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Fundamental Studies of Catalytic Gasification

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FUNDAMENTAL STUDIES OF CATALYTIC GASIFICATION

Summary report on single metal oxide and binary oxide catalysts, their performance in steam gasification and reaction mechanisms.
1985-1990

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TABLE OF CONTENTS

I OBJECTIVE

The major purpose of this project was to find catalysts which will permit steam gasification of carbonaceous material at reasonable rates and at lower temperatures than currently practiced. Rapid catalyst deactivation must be avoided. An understanding of the catalytic mechanism is necessary to provide leads towards this aim.

II EXECUTIVE SUMMARY

- Experiments with steam gasification of graphite in the presence of alkali compounds confirm that at relatively low temperatures (below 600°C) a stoichiometric reaction occurs between carbon, alkali and water forming a phenoxide and hydrogen. The reaction stops when all alkali has been used. At higher temperatures the phenoxide decomposes giving CO_x and alkali hydroxide.
- The decomposition of the phenoxide can be accomplished at low temperatures using a transition metal oxide as a catalyst. Mixtures of an alkali oxide and a transition metal oxide can serve as catalysts for continuous steam gasification of graphite (and chars and coals) at temperatures below 600°C. Preferred combinations are mixtures of potassium and nickel oxides. Sodium and iron oxide may be used.
- Work in the controlled atmosphere chamber of an electron microscope has shown that alkali compounds alone attack carbon in the presence of water in a solid particle-graphite edge contact, leading to channeling. Alkali-transition metal oxide mixtures form low melting eutectica, resulting in a liquid film which attacks the graphite by edge recession. The rate of gasification is much higher for the binary mixture.
- Gasification of carbonaceous materials with steam in the presence of a binary oxide catalyst requires that the catalyst can dissociate water at the gasification temperature. Hydrogen is released and oxygen forms a surface oxide with the carbon, such as a quinone or lactone, which then decomposes thermally giving CO_x.
- Steam gasification in the presence of a binary oxide catalyst produces hydrogen and carbon dioxide in a 2:1 molar ratio with only minor

amounts of CO and traces of methane. The larger than equilibrium CO_2/CO ratio is probably due to a shift reaction.

- Binary oxide catalysts containing a transition metal oxide such as K-Ni-O_x are poisoned by sulfur compounds. In the steam gasification of coals, it has been shown that poisoning occurs with organic sulfur but not with pyritic sulfur in the coal.
- It was found that mixtures of an alkali compound with an earth alkali oxide possess the same characteristics as e.g. K-Ni-O_x catalysts for gasification. Equimolar mixtures of potassium and calcium oxide are only slightly less active than K-Ni-O_x but are much more poison resistant.
- The catalysts are preferentially used in a carbon to binary oxide molar ratio of 1:0.4. They can be applied to the coal or char by impregnation or just by physical mixing.
- A series of chars and of coals were gasified with steam in the presence of binary oxide catalysts. In general coals gasify faster than chars and chars gasify faster than graphite. Complete gasification of the carbon content is obtained. The rate of gasification declines from lignite > subbituminous > bituminous coals.
- Ash components in coals other than sulfur do not appear to greatly affect the catalysis.
- A number of petroleum cokes were catalytically gasified with steam. They behaved much like coals. There appeared to be no major effect of varying metal content of the cokes.
- The amounts of catalyst used can be reduced and it may be possible to use the catalyst on a throw-away basis and not recover it from the ash.

III INTRODUCTION

This project *Fundamentals of Catalytic Gasification* has been carried out at the Lawrence Berkeley Laboratory during the fiscal years 1985-1990. It has been supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, West Virginia 26505. Results which are summarized in this report have previously been reported in greater detail in quarterly and annual reports and in a number of publications which are listed in the Appendix.

IV BACKGROUND

The production of synthesis gas by reaction of various carbonaceous materials with steam has been frequently investigated and is a commercial process. Gasification in the presence of alkali metal compounds has been reviewed by Wen [1]. The mechanism of the catalytic gasification of coal chars has been reviewed by Wood and Sancier in 1984 [2]. The production of low molecular weight gaseous hydrocarbons directly from carbon or from carbonaceous materials provides an intriguing alternative to syngas production with subsequent methanation or liquefaction. The reaction of carbon with water to reproduce methane and carbon dioxide, $2C+2H_2O \rightarrow CH_4+CO_2$, is virtually thermoneutral (ΔG_{298K} = 2.89 Kcal/mol) and thermodynamically feasible at low temperatures. By contrast studies of coal gasification with water have always been carried out at high temperature regimes in order to have efficient production of carbon monoxide and hydrogen, a very endothermic reaction. More recent studies by Exxon researchers [3] reported the production of substantial amounts of methane along with CO and hydrogen during coal gasification using potassium carbonate as a catalyst. These studies employed relatively high temperatures (630-830°C).

