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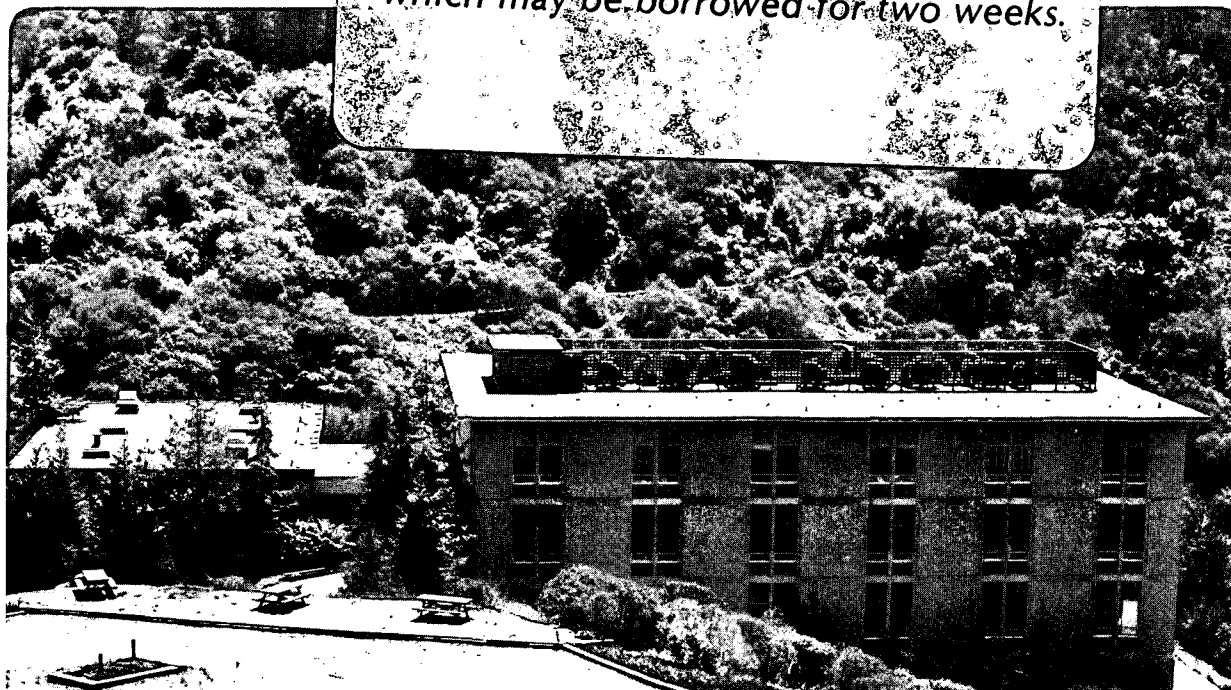
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**Controlled Atmosphere Electron Microscopy Study
of The Gasification of Graphite by Water, Hydrogen and Oxygen
Catalyzed by a Nickel/Potassium Mixture**

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ABSTRACT

The gasification of graphite by H₂O vapor, wet H₂ and wet O₂, catalyzed by a Ni/K mixture has been studied using controlled atmosphere electron microscopy (CAEM). In H₂O vapor the carbon consumption, between 550 and 1100 °C, is catalyzed by an edge recession mode of attack in the $[11\bar{2}0]$ direction, with no sign of deactivation. An activation energy of 30.8 ± 0.9 kcal/mol was obtained in this case. This value is similar to those obtained in kinetic studies of the steam gasification of both graphite and char, using this catalyst. In wet H₂ both channeling and edge recession occur 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 H₂O vapor at 600 °C. In wet O₂, 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.

INTRODUCTION

Recently [1,2], we 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 $550\text{ }^\circ\text{C}$, and have a high resistance to deactivation. 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 $580\text{ }^\circ\text{C}$ ($1.2\text{ ml } H_2/\text{min}$) and a relative low activation energy ($\sim 30\text{ kcal/mol}$).

In this work we 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 environments; 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 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.

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], placing 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]. Ni and K are introduced onto transmission specimens of natural single crystal graphite (Ticonderoga NY) as an atomized spray, using 0.1% solutions of $\text{Ni}(\text{NO}_3)_2$ 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 $\text{Ni}(\text{NO}_3)_2$, and achieve a good metal 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 H_2O at 20 °C. This procedure produces a gas/ H_2O ratio of $\sim 40/1$ in the gas reaction cell.

RESULTS

The nickel-potassium/graphite-water vapor system.

After treating graphite samples loaded with KOH and $\text{Ni}(\text{NO}_3)_2$ at 450 °C in Ar, particle nucleation was observed both on the basal and edge planes. When the sample was treated in a water vapor environment (2 Torr Ar: H_2O 40:1), 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 ± 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 H₂ product in the gas environment. This is in agreement with the results described in the following section.

