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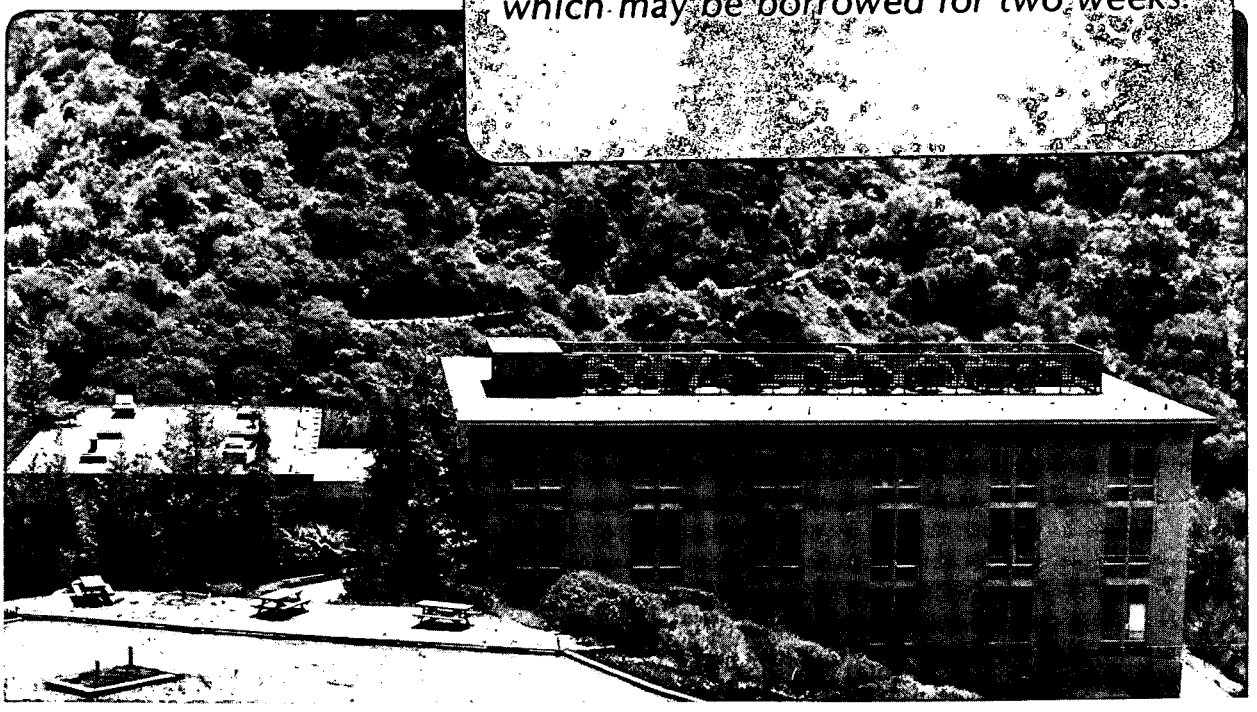

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STEAM GASIFICATION OF CARBONACEOUS SOLIDS CATALYZED BY A MIXTURE OF POTASSIUM AND NICKEL OXIDES BELOW 1000 K

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Introduction

The gasification of carbon with water vapor is an important reaction in the industrial production of H_2, CH_4, CO and CO_2. The use of catalysts is necessary if the process is carried out at temperatures below 1400 K. Two recent reviews discuss the properties of the various catalysts used for this purpose.(1,2) Alkaline and akaline-earth hydroxides and carbonates are the catalysts most commonly studied. These compounds only show catalytic activity at temperatures above 1000 K. Previous work in our laboratory shows that below this temperature KOH reacts stochiometrically with graphite and water vapor to produce H_2 and a stable surface compound.(3) Transition metals, in particular nickel and iron, are able to catalyse this process at temperatures as low as 750 K, but they deactivate much faster than the alkaline and alkaline-earth salts. Several authors have reported that nickel and iron are only active as catalysts for this process if the reaction conditions favors their presence in the metallic state.(4,5)

We have recently reported that several mixtures of a transition metal oxide with potassium hydroxide are excellent catalysts for the gasification of graphite with steam.(6) These catalysts are active at temperatures much lower than the alkaline and alkaline-earth salts and they deactivate more slowly than nickel and iron. In this previous publication it was shown that there is a synergistic effect between the transition metal and potassium.

