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FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION: QUARTERLY REPORT, JAN. 1, 1987-MARCH 31, 1987

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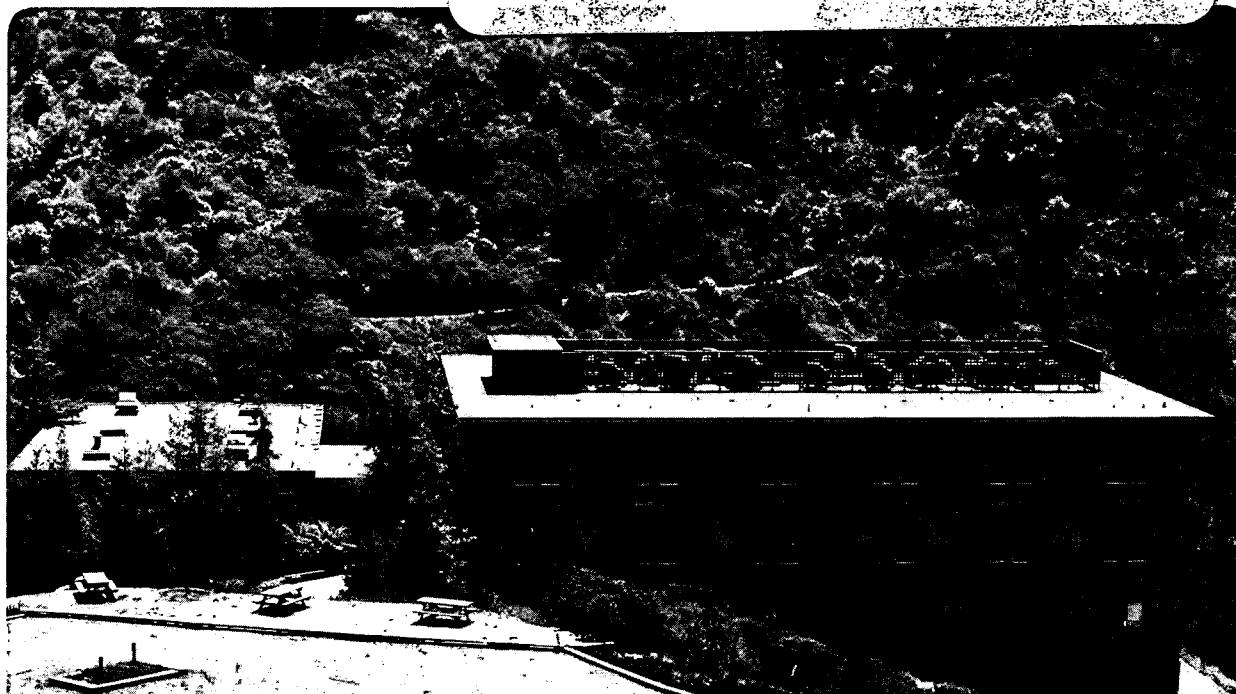
FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION:
Quarterly Report, January 1, 1987–March 31, 1987

H. Heinemann

March 1987

DISCLAIMER

QUARTERLY REPORT

January 1, 1987 – March 31, 1987

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

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Berkeley, CA 94720

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I.   Task Description for FY 1987

This program studies the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrogen and/or synthesis gas. Relatively low temperatures are being used. The catalysts under investigation are compounds of potassium and a transition metal oxide. Major objectives are the extension of the work from chars to coke; the effect of H_2, CO and CO_2 partial pressure on the gaseous product distribution; and the inhibition of catalyst poisoning by ash components.

II.   Highlights

1.   Two papers have been prepared for publication. One deals with controlled atmosphere electron microscopy and the other with catalytic steam gasification of chars. Both papers are appended in draft form.

2.   It has been found that the NiO/KOH catalyst is very active for the Boudouard reaction. Experiments were carried out with CO_2 in the absence of water.

3.   The NiO/KOH catalyst promotes the hydrogenation of CO to methane in the absence of water at 673K and above. Since CO_2 can be reduced to CO by char, CO_2 also can go to methane.

4. A hypothesis has been arrived at that the ratios of $CO/CO_2/CH_4$ obtained during char gasification with steam over NiO/KOH can be controlled by adjusting the water partial pressure. This assumption based on single gas experiments is now being tested.

5. XPS data obtained and described in earlier reports are currently being refined and analyzed and will be included in an additional publication.

III. **Progress of Studies**

a) Reactions of carbonaceous material with H_2, CO and/or CO_2 over a Ni/K catalyst.

Previous reports have mentioned that the steam gasification of carbon catalyzed by Ni/K catalysts favors the formation of H_2 and CO_2, and that in the case of some chars a small fraction of CO is also present. During this quarter the catalytic activity of the Ni/K catalyst for the reaction between these gases and carbon and with each other has been investigated without water being present in the inlet gases. Graphite was used as a carbon source since its equivalence with chars for mechanistic studies had previously been demonstrated.

The results presented here were obtained under high conversion conditions (low flow rates) and the experiments were designed to provide qualitative information. Further experiments are currently being done to obtain kinetic information.

The catalyst was loaded on graphite samples by the incipient wetness method, using KOH and $Ni(NO_3)_2$ solutions. The catalyst loading was equal to 1×10^{-2} mole Ni/mol C with a Ni/K molar ratio equal to 1.0. The catalyst was treated in Ar at $450^{\circ}C$ after loading it to graphite and previous to being exposed to the reactant gases.

In this quarter three reactions were studied: the CO_2 gasification of carbon; the CO disproportionation to CO_2 and carbon; and the hydrogenation of CO_2 in the presence of carbon.

i) CO_2 gasification of carbon/CO disproportionation

Preliminary results indicate that the $Ni(NO_3)_2$/KOH catalyst has excellent properties for the CO_2 gasification of carbon (eq. 1), the reverse Boudouard reaction:

$$CO_2 + C \rightleftharpoons 2CO \qquad (1)$$

When a 1.0 ml/min flow of CO_2 is passed above 673K over a graphite sample loaded with the Ni/K catalyst, CO_2 conversions above 50% were observed and the activity remained constant with time over a 10 hour period at 773K.

The Ni/K mixture is also a good catalyst for the reverse reaction, that is the CO disproportionation to produce CO_2 and C. Signs of deactivation for this reaction were observed, however, after 10 hours at 773K.

ii) CO_2 hydrogenation in the presence of carbon

Since the Ni/K catalyst has excellent properties for CO formation from CO_2 gasification of carbon, it was decided to add H_2 to CO_2 in order to study CH_4 formation.

When 1.0 ml/min flows of H_2 and CO_2 are passed over a Ni/K loaded graphite sample at 673K, CH_4, CO and H_2O were observed as reaction products. These products can be accounted for by the reactions represented by equations (1) and (2).

$$CO_2 + C \rightleftharpoons 2CO \qquad (1)$$

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O \qquad (2)$$
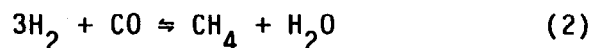
The percentages of CH_4 and CO in the outlet gases varied between 10 and 20% at 673K, depending on the initial ratios of H_2 to CO_2. A higher H_2 concentration in the inlet gases increases the CH_4 fraction and decreases the CO fraction in the products. This suggests that the CH_4 is produced from the reaction between the H_2 and CO that is formed by the CO_2 gasification of carbon (eqs. 1 and 2).

iii) Hypothesis

In previous experiments it has been observed that the Ni/K mixture is an excellent catalyst for steam gasification of carbon solids to form

H_2 and CO_2, but no CH_4 and CO were observed. The results presented in this report indicate that the Ni/K catalyst is active for formation of CH_4 and CO, with H_2O as a by-product, if H_2 and CO_2 are used as reactants. From this observation it is predicted that by changing the water partial pressure, one can control the product distribution obtained from the steam gasification of carbon. At lower partial pressures of water CH_4 and CO will be produced, but as the partial pressure of water increases, these gases are decomposed by steam reforming and water gas shift reactions, and the formation of H_2 and CO_2 is favored.

Experiments are currently being done to test this idea and to obtain kinetic information about the reactions previously described such as rates of reaction, activation energies and partial pressure dependence for the CO_2 gasification of carbon, the CO disproportionation and the hydrogenation of CO_2 in the presence of graphite.

b)   Additional work performed

During this quarter, two publications have been written including the kinetic data on char gasification with steam and the controlled atmosphere electron microscopy results. The data included in this publication has been discussed in previous reports and copies of the publications are appended to this report.

The analysis of XPS results obtained during the last year has continued with the intention of including these data in a publication to be prepared during the next quarter.

APPENDICES

CAEM Study of The Gasification of Graphite by H_2O, H_2 and O_2 Catalyzed by a Ni/K Mixture

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ABSTRACT

The gasification of graphite by H_2O vapor, wet H_2 and wet O_2, catalyzed by a Ni/K mixture has been studied using controlled atmosphere electron microscopy (CAEM). In H_2O vapor the carbon consumption, between 550 and 1100 C, is catalyzed by an edge recession mode of attack in the [11$\overline{2}$0] direction, with no sign of deactivation. An activation energy of 30.8 ± 0.9 Kcal/mol was obtained in this case. In wet H_2 both channeling and edge recession occurr simultaneously. The activation energy obtained was equal to 30 ± 2 Kcal/mol. The catalyst deactivates above 1000 C, but can be regenerated by treating the sample in H_2O vapor at 600 C. In wet O_2, graphite is also gasified by edge recession, but no preferred direction was observed. The catalyst maintains its activity up to 1000 C, and an activation energy of 25 ± 2 Kcal/mol was obtained. These results show that the catalytic properties of the Ni/K mixture are superior to those of Ni and K alone due to a cooperative effect between the components.

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INTRODUCTION

Recently [1,2], we have reported that mixtures of KOH and various transition metal salts were good catalysts for the steam gasification of graphite and char. These catalysts promote the formation of H_2 and CO_2 above 550 C, and have a high resistance to poisoning. Out of all the catalysts studied, the one derived from a mixture of KOH and $Ni(NO_3)_2$ has the best kinetic properties for this reaction. This catalyst, denominated from now on as Ni/K catalyst, shows the highest activity for H_2 production at 580 C (1.2 mlH_2/min) and a relative low activation energy ($\sim$ 30 Kcal/mol).

In this work we have used controlled atmosphere electron microscopy (CAEM) to characterize this catalyst in further detail. We studied the interaction between the Ni/K catalyst and graphite surfaces in three gas enviroments; H_2O vapor, H_2/H_2O, and O_2/H_2O. This technique is an excellent tool to study the surface mobility and wetting properties of the catalyst. It also allows the determination of the carbon mode of attack promoted by the catalyst, and the intrinsic rates of carbon consumption. This last result 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 actives sites.

In this article, our goal is to show that the Ni/K catalyst has distinctive morphological and kinetic properties for carbon gasification. We will describe and discuss these properties in the three gas environments studied, and then compare them to those reported earlier for KOH or Ni metal [3–6], putting emphasis on the advantages of the mixture over the components used alone. We conclude that these advantages are due to a cooperative effect between Ni and K.

EXPERIMENTAL

A detailed description of the CAEM technique can be found elsewhere [7]. Nickel and potassium are introduced onto transmission specimens of natural single crystal graphite (Tincoredoga NY) as an atomized spray, using 0.1% solutions of $Ni(NO_3)_2$ and KOH. Samples were then dried in air and introduced in the environmental cell.