The nickel - potassium/graphite - wet hydrogen system.

The catalytic effect of Ni/K mixtures on the gasification of graphite on a H₂:H₂O 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 H₂ 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 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 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 ± 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 H₂ 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 H₂/H₂O treatment (open circles), are identical to those obtained after a heat treatment in Ar, (black dots).

The nickel-potassium/graphite-wet oxygen system.

Treatment of nickel/potassium specimens in 2.0 Torr of wet O₂ (O₂:H₂O 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 H₂ and wet Ar, the recession in wet O₂ 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 O₂ the catalyst spreads and promotes the carbon attack by an edge

recession mode. In wet H₂ 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)

$$\gamma_{sg} > \gamma_{lg} + \gamma_{sl} \quad (1)$$

This is the case in H₂O vapor and O₂/H₂O environments, but there are differences in catalyst behavior between these two cases. In wet O₂, 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 O₂, 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 H₂O vapor, below 650 °C the catalyst interacts with a larger fraction of clean edges than in the O₂ case because the sticking coefficient of water on graphite is much smaller than that of O₂ [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, H₂ 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 these two cases is the direction of the edge recession attack. In wet O₂ 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 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 [12] that because steam adsorbs 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 H₂, 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 channeling 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 H₂ [4] and K salts are not active for carbon gasification in reducing environments [14]. Furthermore, this mode of attack has not been previously reported in reducing environments. This interaction is suppressed above 1000 °C in H₂, and can be regenerated by treating the sample in H₂O 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 H₂O 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 H₂ 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 O₂ 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 O₂-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 $\text{Fe}(\text{NO}_3)_3/\text{Na}_2(\text{CO}_3)$ mixtures [18] show that this catalyst is more active than either $\text{Fe}(\text{NO}_3)_3$ or $\text{Na}_2(\text{CO}_3)$ 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

We studied the catalytic properties of Ni/K mixtures in H_2O , $\text{H}_2/\text{H}_2\text{O}$ and $\text{O}_2/\text{H}_2\text{O}$ atmospheres by CAEM. 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 1000°C . This mixture shows superior catalytic properties than either Ni or K used independently, due to a cooper-

ative effect between the components.

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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 in 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 length of the curves indicates the temperature range studied.