This communication summarizes recent results in the study of this type of catalyst. We have focused on the use of mixtures of potassium hydroxide and nickel oxide, since they showed the highest activity of all the systems previously studied.(6) A kinetic study of the gasification of several chars and the dependence of the ratio of potassium to nickel on the rate of graphite gasification are presented. Also the interaction between nickel and potassium is studied using X-ray Photoelectron Spectroscopy (XPS).

Experimental

The gasification rates of graphite and five different chars have been obtained. The chars pretreatment, elemental composition and ASTM rank are summarized in Table 1. Nickel and potassium were loaded on the carbon substrate by incipient wetness using solutions of $Ni(NO_3)_2$ and KOH. A detailed explanation of the sample treatment after catalyst loading is given in a previous publication.(6)

A detailed explanation of the equipment used in these studies is given elsewhere.(6,7) The kinetic studies were done in a fixed bed flow reactor with an online gas chromatograph used for product analysis. The total gas production as a function of time was determined using a gas burette after the steam was condensed. The XPS study was done in an Ultra High Vacuum (UHV) chamber coupled to a high pressure cell. This apparatus allowed us to treat the sample under reaction conditions and to further transfer it to UHV for surface characterization without exposure to air.

All the kinetic results were obtained in isothermal experiments. The steam flow through the sample was equivalent to 1 ml of liquid water per minute. The reactor diameter was 0.6 cm. The reaction temperature was measured using a chromel-alumel thermocouple in contact with the external wall of the reactor. At the beginning of each experiment, a stabilization period of 15 min was allowed before data was collected. The principal reaction products were H_2 and CO_2. The gasification rates were determined measuring the H_2 production because its solubility in water is much smaller than that of CO_2. The carbon conversions were determined by dividing the number of H_2 moles produced by two times the initial number of carbon moles.

The XPS experiments were carried out using a Mg-anode source (hv = 1253.6 eV). The data was collected using a detector pass energy equal to 40 eV. The position of the peaks was calibrated with respect to the position of the C_{1s} peak of graphite (binding energy = 284.6 eV).

Results

The rate of graphite gasification as a function of time has been studied at 893 K for several mixtures of nickel and potassium oxides and for the components deposited alone. Some of the results are shown in Figure 1. The activity corresponding to nickel deposited alone is given by Curve A. A very fast initial activity is observed, but the sample deactivates almost completely after two hours, giving a total carbon conversion of 20%. When potassium is deposited alone from a KOH solution, no steady state gasification rate is observed after 15 min of initiating the experiment. Curve B shows the rate when nickel and potassium oxides are codeposited on graphite with a Ni/C molar ratio equal to 1.0×10^{-2} and a Ni/K molar ratio equal to 0.1. Initially, the steady state rate is two orders of magnitude lower than that of nickel deposited alone (Curve A), but after 6.0 hours the Ni-K mixture has kept its initial activity while Ni alone has deactivated completely. The carbon conversion for this catalyst after 6.0 hours is 2.5%, ten times lower than that of nickel alone. But when the experiment represented by Curve B was followed 400 hours, a total carbon conversion of 20% was obtained and the catalyst was still active. When a mixture of nickel and potassium oxides is deposited on graphite with a Ni/K molar ratio equal to 10.0 and a Ni/C molar ratio equal to 1.0×10^{-2}, an initial rate similar to that of nickel deposited alone is obtained (Curve C), but instead of deactivating completely after two hours, the rate levels out at the same rate obtained with the 1:10 Ni:K mixture (Curve B). These results indicate that for the 10:1 Ni:K mixture only a fraction of the total nickel loading interacts with potassium. The remaining fraction behaves like Ni metal and it is completely inactive after one hour. The reaction rate decreases faster than in Curve A because there is less free nickel on the surface.