Prior to exposing the sample to the reactant gases, it was heated in Ar at 450 C for 30 min to decompose the $Ni(NO_3)_2$, and achieve a good particle nucleation. Particles grew to an average size of 15 nm in diameter.

The gases used, Ar, H_2 and O_2, were obtained from Scientific Gas Products, Inc. with stated purities of 99.999 %, and were used without further purification. H_2O vapor was introduced into the system by allowing a carrier gas to flow through a bubbler containing deionized water at 20 C. This procedure produces a gas/H_2O ratio of $\sim 40/1$ in the gas reaction cell.

RESULTS

Nickel-potassium/graphite-steam

After treating graphite samples loaded with KOH and $Ni(NO_3)_2$ at 450 C in Ar, particle nucleation was observed both on the basal and edge planes. When the sample was treated in a steam environment, the particles located on the graphite edge region underwent a transformation from non–wetting condition to wetting condition between 475 and 525 C. 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 (2.5 nm).

On continued heating to 555 C 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 675 C. Figs. 1a and 1b show a two picture sequence illustrating this mode of attack.

The edge recession involved the whole area and the various fronts of attack where separated by 60n degree angles, in the direction parallel to the $[11\bar{2}0]$ crystallographic orientation of the graphite structure. The orientation was determined by referring the position of the fronts of attack to that of twin bands, which are always present in the graphite in the $[10\bar{1}0]$ direction.

The rate of edge recession increased continuously when the temperature was raised from 675 to 1100 C, and no evidence of deactivation was observed. A quantitative analysis of the rates of edge recession as a function of temperature is shown in Fig. 2 in the form of an Arrhenius plot. An activation energy of 30.8 $\pm$ 0.9 Kcal/mol was obtained. This value is consistent with the one obtained from kinetic studies using a flow reactor system [1].

At temperatures above 955 C, occasionally, a change in the mode of attack was 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.

Nickel – potassium/graphite – wet hydrogen

The catalytic effect of Ni/K mixtures on the gasification of graphite on a $H_2:H_2O$ 40:1 atmosphere was studied on samples that had been either gasified in steam at 1000 C or heat treated in Ar at 450 C. 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 when the specimens were heated in 2.0 torr of wet H_2 were observed at 545 C. It took the form of relatively straight channels which were created by catalyst particles that had nucleated along the edges of graphite.

When first formed the channels remained parallel-sided, and as the temperature was raised to 565 C, they started to acquire a fluted appearance.This is the result of active particles spreading along the channel walls, which then proceeded to catalyze the reaction by an edge recession mode. (See region indicated by arrows in Figures 3a and 3b)

On raising the temperature to 675 C many of the previously inactive particles located on the graphite basal plane started to exhibit mobility. When this 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 Fig 4 in the form of an Arrhenius plot. An activation energy of 30 $\pm$ 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 (600 - 1100 C). Below 900 C 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 1100 C the edge recession tent to slow down and in some regions it stopped completely, leaving channeling as the only mode of attack.

The edge recession activity could be regenerated by treating the sample in wet Ar at about 600 C. The wet H_2 treatment did not affect the properties of the Ni/K mixture for promotion of the edge recession mode of attack of steam. Figure 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).

Nickel-potassium/graphite-wet oxygen

Treatment of nickel/potassium specimens in 2.0 torrs of wet oxygen (O_2:H_2O 40:1) at 605 C 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 665 C, 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 Fig 5).

In contrast with the behavior observed in wet hydrogen and wet argon, the recession in wet O_2 did not appear to follow any preferred direction. Also, in this case the catalyst attack continued up to 1015 C, there being 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 Fig. 6).

DISCUSSION

The Ni/K 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.

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}). (Equation 1)

$$\gamma_{sg} > \gamma_{lg} + \gamma_{sl} \tag{1}$$

This is the case in H_2O vapor and O_2/H_2O environments, but there are differences in catalyst behavior between these two cases. In wet O_2, at 500 C, the catalyst forms particles that only wet the carbon surface, and as the temperature raises above 650 C these particles spread over the edge planes. In wet Ar the opposite behavior is observed. The catalyst spreads at temperatures as low as 500 C, and as the temperature approaches 1000 C, 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 [8,9]. This lowers the gas-solid surface tension (γ_{sg}) to such a level that equation 1 is no longer satisfied, and particle nucleation is favored. These species desorb from the surface between 600 and 700 C [8,9], and since the surface free energy of clean edge planes of graphite is much higher than that of the catalyst [10,11], spreading becomes now favored. In H_2O vapor, below 650

C the catalyst interacts with a larger fraction of clean edges than in the O_2 case because the sticking coefficient of water on graphite is much smaller than that of O_2 [8]. For this reason, in the wet Ar case the catalyst spreading over the edge surfaces is observed as soon as the Ni/K mixture becomes mobile. As the temperature approaches 1000 C, H_2 formed in the carbon-water reaction builds up in the cell. This changes the wetting properties of the catalyst, and favors particle nucleation.

A second difference between this 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 [11]. At this point, unfortunately, we do not know the reasons for this preferential direction. Several suggestions have been proposed in the literature, but they do not explain all the cases studied. It has been suggested [12] that because steam adsorbes preferentially at "arm chair" sites [13], the carbon gasification is favored in a $[11\bar{2}0]$ direction, but this is not always the case, since there are several cases in which transition metals catalyze the water attack of carbon in the $[10\bar{1}0]$ direction. It has also been suggested [11] 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 is spread over the whole edge area and carbon attack is only promoted in a particular direction.

In wet H_2, between 600 and 1000 C, both edge recession and channeling modes of attack are observed simultaneously, because a fraction of the catalyst spreads upon the edges, while the rest only wets them. The chanelling attack is probably due to Ni metal, since the characteristics observed in our study are very similar to those reported previously when

Ni was deposited alone on graphite [4]. The edge recession, on the other hand, can only be explained as the result of the interaction between Ni and K, because Ni deposited alone does not show any evidence for this mode of attack in wet H_2 [4] and K salts are not active for carbon gasification in reducing environments [14]. This interaction is suppressed above 1000 C in H_2, and can be regenerated by treating the sample in H_2O vapor at 600 C, as shown in Figure 2.

The catalytic properties of the Ni/K mixture for carbon gasification are superior to those of Ni or K alone. In the H_2O vapor–graphite reaction the clearest advantage of the Ni/K mixture is its resistance to poisoning. CAEM [3,5] and flow reactor [15,16] studies show that both K and Ni deactivate when used as catalysts for steam gasification of graphite below 1000 K. On the contrary, this study shows that the Ni/K mixture does not show any sign of deactivation in wet Ar up to 1100 C. This result is in agreement with flow reactor studies reported elsewhere [1]. In wet H_2 the intrinsic activity of the Ni/K mixture is two times higher than the one reported for Ni alone, while K salts are inactive. Furthermore, the Ni/K mixture favors an edge recession mode of attack and Ni 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 K alone and Ni/K are similar and neither of them deactivate. There are differences, however, between these two systems. The activation energy in the Ni/K case (22 Kcal/mol) is lower than the one reported for K alone (30 Kcal/mol), and even though both promote an edge recession mode of attack for the O_2–graphite reaction, in the Ni/K case there is no preferential direction of attack, while in the case of K alone the carbon consumption occurs parallel to the $[10\bar{1}0]$ direction.

The distinct catalytic properties of the Ni/K mixture are due to a cooperative effect between the components. In the case of steam gasification this conclusion is also supported

by flow reactor studies both in graphite and char [1,2]. This cooperative effect has also been observed in other systems. In steam only, CAEM studies of Pt/Ba [17] indicate that this mixture is more resistant to poisoning than the components used independently, and flow reactor studies of $Fe(NO_3)_3/Na_2(CO_3)$ mixtures [18] show that this catalyst is more active than either $Fe(NO_3)_3$ or $Na_2(CO_3)$ alone. In wet H_2, mixtures of K_2SO_4 and $FeSO_4$ form a molten phase at 650 C and this phase has a higher steady state activity and an improved CH_4 selectivity than the components used alone [19].

A CAEM study of the catalytic activity of Ni/Ca mixtures for carbon gasification in wet Ar were reported previously [5]. This catalyst shows several similarities with the Ni/K catalyst for the H_2O vapor–graphite reaction. The catalytic properties of the Ni/Ca mixture, as in the case of Ni/K, can only be explained by the interaction between the components. Both systems spread over the edge surfaces of carbon between 500 and 600 C, 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. Ni/K, however, is more active than Ni/Ca and it has a much lower activation energy.

SUMMARY

In summary, we have studied the catalytic properties of Ni/K mixtures in H_2O, H_2/H_2O and O_2/H_2O atmospheres by CAEM. In H_2O and O_2/H_2O environments an edge recession mode of attack is favored, and no sign of deactivation was observed. In H_2/H_2O both edge recession and channeling occur simultaneously and the catalyst deactivates above 1000 C. This mixture shows superior catalytic properties than either Ni or K used independently, due to a cooperative effect between the components.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1: Sequence of photographs taken from the CAEM video display, showing the edge recession attack of carbon in H_2O vapor at 900 C. The time between Fig. 1a and Fig. 1b is 3 sec.
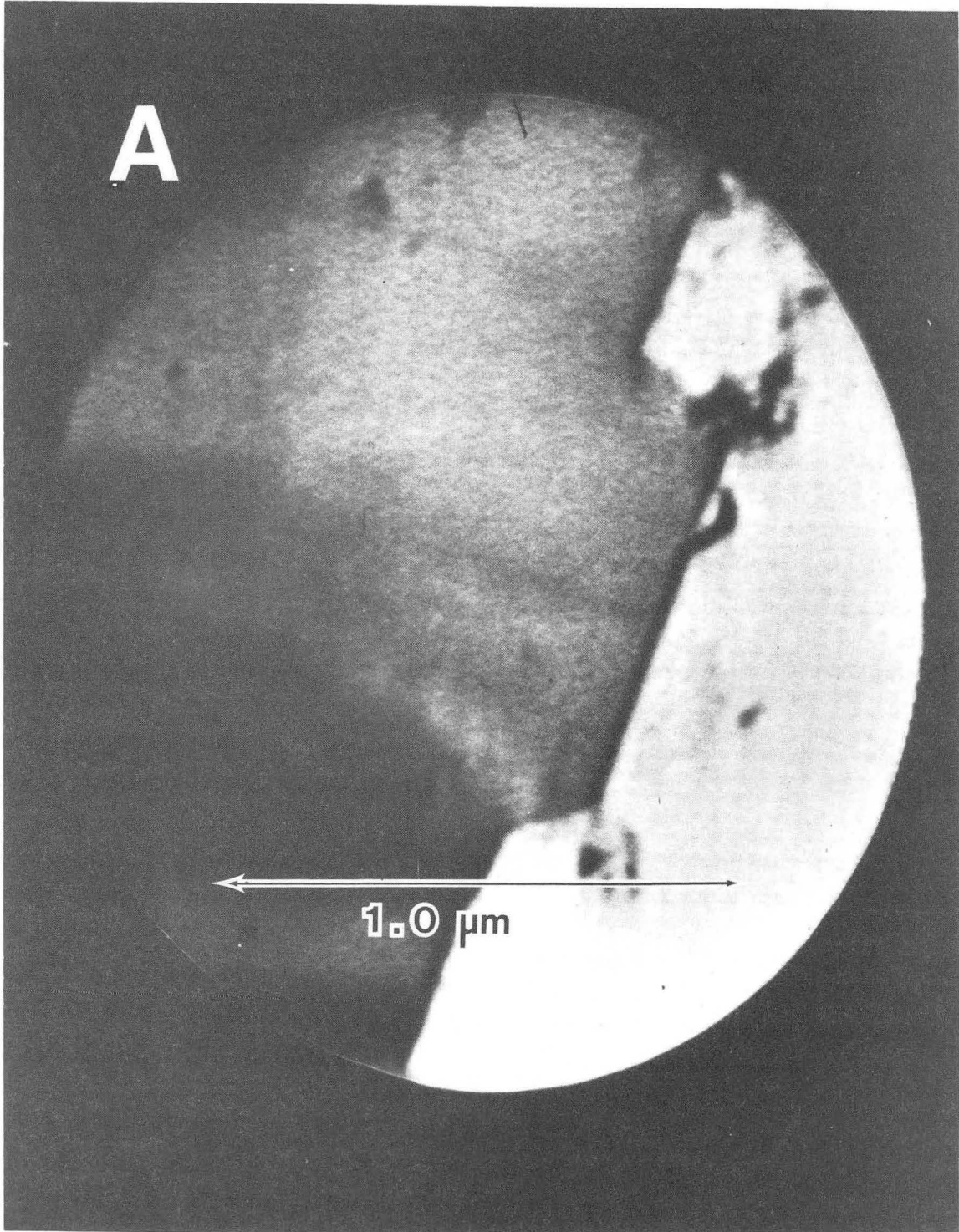
Figure 2: Arrhenius plot of Ni/K catalyzed edge recession rates of graphite in 2 torr of wet Ar. The black dots represent the results obtained after heat treating the sample is Ar for 30 min at 450 C. The open circles represent the results obtained after treating the sample in 2 torr of wet H_2 at 1100 C. Results previously reported for KOH and Ni metal are included for comparison purposes. The lenght of the curves indicates the temperature range studied.