V EXPERIMENTAL

1) Equipment. The work carried out in this project involved primarily three types of equipment:

a) A flow reactor as shown in Fig. 1. This type of reactor system with either a horizontal or a vertical reactor and furnace was used for all kinetic studies. All work was at atmospheric pressure unless otherwise noted.

b) A high pressure-low pressure ultra-high vacuum cell [4], operating at a base pressure greater than 10^{-9} torr (Fig. 2). It is equipped to determine surface composition analysis by Auger

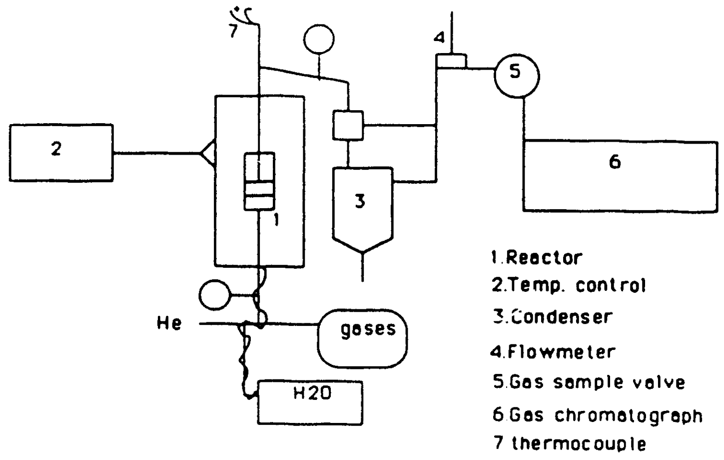

Fig. 1. Diagram of flow reactor system.

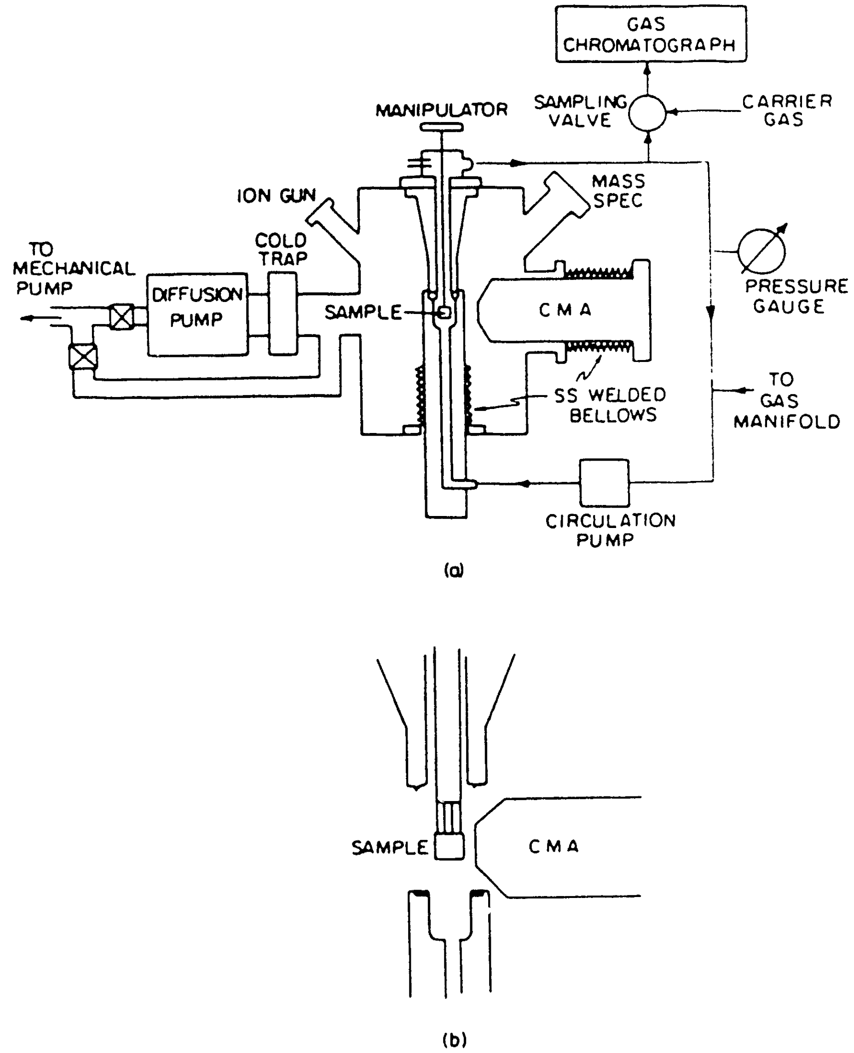

Fig. 2 High pressure-low pressure ultra-high vacuum cell.

