_2 (mass 44 amu) is also evolved. Figure 7.11 shows two maxima at *ca.* 460 and 690 K, and a tail around 900 K. The intensities in figure 7.11 are expanded by a factor of 20 compared to figures 7.9 and 7.10. By raising the adsorption temperature at least three other peaks at 573, 793 and 923 K are observed, so that a total of five different chemisorbed species yielding CO_2 are isolated (figure 7.12). The adsorption of a mixture of 47% $^{18}\text{O}_2$ and 53% $^{16}\text{O}_2$ produces TPD features of masses 44 amu (C^{16}O_2), 46 amu ($\text{C}^{16}\text{O}^{18}\text{O}$) and 48 amu (C^{18}O_2) (figure 7.13). As for CO_2 adsorption, total scrambling occurs, since the intensities for the mass 44 amu, 46 amu and 48 amu signals are respectively 33, 19 and 48% for the 433 K peak, and 31, 24, and 45% for the 693 K peak, as shown in figure 7.13. The theoretical values for total isotope mixing are 28, 22 and 50% respectively. Similar isotopic ratios were measured for the other TPD features at 573, 793 and 903 K, and are not reproduced here.

The O_{1s} XPS signal after extensive O_2 exposure (250 Torr O_2 for 5 min at 803 K) is shown in figure 7.14 curve A. The peak is centered around 532 eV, and is similar to that obtained after CO chemisorption, although more intense. No difference in the C_{1s} signal is observed after this treatment, as compared with clean graphite. In agreement with the TPD results (figure 7.9), oxygen on the surface desorbs thermally and the clean surface is recovered after flashing the graphite sample to 1353 K, as shown by the decrease in the O_{1s} signal (curves B to D in figure 7.14). Variations in the position of the maximum with flashing temperature are within experimental error.

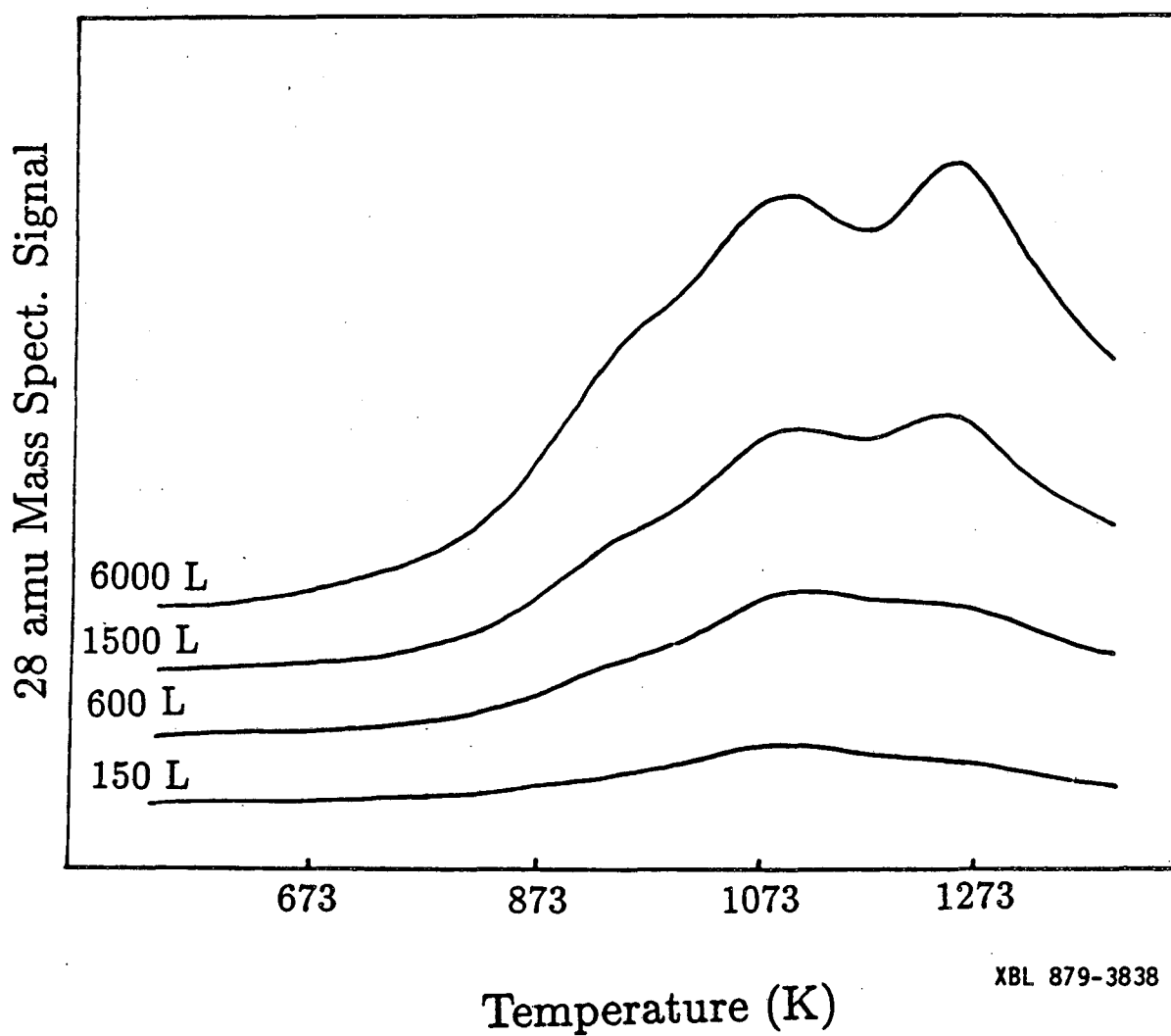


Figure 7.9: Mass-28 amu TPD spectra after adsorption of various O_2 doses on graphite at room temperature.

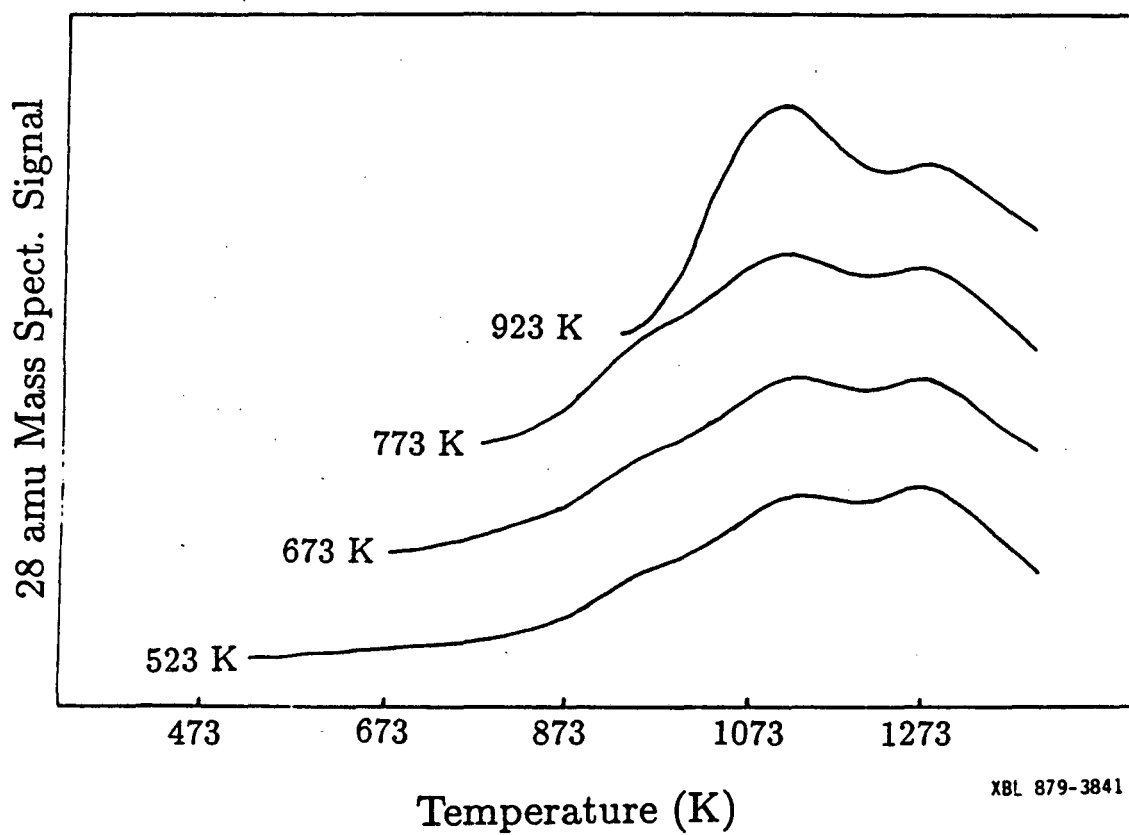


Figure 7.10: Mass-28 amu TPD spectra after 1500 L (5×10^{-5} Torr for 30 s) O_2 exposure to graphite at various temperatures.