Figure 3: Sequence of photographs, showing the modes of attack in 2 torr of wet H_2. The region indicated by the arrows shows the recession of the channel walls, as described in the text (see results). Also notice the simultaneous carbon attack by edge recession and channeling in the lower part of the photographs. The time between Fig 3a and 3b is 1 sec.

Figure 4: Arrhenius plot of Ni/K catalyzed edge recession rates of graphite is 2 torr of wet H_2. The results previously obtained for the channeling mode of attack of Ni metal are included for comparison. The lenght of the curves indicates the temperature range studied.
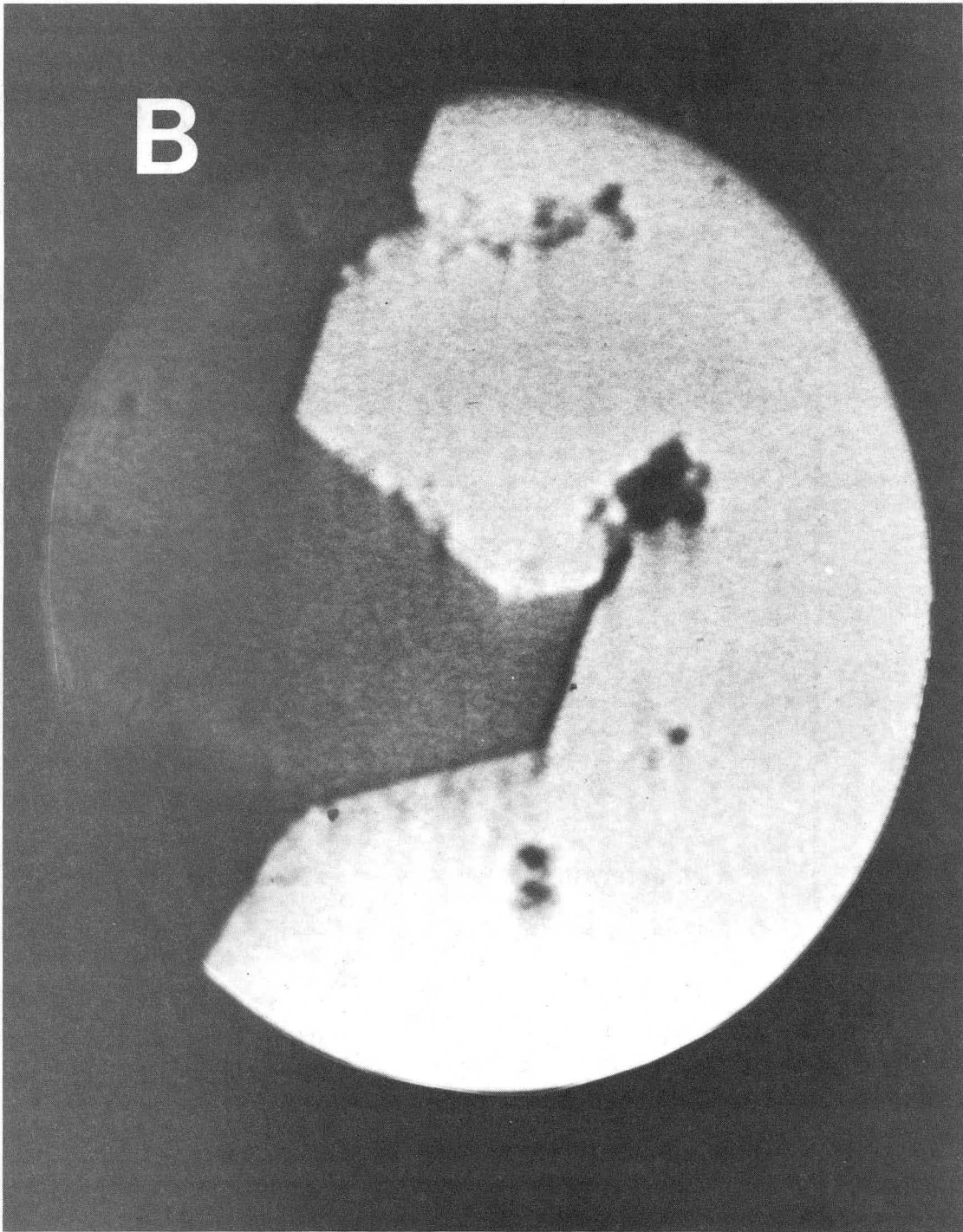
Figure 5: Sequence of photographs in wet O_2 at 650 C, showing the irregular channels formed befrore catalyst spreading. Notice also the erosion of the edges, which is the first indication of edge recssion attack. The time between photographs is 10 sec.