The rate of gasification of several chars with steam was studied as a function of time in the presence of a 1:1 mixture of nickel and potassium oxides. A description of the five chars studied is given in Table 1. For all of them, the steady state rate after 1.0 hour is at least one order of magnitude higher than that of graphite (see Figure 2a). This is reflected in a much higher carbon conversion after 6.0 hours (see Figure 2b), even though by then the char steam gasification rates have decreased to values similar to those of graphite.

A comparison of the gasification rates for a 1:1 mixture of potassium and nickel oxides with that of the components deposited alone is given in Figures 3a and 3b for two of the chars studied (Illinois No. 6 High Temp. Treat. and

Montana). In the case of Illinois No. 6 char, it is clear that the mixture is more active than the sum of the rates of the components deposited alone. (Compare Curves A and D in Figure 3a.) In contrast to the results obtained with graphite, the mixture in this case is more than two times as active as nickel deposited alone. For Montana subituminous char the rate of gasification of the mixture is similar to that of nickel alone and higher than that of potassium (see Figure 3b).

A surface science study of the interaction of potassium, nickel and carbon in the presence of water is currently being done and some preliminary results are included in this communication. XPS of the $Ni_{2p_{3/2}}$ signal of two systems, a 1:1 Ni:K mixture codeposited on graphite and nickel deposited alone have been obtained after exposing them to 24 torrs of water vapor at 950 K. The kinetic results show that at this temperature both systems are catalytically active. Figure 4 Curve A shows the spectrum corresponding to nickel deposited alone. There is a peak at 854.2 eV with a small satellite peak at 862.7 eV. This is characteristic of nickel in the metallic state and agrees with results obtained by us for nickel foil. The shoulder at 857.5 eV is due to small amounts of NiO in the sample. When nickel and potassium are codeposited on graphite (Curve B in Figure 4) the binding energy of the $Ni_{2p_{3/2}}$ XPS peak is at 856.4 eV. This indicates that nickel is present in its +2 oxidation state. The much larger satellite peak at 864.6 eV also shows that nickel forms an oxide at this temperature in the presence of potassium. The lower binding energy of the $Ni_{2p_{3/2}}$ peak in the nickel-potassium mixture compared to NiO shows that there is an electronic interaction between nickel and potassium.

Discussion

The kinetic results presented in this paper indicate that mixtures of potassium and nickel oxides are good catalysts for the gasification of carbonaceous solids with steam. The high reaction rates and carbon conversions obtained with the several chars studied (Figures 2 and 3) and the graphite gasification activity after 400 hours support this conclusion.

In a previous publication we concluded that there is a cooperative effect between potassium and nickel in this catalyst.(6) The results in this paper present the clearest evidence obtained so far for this effect. In Figure 3a the gasification rate of Illinois N-6 char in the presence of the mixed catalyst is higher than that of the mathematical sum of the rates of the components deposited alone. The XPS results in Figure 4 show that nickel deposited alone is active as a gasification catalyst when it is present in the metallic state, while in the nickel-potassium mixture, the nickel is catalytically active being in the +2 oxidation state. Also, the shift to lower binding energies for the $Ni_{2p_{3/2}}$ peak in the potassium-nickel catalyst when compared to the position of the NiO peak is evidence for chemical interaction between nickel and potassium. We propose that this synergistic effect is due to the formation of a mixed oxide (K_xNi_yO) that is not readily reduced by carbon under our reaction conditions (< 1000K). There is evidence in the literature for the presence of several nickel-potassium mixed oxides,(8) but we do not have enough information to decide which one of them is present in our system.

The results presented in Figure 1 show that there is no interaction between the nickel metal catalyst and this potassium-nickel mixed oxide. When the ratio of nickel to potassium is high enough to allow the coexistence of these two catalysts on the graphite surface, the catalytic behavior observed can be explained by just adding the rates of the two catalysts; i.e. a very

high initial rate due to nickel metal that decays to a lower value and then remains constant for a long period of time due to the catalytic activity of the nickel-potassium mixed oxide.

