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FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION:
Quarterly Report, October 1, 1986-December 31, 1986

H. Heinemann

December 1986

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QUARTERLY REPORT

October 1, 1986 - December 31, 1986

FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

Principal Investigator: Heinz Heinemann

Lawrence Berkeley Laboratory
University of California
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. Activation energies for K/Ni catalysed steam gasification of graphite and of chars are identical, indicating the same mechanism prevails though rates are much higher for chars. This permits extrapolation of findings in high vacuum equipment from graphite to chars.

2. The CO/CO_2 ratio of gases produced along with hydrogen varies with different chars. The ratio is 0.8 for Illinois #6 char and 0.08 for North Dakota char. Methane production is several orders of magnitude smaller and ceases after about 2 hours.

3. Comparison of K/Ni catalyst for steam gasification of Ilinois #6 char with K or Ni alone indicates:

   a) K alone produces much higher CO/CO_2 ratios than K/Ni (3.5 vs. 0.8) and therefore less hydrogen; activation energies for K catalyst are much higher than for K/Ni.

   b) Ni alone is almost inactive for the steam gasification of Illinois #6 except for the short first period of operation. The H_2 production rate for Ni alone as in the case of K alone is lower than that for K/Ni.

4. Montana char treated with aqua regia to remove ash components prior to impregnation wit K/Ni has 75% of the activity of untreated char but exhibits little deactivation with time so that it gasifies better than untreated char after a few hours.

5. Controlled atmosphere electron microscopy studies have been extended to wet hydrogen and wet oxygen treatments of K/Ni impregnated graphite.

III. Progress of Studies

For the sake of clarity, a few observations which were previously reported are repeated in this section.

A. Char Gasification Catalyzed by K/Ni Mixtures

The steam gasification of all the chars (Table 1) catalyzed by a K/Ni mixture shows the same general pattern, even though there are some differences in product distribution.

The gas products include H_2, CO, CO_2 and a slight amount of CH_4. Fig. 1 shows, as an example, the rates of production of these four gases as a function of time for the gasification of Illinois #6 char at 893 K. These results are analogous to those observed for the other two chars. After the first hour of reaction, the production rate of hydrogen containing gases is equal to 2.0 times the rate of those containing oxygen indicating that there is a mass balance at this temperature.

The product distribution obtained from the gasification of each char is shown in Fig. 2. H_2 is the main hydrogen containing gas product. Very little CH_4 is produced, and only within the first two hours of reaction. The ratio of CO to CO_2 varies from char to char, going from .80 in the case of Illinois #6 char to .080 in the case of North Dakota char. Due to the stochiometry of Eqs. 1 and 2, this ratio affects the total number of moles of H_2 that are produced per mol of carbon that is gasified, ranging from 1.54 in the case of Illinois #6 char to 1.91 in the case of North Dakota char.

$$C + 2H_2O \longrightarrow 2H_2 + CO_2 \qquad (1)$$

$$C + H_2O \longrightarrow H_2 + CO \qquad (2)$$

Fig. 1 also shows that the rate of gasification of all gases decreases with time. Several reasons can be responsible for this behavior. One of them is that the rate of reaction depends on the number of active sites in the carbon substrate, which diminishes as the reaction progresses. This dependence can be expressed according to Eq. 3, assuming that the morphology of the substrate does not change during the process.

$$-\frac{dC}{dt} = k\,(1 - X)^m \qquad (3)$$

dC/dt is the rate of carbon conversion and X is the fraction of carbon gasified or "carbon burn off". If the rate depends on the concentration of active sites, the reaction order with respect to carbon (n) should be between 0.75 and 1.00.

The data necessary to evaluate Eq. 3 can be obtained from the results shown in Fig. 1. The sum of the rates CO, CH_4 and CO_2 production is equal to dC/dt, and the integration of dC/dt as a function of time gives the carbon conversion (X). Then, from Eq. 3, the slope of ln(dC/dt) versus ln(1-X) is equal to the reaction order with respect to the carbon (n).

The values of n obtained for the three cases are less than 0.4. (See Table 2.) As mentioned previously, a value n higher than 0.75 would be expected if the rate of gasification depended on the number of active sites in the carbon, therefore it is concluded that this is not the reason for the decrease in rate.

Another possibility for the decrease in rate is catalyst deactivation. In a previous report[1] (see Fig. 3) the rates of H_2 production were compared for the steam gasification of Montana char samples that have not been treated in aqua regia overnight, previous to the loading of Ni/K catalyst. The sample that has not been treated in aqua regia deactivates in a fashion similar to that already described for Illinois #6 char, while the one that has been treated in aqua regia maintains 75 percent of its initial activity after 600 min. It should also be noted that 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 K/Ni catalyst by interaction with some char component that can be removed by aqua regia treatment. Furthermore, a plot of ln(dC/dt) vs. ln(1-X) for the char treated aqua regia gives a value of n close to zero (see Table 2), indicating again that at these catalyst loadings and up to a carbon conversion of 50 percent the rate is independent of the carbon active site concentration.

The rates of steam gasification and product distribution as a function of temperature have been studied for the three chars. Since the initial rate of gas production decreases very fast with time, the reaction was carried out isothermally at 893 K for 4 hours before the temperature was raised. After this period, the absolute changes in rate with time at 893 K were small enough to allow obtaining a reasonable estimate of the activation energies. The rates of gas production as a function temperature obtained for Illinois #6 char are shown in Fig. 4 in

the form of an Arrhenius plot, and the activation energy values obtained for H_2, CO and CO_2 production in all three cases are summarized in Table 2. The activation energy for H_2 production is very similar for all the chars ($\sim$29 Kcal/mol) and in the cases of Illinois #6 and North Dakota chars it is lower than those of CO and CO_2 formation. Also the activation energy values for H_2 and CO_2 formation on all chars are similar to those obtained with graphite, suggesting that the latter is a good model for the studies of the catalyzed steam gasification of chars. The two chars that produce a ratio of CO to CO_2 lower than 0.1, that is, North Dakota and Montana chars, show a larger activation energy for CO formation than the CO_2 formation, while Illinois #6 char, that produces a CO to CO_2 ratio close to one shows activation energies for the formation of these two gases. This indicates that the product distribution in all the cases is controlled by the activation barrier for formation of the products, rather than by pre-exponential factors.