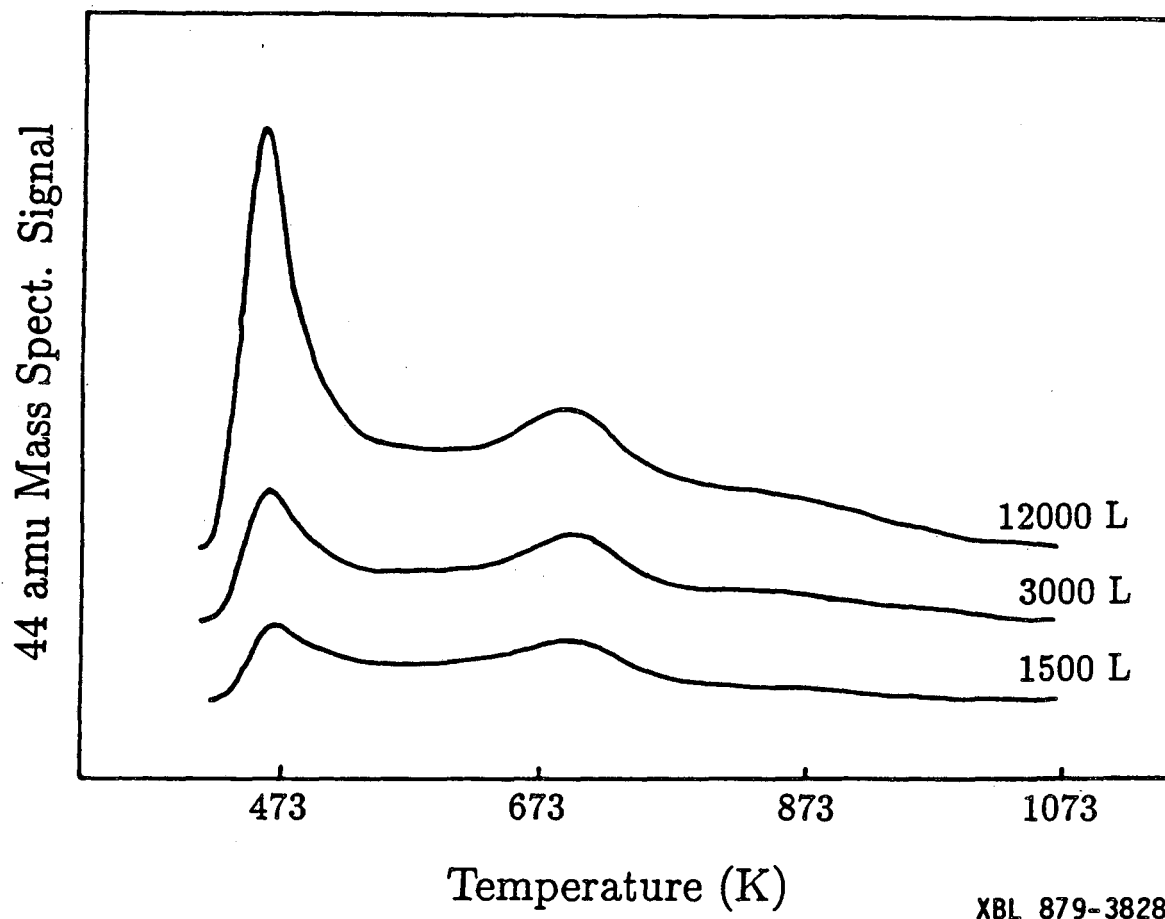


Figure 7.11: Mass-44 amu TPD spectra after adsorption of various O_2 doses on graphite at room temperature.

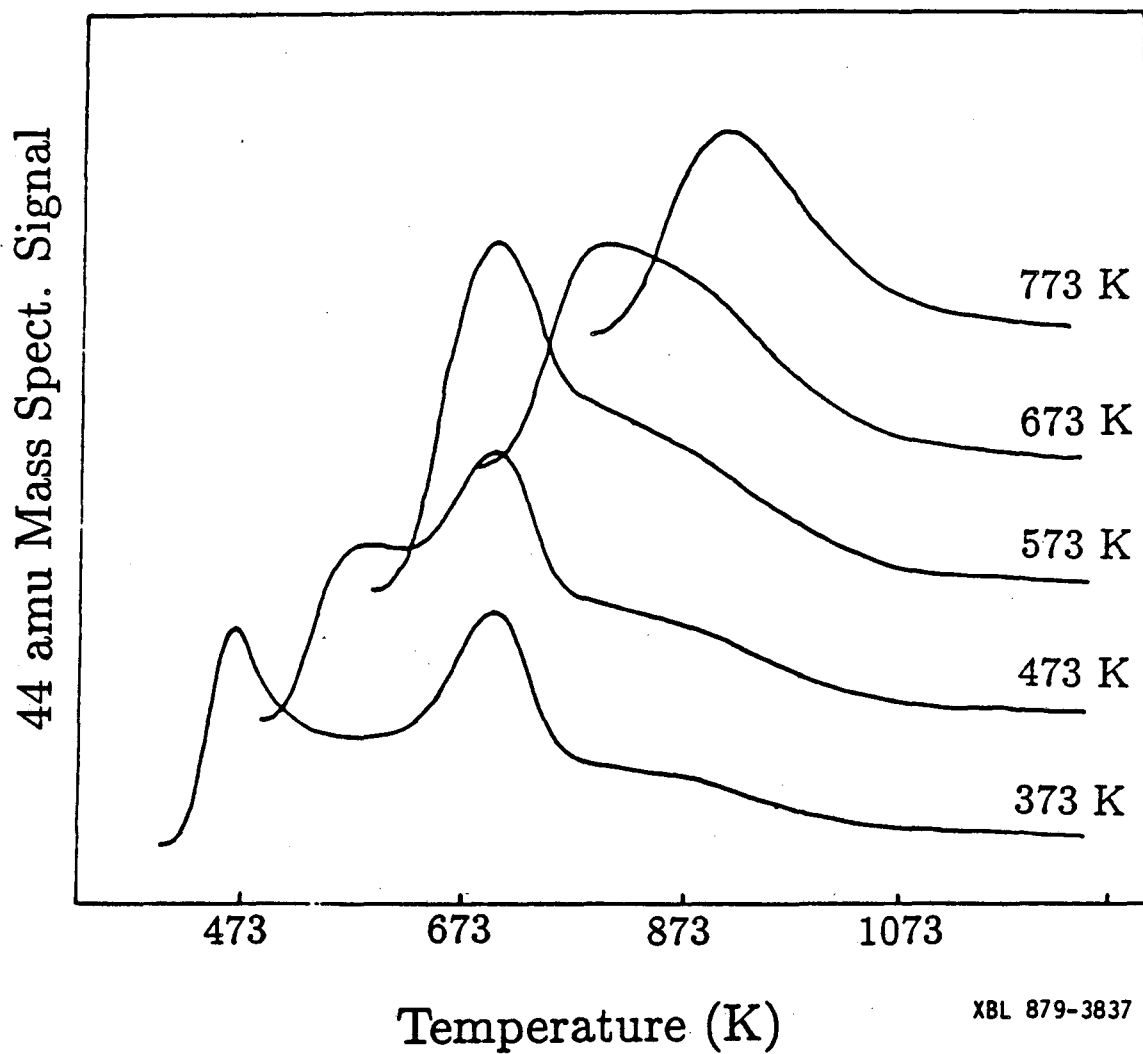


Figure 7.12: Mass-44 amu TPD spectra after 900 L (6×10^{-5} Torr for 15 s) O_2 exposure to graphite at various temperatures.