Mixtures of transition metals and alkaline metals as catalysts for steam gasification of various carbon sources have been reported previously. Wigmams and Moulijn(9) reported that there was no interaction between nickel and K_2CO_3 for the steam gasification of chars at 1023 K. Similar results were obtained in our laboratory when the gasification of graphite was studied above 1000 K. Also, XPS data obtained in our laboratory show that at 1000 K the nickel is present in the metallic state, even in the presence of potassium. We suggest that these results are due to the decomposition to this mixed oxide and reduction of the nickel by carbon. In contrast with the results reported by Muolijn and Wigmams, a cooperative effect between a transition metal and an alkaline metal has been reported by other authors. Adler and Hüttinger(10) found that mixtures of $FeSO_4$ and K_2SO_4 deposited on PVC coke were better catalysts than the salts deposited alone. Also, Suzuky et. al.(11) reported that $Na(HFe(CO)_4)$ is a good catalyst for the gasification of various coals with steam. They suggest that this high activity is due to the interaction between iron and sodium.

Further work is currently being done to obtain more direct evidence of the existence of these mixed oxides and to characterize and understand their catalytic behavior toward carbon gasification.

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TABLE 1

Characteristics of Coal Char and Graphite Samples Used in this Study

Name	ASTM Rank[a]	Pretreatment	Analysis (wt%)[b]					
			C	H	N	O	S[c]	Ash[d]
Western Kentucky Washed (WK)	HV.B.Bit.	Unspecified	72.3	3.2	1.4	7.9	3.2	12
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 High Temp. (I 6 HT)	HV.C. Bit.	Heated Under He T = 1300K	-	-	-	-	-	-
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
Graphite UCP-2		None	100	0	0	0	0	0

[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 12.