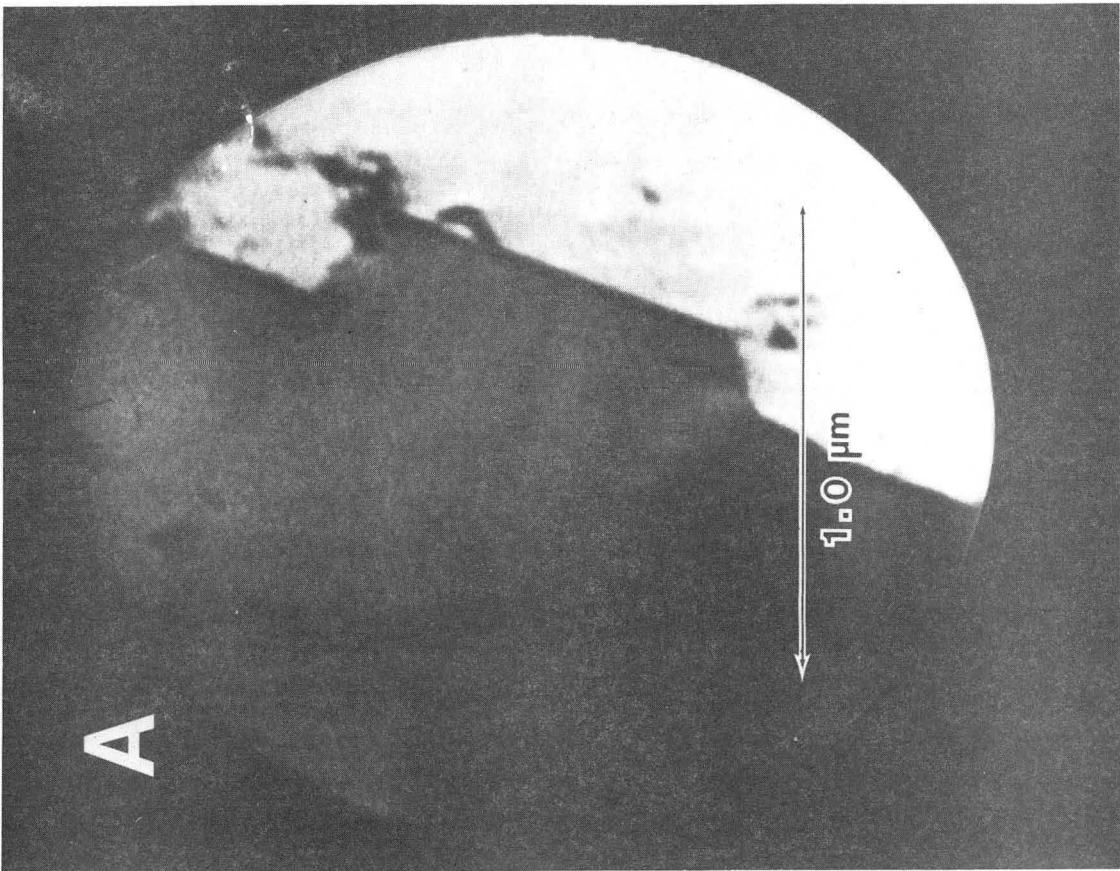
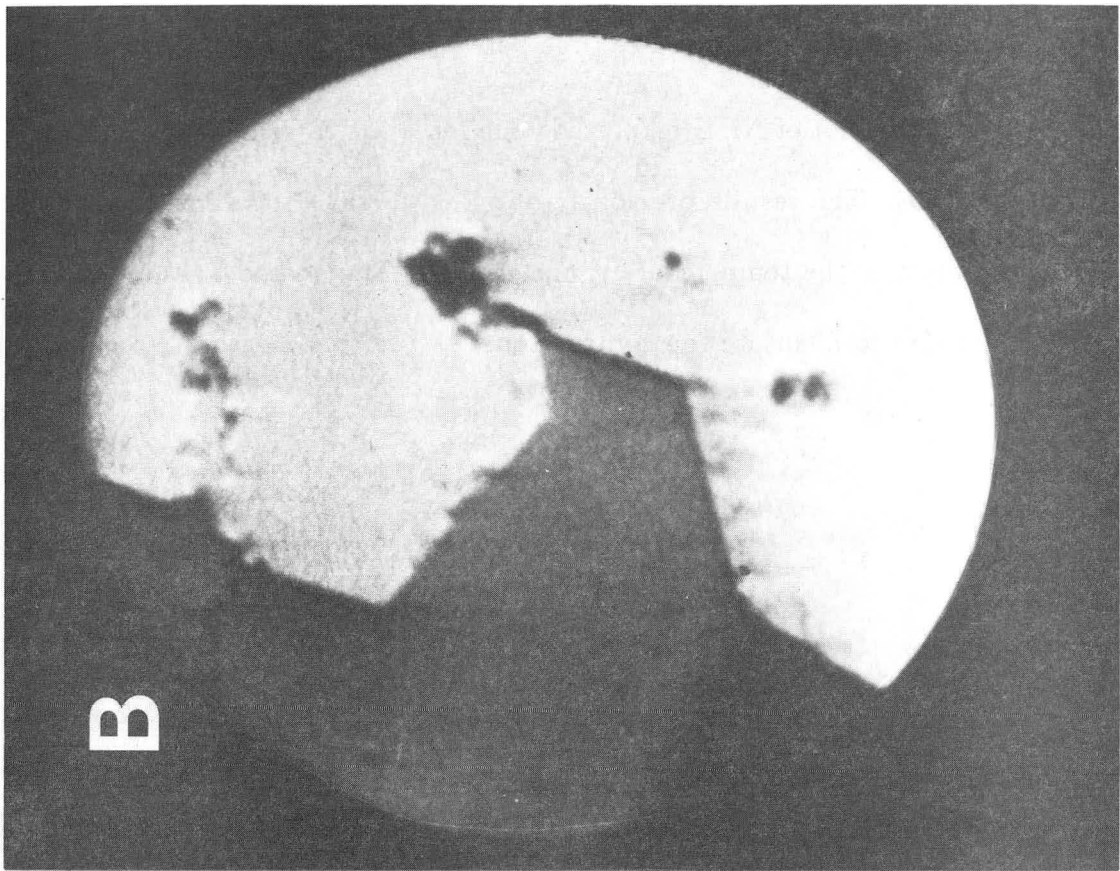
Figure 3: Sequence of photographs, showing the modes of attack in 2 Torr of wet H_2 . The region indicated by the arrows shows the recession of the channel walls, as described in the text (see results). Also notice the simultaneous carbon attack by edge recession and channeling in the lower part of the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

Figure 4: Arrhenius plot of Ni/K catalyzed edge recession rates of graphite in 2 Torr of wet H_2 . The results previously obtained for the channeling mode of attack of Ni metal are included for comparison. The length 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 before catalyst spreading. Notice also the erosion of the edges, which is the first