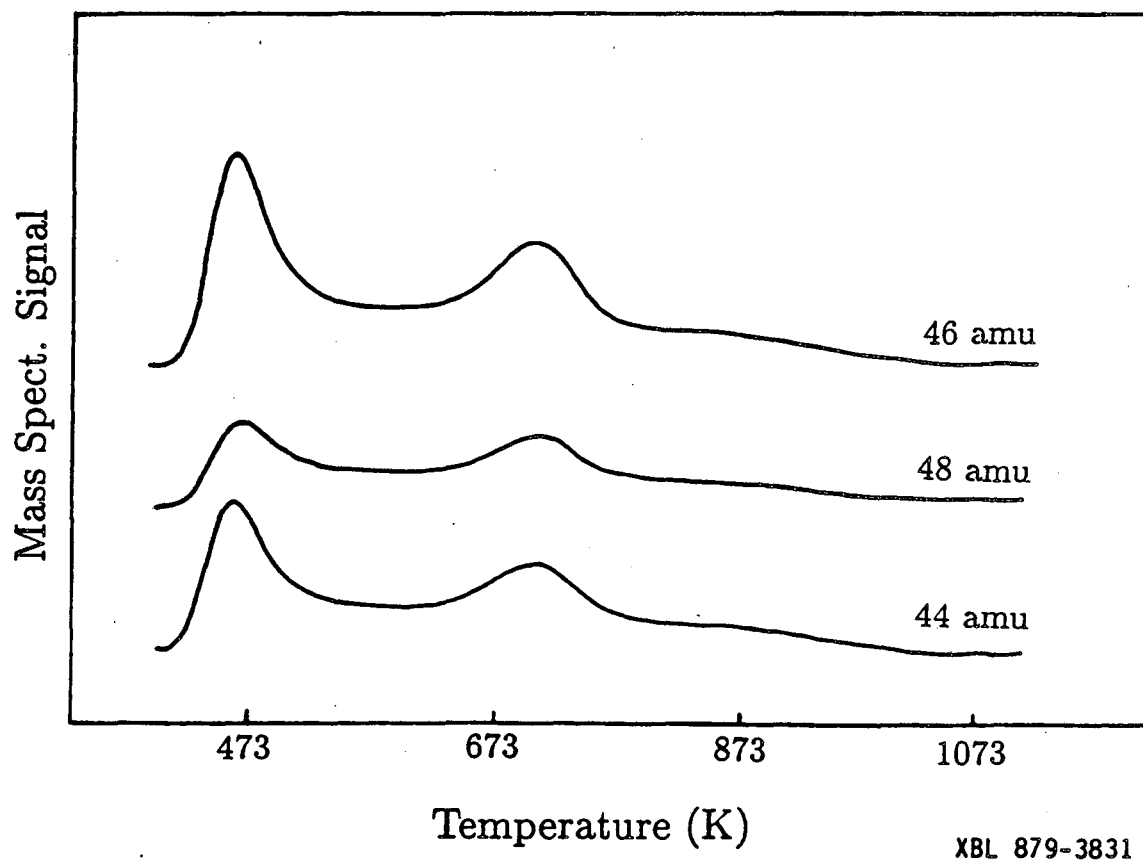


Figure 7.13: TPD spectra after exposing a clean graphite surface to 900 L (6×10^{-5} Torr for 15 s) of a mixture of $^{16}\text{O}_2$ (53%) and $^{18}\text{O}_2$ (47%) at room temperature.

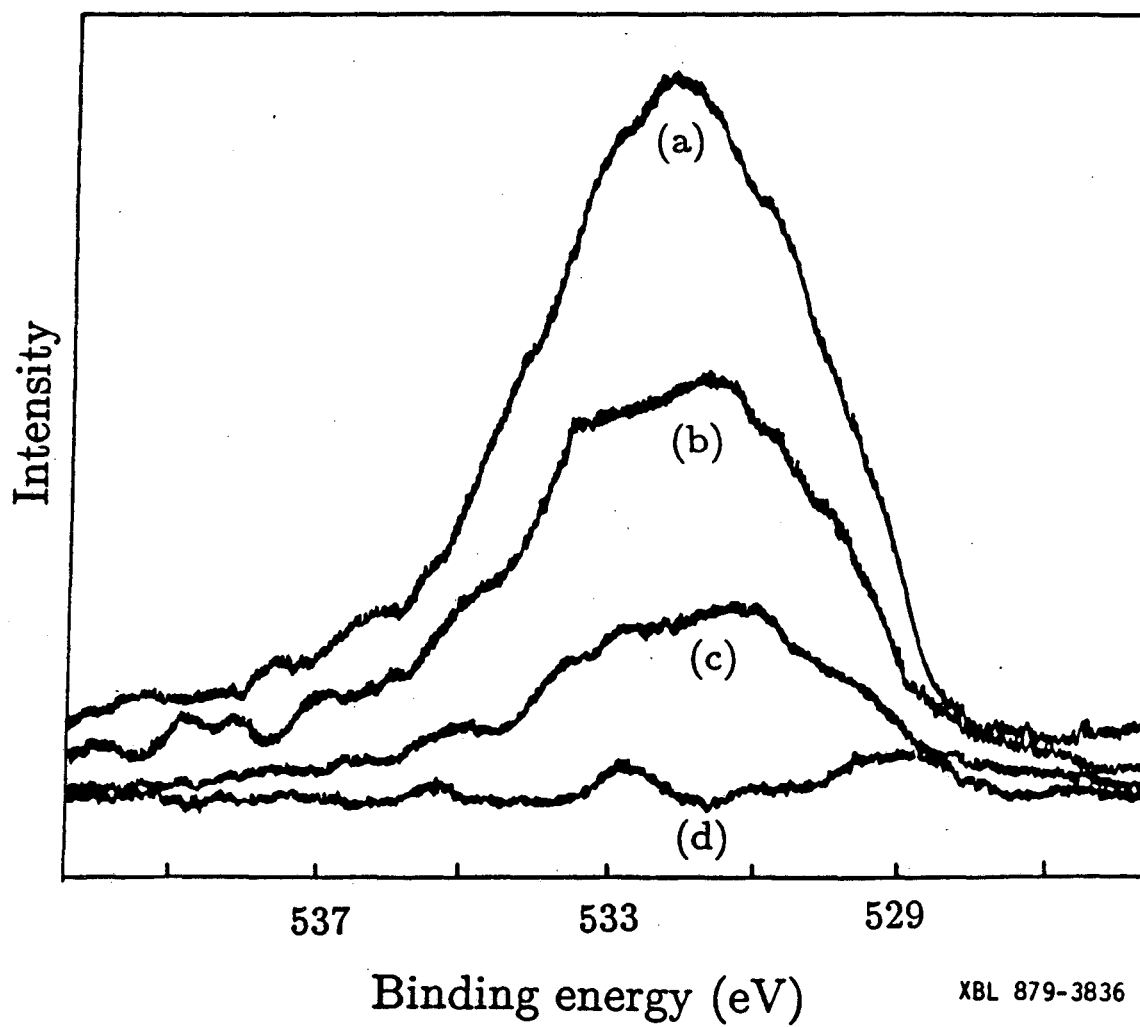


Figure 7.14: O_{1s} XPS spectrum of the graphite surface, (a) after exposure to 250 Torr of O₂ at 803 K for 5 min, and after flash at (b) 993 K, (c) 1113 K, and (d) 1353 K.

7.2.5 H₂O Adsorption

Under similar conditions, adsorption of H₂O on clean graphite is much lower than for O₂ and CO₂ adsorption. Exposures to high H₂O pressures (> 1 Torr) are necessary to detect the desorption products in TPD experiments. The TPD signal at mass 2, 44 and 28 amu, corresponding to the desorption of H₂, CO₂ and CO after exposure to 20 Torr of H₂O for 60 s are reproduced in figure 7.15. H₂ is evolved at high temperatures (*ca.* 1300 K). CO₂ desorbs in a broad peak at temperatures between 350 and 750 K. CO shows the usual feature centered around 1093 K, with a shoulder at lower temperatures, and a small peak near 1300 K. Two other peaks of mass 28 amu are observed at around 500 and 700 K. These peaks are not present after O₂ or CO₂ chemisorption, and are likely to be C₂ hydrocarbons. Other hydrocarbons are also produced. Figure 7.16 shows the TPD spectra taken after H₂O adsorption (20 Torr for 60 s), for masses corresponding to C₁ (15 amu), C₂ (26-30 amu), C₃ (39-41 amu) and C₆ (78 amu) hydrocarbons. The scale in figure 7.16 is expanded by a factor of 10 compared with figure 7.15.

The integrated intensity of the H₂ peak is slightly less than one third of the total CO produced, while the low temperature CO₂ signal, not well resolved, corresponds to less than one tenth of the total CO signal.

In order to increase the total amount of H₂O adsorbed, physical wetting of the clean graphite was carried out, using the procedure described in chapter 2. In figure 7.17 the O_{1s} signal of the wetted surface is reproduced, and compared to the signal obtained after exposure to 20 Torr of H₂O vapor for 60 s. It is immediately apparent that the wetted surface contains much more oxygen than the one exposed only to H₂O vapor. The binding energy of the O_{1s} signal after H₂O wetting (533 eV) is higher than that observed after O₂ chemisorption (532 eV).