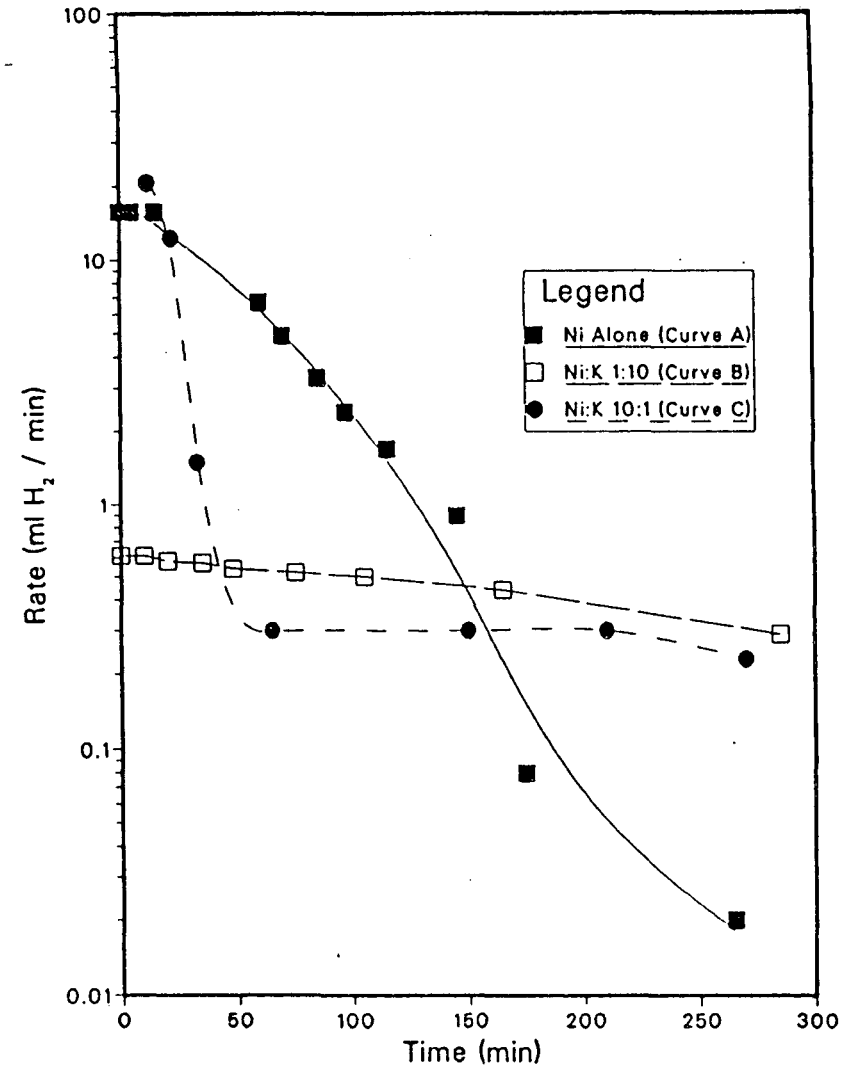
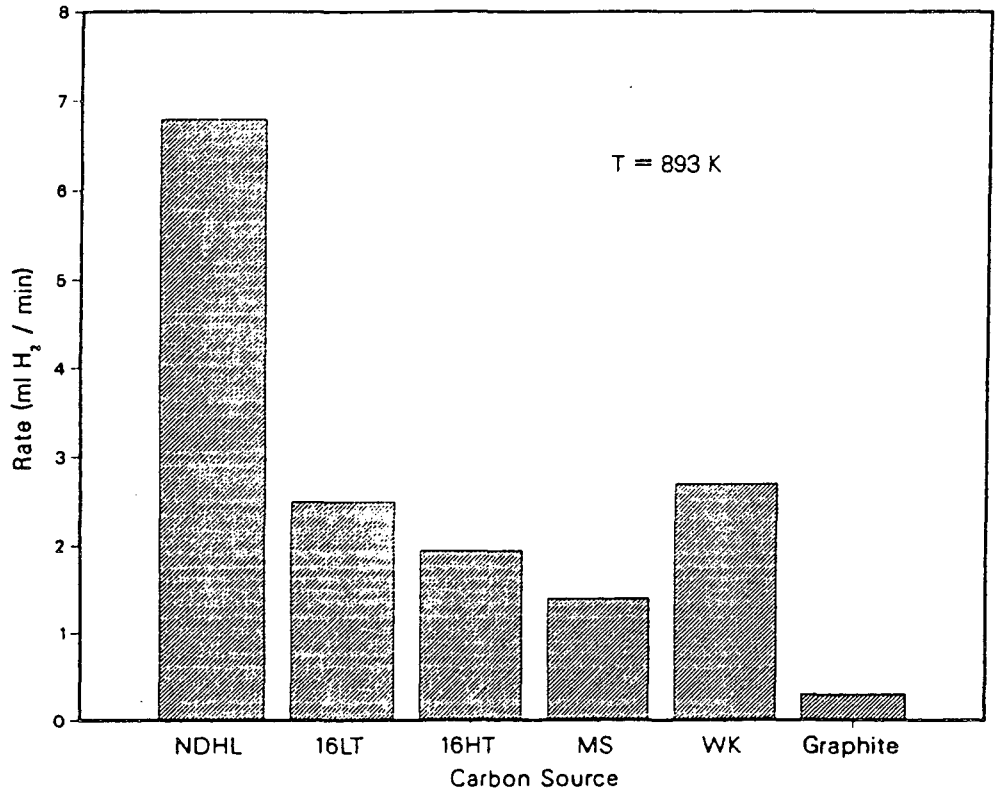


Figure 1: Steam gasification rates of graphite at 893 K catalyzed by three different compounds: nickel metal (Curve A) and two mixtures of nickel and potassium oxides, Ni:K 1:10 (Curve B) and Ni:K 10:1 (curve C). In all cases the Ni/C molar ratio is equal to 1.0 $\times 10^{-2}$.