B. Char Gasification Catalyzed by K Deposited Alone

The steam gasification of Illinois #6 char catalyzed by KOH was studied isothermaly at 893 K and as a function of temperature in order to compare results with those obtained for K/Ni mixture.

Fig. 5 shows the rates of gas production for H_2, CO and CO_2 and CH_4 as a function of time at 893 K. As in the case of K/Ni catalyst, the rate of hydrogen containing gases (Eq. 4) is equal to two times the rate of those containing oxygen, indicating that at this temperature there is a mass balance. The ratio of CO to CO_2 in this case is much

higher than that obtained with the Ni/K catalyst. (pCO/pCO_2 is equal to 3.5 in the case of K alone and 0.80 in the case of Ni/K.) The moles of H_2 produced per mol of carbon consumed are therefore lower in this case (1.3 mol H_2/mol no. C) than in the Ni/K case (1.61 mol H_2/mol no. C).

Fig. 5 also shows that as in the case of the Ni/K catalyst, when K is deposited alone there is a decrease in the reaction rate as a function of time. When ln(dC/dt) is plotted versus ln(1-X), a value of n equal to 0.28 is obtained. Again, as in the case of the Ni/K mixture, the decrease in rate should be attribute to a deactivation or loss of catalyst rather than to a dependence in the carbon active-site concentration.

The rate of H_2, CO and CO_2 production was studied as a function of temperature between 853 and 993 K. As in the case of Ni/K mixture, since the initial state of reaction decreases fast with time, the reaction was initially carried out isothermally at 893 K for 4 hours and then the temperature was increased. The activation energies for H_2, CO and CO_2 production are summarized in Table 2. Their values are much higher than those obtained for the Ni/K catalyst. The H_2 activation energy is 32 Kcal/mol higher than that obtained with the Ni/K catalyst, the CO activation energy is 19 Kcal/mol higher, and the CO_2 activation energy is 43 Kcal/mol higher. From Table 2 also notice that the activation energy for CO formation obtained for K alone (55.3 Kcal/mol) is lower than that for CO_2 formation for the same catalyst (78.2 Kcal/mol), while in the case of the Ni/K catalyst the values are similar. This is reflected in the ratios of CO to CO_2 obtained with

each catalyst, suggesting that the product distribution in this case is also controlled by the energy barriers for formation of the products.

C. Char Gasification Catalyzed by Ni Deposited Alone

Ni deposited alone from the impregnation to incipient wetness of $Ni(NO_3)_2$ has been studied as a catalyst for the steam gasification of Illinois #6 and Montana chars.

Fig. 6 shows that Ni alone is almost inactive for the steam gasification of Illinois #6 char. Also notice that for this char, the sum of the H_2 production rates for Ni deposited alone and K deposited alone (Fig 5 Curve A plus Fig. 6 Curve A) is lower than the H_2 rate obtained for the K/Ni mixture (Fig. 1 Curve A), indicating the existence of a cooperative effect between Ni and K in the mixture.

In the previous report [1] it was shown that in the case of Montana Char, (Fig. 7 Curve B) the activity of Ni deposited alone is similar to that of the Ni/K mixture (Fig 3. Curve A), however, if the sample is treated in aqua regia previous to the Ni loading the catalyst becomes inactive (Fig. 6 Curve C), suggesting that the activity of Ni on the untreated sample was due to its interaction with some component in the char that can be eliminated by aqua regia treatment.

D. Controlled Atmosphere Electron Microscopy

In the annual report for fiscal year 1986 (September '86) a controlled atmosphere electron microscopy study was presented for the

gasification of graphite with steam catalyzed by Ni/K mixture. In the present report additional work is included using mixtures of H_2 and H_2O vapor and O_2 and H_2O vapor as reactant gases.

i) Nickel-Potassium/Graphite - Wet Hydrogen

The first signs of catalylic attack, when the specimen were heated in 2.0 Torr wet hydrogen, was observed at 545°C; and this took the form of relatively straight channels which were created by catalyst particles which had nucleated along the edges of the graphite. When first formed the channels remained parallel-sided, however, as the temperature was raised to 565°C they started to acquire a fluted appearance. This was a result of active particles spreading along the channel walls and proceeding to catalyze the reaction by the edge recession mode.

On raising the temperature to 675°C many of the previously inactive particles located on the graphite basal plane started to exhibit mobility. If these particles encountered an edge, they underwent a rapid spreading action, and this resulted in the subsequence removal of carbon by edge recession. Continous observation of this process showed that the edges moved back in a very uniform manner, in directions parallel to the $(11\bar{2}0)$ crystallographic orientations. The reaction was continued up to a maximum temperature of 1000°C, a condition where the rate of edge recession appeared to have slowed down and in some cases movement had stopped. Regeneration of catalytic activity could be achieved by heating in 2 Torr wet argon at about 600°C.

It is interesting to compare the behavior of this system with that exhibited by nickel under the same conditions.[3] In the latter reaction, catalytic attack occurred by the channeling mode and remained the exclusive form of attack up to about 1000°C. At this temperature, the channeling particles underwent an unusual loss in activity which was associated with the spreading of material along the sides of channels created at lower temperatures. In this case it was also possible to restore catalytic activity by replacing the hydrogen with a pure steam environment. Based on these observations, it would appear that although potassium enhances the wetting characteristics of nickel in a hydrogen atmosphere (i.e., catalytic attack proceeds by edge recession rather than channeling) it does little to suppress the deactivation step.