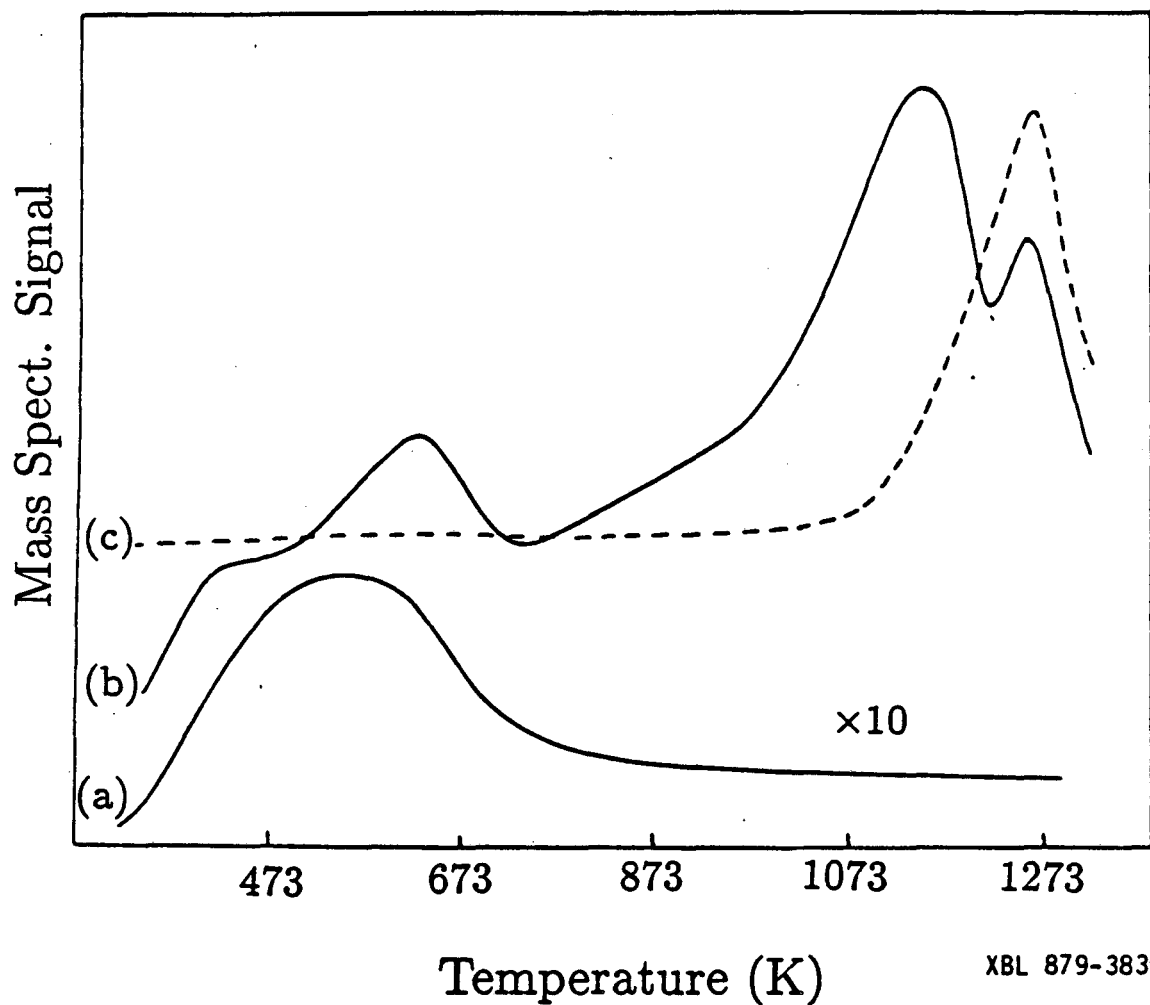


Figure 7.15: TPD spectra after exposing a clean graphite surface to 20 Torr H_2O for 1min at room temperature. (a) mass 44 amu, (b) mass 28 amu and (c) mass 2 amu.

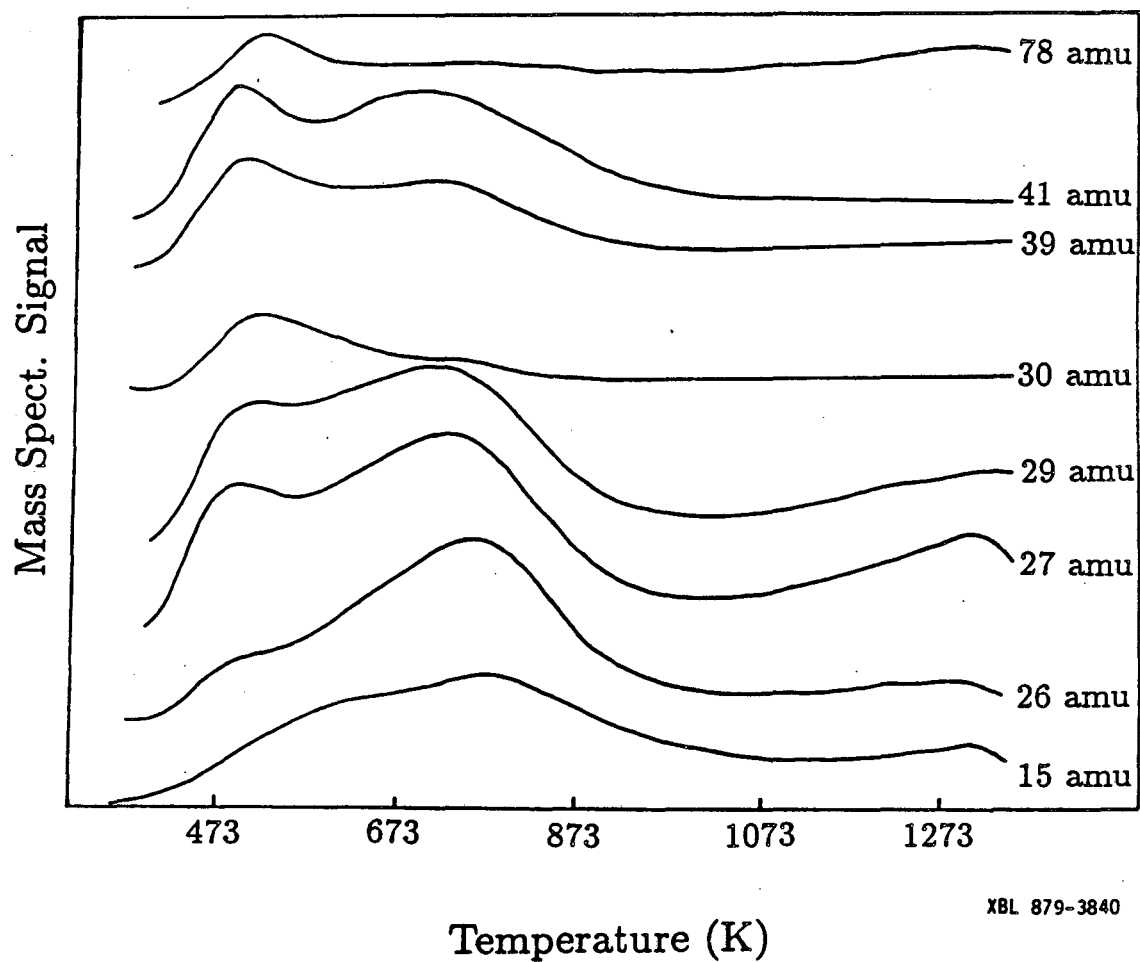


Figure 7.16: TPD spectra after exposing a clean graphite surface to 20 Torr of H_2O for 1min at room temperature. The scale is expanded by 10, compared with figure 7.15.

After physical wetting, the C_{1s} XPS signal shows a tail located in the higher binding energy region (curve A in figure 7.18). The subtraction of the signals from the wetted and clean samples (curve C) shows a maximum at *ca.* 287 eV, 2 eV higher than the peak position for the graphite signal. This shift is typical of that observed for weakly oxidized carbon atoms [16]. The integrated intensity of this difference is about 20% of that from the clean surface. Thermal decomposition of the wetted surface occurs at 623 K (figure 7.19), and the decomposition product is mostly H_2O , as observed by TPD. After flashing at 663 K, the O_{1s} signal intensity decreases considerably, and shifts to 532 eV. This signal is, however, still larger than that observed after exposure to 20 Torr H_2O vapor. The signal vanishes after heat treatment above 1000 K (figure 7.17).