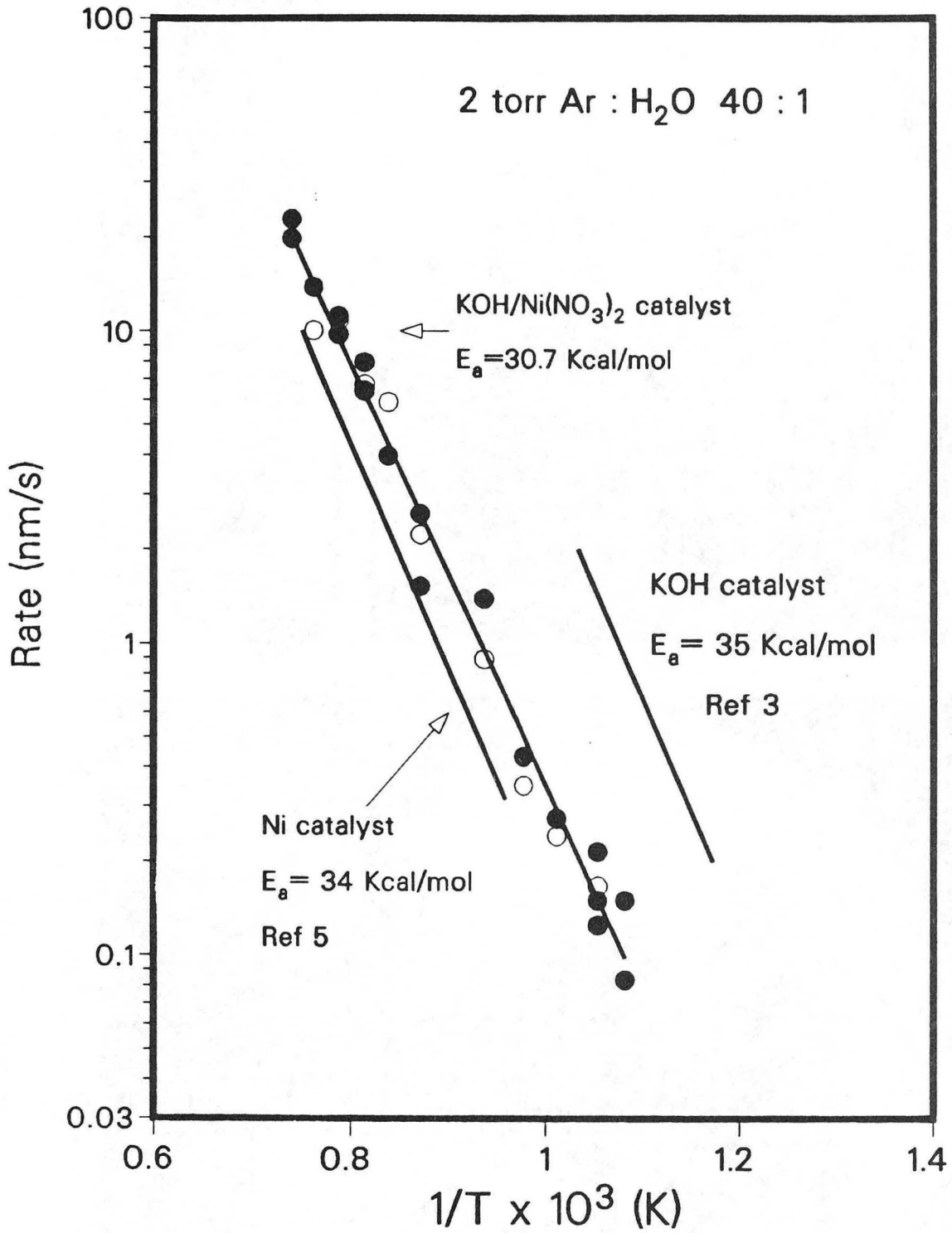
indication of edge recession attack. The time between photographs is 10 sec.

Figure 6: Arrhenius plot of Ni/K catalyzed edge recession rates of graphite consumption in 2 Torr of wet O₂. The results previously obtained for KOH are included. The length of the curves indicates the temperature range studied. The dotted lines are extensions of the curves, included to facilitate the comparison.