The variation in the edge recession rate was determined as a function of temperature and this data is presented in the form of an Arrhenius plot in Fig. 7. From the slope of this line, it has been possible to evaluate an apparent activation energy fo 26.2 kcal/mole; which is identical to that obtained for the nickel/graphite-wet hydrogen system.[3]

ii) Nickel-Potassium/Graphite-Wet Oxygen

Treatment of nickel-potassium/graphite specimens in 2.0 Torr wet oxygen resulted in the formation of shallow channels at 605°C. During this stage of the reaction, the channels followed random pathways and tended to remain parallel-sided throughout these propagation period. As the temperature was raised to 665° catalyst particles at the head of

the channels gradually disappeared due to spreading of material along the walls of the channels which then proceeded to undergo lateral expansion. At the same time particles which come into contact with edges immediately underwent spreading and following this action the coated edges started to gasify, but in contrast to the equivalent behavior in wet hydrogen the recession did not appear to follow any preferred direction. A further difference in this reaction compared to the behavior in either steam are wet hydrogen was that catalytic attack continued in uninterupted fashion up to 1015°C, there being no evidence for deactivation of gasifying edges.

From the Arrhenius plot of the variation of the rate of edge recession with temperature (Fig. 8), it has been possible to derive an apparent activation energy of 24.8 kcal/mole. Examination of this data reveals that the mixed catalyst exhibits a higher intrinsic activity than either of its single component for the graphite-oxygen reaction.

E. References

1. Annual Report, September 1986, LBL-22196.

2. J. Carrazza, W. T. Tysoe, H. Heinemann and G. A. Somorjai, J. Catal., 96, 234 (1985).

3. R. T. K. Baker and R. D. Sherwood, J. Catal., 70, 198 (1981).

TABLE 1

Characteristics of Coal Char and Graphite
Used in Study

Char Name	ASTM Rank[a] of Parent Coal	Pretreatment	Analysis (wt%)[b] C	H	N	O	S[c]	Ash[d]
North Dakota Husky (NDHL)	Lignite	Partial Steam Gasification T = 1200K	71.2	1.1	0.37	13-17	2.0	8-12[e]
Montana (MS)	Subbituminous	Partial Steam gasification: T = 1200K	66.0	1.1	0.20	-	0.92	-
Illinois N-6 Low Temp. (I 6 LT)	HV.C. Bit	Pregasifier Heater T 670K	72.0	3.3	1.5	10.9	2.6	9.1

[a]HV. = High volatility B and C indicate bituminou classes.
[b]Dry Mineral water containing basis. Oxygen by difference.
[c]Total Sulfur.
[d]By low temperature technique (oxygen plasma).
[e]Not measured. Range of values reported in reference 12.

TABLE 2

Activation Energies and n Values Obtained for the Ni/K and K Alone Catalysts

Char	Catalyst	H_2	CO_2	CO	n*
Illinois #6	K/Ni	28.6 ± 0.6	36.0 ± 0.6	35.0 ± 0.4	0.37
Illinois #6	K	60.8 ± 1.8	48.1 ± 2.3	55.3 ± 1.7	0.28
Montana	K/Ni	28.7 ± 1.2	28.4 ± 0.6	43.0 ± 0.7	0.23
North Dakota	K/Ni	29.2 ± 0.6	36.8 ± 0.3	49.8 ± 0.8	0.48
Montana ≠	K/Ni	-	-	-	0.10

*See Eq. 3

≠ Treated with aqua regia.

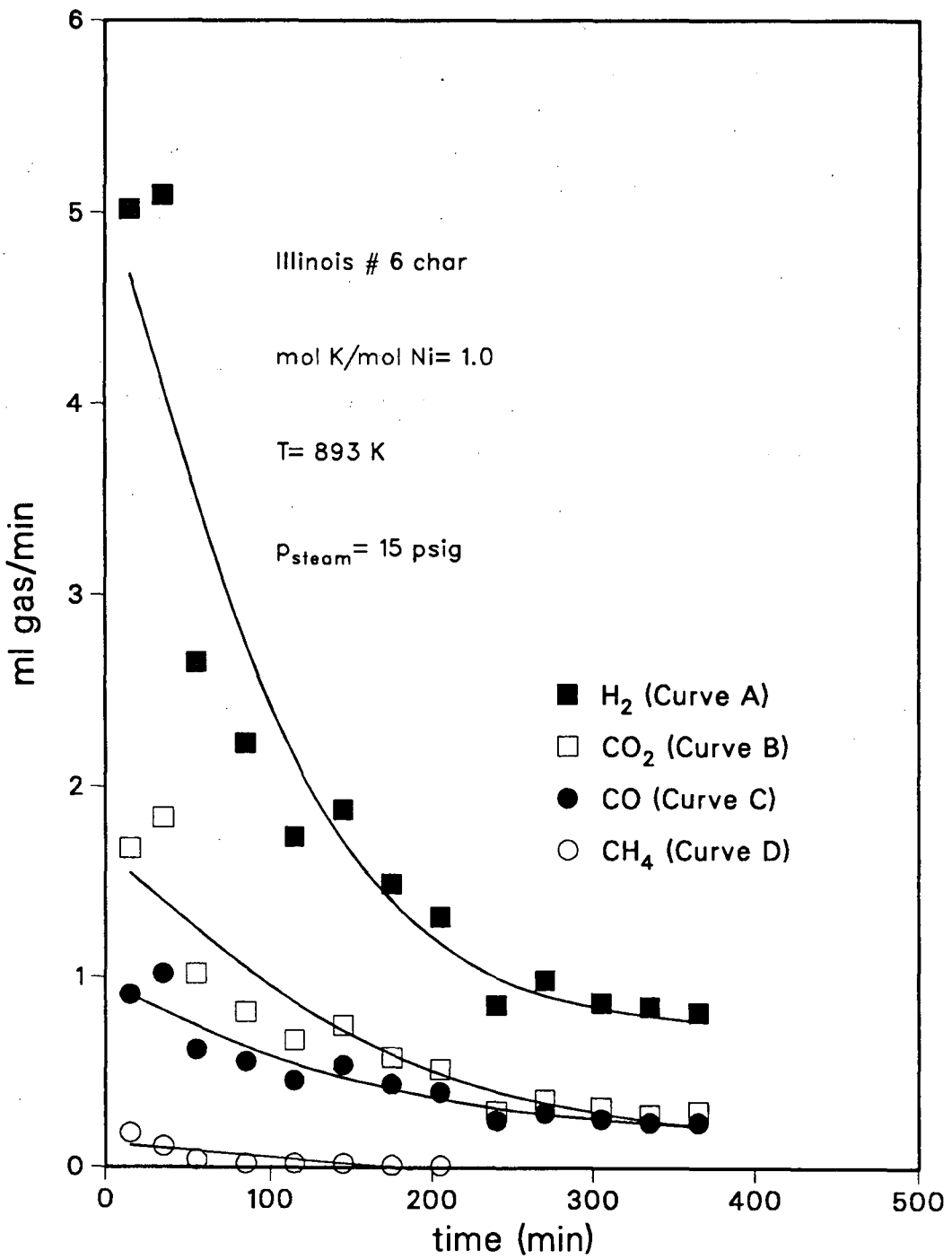
Illinois # 6 char
mol K/mol Ni= 1.0
T= 893 K
P_{steam}= 15 psig
H_2 (Curve A)
CO_2 (Curve B)
CO (Curve C)
CH_4 (Curve D)
ml gas/min
time (min)
0
1
2
3
4
5
6
0
100
200
300
400
500