7.3 Discussion

Figure 7.2 shows that after CO adsorption, CO desorbs in two temperature regions. When CO is adsorbed at room temperature, desorption peaks at 393, 503 and 673 K are observed, and when CO is adsorbed above 773 K, TPD peaks at 973 and 1093 K are obtained. These results suggest that the desorption of two distinct surface species. The high temperature species is also observed after CO_2 , O_2 and H_2O adsorption (figures 7.5, 7.11 and 7.15), and even though the CO low temperature species have not been reported after adsorption of other gases on graphite, desorption of CO from metal surfaces usually occurs in this temperature region (300-700 K) [30]. When ^{13}CO is adsorbed on clean graphite, no ^{12}CO is produced at high temperatures. This indicates that, even though the CO interacts strongly with the graphite surface, it does not dissociate.

Figure 6.4 shows that the major desorption product after CO_2 adsorption is

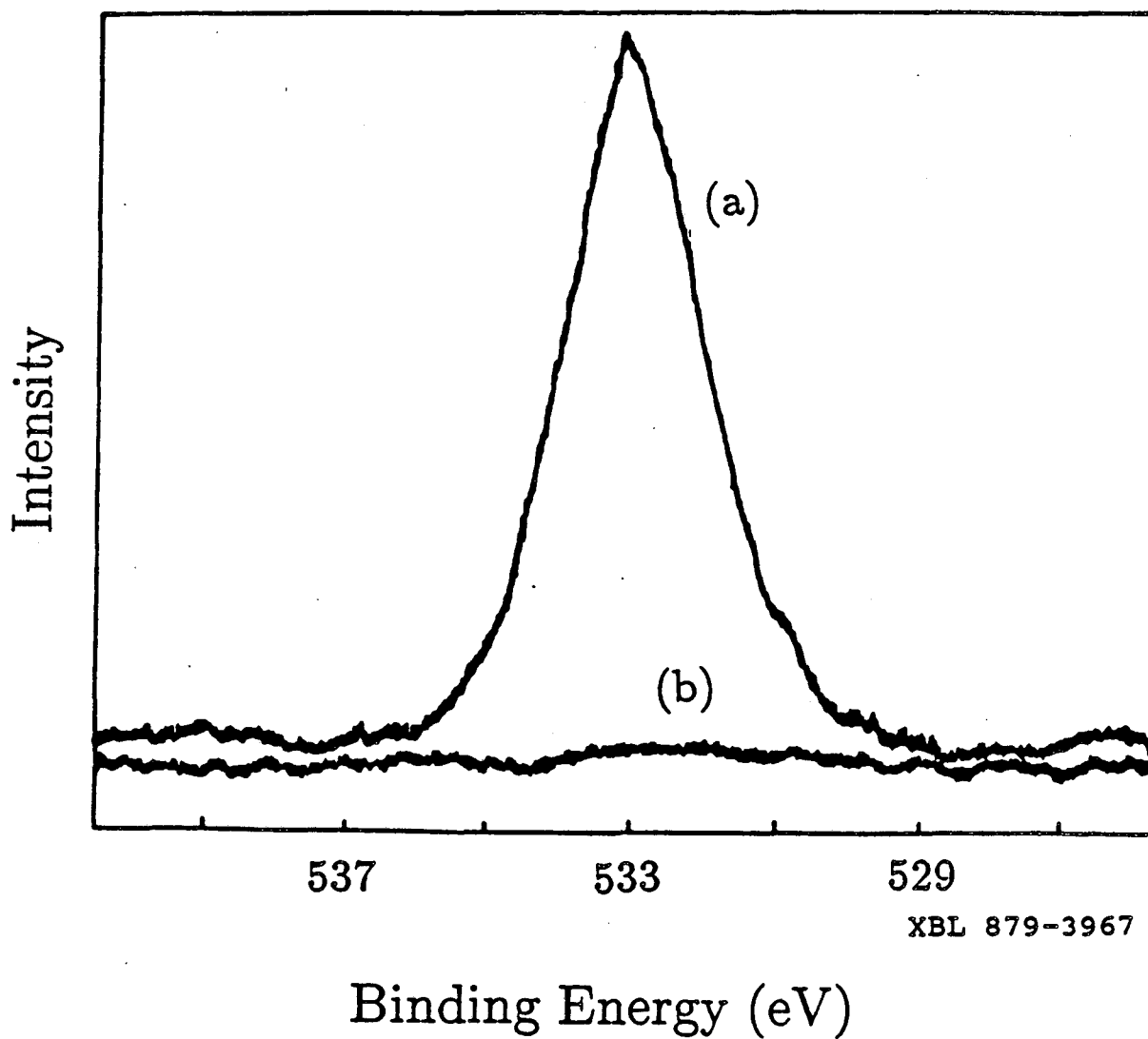


Figure 7.17: O_{1s} -XPS signal of a graphite surface after (a) wetting with H_2O and (b) exposure to 20 Torr of H_2O vapor for 60 s.

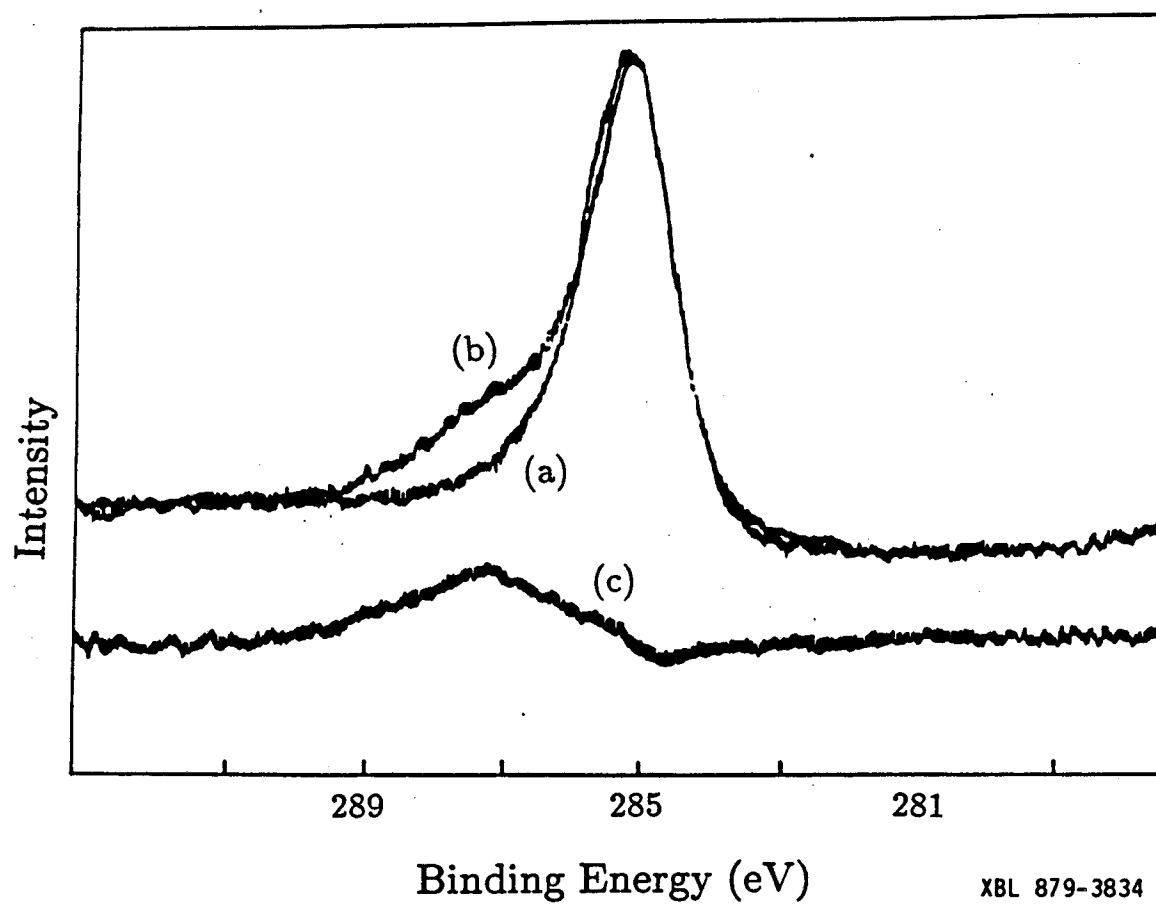


Figure 7.18: C_{1s} -XPS signal of (a) a clean graphite surface, and (b) after wetting with H_2O . Curve (c) is the difference between curves (a) and (b).