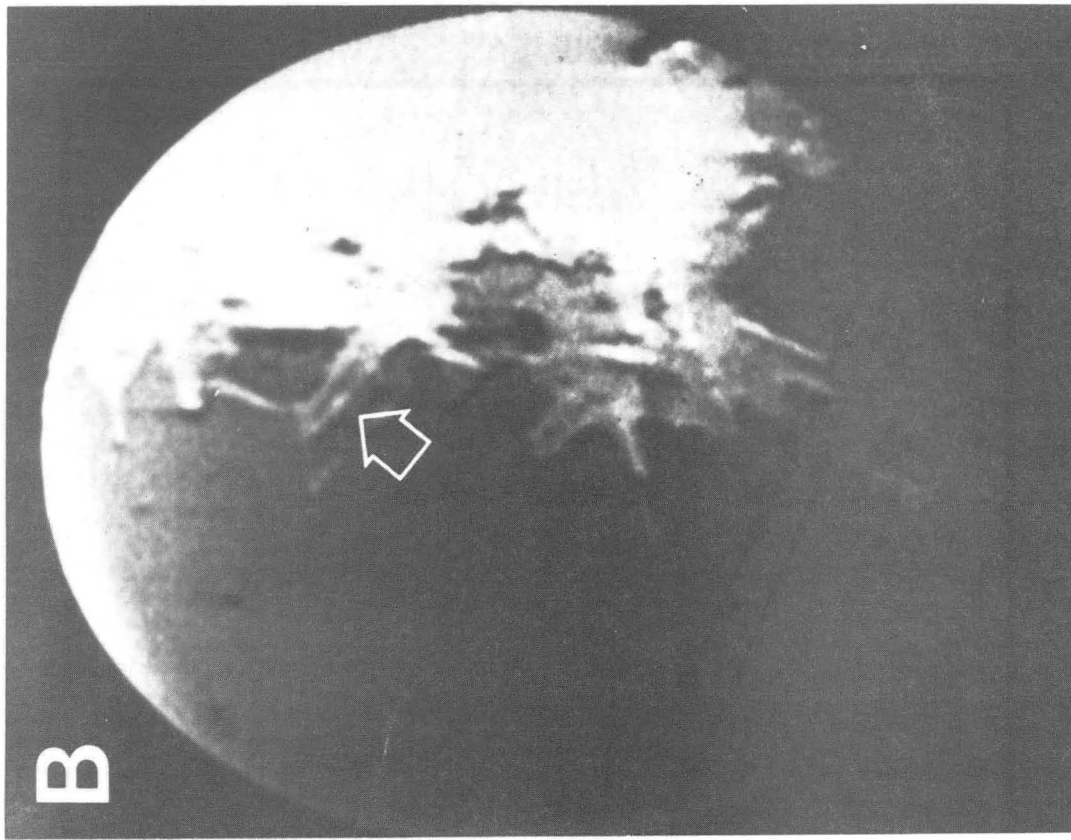
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Fig. 1A,1B