electron spectroscopy and by XPS. The system is also equipped with a high pressure cell which isolates the sample and permits the performance of chemical reaction studies at high pressure without removing the sample from the UHV chamber. The product distribution is monitored by gas chromatography with a thermal conductivity detector.

c) A controlled atmosphere electron microscope (CAEM). All work in this equipment was with graphite to prevent fogging of the chamber which would occur with coals or chars.

Transparent flakes of graphite were prepared by attaching the graphite to a glass slide using low-melting-point wax and repeatedly cleaving the graphite along its basal plane with adhesive tape until only a small section was left stuck to the glass slide. The section was released using acetone, picked up on a gold 500-mesh grid, and allowed to dry in air. The graphite was then impregnated with K and/or Ca nitrate and the flow reactor system described was used to decompose the salts.

Unless otherwise described, the experiments were performed in a KRATOS EM-1500 transmission electron microscope at the National Center for Electron Microscopy at the Lawrence Berkeley Laboratory.

A Gatan single-tilt heating stage was used in a Gatan environmental cell. Argon was bubbled through water and the water vapor/argon mixture was fed directly into the cell at a pressure of 3 torr. The microscope was operated at its maximum accelerating voltage, 1.5 MeV, and dynamic images were displayed and recorded via a video camera.

A detailed description of the CAEM technique can be found elsewhere [5].

2) Catalysts. Catalysts used in this work were primarily mixtures of alkali and transition metal oxides and of alkali and earth alkali oxides. For comparison purposes alkali oxides alone were used. The preferred alkali was potassium, although sodium was found to possess equivalent activity. The preferred transition metal was nickel and the preferred earth alkali was calcium.

The catalysts were prepared by mixing aqueous solutions of the nitrates and impregnating the carbonaceous substrate with the solution to deposit 1-3 mol % of the mixed oxide. The impregnated carbon was dried and the nitrate decomposed by heating. It was found that hydroxides, carbonates and oxalates could be employed with equal catalyst efficiency, but that for carbonates a calcination temperature above 900°C was required to convert the carbonate to oxide. The preferred catalyst to carbon ratio was 0.04.

The mixed catalysts had eutectic melting points and at the usual operating temperature (525-630°C) formed a liquid film on the substrate. It was even possible to mix the dry salts, add them to the carbon and heat to reaction temperature.

3) Operating Conditions. All work in the flow reactor was at atmospheric pressure. The temperature in the impregnated carbon sample was controlled to ±5°C. The range of gasification temperatures was 550-700°C. Steam was introduced at close to reaction temperature by vaporizing and preheating water charged from a syringe pump at controlled rates. The standard rate of water charged is 8cc/g catalyst/hr.

VI RESULTS

1) CATALYTIC STEAM GASIFICATION OF GRAPHITE

a) Alkali or Earth Alkali Catalysts

In this project the gasification of graphite has been studied in the presence of alkali hydroxide and in some cases of earth alkali hydroxide at temperatures in the range 230-525°C and atmospheric pressure. We have used graphite as a carbon source because of its lack of hydrocarbonaceous material and in order to be sure that all hydrogen produced as hydrogen or in hydrocarbons was derived from hydrogen in water.

Early work in the high pressure-low pressure cell indicated that methane could be produced at temperatures as low as 200°C in the presence of potassium hydroxide [6] as indicated in Fig. 3. Figure 4 shows the methane production with various alkali hydroxides. While the rate of methane production is small, it becomes appreciable if one assumes that not all the geometric surface area of graphite is available for attack and that the attack probably takes place on the edges of the graphite.