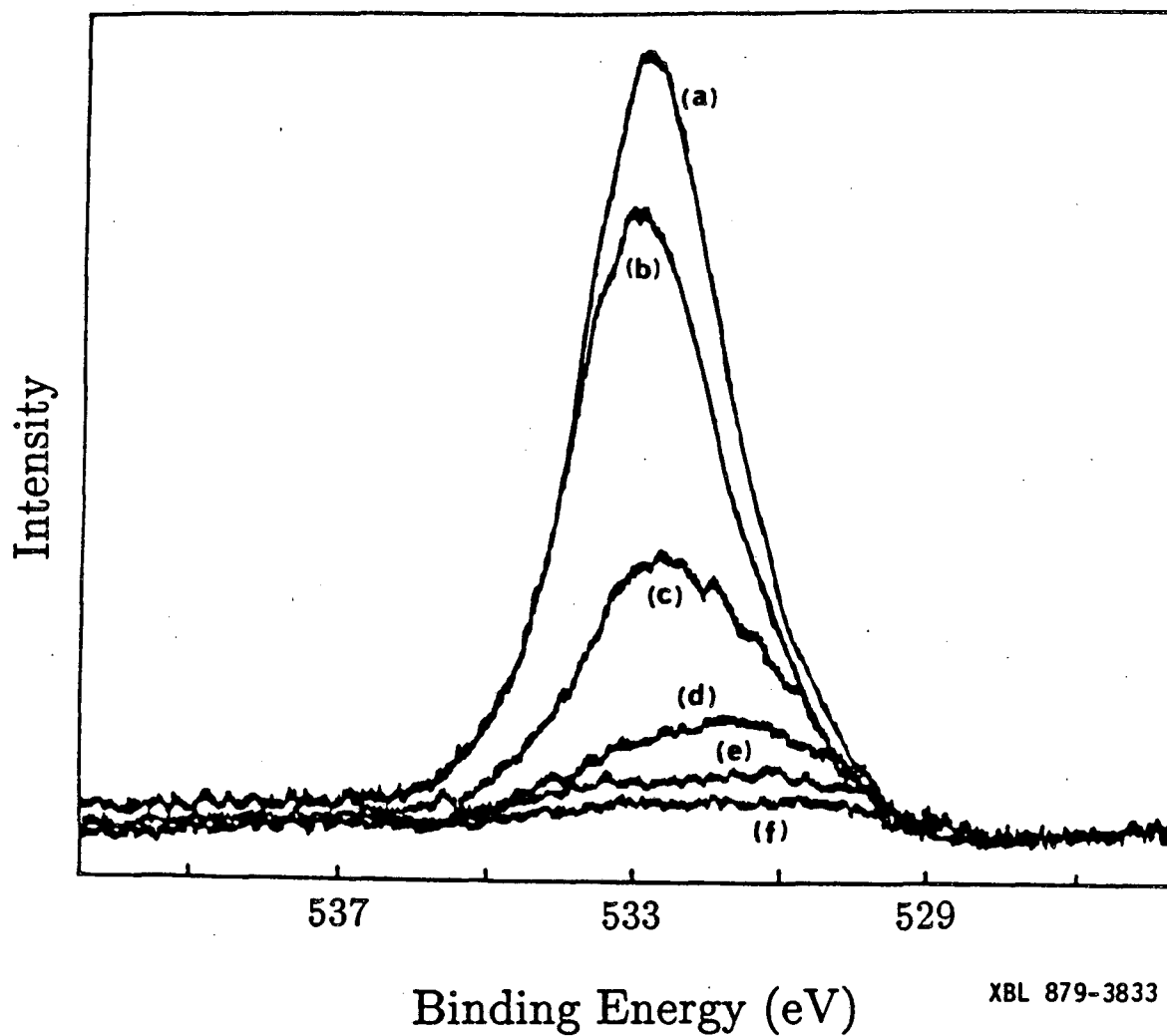
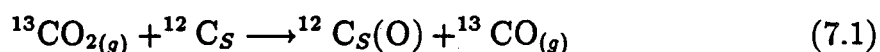


Figure 7.19: O_{1s}-XPS signal of a graphite surface, (a) after surface wetting, and after flash at (b) 523 K, (c) 593 K, (d) 663 K, (e) 803 K and (f) 1013 K.

CO at high temperatures. This figure also shows that the adsorption of $^{13}\text{CO}_2$ favors the desorption of ^{12}CO at high temperatures, indicating the dissociation of CO_2 , and the incorporation of one oxygen atom in the carbon lattice, to desorb ^{12}CO at high temperatures. This agrees with the mechanism proposed earlier by several authors [6,28,31].



where the $^{12}\text{C}_S(\text{O})$ species is likely to be the same high temperature species obtained after CO adsorption. The above reaction implies the release of ^{13}CO . The molecule could readsorb on the surface, but this is a very low probability event. For this reason, the area of the mass 29 amu peak in figure 6.4 is much lower than that of the mass 28 amu peak.

The O_{1s} signal shows a maximum at a binding energy of 532 eV after O_2 and CO adsorption (figure 7.14). This suggests, as in the case of the TPD results, that similar surface species are formed after adsorption of these gases. The peak position at 532 eV is lower than that reported for covalent non-polarized oxygen bonds (534 eV), and higher than that reported for compounds containing O^- (531 eV) [32], suggesting the formation of a polarized carbon-oxygen covalent bond.

CO_2 (44 amu) is also produced after adsorption of O_2 , H_2O , CO_2 or CO (figures 7.3, 7.4, 7.11 and 7.15), although in smaller amounts than CO (28 amu). Whereas only three desorption peaks at 443, 673 and 923 K are observed after CO adsorption (figure 7.3), five peaks can be resolved after O_2 adsorption, at 463, 573 K, 693, 793 and 903 K (figure 7.12). These various peaks are attributed to the desorption of the same type of species, but from different chemisorption sites.

TPD after H_2O exposure does not show such well resolved peaks. Instead, a broad continuum from 350 to 750 K is observed (figure 7.15), which is likely to originate from the same kind of species as after O_2 , CO_2 and CO adsorption.

After either O_2 or CO_2 chemisorption, complete oxygen scrambling is observed in the CO_2 desorbed, as indicated by isotope experiments (figures 7.5 and 7.13). This indicates that in both cases CO_2 is produced from the interaction of two adsorbed molecules. A possible mechanism for the formation of CO_2 is given later in the discussion.

Assuming a frequency factor of 10^{13}s^{-1} , Redhead's equation [33] can be used to estimate the desorption energies from the peak temperatures in a TPD experiment. The values obtained for the CO and CO_2 species observed are summarized in Table 7.1. A comparison between these values and the activation energies obtained in kinetic experiments for CO_2 gasification and the Boudouard reaction indicate that both reactions are controlled by the desorption of the products. The activation energy for CO_2 gasification (67 kcal/mol) from kinetic experiments agrees with the one obtained from the desorption temperature for CO formation after CO_2 exposure (64 kcal/mol). Also, the activation energy derived from the Boudouard reaction (24 kcal/mol) coincides with the lower limit in activation energy derived from desorption of CO_2 after CO adsorption (28 kcal/mol).

TPD experiments after H_2O adsorption show that H_2 is evolved at very high temperatures (*ca.* 1300 K), in agreement with results obtained by Matsumura *et al.* [27]. From the integrated intensities, the amount of H_2 evolved accounts for less than one third of the total CO produced. The amount of hydrogen obtained from the desorbing hydrocarbons is one order of magnitude less than the H_2 evolved. After H_2O chemisorption, the two hydrogen atoms produced can either recombine

Table 7.1: Desorption temperatures and activation energies for desorption of CO and CO₂ after adsorption of CO, CO₂, O₂ and H₂O.

Adsorption gas	Adsorption temp (K)	Desorption product	Desorption temp (K)	E_{des}^a (kcal/mol)
CO	> 750	CO	973–1253	64–83
CO ₂	room temp			
O ₂	323–923			
H ₂ O	room temp			
CO	323–573	CO	393–673	25–44
CO	373–723	CO ₂	443–923	28–60
CO ₂	room temp		423	27
O ₂	323–923		463–923	28–60
H ₂ O	room temp		350–850*	21–51

* One broad feature.

and evolve as H_2 , or form carbon-hydrogen bonds on the surface, which then decompose around 1300 K.

Since hydrocarbon evolution after H_2O exposure occurs between 350 and 650 K, it probably only involves breaking of carbon-carbon single bonds, rather than the more stable aromatic bonds. To account for such behavior, the existence of aliphatic fragments such as $-CH_2-$, $-CH_3$, or even $-C_2H_5$ functionalities is proposed. Their thermal decomposition would lead to radical formation, which would yield hydrocarbon molecules after recombination. The origin of the two maxima around 450 and 650 K (figure 7.16) remains unexplained.