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Fig. 2



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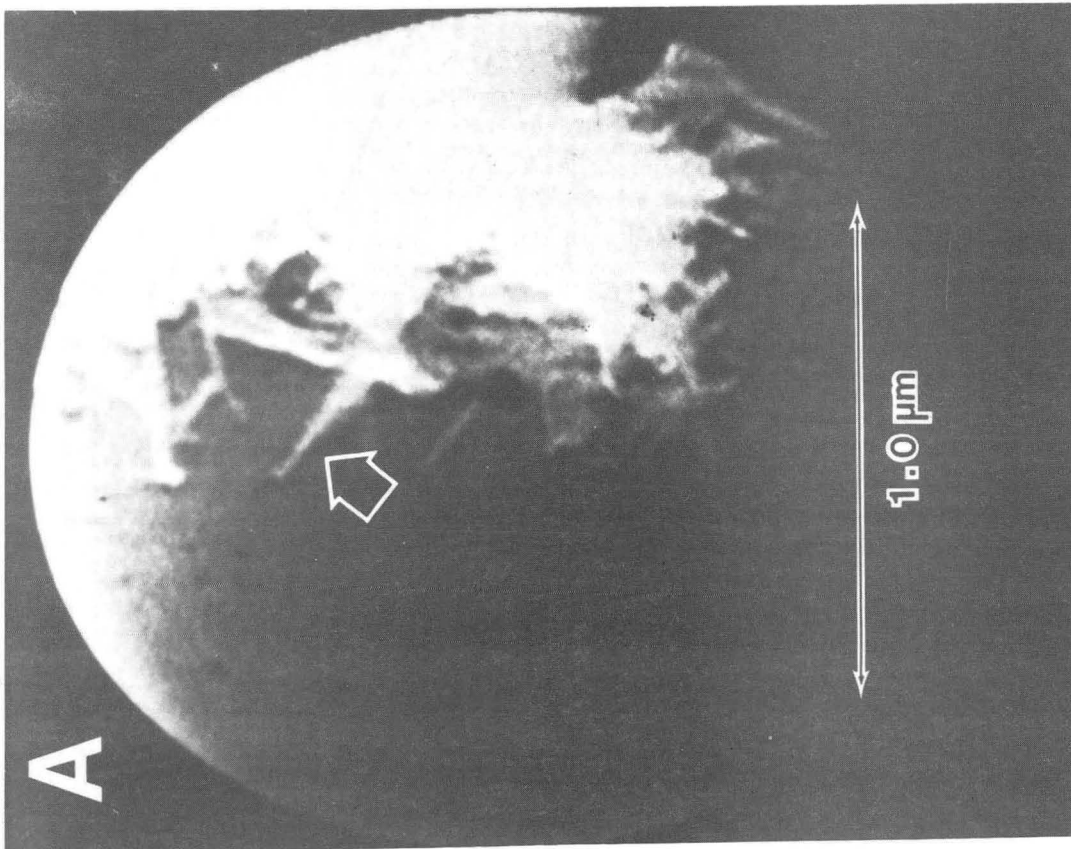