Figure 6: Arrhenius plot of Ni/K catalyzed edge recession rates of graphite comsumption in 2 torr of wet O_2. The results previously obtained for KOH are included. The lenght of the curves indicates the temperature range studied. The dotted lines are extensions of the curves, included to facilite the comparison.
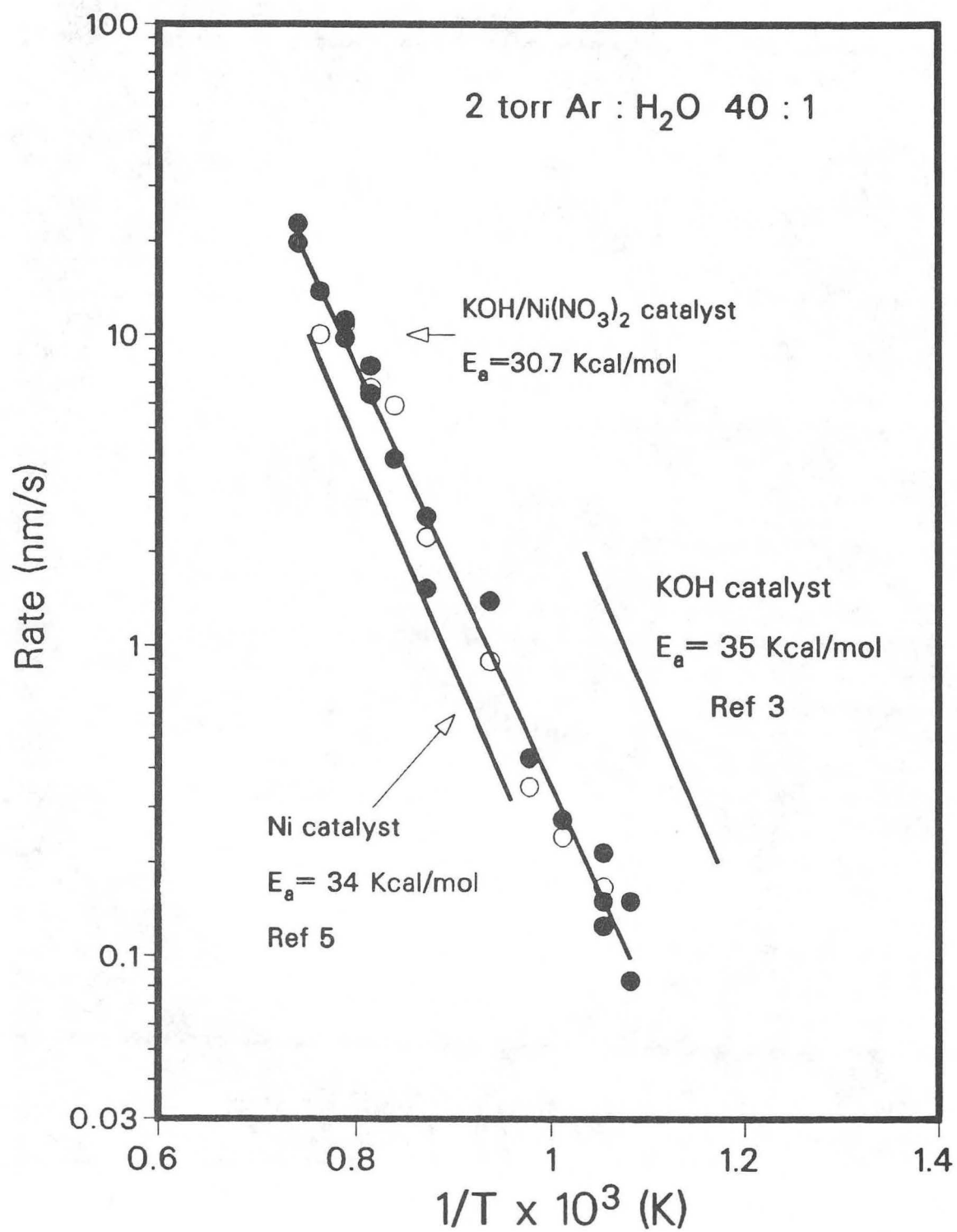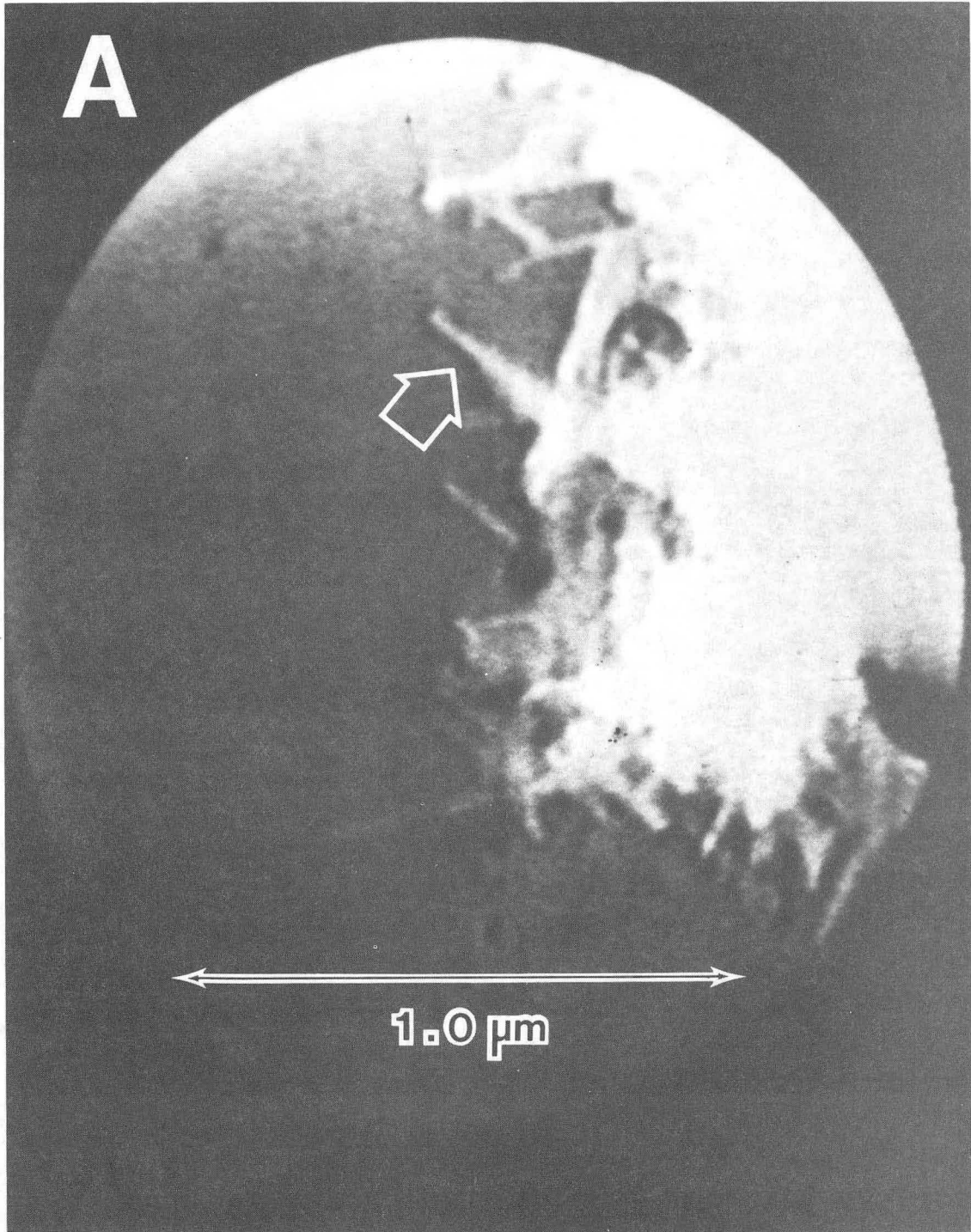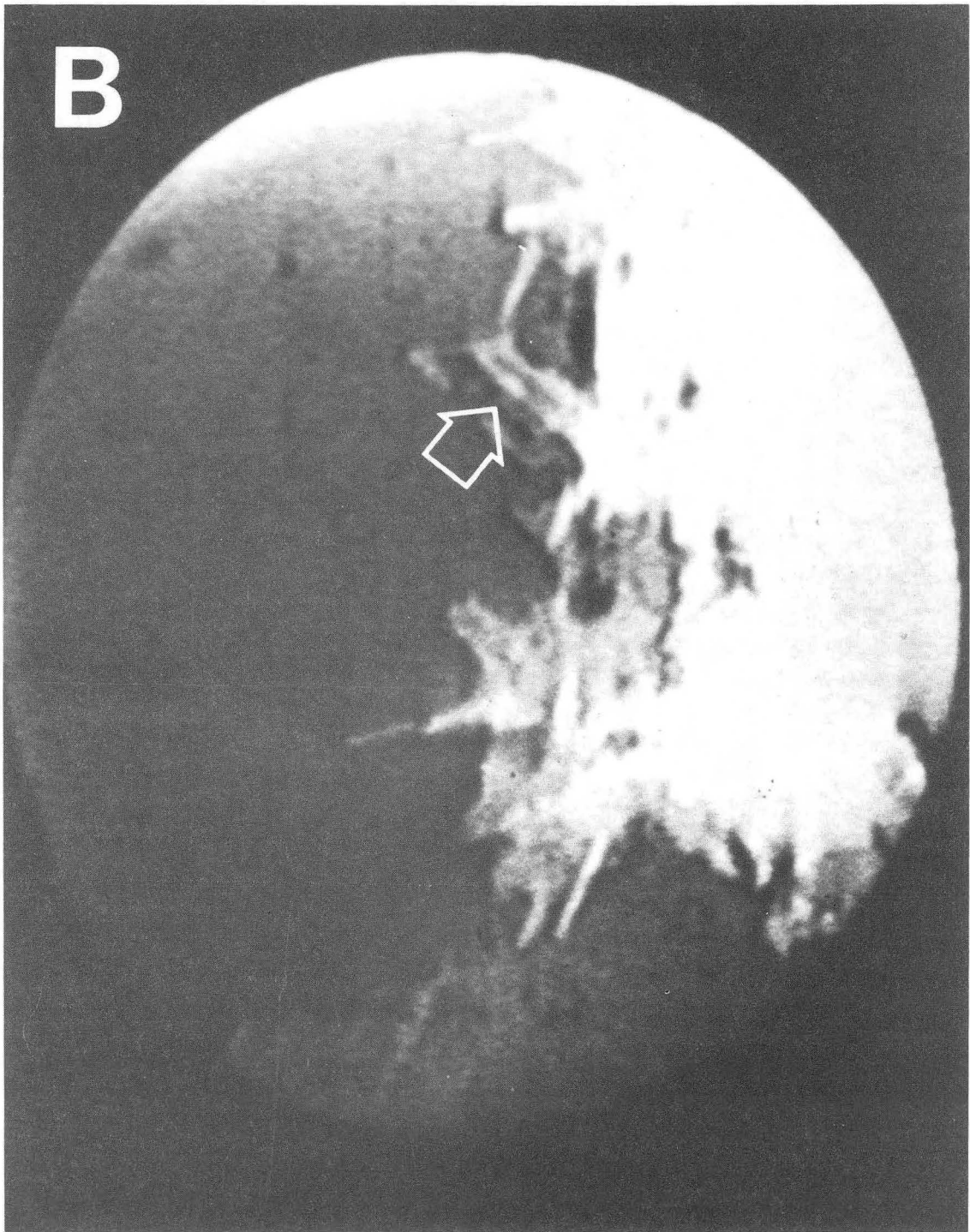
XBB867-5378A

Fig. 1A

XBB867-5379A

Fig. 1B

2 torr Ar : H_2O 40 : 1

KOH/Ni$(NO_3)_2$ catalyst

E_a=30.7 Kcal/mol

KOH catalyst

E_a= 35 Kcal/mol

Ref 3

Ni catalyst

E_a= 34 Kcal/mol

Ref 5

Rate (nm/s)

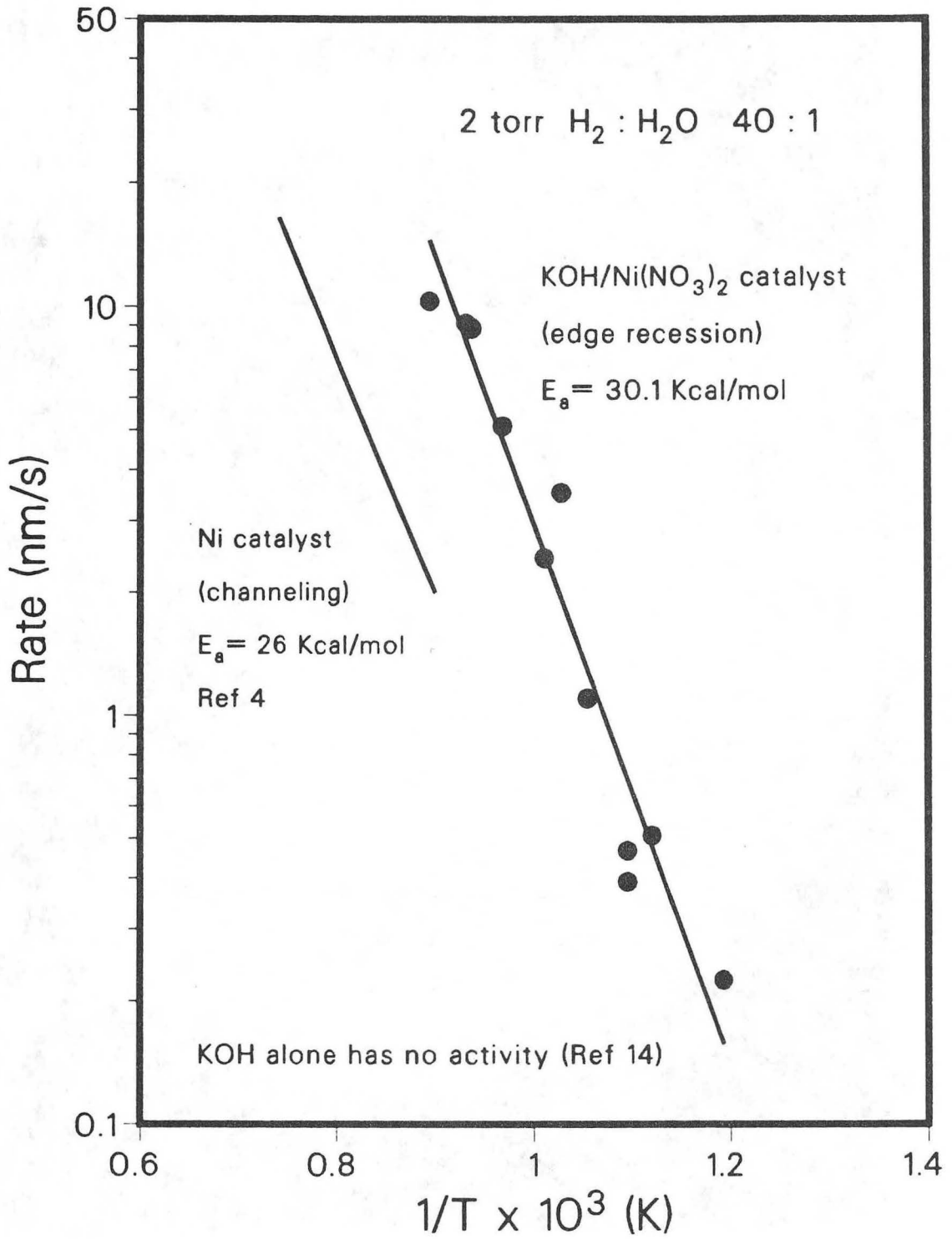1/T x 10^3 (K)