Figure 1

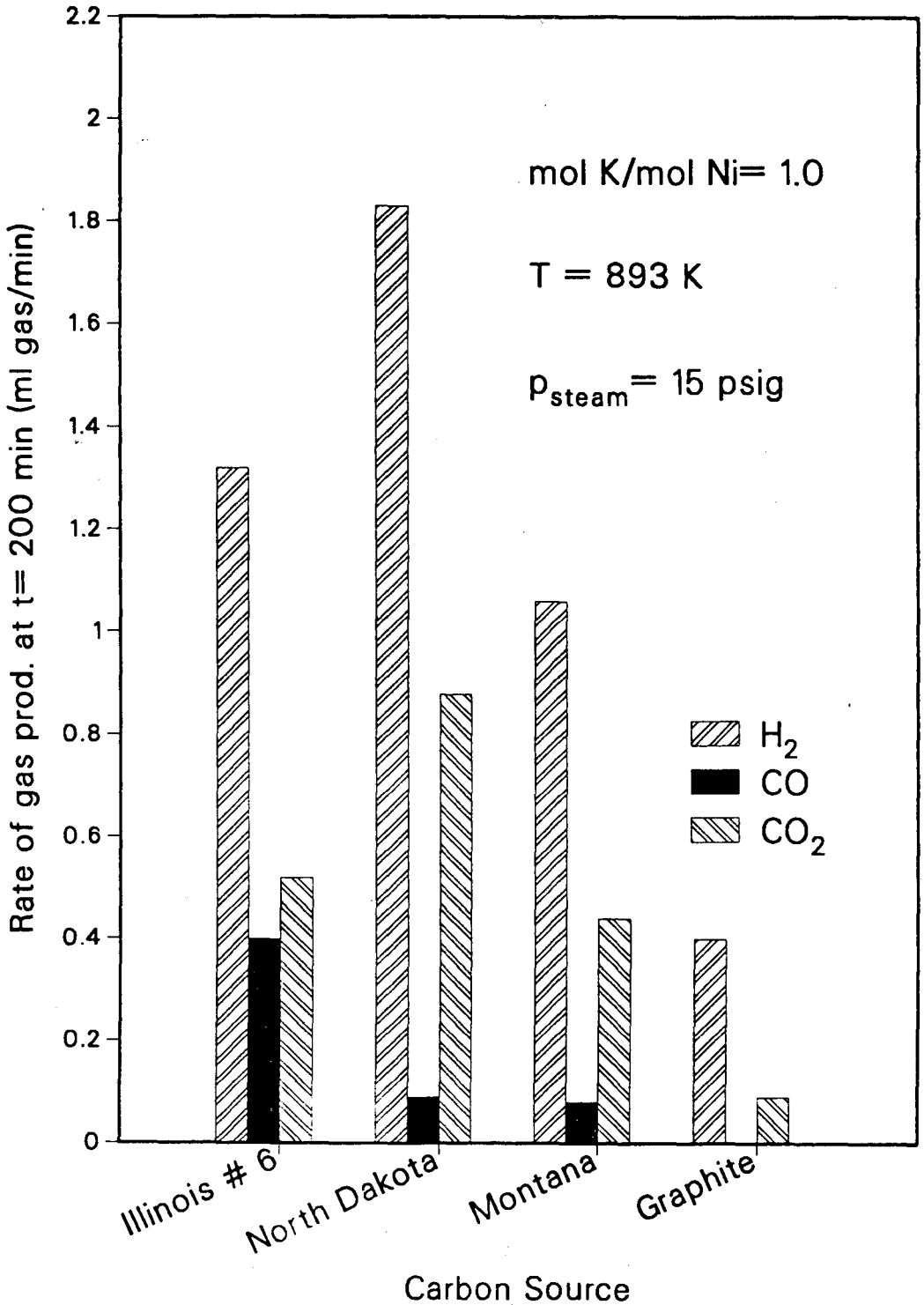
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Rate of gas prod. at t= 200 min (ml gas/min)
mol K/mol Ni= 1.0
T = 893 K
p_{steam}= 15 psig
H_2
CO
CO_2
Illinois # 6
North Dakota
Montana
Graphite
Carbon Source