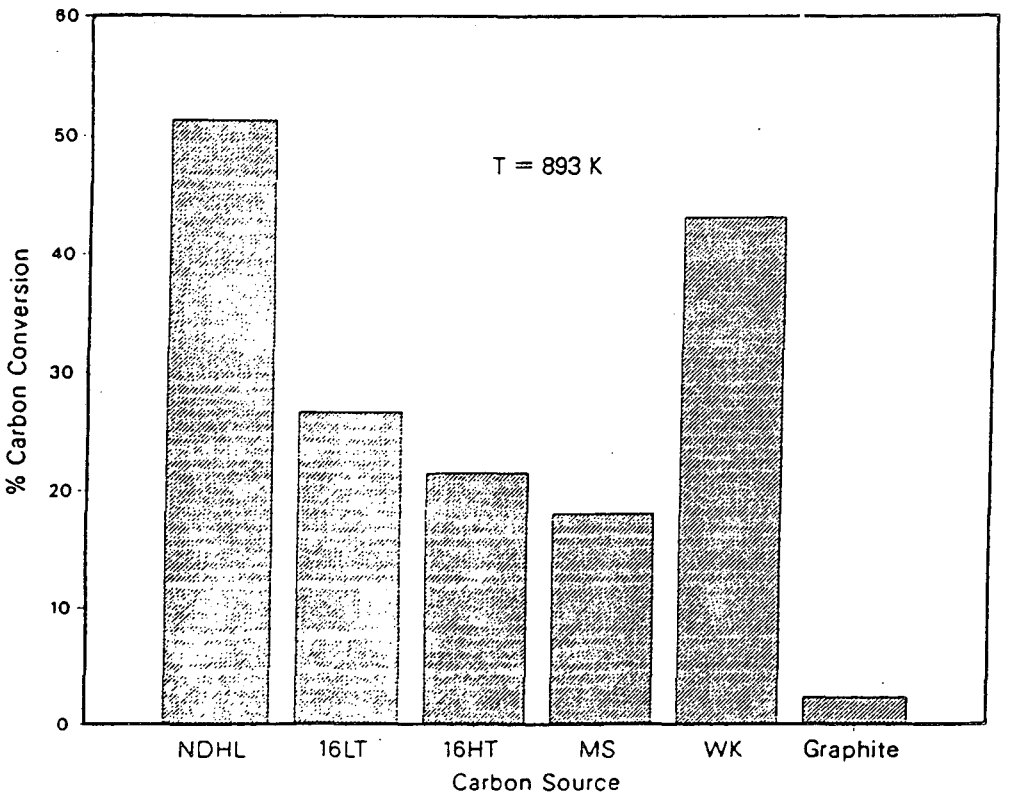


Figure 2a (Top). Steady state steam gasification rates of several carbonaceous solids after 1.0 hours when a mixture of nickel and potassium oxides is used as a catalyst.
Figure 2b (Bottom). Percentage of carbon conversion obtained after 6.0 hours when the same catalyst is used.