XBL 873-1273

Fig. 2

XBB871-50A

Fig. 3A

XBB871-49A

Fig. 3B

Fig. 4
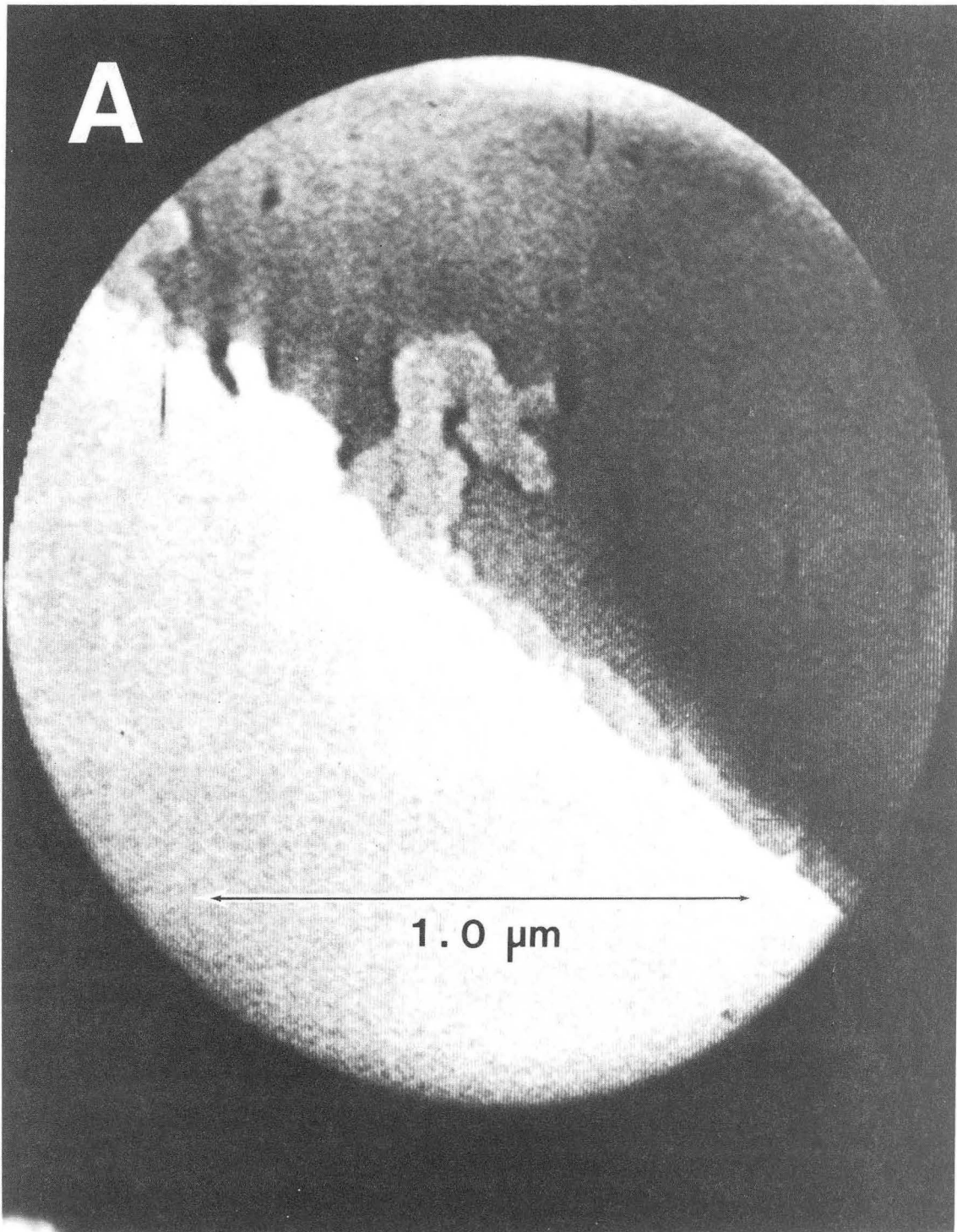
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XBB871-51A

Fig. 5A
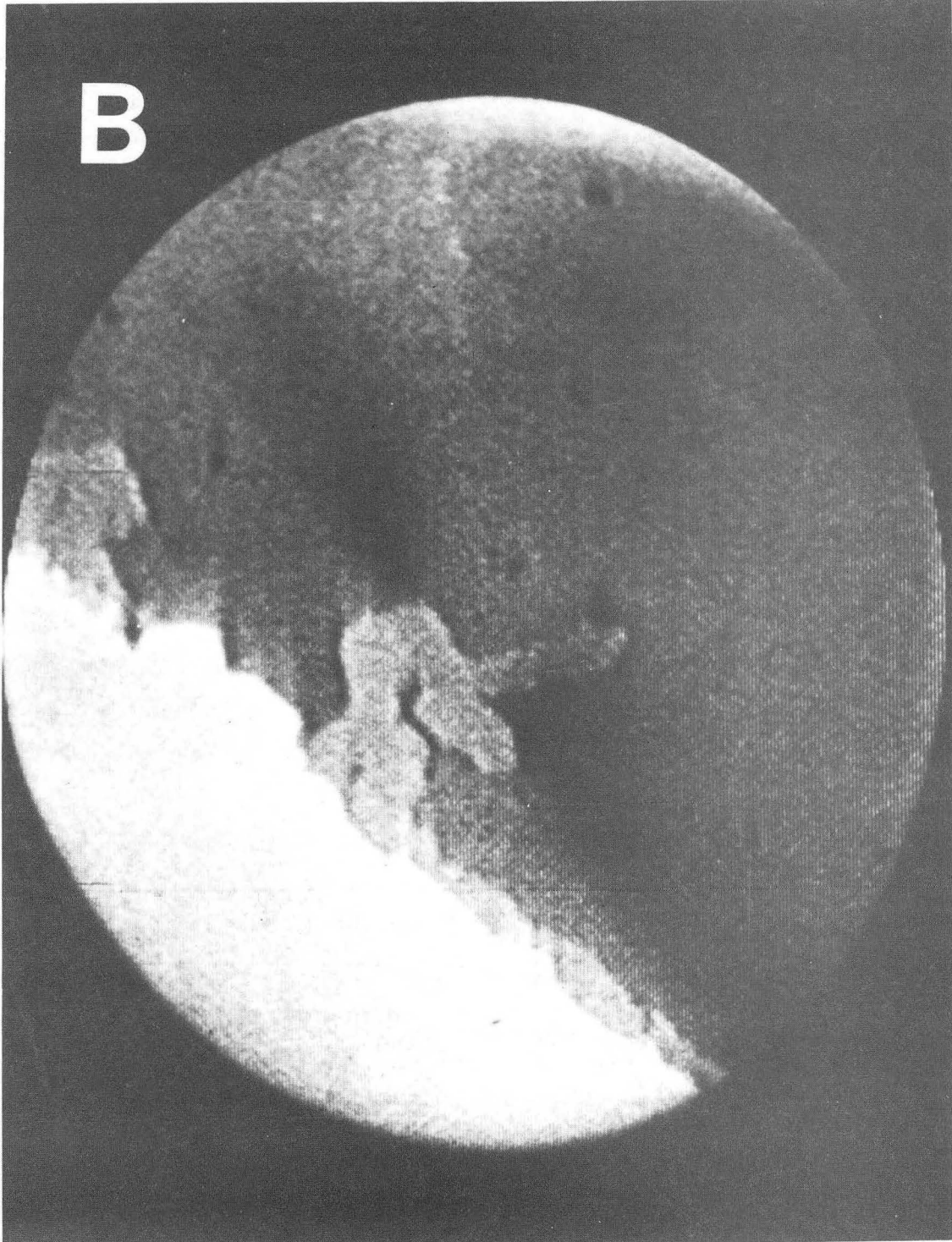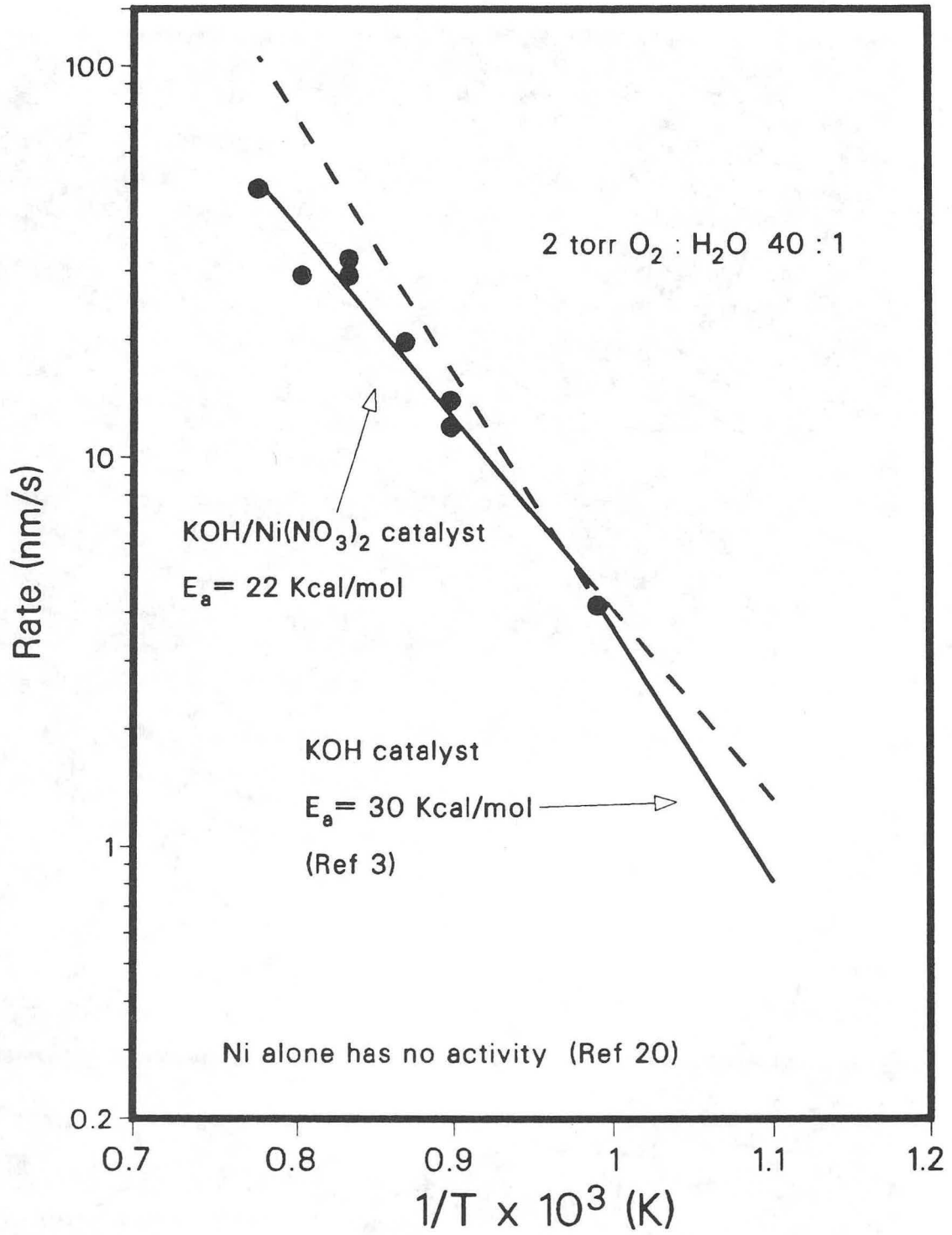
XBB871-52A

Fig. 5B

2 torr $O_2 : H_2O$ 40 : 1

KOH/Ni(NO$_3$)$_2$ catalyst

E_a = 22 Kcal/mol

KOH catalyst

E_a = 30 Kcal/mol

(Ref 3)

Ni alone has no activity (Ref 20)

Rate (nm/s)

$1/T \times 10^3$ (K)

XBL 873-1272

Fig. 6

Kinetic Study of The Catalyst Derived From Mixtures of KOH and Ni(NO$_3$)$_2$ for Steam Gasification of Char

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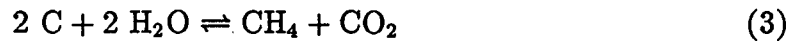[2]*Department of Chemical Engineering, University of California Berkeley, CA 94720
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Abstract

The kinetic properties of a catalyst derived from a mixture of KOH and Ni(NO$_3$)$_2$ for steam gasification of three chars are presented. H$_2$, CO$_2$ and small amounts of CO and CH$_4$ are the reaction products. The product distribution is controlled by the activation energies for formation of the gases. The activation energies for H$_2$ and CO$_2$ formation are 29 and 36 Kcal/mol respectively. The catalyst derived from the KOH/Ni(NO$_3$)$_2$ mixture has better catalytic properties, due to a cooperative effect between nickel and potassium, than catalyst derived by loading the components alone. The mixture has a higher activity and lower activation energies for H$_2$ and CO$_2$ production than KOH alone, and higher resistance to deactivation than Ni(NO$_3$)$_2$ alone. Since char and graphite gasification have the same activation energies, it is concluded that there is a common mechanism for their gasification catalyzed by the KOH/Ni(NO$_3$)$_2$ mixture.