Figure 2

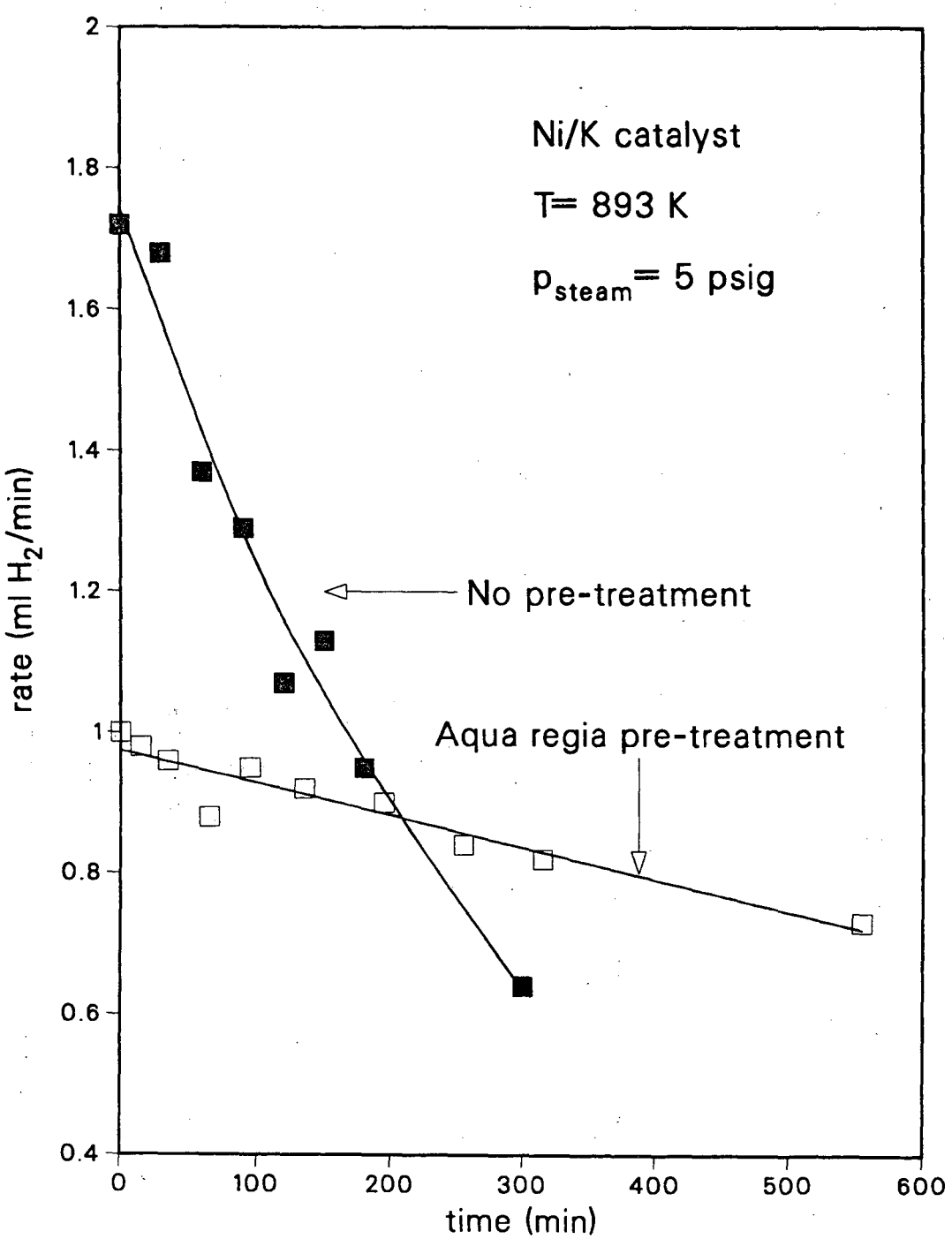
Ni/K catalyst
T= 893 K
p_{steam}= 5 psig
No pre-treatment
Aqua regia pre-treatment
rate (ml H_2/min)
time (min)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0
100
200
300
400
500
600

Figure 3

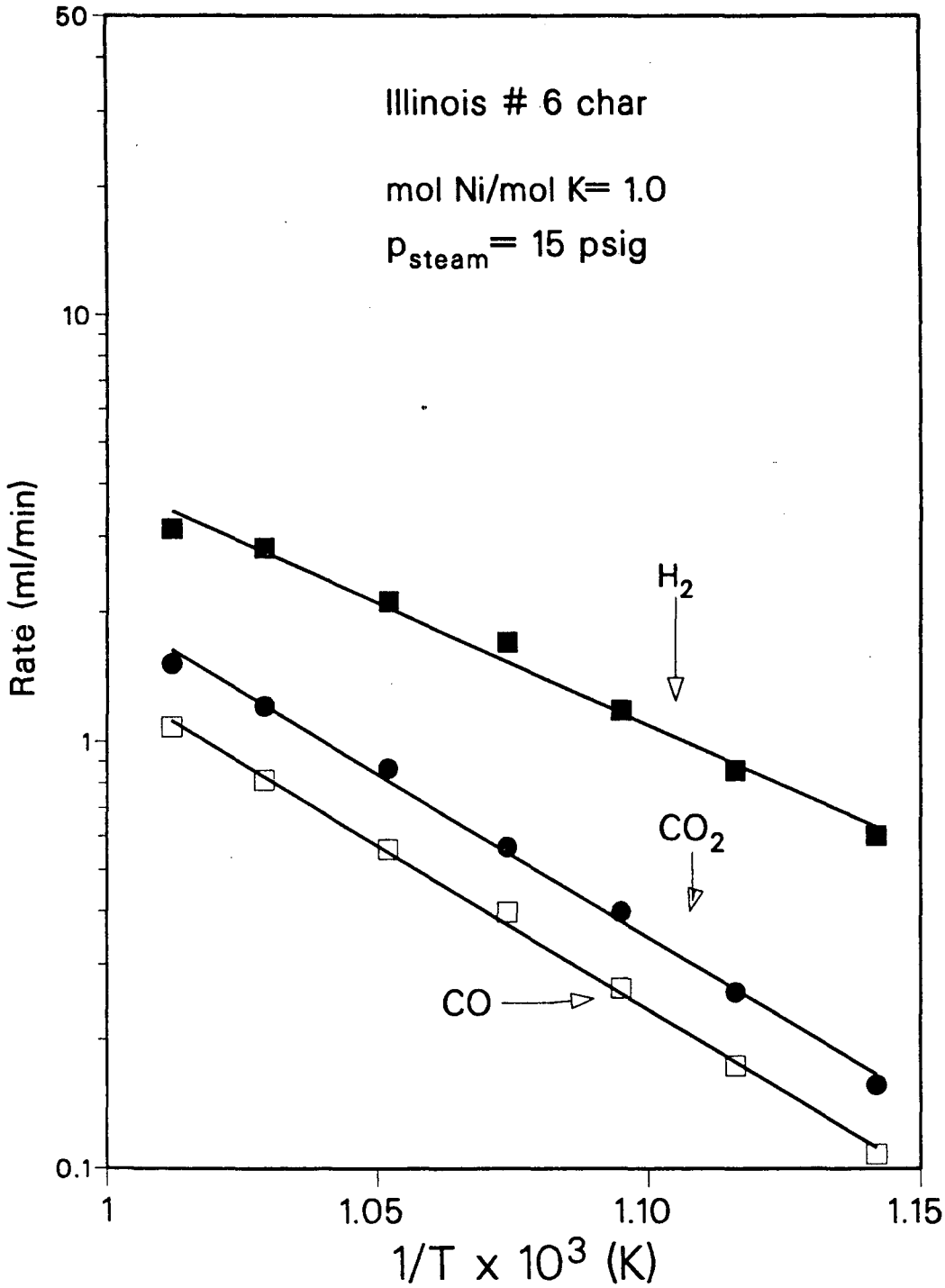
Illinois # 6 char
mol Ni/mol K= 1.0
p_{steam}= 15 psig
50
10
1
0.1
Rate (ml/min)
H_2
CO_2
CO
1
1.05
1.10
1.15
$1/T \times 10^3$ (K)