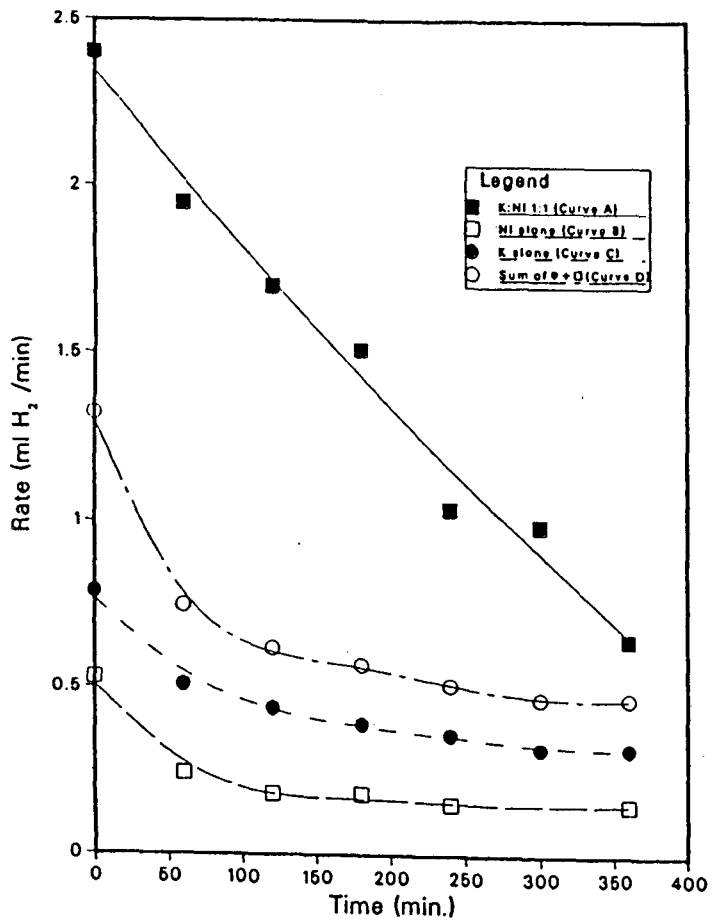


Figure 3a

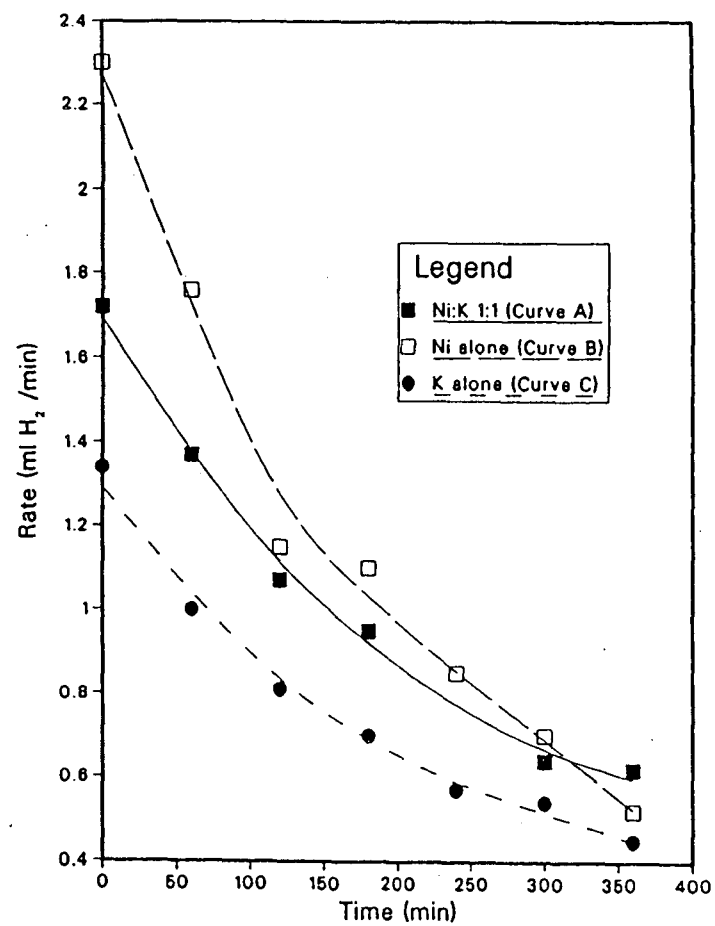


Figure 3b

Figure 3: Steam gasification rates at 893 K for two chars, Illinois N° 6 High Temp. (left) and Montana (right), catalyzed by three different compounds, a 1:1 mixture of nickel and potassium (Curve A), nickel alone (Curve B) and potassium alone (Curve C). In figure 3a, Curve D is the mathematical sum of curves B and C.