1 INTRODUCTION

Thermodynamic considerations indicate that the gasification of carbon solids with steam should yield mostly H_2 CO_2 and CO above 700 K, and CH_4 and CO_2 below this temperature (Equations 1–3). The ratio of H_2/CH_4 produced is strongly dependent on temperature, H_2 being favored above 700 K (p_{H_2}/p_{CH_4} is equal to 0.06 at 500 K, 1.5 at 700 K, and 23.2 at 1100 K). In addition, as a H_2 by-product, the formation of CO_2 is favored between 700 and 950 K, and the formation of CO is favored above 950 K. (p_{CO_2}/p_{CO} is equal to 35.8 at 700 K and 0.07 at 1100 K).

$$C + 2\,H_2O \rightleftharpoons 2\,H_2 + CO_2 \tag{1}$$

$$C + H_2O \rightleftharpoons H_2 + CO \tag{2}$$

$$2\,C + 2\,H_2O \rightleftharpoons CH_4 + CO_2 \tag{3}$$

When gasification is carried out for H_2-production purposes, the formation of CO_2 as a by-product is preferred over the formation of CO for technological reasons. First, the number of moles of H_2 per mol of carbon consumed is doubled when CO_2 is the by-product; second, it is easier to separate H_2 from CO_2 than it is from CO; and third, the energy requirements for the formation of H_2 and CO_2 are lower than for the formation of H_2 and CO.

Kinetic barriers are the dominant constraints for the steam gasification of carbon, thus various catalysts have been utilized to reduce the temperature necessary

to carry out this reaction. Alkaline and alkaline-earth hydroxides, carbonates and oxides have been the catalysts most widely studied [1]. For graphite gasification they are active above 1000 K, and their activity remains constant up to high carbon conversions. In the case of char gasification, however, these catalysts are required in large amounts ($\sim$ 30 %), and their recovery after reaction is difficult, because they form stable compounds with alumino-silicates and minerals present in the char [2].

Recently we have reported that catalysts derived from mixtures of KOH and several transition metal salts were effective for steam gasification of graphite [3]. The most active mixture was derived from KOH and $Ni(NO_3)_2$. Its activity was measurable at temperatures as low as 850 K, with H_2 and CO_2 as major products. At this temperature the $Ni(NO_3)_2$/KOH mixture was still active after 100 hours, while KOH was completely inactive, and the catalyst derived from $Ni(NO_3)_2$ alone deactivated after one hour.

In this article we extend our previous study to include the gasification of char. We have compared the kinetic properties of the catalyst derived from $Ni(NO_3)_2$/KOH mixture with those derived from KOH and $Ni(NO_3)_2$ used alone. The results show that the $Ni(NO_3)_2$/KOH mixture is a better catalyst for char gasification. It has a higher activity and lower activation energy for H_2 and CO_2 production than KOH alone, and it is more resistant to deactivation than $Ni(NO_3)_2$ alone. Also, for this mixture, the product distribution and activation energies for char gasification are

similar to those previously obtained with graphite, suggesting that the same mechanism of gasification applies to both carbon substrates.

2 EXPERIMENTAL

The experiments were carried out in a fixed bed flow reactor system (Fig. 1). Steam was produced by pumping water through a heated element, and then introduced into a knock-out container used to separate the condensed water and to dampen the pulsations in flow due to the pump. The reactor was an alumina tube of 1.26 cm diameter, inside of which there was a small alumina cartridge containing the sample (See insert in Fig. 1). The outside diameter of the cartridge was machined to match the inside diameter of the reactor tube. This assured that all steam was forced to flow through the sample. The temperature was measured with a chromel-alumel thermocouple in contact with the external walls of the cartridge. To avoid losses of fine carbon particles during experiments, the cartridge was sealed using a ceramic cement. The pressure inside the reactor was controlled using valve 3. The outlet gases were cooled with a condenser, so that the gases reached room temperature at the outlet. The total gas production was measured with a gas buret and the product distribution determined with an on-line gas chromatograph and a sampling valve, using He as the carrier gas . The sampled gases were separated by a 10 foot long-1/8 inch wide Carbosieve SII column and detected using a thermal

conductivity detector.

Samples of 0.6 g of char were used as carbon substrates. The elemental analysis, coal precursor and pretreatment of the three chars used is given in Table I. They will be named according to their coal precursor; Illinois #6, North Dakota and Montana chars.

The catalyst was loaded onto the char by incipient wetness using KOH and $Ni(NO_3)_2$ solutions. The KOH and $Ni(NO_3)_2$ loadings were equal to 3.74 and 11.3 wt % respectively. This loadings correspond to a K/C and Ni/C molar ratios of approximately 1.0×10^{-2}, and therefore a Ni/K molar ratio of 1.0 in the case of the mixture.

The sample was initially heated in Ar to treat the cement used to seal the cartridge, and to decompose the $Ni(NO_3)_2$. The treatment involved intervals of 30 min at 363, 393, 643 and 723 K. After this treatment, steam was immediately introduced by closing valve 2 and opening valve 1 (See Fig. 1). The temperature was kept at 723 K until no more Ar was collected in the gas buret ($\sim$ 10 min), and then it was raised to the reaction value. After the reaction conditions were achieved, a 15 min was elapsed before data was collected to allow the system to reach steady-state conditions. Rates were determined by collecting gas for 10 min, after which a gas chromatograph sample was taken to determine the product distribution.

3   RESULTS

3.1   Catalyst derived from the $Ni(NO_3)_2/KOH$ mixture

The gas products obtained in the steam gasification of the three chars studied are H_2, CO_2, CO and a slight amount of CH_4. After the first hour, and in all the cases, the product distribution remains constant with time and a mass balance is established. The rates of formation of these four gases as a function of time are shown in Figs. 2, 3 and 4 for the steam gasification of Illinois #6, North Dakota and Montana chars respectively. By comparing the rates shown in these figures it is clear that the ratio of CO_2 to CO produced depends on the char (see Table II), and due to the stoichiometry of Equations 1 and 2 this ratio affects the total number of moles of H_2 that are produced per mol of carbon that is gasified. The steam gasification of North Dakota and Montana chars produces almost 2.0 moles of H_2 per mol of carbon consumed, since CO_2 is the main oxygen containing product, while the steam gasification of Illinois #6 char produces 1.6 moles of H_2 per mol of carbon consumed, because CO_2 and CO are produced in a ratio equal to 1.47.

The rate of H_2 production is also dependent on the carbon source. This is reflected in the total H_2 production obtained after 4 hours at 893 K (See Table II). For North Dakota char gasification this volume (663 ml) is two times higher than that of Montana char (337 ml) and six times higher than the volume previously obtained for graphite (95 ml) [3], even though the product distribution for these

three carbon sources is similar.

Fig 2, 3 and 4 also show that the rate of formation of all the gases decreases with time. This can be prevented by treating the carbon substrate in aqua regia overnight previous to the catalyst loading. This is shown in Fig. 5 for the case of Montana char. The $Ni(NO_3)_2/KOH$ mixture maintains 75 % of its initial activity after 600 min when the substrate is pretreated in aqua regia while its activity decreases by a factor of three after 200 min when the sample has not been treated. Also, beyond 200 min the rate of gasification of the treated sample becomes higher than that of the untreated one. These results suggest that the decrease in rate of char gasification is due to the deactivation of the $Ni(NO_3)_2/KOH$ catalyst by interaction with some char component that can be removed by the aqua regia treatment.

The dependence of the rates of steam gasification upon temperature has been determined for the three chars. Since the initial rate of gas production decreases rapidly with time, the reaction was carried out isothermally at 893 K for four hours before the temperature was increased. After this period the variations in rate with time at 893 K are small enough to allow the determination of the activation energies. The measurements were carried out in a temperature range where the product distribution does not vary significantly (873 to 993 K) and in a total time period of one and a half hours to diminish the effect of deactivation.

The rates of gas production as a function of temperature for Illinois #6 char are

shown in Fig. 6 in the form of an Arrhenius plot and the activation energy values for H_2, CO_2 and CO production obtained for the three chars are summarized in Table III. The activation energy for H_2 production is the same in all the cases (29 Kcal/mol), and the activation energies for formation of CO and CO_2 varies with the char. The gasification of the chars that produce much more CO_2 than CO, that is Montana and North Dakota, also show lower activation energies for CO_2 than for CO production. (28.4 vs. 43.0 Kcal/mol in the case of Montana, and 36.8 vs. 49.9 Kcal/mol in the case of North Dakota). Illinois #6 char, which produces a ratio of CO_2 to CO close to one, shows similar activation energies for CO_2 and CO production (36.0 and 35.4 Kcal/mol respectively). These results indicate that the product distribution is controlled by the activation energy for formation of the gases.

Table III also shows that the activation energies for H_2 and CO_2 production for the three chars are similar to the ones obtained previously for graphite [3], suggesting that there is a common mechanism for the gasification of all these carbon sources and that graphite is a good substrate model for its study.

3.2 Catalyst derived from KOH deposited alone

The steam gasification of Illinois #6, North Dakota and Montana chars catalyzed by KOH alone was studied isothermally at 893 K and as a function of temperature in order to compare the results with those obtained for the $Ni(NO_3)_2$/KOH mixture.

Fig. 7 shows the rates of gas production for H_2, CO, CO_2 and CH_4 as a function of time at 893 K for the steam gasification of Illinois #6 char. As in the case of the $Ni(NO_3)_2/KOH$ catalyst, a mass balance is established after the first hour of reaction. The ratio of CO_2 to CO in this case is lower than the one obtained with the $Ni(NO_3)_2/KOH$ catalyst, (p_{CO_2}/p_{CO} is equal to 0.29 in the case of KOH alone and 1.47 in the case of $Ni(NO_3)_2/KOH$) and therefore the moles of H_2 produced per mol of carbon consumed are lower in this case (1.30 mol H_2/mol carbon) than in the $Ni(NO_3)_2/KOH$ case (1.56 mol H_2/mol carbon) (See Table II).

Fig 8 shows the results obtained for the gasification of North Dakota char at 893 K. The results are analogous to those obtained with Montana char, and because of this they will be presented together. For these two chars the product distribution obtained when the reaction is catalyzed by KOH is very similar to the one obtained with the $Ni(NO_3)_2/KOH$ catalyst (See Table II). The ratio of CO_2 to CO produced in the gasification of both chars is the same as for the $Ni(NO_3)_2/KOH$ catalyzed reaction, but the catalytic activity of KOH alone for the steam gasification of these two chars is lower than that of the $Ni(NO_3)_2/KOH$ catalyst. A comparison of curves A in Figs. 3 and 8 shows that the rate of H_2 production obtained with KOH alone is almost a factor of two lower than the one obtained with the $Ni(NO_3)_2/KOH$ mixture. This is also reflected in the total H_2 production after 4 hours, as shown in Table II. The H_2 volume produced at 893 K with the KOH catalyst (170 ml in the

case of Montana and 449 ml in the case of North Dakota) is almost half the volume

obtained with the $Ni(NO_3)_2/KOH$ catalyst (337 ml in the case of Montana and 663

ml in the case of North Dakota).