Figure 4

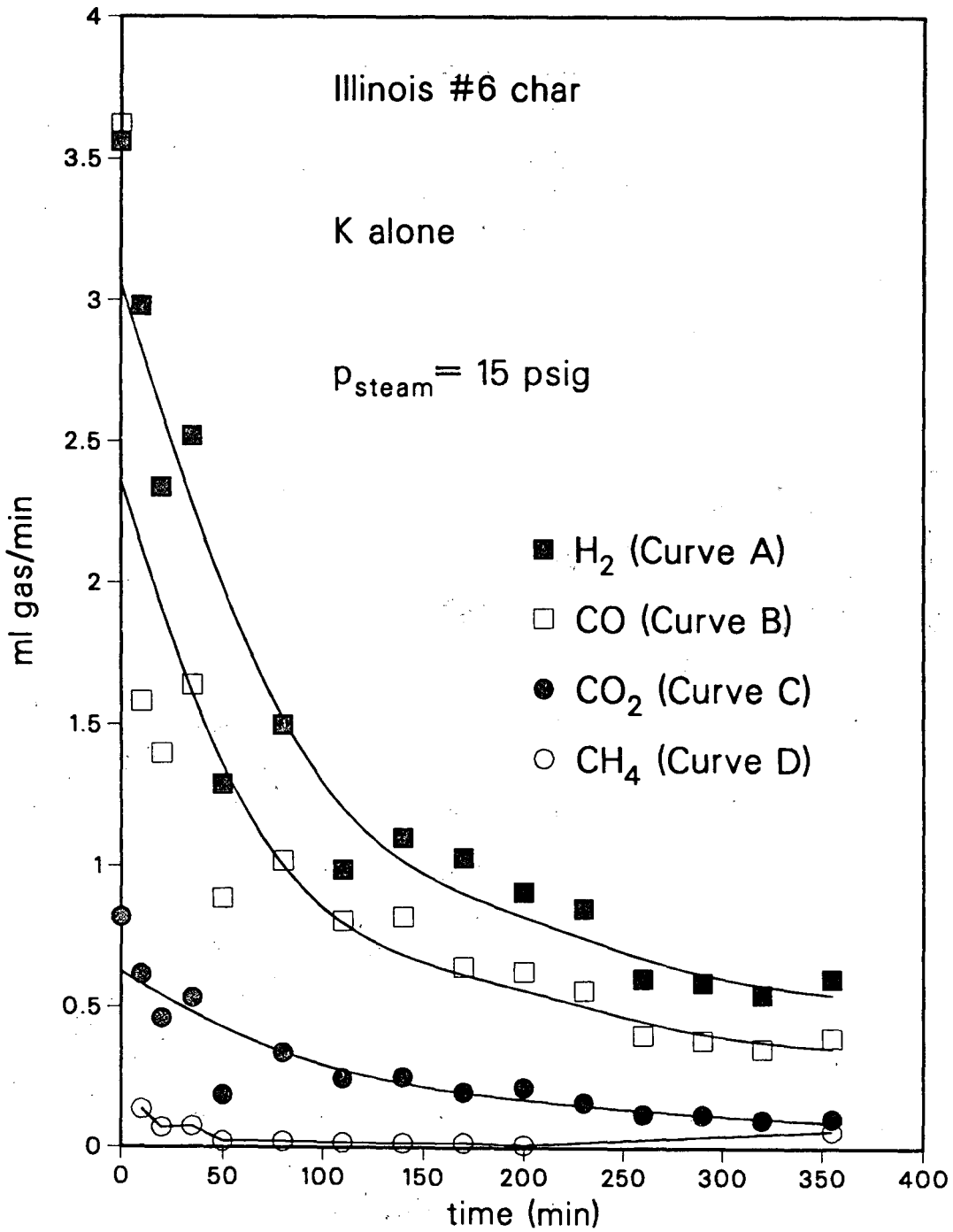
Illinois #6 char
K alone
p_{steam}= 15 psig
H_2 (Curve A)
CO (Curve B)
CO_2 (Curve C)
CH_4 (Curve D)
ml gas/min
time (min)
0
0.5
1
1.5
2
2.5
3
3.5
4
0
50
100
150
200
250
300
350
400