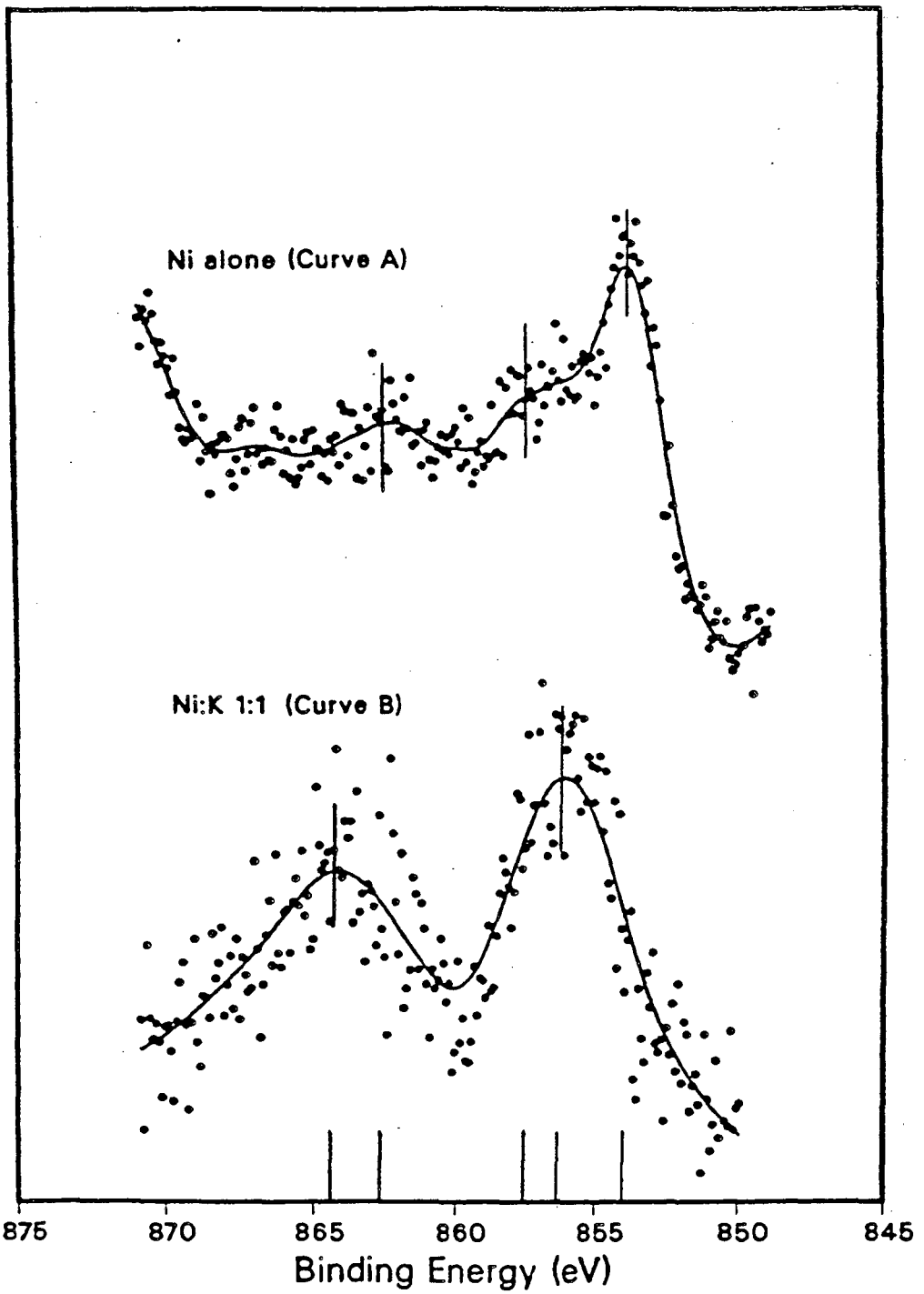


Figure 4. $Ni_{2p3/2}$ XPS of nickel (Curve A) and a 1;1 Ni:K mixture (Curve B) deposited on graphite. The spectra was taken after exposing the samples to 24 torr of water at 923 K for 15 min.

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