The rates of H_2, CO_2 and CO production were studied as a function of tem-

perature between 853 and 993 K for Illinois #6 and North Dakota chars. The

activation energies obtained are summarized in Table III. Their values are in both

cases much higher than that obtained with the $Ni(NO_3)_2/KOH$ catalyst. In the case

of Illinois #6 the H_2 activation energy (60.8 Kcal/mol) is 32 Kcal/mol higher than

that obtained with the $Ni(NO_3)_2/KOH$ catalyst, the CO activation energy (55.3

Kcal/mol) is 19 Kcal/mol higher, and the CO_2 activation energy (78.1 Kcal/mol)

is 43 Kcal/mol higher. From Table II also notice that the activation energy for CO

formation obtained for KOH alone on Illinois #6 is lower than the one for CO_2

formation, while in the case of the $Ni(NO_3)_2/KOH$ catalyst the values are similar.

This is reflected in the ratios of CO_2 to CO obtained with each catalyst, suggesting

that the product distribution in the case of the KOH alone catalyzed reaction is

also controlled by the activation energy of formation of the products.

3.3 Catalyst derived from $Ni(NO_3)_2$ deposited alone

While $Ni(NO_3)_2$ alone is completely inactive for the steam gasification of Illinois #6

char, its catalytic properties for the steam gasification of North Dakota and Montana

chars are similar to those of the $Ni(NO_3)_2/KOH$ mixture. Table III shows that, at

893 K, the two catalysts give the same product distribution ($p_{CO_2}/$ p_{CO} is equal to 4.35 for $Ni(NO_3)_2$ alone and 5.26 for $Ni(NO_3)_2/KOH$ in the case of Montana char), and comparable activities for H_2 production. ($Ni(NO_3)_2$ alone produces 314 ml of H_2 in 4 hours for Montana char gasification while $Ni(NO_3)_2/KOH$ produces 337 ml under the same conditions). Fig. 9 also shows that, as in the case of $Ni(NO_3)_2/KOH$, the rate of H_2 production decreases as a function of time. A treatment of the char in aqua regia previous to the $Ni(NO_3)_2$ loading also eliminates the decrease in rate with time. In contrast with $Ni(NO_3)_2/KOH$, however, if the char is treated in aqua regia previous to the $Ni(NO_3)_2$ loading, the catalyst loses most of its activity (see Fig. 9), suggesting that the $Ni(NO_3)_2$ activity on the untreated sample was due to its interaction with some inorganic constituent in the char.

The activation energy for gasification of North Dakota char loaded with $Ni(NO_3)_2$ was determined for samples that either had or had not been pretreated in aqua regia. The results are summarized in Table III. The values do not change after the aqua regia pre-treatment and they are similar to those obtained with the $Ni(NO_3)_2/KOH$ catalyst. (33.6 Kcal/mol for H_2 production, 38.2 Kcal/mol for CO_2 production and 48.5 Kcal/mol for CO production). As in the case of $Ni(NO_3)_2/KOH$ and KOH alone, the product distribution is controlled by the activation energy for formation of the products.

4 DISCUSSION

The catalytic properties of the $Ni(NO_3)_2/KOH$ mixture for steam gasification of char are different than those of either KOH or $Ni(NO_3)_2$ alone. Higher H_2 production rates, higher ratios of H_2 produced per carbon consumed and lower activation energies are the three main advantages of using this mixture as a catalyst for the process.

The amount of H_2 produced in four hours at 893 K is almost 2.0 times higher when the reaction is catalyzed by the $Ni(NO_3)_2/KOH$ mixture than when it is catalyzed by KOH. This is due to either higher carbon conversions, or higher ratios of CO_2 to CO in the products. In the case of Illinois #6 gasification the total carbon conversion after 4.0 hours obtained for KOH and $Ni(NO_3)_2/KOH$ are similar ($\sim$ 30%), but the latter favors a larger proportion of CO_2 in the gas products, which due to the stoichiometry of Eq. 1 involves a larger H_2 production. In the other two cases, that is Montana and North Dakota char gasification, the product distribution is the same but the H_2 activity of the $Ni(NO_3)_2/KOH$ catalyst at 893 K is higher. Beside the higher activity, the $Ni(NO_3)_2/KOH$ catalyst has a much lower activation energy for formation of H_2 and CO_2 than KOH. These two characteristics, which are probably related, make the $Ni(NO_3)_2/KOH$ catalyst more suitable for H_2 production at temperatures between 800 and 1000 K than KOH.

While $Ni(NO_3)_2$ deposited alone is completely inactive for steam gasification of

Illinois #6 char, it shows similar catalytic properties for the steam gasification of North Dakota and Montana chars to the $Ni(NO_3)_2/KOH$ mixture. Both catalysts show a similar product distribution, H_2 production rates at 893 K and activation energies for formation of H_2 and CO_2. The main difference between $Ni(NO_3)_2$ alone and combined with KOH is observed when either of these two chars is pretreated in aqua regia. While the H_2 production rate at 300 min of the pretreated char catalyzed by $Ni(NO_3)_2/KOH$ is 30 % higher than that of the untreated sample, in the case of $Ni(NO_3)_2$ alone it is four times lower. The aqua regia pretreatment prevents the catalyst deactivation in the case of the $Ni(NO_3)_2/KOH$ catalyst, but it has the opposite effect on the $Ni(NO_3)_2$catalyst. This suggests that the interaction of $Ni(NO_3)_2$ loaded alone with some char component provides similar catalytic properties to this component as those of the $Ni(NO_3)_2/KOH$ mixture. When the char is treated in aqua regia, this component is extracted from the char and $Ni(NO_3)_2$ loaded alone is exposed to the interaction of some other component in the char that causes its almost complete deactivation. In the case of $Ni(NO_3)_2/KOH$, the nickel-potassium interaction prevents this deactivation process, which is reflected in the high activity observed even after 10 hours of reaction ($\sim$ 50 % carbon conversion).

In all the cases studied the product distribution obtained for steam gasification reaction catalyzed by the $Ni(NO_3)_2/KOH$ mixture is controlled by the activation energy for formation of H_2, CO and CO_2. It is interesting to compare the activation

energies obtained in this study with those obtained for the desorption of H_2, CO and CO_2 from a carbon surface after adsorption of water in the absence of catalyst. These values have been determined from analysis of the peak temperatures in TPD experiments done in our laboratory [4] and elsewhere [5]. They range from 40 to 55 Kcal/mol for CO_2 desorption, from 55 to 85 Kcal/mol for CO desorption and from 70 to 75 Kcal/mol for H_2 desorption. These studies concluded that the dissociation of water on clean carbon surfaces involves the formation of several oxygen containing surface species whose decomposition at high temperatures leads to the preferential desorption of either CO_2 or CO. The activation energy for H_2 and CO_2 production obtained in this work when the reaction is catalyzed by $Ni(NO_3)_2/KOH$ (Table III) are always below the ranges for desorption from the clean surfaces, suggesting that the catalyst affects the stability of the surface species formed after adsorption of water and lowers the desorption temperature of these two gases. In the case of CO, for three of the four carbon substrates studied, that is graphite, North Dakota char and Montana char, the activation energy for formation of this gas falls within the range reported earlier for its desorption from the clean surface, implying that the $Ni(NO_3)_2/KOH$ catalyst does not affect the stability of the CO precursor on the surface and therefore the production of CO in the products is very small. In the Illinois #6 steam gasification CO and CO_2 are produced with the same activation energy, and in a ratio close to 1.0. The activation energies obtained are lower than

in the absence of catalyst. In this case, CO and CO_2 could be produced from the same surface precursor, which can decompose by two different routes due to its interaction with the $Ni(NO_3)_2$/KOH catalyst.

At this point we do not have an atomic level physical picture of how the $Ni(NO_3)_2$/KOH mixture affects the stability of these surface species, but it is clear that its catalytic properties are due to a cooperative effect between the components. This conclusion was also reached in a previous publication when the catalytic activity of mixtures of KOH with either $Ni(NO_3)_2$ or $Fe(NO_3)_3$ were studied for the steam gasification of graphite. It was shown then that these mixtures had a higher resistance to poisoning than either $Ni(NO_3)_2$ or $Fe(NO_3)_3$ deposited alone and a higher activity than KOH deposited alone, due to a cooperative effect between potassium and the transition metal. This effect has also been reported by other authors. Adler et. al. [6] have shown that mixtures of K_2SO_4 and $FeSO_4$ had higher activity for H_2/H_2O gasification of carbon than either K_2SO_4 or $FeSO_4$ and Susuky et. al. [7] found that mixtures of $Na_2(CO_3)$ and $Fe(NO_3)_3$ mixtures were better catalysts for the steam gasification of low ash-low sulphur chars than either of the components used by itself.

Based on surface characterization studies, we propose that the properties of the $Ni(NO_3)_2$/KOH mixture are those of a mixed oxide (K_xNi_yO). X-ray Photoelectron spectra of $Ni(NO_3)_2$/KOH mixtures deposited on graphite after exposition to water

vapor at 923 K [8] shows the presence of a $Ni_{2p_{3/2}}$ peak with binding energy similar to that of NiO (856.2 eV) but with a very low satellite peak at 862.5 eV, which is typical spectrum of a low spin Ni(II) compound [9], such as K_xNi_yO. Also, Controlled Atmosphere Electron Microscopy studies of $Ni(NO_3)_2$/KOH mixtures loaded on graphite [10] show that in the presence of steam and above 823 K, the mixture wets and spreads over the edges of graphite, catalyzing the steam attack of the carbon by an edge recession mode up to 1400 K, and without deactivation.

The results obtained for the steam gasification of chars are very similar to those obtained previously on graphite, suggesting that there is a common mechanism for these two carbon substrates. Tables II and III show that both carbon substrates show the same product distribution and activation energy for this reaction, and we have already concluded that the catalytic properties of the $Ni(NO_3)_2$/KOH mixture in both cases are due to a cooperative effect between nickel and potassium. Graphite is, then, a good model for fundamental studies of the catalytic properties of this mixture on the steam gasification of carbon. This in an important conclusion because it allow us to extrapolate the surface characterization studies done on graphite with this catalyst to the char case. The use of graphite as a substrate is advantageous because the results obtained are not complicated by contributions due to the presence of the other components in the char.

5 SUMMARY

In this work we have demonstrated that the $Ni(NO_3)_2/KOH$ mixture has properties for H_2 production from the steam gasification of three different chars, which are superior to the use of the catalyst components separately. This is due to a cooperative effect between nickel and potassium. The mixture has a higher activity and lower activation energy than KOH used alone, and a higher resistance to deactivation than $Ni(NO_3)_2$ alone. We have also concluded that there is a common mechanism for the gasification of char and graphite catalyzed by the $Ni(NO_3)_2/KOH$ mixture.

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Table I: Characteristics of Coal Char Samples Used in this Study.