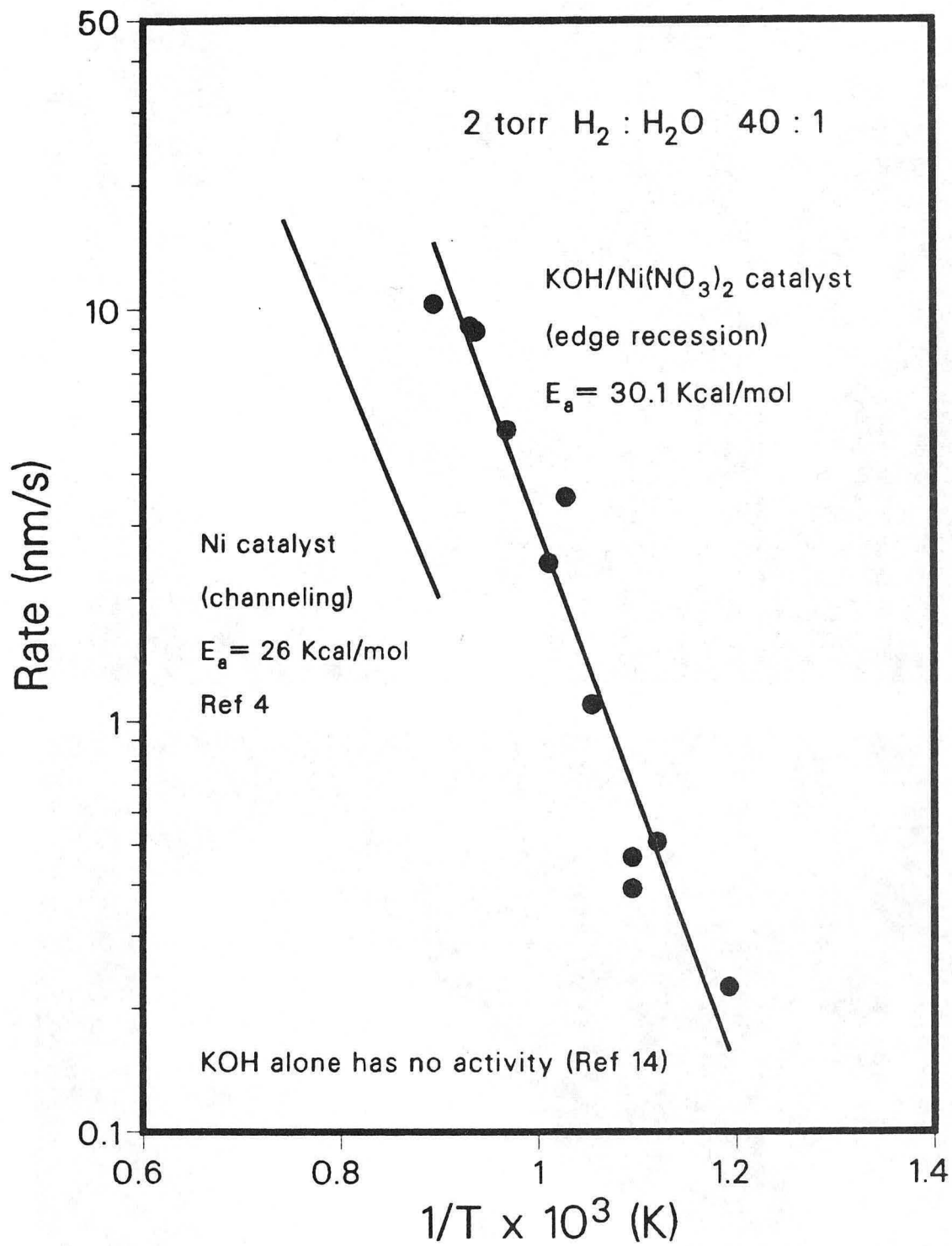
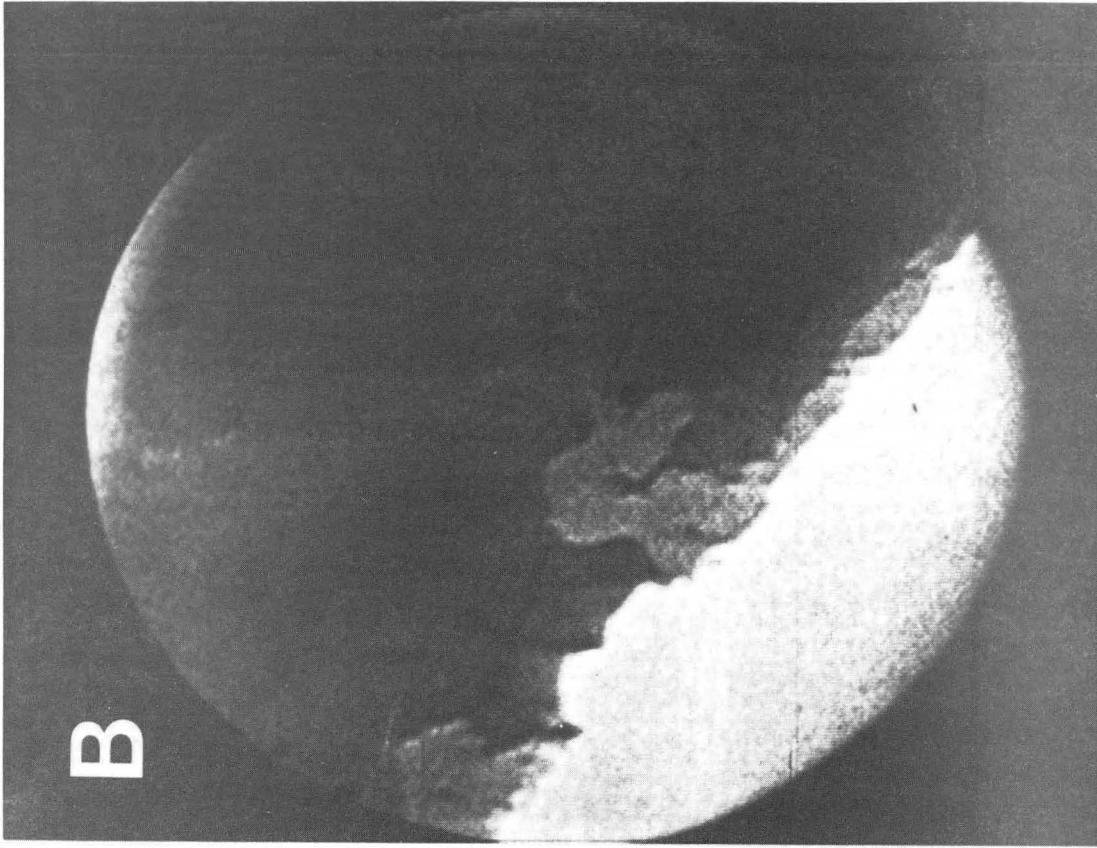
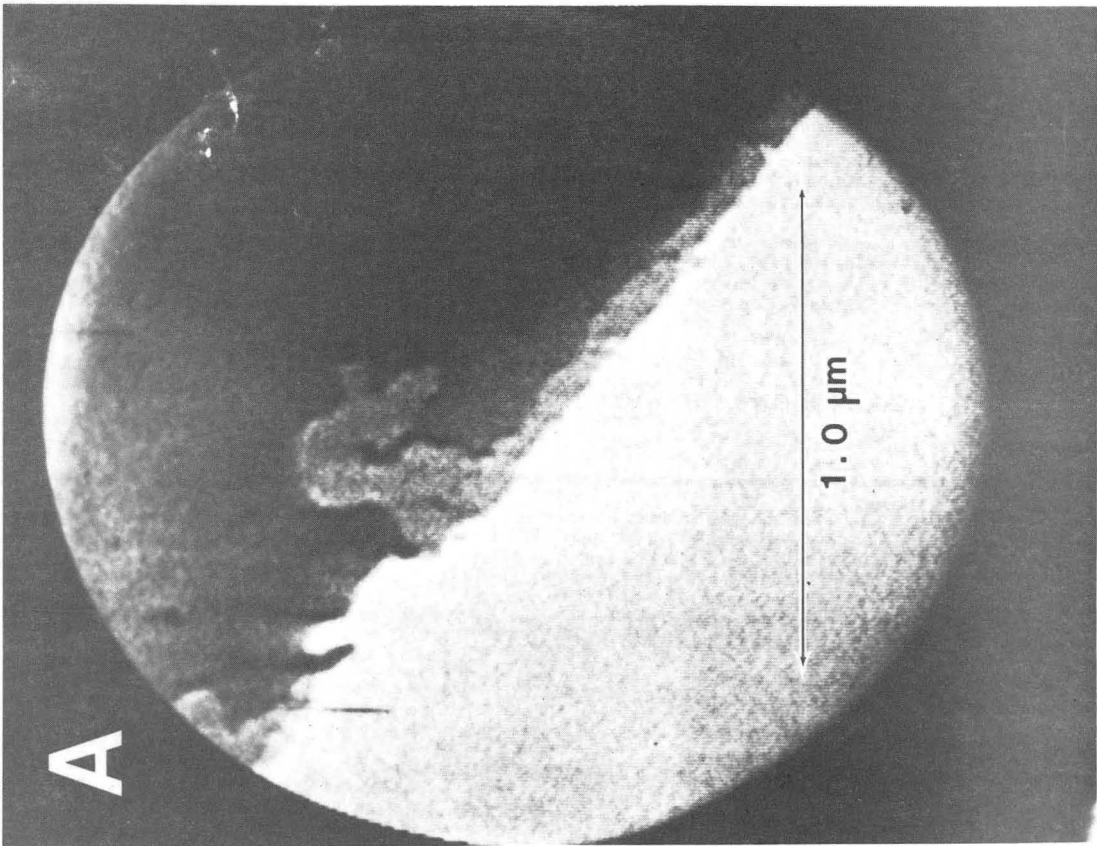