Figure 5

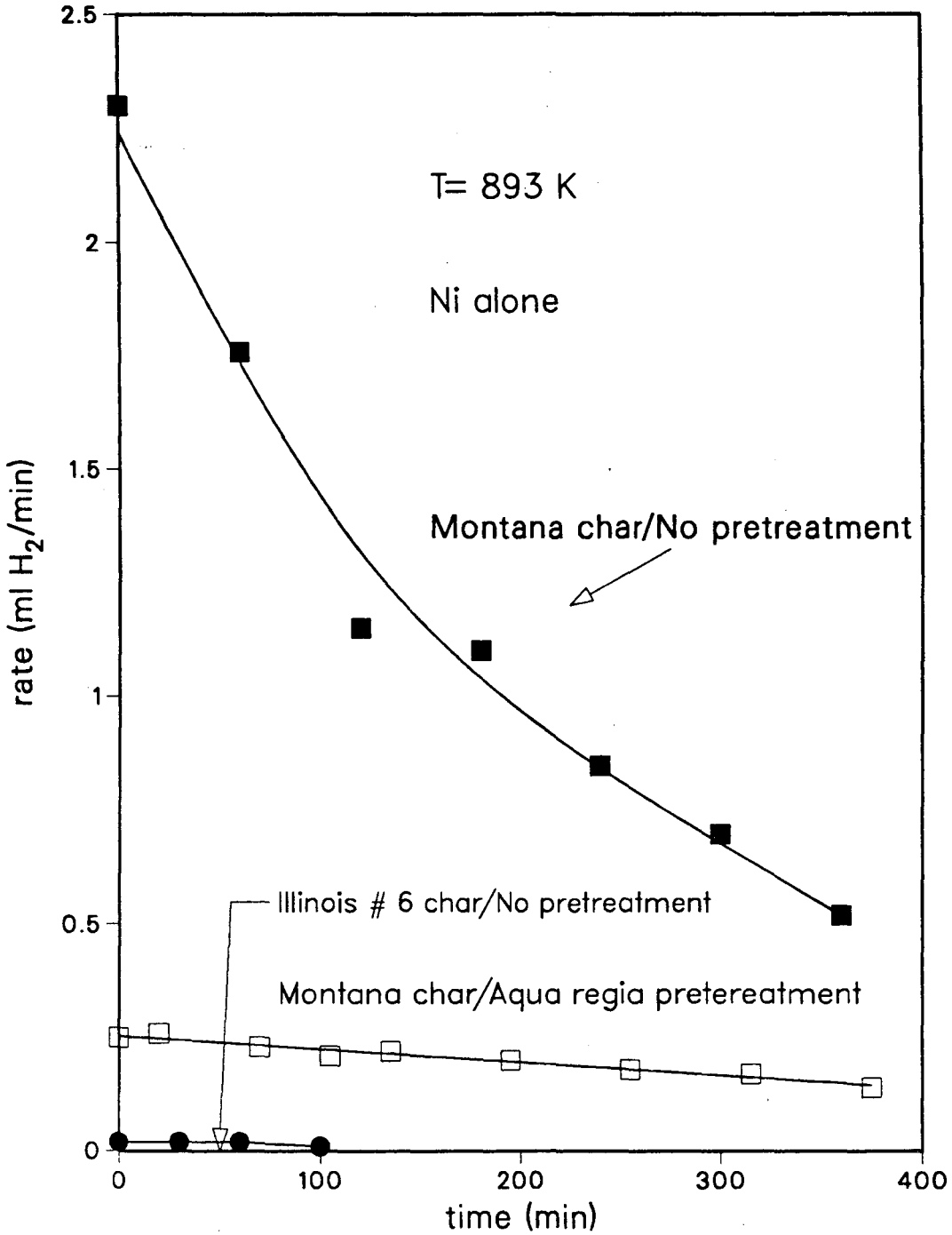
2.5
2
1.5
1
0.5
0
rate (ml H_2/min)
T= 893 K
Ni alone
Montana char/No pretreatment
Illinois # 6 char/No pretreatment
Montana char/Aqua regia pretereatment
0
100
200
300
400
time (min)

Figure 6

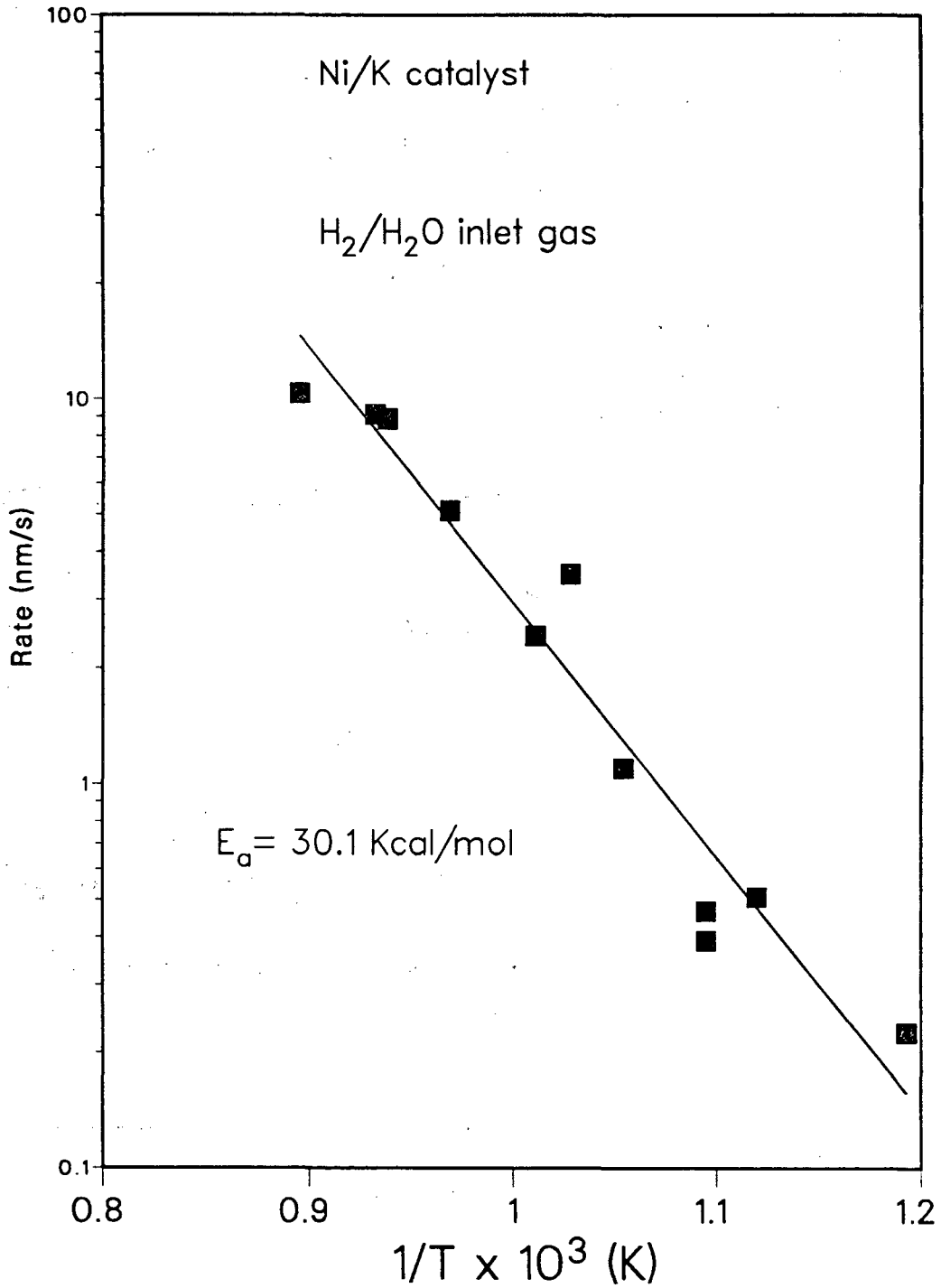
Ni/K catalyst
H_2/H_2O inlet gas
E_a= 30.1 Kcal/mol
Rate (nm/s)
100
10
1
0.1
0.8
0.9
1
1.1
1.2
$1/T \times 10^3$ (K)