As mentioned in the introduction, there has been a great number of studies on surface oxides adsorbed on carbon. Based on spectroscopy methods, these studies have proposed the existence of various types of surface groups. Our results imply that some of these species are present on the graphite surface after CO , CO_2 , O_2 and H_2O adsorption. It would be interesting, then, to assign the various TPD features obtained in this work to plausible surface species. As previously mentioned, analysis of TPD data provides information about the desorption energy of the surface species involved, which is related to the strength of the bonds involved in the desorption process. By comparing these values with bond energies in similar organic compounds, tentative assignments of the various desorption features to surface species can be made.

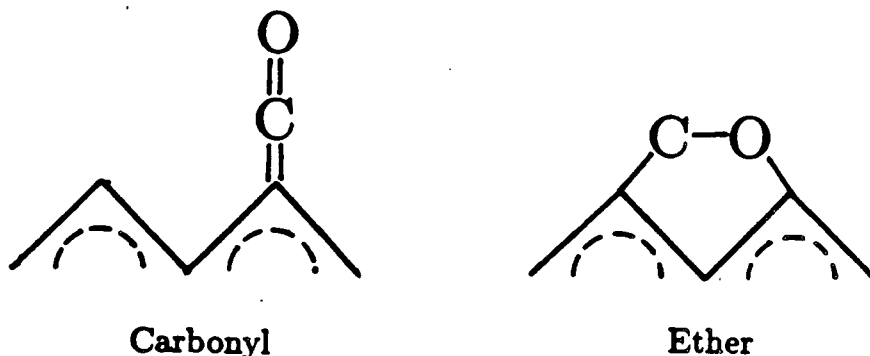
It should be noted, however, that it is difficult to obtain precise values of the bond energies on the graphite surface, based on desorption energies calculated from TPD experiments. First, desorption energies are the sum of the activation energies for desorption and the surface bond energy. The activation energy for desorption is very low in the case of CO desorption from metal surfaces [30], but

it is known to be of the order of 10 kcal/mol [4] or greater [9] for O_2 adsorption on graphite. In addition, Sanderson has pointed out [34] that the reorganizational energy of radicals after breaking the surface bond is an important contribution to the desorption energy, and in the case of graphite this energy is expected to be considerable, due to electron delocalization. Another complication to the determination of the bond strengths from TPD experiments is that the edges of the graphite particles contain various adsorption sites that lead to species of different stability, whose desorption will broaden the TPD features [12]. For example, theoretical calculations [35] have shown that arm-chair sites are less reactive than zig-zag sites but give more stable species after adsorption. It is thus expected that TPD features from surface species adsorbed on zig-zag structures would be more intense, and appear at higher temperatures than those from arm-chair structures.

Despite the complexity of the surface structure and the large number of variables involved in the desorption energy, it can be assumed that surface species of the same type, adsorbed on different sites, desorb in the same temperature range. Some qualitative trends, thus, can be established. For example it is expected to be easier to break a non aromatic carbon-carbon bonds (~ 80 kcal/mol), than a bond in the graphite lattice (~ 115 kcal/mol); and that at temperatures below 1500 K, carbon-oxygen single bonds can be thermally dissociated (~ 85 kcal/mol), but double bonds cannot (~ 175 kcal/mol).

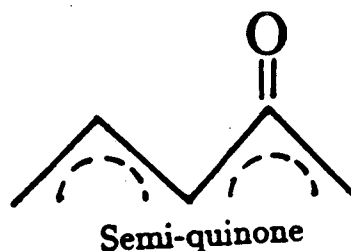
Based on the TPD features observed, three types of surface species can be suggested after adsorption of CO , CO_2 , H_2O and O_2 on graphite. The low temperature (373-673 K) CO precursor observed after CO adsorption, the high temperature CO precursor (973-1273 K) observed after adsorption of all four gases and the CO_2 precursor (473-873 K) also observed after adsorption of all four gases.

The low temperature CO precursor is likely due to weakly bound species such as carbonyl and/or ether groups. The low desorption temperature of this species suggests that no graphitic carbon-carbon bonds are broken during the process.



To the knowledge of the authors, carbonyl species adsorbed on carbon have never been cited in the literature before, but analogy with CO species adsorbed on single crystal-metal surfaces [30] makes them favorable candidates. The transformation into ether groups is only a ring closure and appears energetically favored. The lack of spectroscopic data, however, prevents any further comment.

The high temperature CO precursor is assigned to a semi-quinone species.



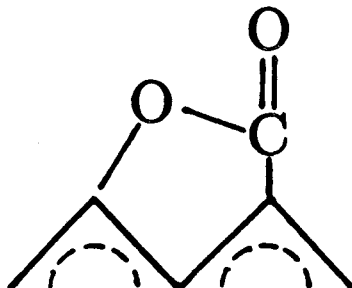
The high stability of quinone groups in polycyclic aromatic compounds [36] gives strong support to the existence of semi-quinone groups on the graphite surface. The desorption of this species involves the breaking of two carbon-carbon bonds in the graphite lattice, and explains the high desorption temperature. In

the case of CO_2 , H_2O and O_2 adsorption, this species might be formed by reaction between an oxygen atom and a carbon atom, but in the case of CO adsorption there is no dissociation, and this species is formed by insertion of a molecule in the graphite lattice. This insertion requires graphitic carbon-carbon bond breaking both for the formation and desorption of the species, and explain why the formation is such a highly activated process, and why the desorption occurs at such high temperatures.

Although proposed earlier by several authors [12,13,15,16,17], hydroxyl or phenol groups do not appear to be good candidates for surface species after H_2O adsorption, based on our TPD results. The high similarities on the CO desorption signal, after exposures to either O_2 , CO_2 , CO or H_2O is a good indication that the same type of species (possibly a semi-quinone) is produced in all cases, as Kelemen and Freund pointed out [10]. The keto-enolic equilibrium, totally displaced towards the ketonic form for polycyclic aromatic compounds of high order [36] is another argument in favor of the nonexistence of phenol groups on the graphite surface.

At this point it is important to comment on the nomenclature used to identify these species. The name carbonyl has been employed to identify the low temperature CO species, rather than ketone, in agreement with IUPAC rules [37]. It must not be confused with the CO high temperature species. Most authors refer to this high temperature species as carbonyl, but a more specific determination, such as ketone or oxo [38], or better semi-quinone, has been chosen in this work, in order to emphasize the strong conjugation with delocalized electrons as encountered in quinoid structures.

The CO₂ precursor is assigned to a lactone group.



Lactone

The formation of CO₂, from the decomposition of this species is analogous to decarboxilation reactions, which are very well known in organic chemistry [39]. This chemical species has been proposed by several authors [6,8,13,25], and the TPD results presented here suggest the existence of five different adsorption sites for this species, having activation energies for desorption ranging from 26 to 53 kcal/mol.

Based on the results presented, a general scheme for the desorption products after O₂, CO₂, H₂O and CO adsorption is proposed (figure 7.20). In all the cases studied, the desorption of CO at high temperatures is the main feature in the TPD experiments. It is thus proposed that the main pathway for adsorption of the reactants is the formation of a high temperature precursor species, possibly the semi-quinone. The activation energy for adsorption depends on the molecule itself, the site on which it adsorbs, and the coverage. O₂ dissociates to give two CO precursors, CO₂ yields a CO precursor and a gaseous CO molecule, and H₂O produces two hydrogen atoms which can either recombine (the more probable event) or form carbon-hydrogen bonds (the less probable event). The latter bonds can be aromatic, and desorb as H₂ around 13)) K, or aliphatic and yield hydrocarbons at lower temperatures.

If the temperature is lower, say below 900 K, thermal decomposition of the CO precursor cannot occur, and only the formation of the CO₂ precursor (lactone group) is possible. The total oxygen scrambling observed after O₂ and CO₂ adsorption can be explained by an equilibrium between the CO and CO₂ precursors in the presence of the reactant gas. Since in the TPD experiments the amount of CO desorbed is much higher than the amount of CO₂, this equilibrium is probably shifted towards the formation of the more stable CO precursor.

More spectroscopic data is necessary in order to support the assignment of the two CO and the CO₂ precursors to a carbonyl, a semi-quinone and a lactone group respectively. Vibrational techniques such as infrared, Raman or high resolution electron energy loss spectroscopy (HREELS) under UHV conditions could bring fruitful indications.

In all the cases studied, the sticking coefficient of the gases is very low. The highest coverages, at a given exposure, were obtained after O₂ chemisorption, and even in this case no changes in the C_{1s} XPS peaks were observed, when compared with those for clean graphite. This indicates that only a few percent of the total carbon atoms are bonded to chemisorbed oxygen, even after high exposures (250 Torr for 60 s at 773 K), suggesting that the adsorption is highly activated.