Fig. 3A,3B



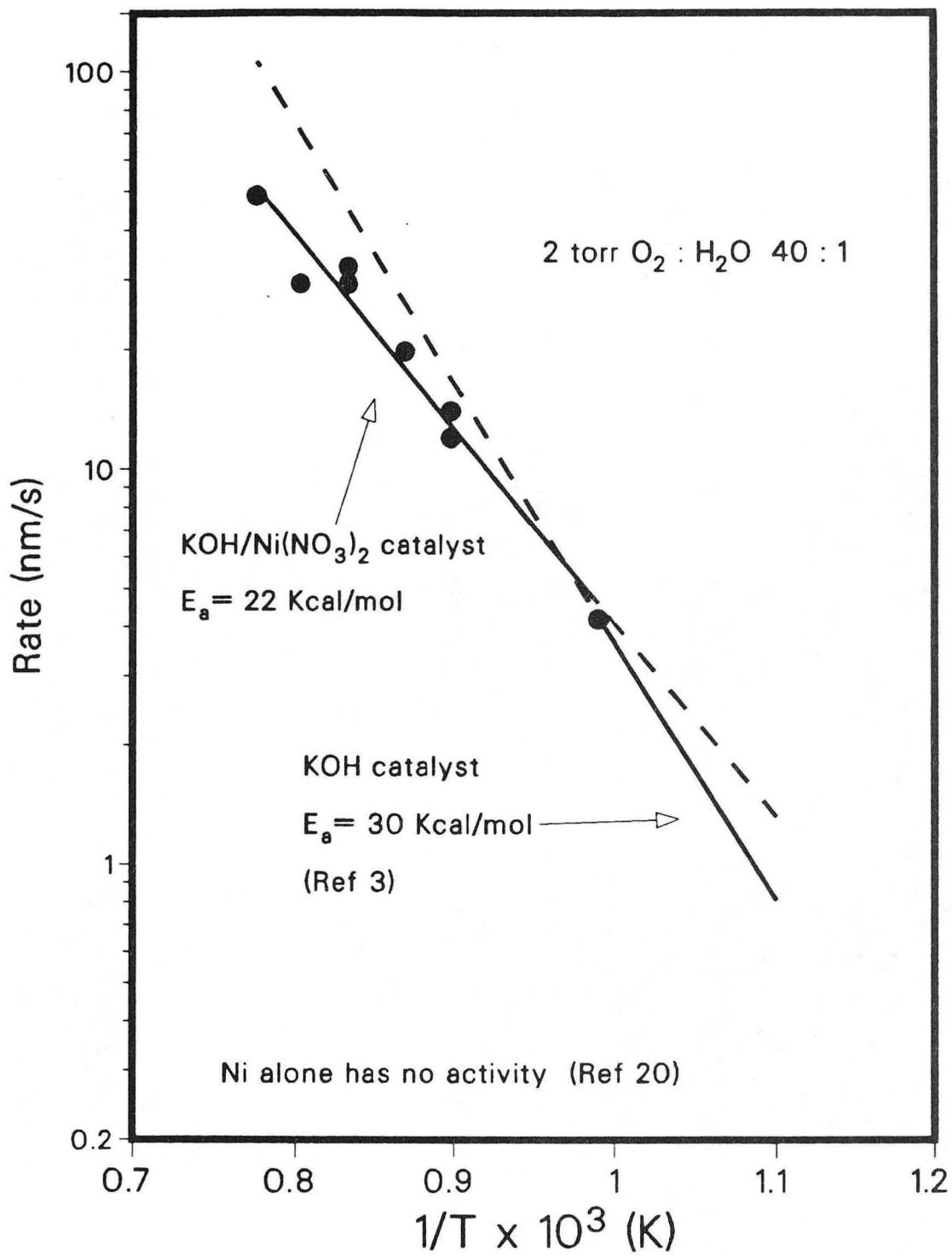
XBL 873-1271

Fig. 4



XBB 871-52B

Fig. 5A,5B



XBL 873-1272

Fig. 6

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