Figure 7

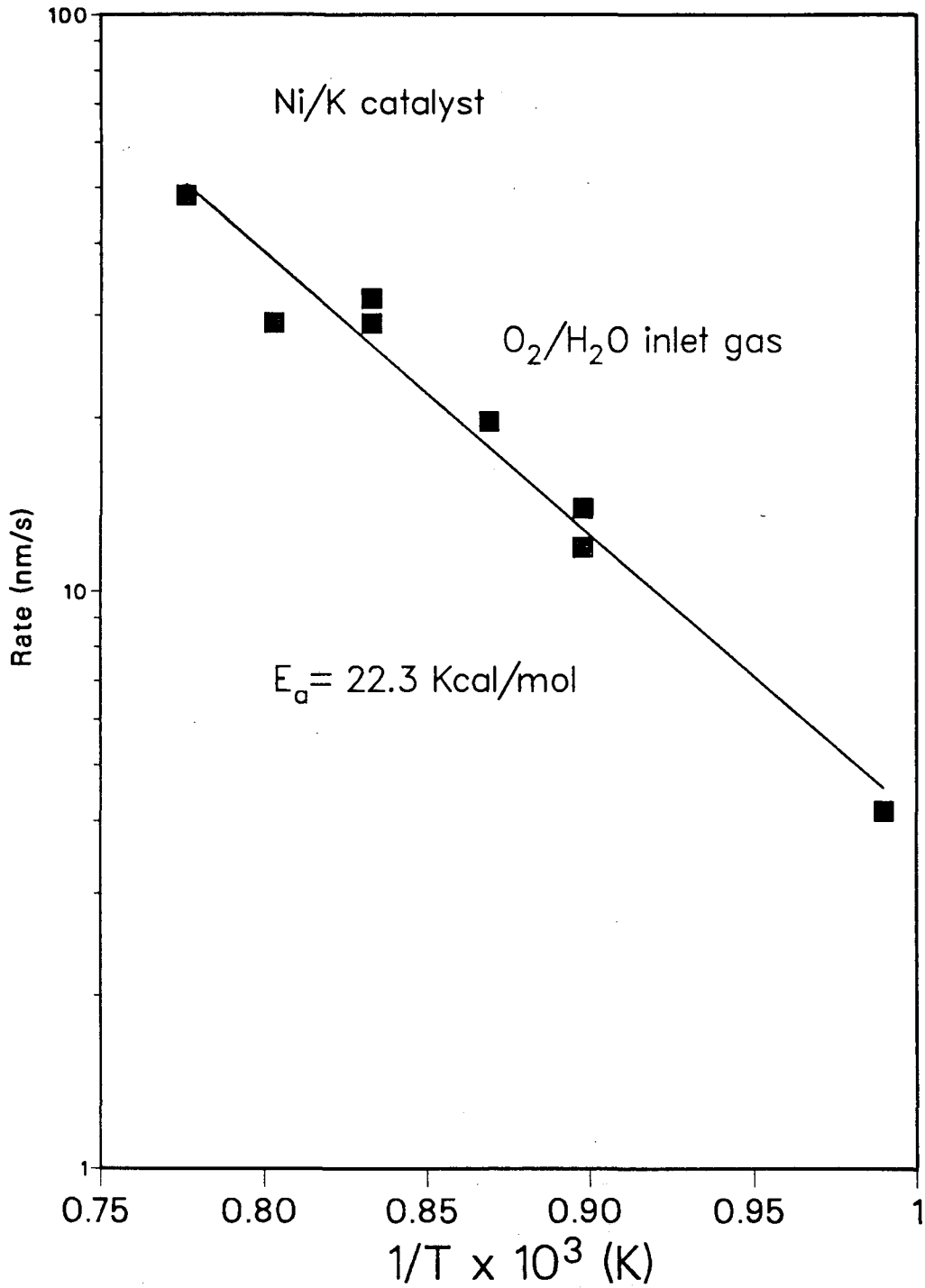
Ni/K catalyst
O_2/H_2O inlet gas
E_a= 22.3 Kcal/mol
Rate (nm/s)
100
10
1
0.75
0.80
0.85
0.90
0.95
1
$1/T \times 10^3$ (K)

Figure 8

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