Despite the low coverages, strong TPD signals were observed. From these signals, in principle, activation energies of adsorption can be determined by studying variations in coverage with adsorption temperature, at a given exposure. In practice the imprecision in the intensity measurement of a group of broad and overlapping peaks makes accurate determinations difficult. Some qualitative information, however, can still be obtained. For example, for O₂ chemisorption, the 1093 K CO

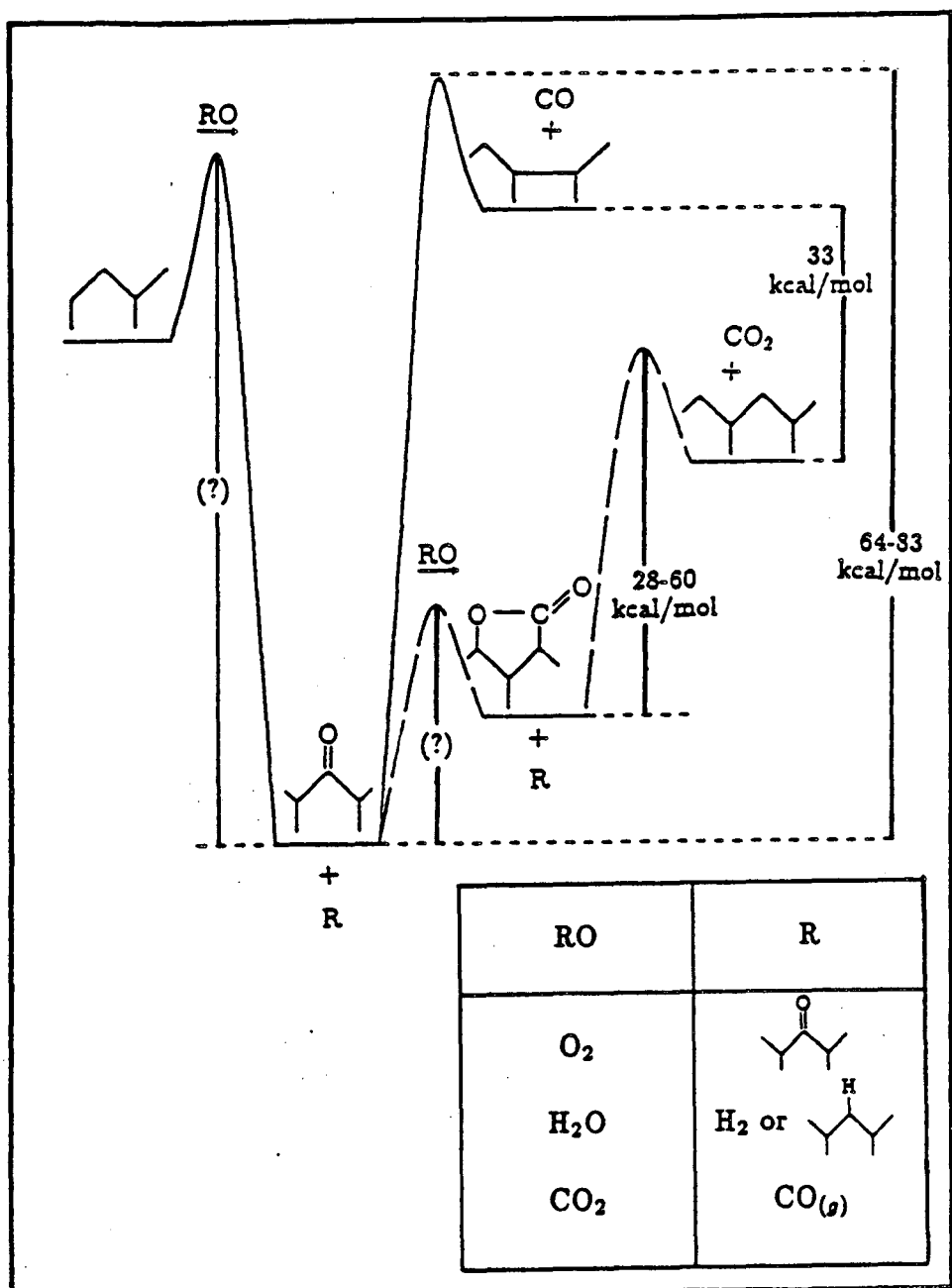


Figure 7.20: General schematic mechanism for graphite gasification reactions.

peak intensity varies with temperature, and the 1253 K peak intensity is almost independent of temperature (figure 7.6), whereas in the case of CO₂ chemisorption, the change in intensity of the 1253 K peak with adsorption temperature is larger than that of the 1093 K peak. This indicates that the activation energy for adsorption is dependent on both the type of molecule and type of site.

The physical wetting of clean graphite by liquid H₂O favors the formation of different surface species than those formed after the adsorption of H₂O vapor. After physical wetting, the amount of H₂O adsorbed is much higher. This is clearly shown by the appearance of a shoulder at 287 eV in the C_{1s} XPS signal, amounting to 20% of the carbon signal (figure 7.18). In contrast, the signal obtained after H₂O vapor adsorption is the same as that for clean graphite, indicating that in this case, only a very small fraction of the carbon atoms interact with H₂O. The position of the shoulder after physical wetting is characteristic of slightly oxidized carbon atoms as in compounds such as alcohol or ethers. The O_{1s} signal (figure 7.17) shows a large peak centered at 533 eV. This value is 1 eV higher than that observed after O₂ and CO adsorption, and indicates a weaker electron transfer from the carbon to the oxygen atom, which is consistent with the C_{1s} result.

The desorption at rather low temperatures (623 K) (figure 7.19), giving H₂O as the main component, again suggests a weakly bound species. Phenolic groups can be ruled out since they would show an O_{1s} signal at lower binding energies (531 eV). Also, the recombination of a C-OH and C-H group to recover the H₂O molecule should occur at much higher temperatures, since it involves the breaking of a carbon-hydrogen bond in the graphite ring. The proposed species is a solvate between H₂O and the edge carbon atoms with bond energies about 35 kcal/mol, as given by the desorption temperature [33].

After heating above 650 K, the O_{1s} binding energy shifts toward 532 eV. This indicates that a fraction of the chemisorbed H_2O is able to dissociate and form CO precursor species on the surface. The intensity of this signal is higher than that observed after H_2O vapor adsorption, and shows that physical wetting increases the H_2O dissociative chemisorption.

The reaction of H_2O with graphite is of great interest for the gasification of carbon solids. High temperature non-catalyzed reactions, to give CO and H_2 probably proceeds along the high temperature route of figure 7.20, that is via the formation of the CO precursor and H_2 recombination.

To lower the temperature required to run this process, ways to facilitate the formation of the CO_2 precursor, and its further decomposition must be found. Also of great importance, and probably related to the previous point, is the accessibility of the H_2O molecule to the active sites on the graphite-grain edges. XPS studies show that the H_2O vapor, at least at room temperature, cannot wet the surface in a significant fashion, whereas physical H_2O wetting covers 20% of the total number of sites (figures 7.18 and 7.17). One must therefore find ways to increase the surface wettability (sticking coefficient) by decreasing the activation energy for adsorption. There is no doubt that KOH, apart from other possible catalytic properties, can provide such an action, owing to its hydrophilic properties. Additional TPD and XPS measurements must be systematically undertaken on the graphite/KOH system in order to obtain a better understanding of the catalytic reaction mechanism. Preliminary experiments on this system tend to suggest that the catalyst does not change the decomposition temperature, but rather, enhances dramatically the intensities of the TPD peaks. That is, the chemistry does not change, and only the H_2O sticking coefficient increases. If confirmed, these obser-

ations would be of great interest.

7.4 Summary

CO, CO₂, O₂ and H₂O chemisorption yield the same CO precursor on three different sites, decomposing at 973, 1093 and 1253 K. This species has been tentatively assigned to a semi-quinone functional group. As by-products of the CO precursor, CO₂ adsorption gives gaseous CO, and H₂O adsorption gives hydrogen atoms that either recombine to form H₂, or form carbon-hydrogen bonds analogous to those in benzene or in aliphatic hydrocarbons. The first type decomposes around 1300 K to produce H₂, and the second produces hydrocarbons below 750 K.

A small fraction of the CO precursors react with the adsorbing gas to produce the CO₂ precursor, which then decomposes thermally between 450 and 870 K. A lactone species has been proposed as the CO₂ surface precursor.

CO adsorbed at room temperature leads to the formation of a weakly bound species, assigned to a carbonyl group, which desorbs at 473 K as CO. H₂O physical wetting also leads to a weakly bound species, suggested to be a hydrate, and desorbs at 623 K as H₂O.

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