Char Name	ASTM Rank[a] of Parent Coal	Pretreatment	Analysis (wt%)[b]					
			C	H	N	O	S[c]	Ash[d]
Western Kentucky	HV. B Bit.	Unspecified	72.3	3.2	1.4	7.9	3.2	12
North Dakota	Lignite	Partial Steam Gasification T=1200 K	71.2	1.1	0.37	13-17	2.0	8-12[e]
Illinois #6	HV. C Bit	Pregasifier Heater T > 670 K	72.0	3.3	1.5	10.9	2.6	9.1

[a] HV.= High volatility B and C indicate bituminous classes.

[b] Dry mineral matter containing basis. Oxygen by difference.

[c] Total sulfur.

[d] By low temperature technique (oxygen plasma).

[e] Not measured. Range of values reported in reference 11.

Table II: Product distribution obtained with the three chars and three catalysts studied.

Carbon source	Catalyst	p_{CO_2}/p_{CO}	H_2 prod.[a]
Illinois # 6		1.47	458
North Dakota		10.0	663
Montana	$KOH/Ni(NO_3)_2$	5.26	337
Graphite[b]		33.3	95
Montana[c]		.77	173
Illinois # 6		0.29	322
North Dakota	KOH	9.09	170
Montana		5.26	449
Illinois # 6		–	0
Montana		4.35	314
Montana[c]	$Ni(NO_3)_2$	1.11	55
North Dakota		8.33	511
North Dakota[c]		7.14	342

[a]ml of H_2 produced in 4.0 hours at 893 K.

[b]Taken from reference 3.

[c]Treated in aqua regia.

Table III: Activation energies obtained with the three catalysts studied

Carbon source	Catalyst	Activation Energy (Kcal/mol)		
		H_2	CO_2	CO
Illinois # 6		28.6 ± 0.6	36.0 ± 0.4	35.4 ± 0.4
North Dakota	$KOH/Ni(NO_3)_2$	29.2 ± 0.6	36.8 ± 0.3	49.9 ± 0.8
Montana		28.7 ± 1.2	28.4 ± 0.6	43.0 ± 0.7
Graphite[a]		25.2 ± 0.8	34.0 ± 1.3	65 ± 8
Illinois # 6	KOH	60.8 ± 1.8	78.1 ± 2.3	55.3 ± 1.7
North Dakota		54.8 ± 2.0	65.7 ± 2.6	80.4 ± 2.1
North Dakota	$Ni(NO_3)_2$	33.6 ± 0.6	38.2 ± 0.7	48.5 ± 1.9
North Dakota[b]		27.3 ± 1.7	40.8 ± 1.0	59.7 ± 2.9

[a] Taken from reference 3.

[b] After aqua regia treatment.

FIGURE CAPTION

Figure 1: Diagram of the experimental apparatus.

Figure 2: Rates of gas production as a function of time for the steam gasification of Illinois # 6 char catalyzed by a mixture of $Ni(NO_3)_2$ and KOH at 893 K.
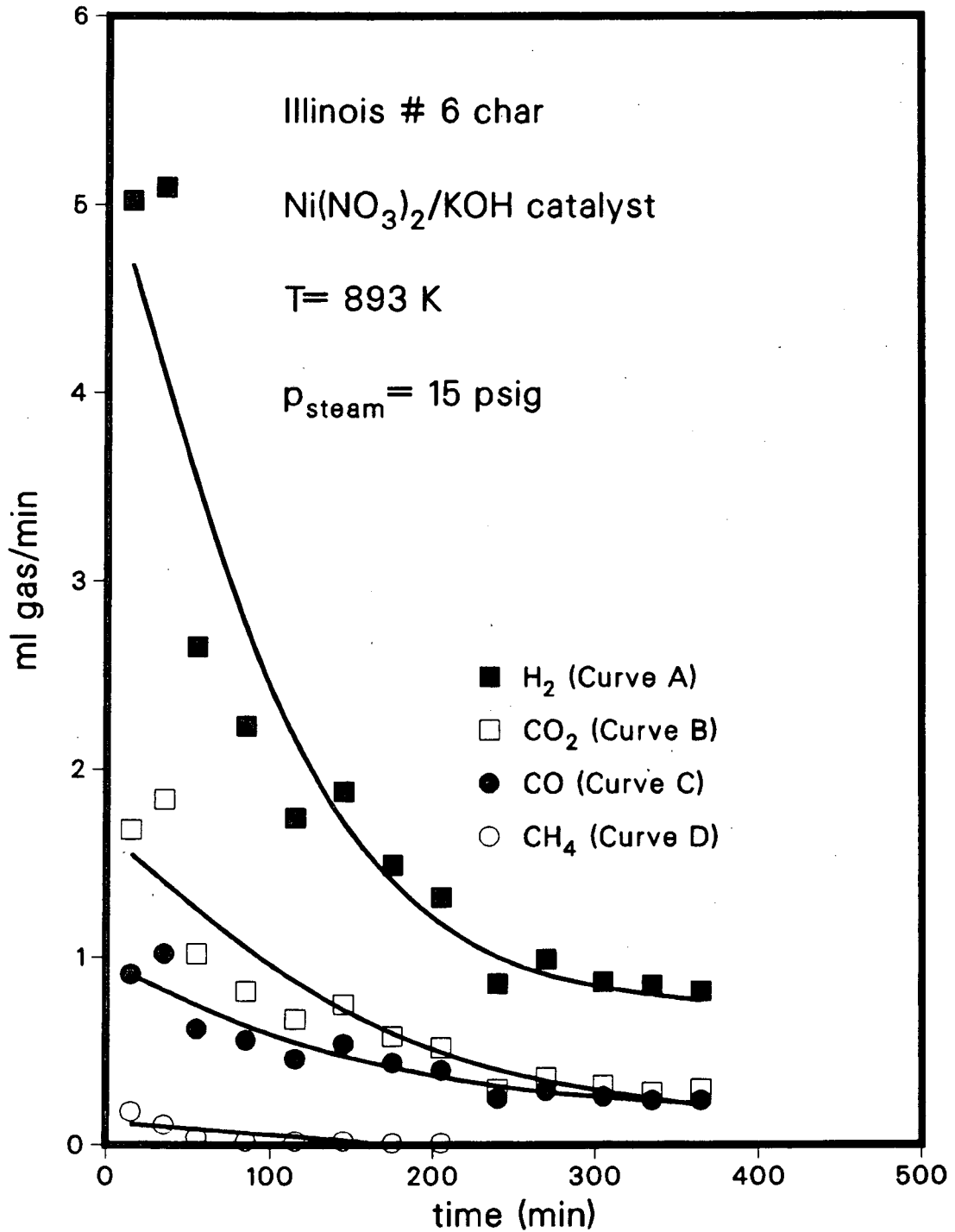
Figure 3: Rates of gas production as a function of time for the steam gasification of North Dakota char, catalyzed by a mixture of $Ni(NO_3)_2$ and KOH at 893 K.

Figure 4: Rates of gas production as a function of time for the steam gasification of Montana char, catalyzed by a mixture of $Ni(NO_3)_2$ and KOH at 893 K.

Figure 5: Effect of the aqua regia pretreatment of Montana char on the catalytic activity of the $Ni(NO_3)_2$/KOH mixture.

Figure 6: Arrhenius plots of the temperature dependence of the rates of gas production from the gasification of Illinois # 6 char catalyzed by a mixture of $Ni(NO_3)_2$ and KOH.

Figure 7: Rates of gas production as a function of time for the steam gasification of Illinois # 6 char, catalyzed by KOH at 893 K.

Figure 8: Rates of gas production as a function of time for the steam gasification of North Dakota char, catalyzed by KOH at 893 K.

Figure 9: Rates of H_2 production as a function of time for the steam gasification of Illinois # 6 char and Montana char with and without being treated in aqua regia, catalyzed by $Ni(NO_3)_2$ at 893 K.
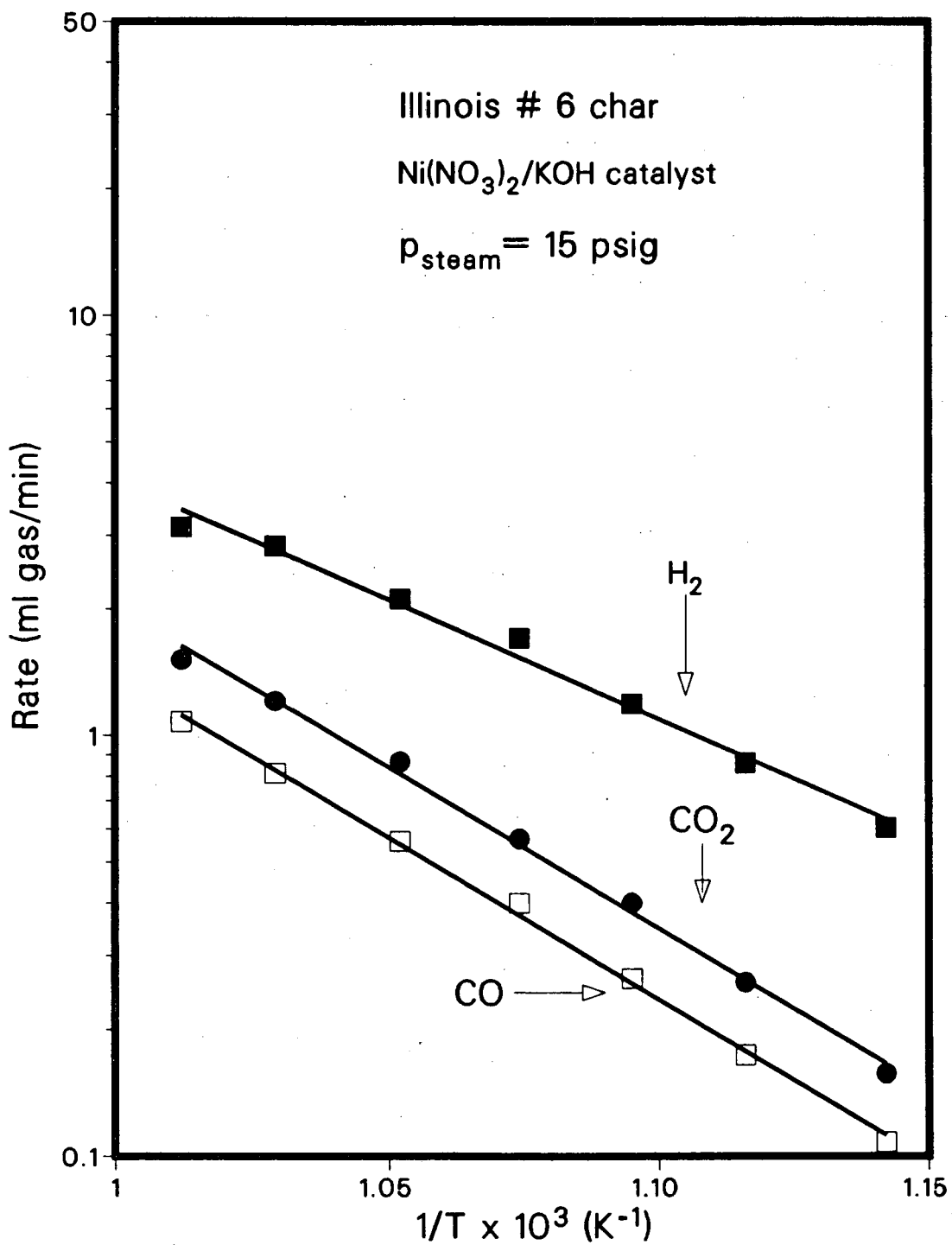
Fig. 1

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Fig. 2

Fig. 3

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Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9