We have carried out gasification studies in the environmental cell of a transmission electron microscope similar to the studies that were previously carried out by Baker [5] who gasified graphite crystals in the presence of nickel and hydrogen and showed that gasification occurred by "basal plane penetration in imperfect regions or by altering the rate of reaction at edges or steps." In our studies thin specimens of highly oriented pyrolithic graphite were obtained by cleavage of graphite crystals. Potassium hydroxide was introduced onto the surface of the graphite by dipping the specimen supported on copper or nickel grids into a .38M solution of potassium hydroxide and then dried. Transmission electron microscopy was carried out in a Hitachi 650 keV microscope [7]. Argon at about 1 atm pressure was bubbled through water at room temperature giving an argon/water ratio of about 40/1 and then introduced into the environmental cell to give a pressure of 50 Torr. At 500°C the potassium hydroxide was dispersed as particles of 0.1 to 0.5 microns in diameter on the surface of the graphite. Figures 5 and 6 show micrographs recorded 11 minutes apart taken from a sequence showing the channel growth at 770K. Channels are evident in two adjacent graphite crystals emanating from the edges of the crystal, each channel with a particle at its head. As the reaction continues the particles move and the length of the channels increase. The channels remain roughly parallel sided indicating that there is little effect of uncatalyzed reaction at the channel edges or of wetting of the channels sides by catalytic material. Intercallation of potassium into the graphite does not appear to play a role in the gasification. Samples of potassium intercallated graphite ($C_{24}K$) were subjected to reaction with water at 300°C and exhibited an appreciably lower methane production than graphite impregnated with potassium hydroxide [8]. Both AES and XPS studies of potassium intercallated graphite also indicated that potassium diffuses to the surface under the influence of the electron beam. The intensity of the potassium peak decreased upon heating.

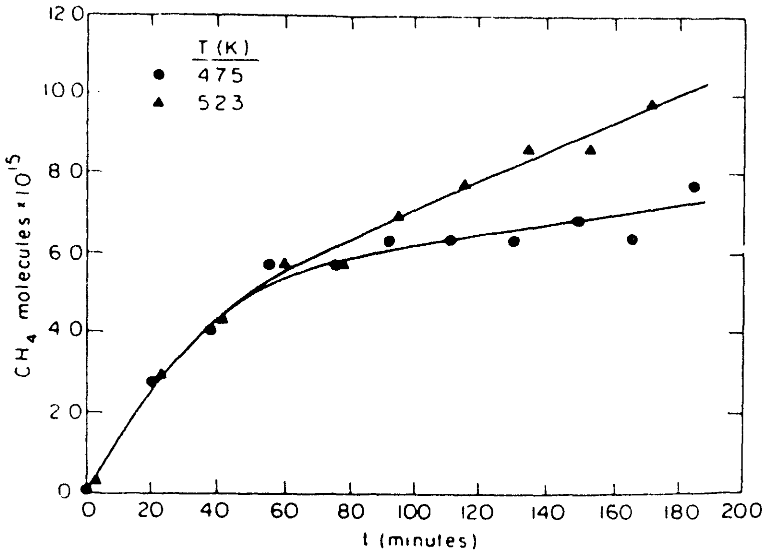

Fig. 3 CH4 production as a function of temperature in the presence of KOH.

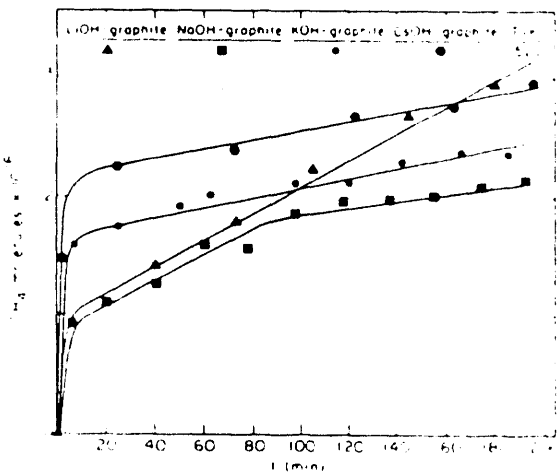

Fig. 4 CH4 production with various alkali hydroxides.

Fig. 5 Micrograph of KOH catalyzed reaction.

Fig. 6 Micrograph of KOH catalyzed reaction ten minutes later.

It was also observed when using calcium hydroxide for the gasification of graphite that a new photoelectron emission peak corresponding to a C_{1s} electron binding energy of 290 eV is formed representing a more reactive form of carbon probably in connection with oxygen. As will be shown later, this probably constitutes a phenoxide species also observed by Mims and Pabst [3].

In experiments with the flow reactor shown in Fig. 1 it was found that two regimens of gas production prevailed as illustrated in Fig. 7. In the first hydrogen, methane and higher hydrocarbons were produced with almost no carbon monoxide or carbon dioxide production. In the second regime hydrogen and CO were produced at a lower rate [9]. The first regime prevails until exactly one-half mole of hydrogen as either hydrogen or in hydrocarbon has been produced per mole of KOH present. This then would indicate that one is dealing with a stoichiometric reaction in which carbon reacts with potassium hydroxide to form a phenoxide and one-half mole of hydrogen which in turn may react with carbon to form hydrocarbons. Such a reaction can be described as: $5C+4KOH \rightarrow 4COK+CH_4$. The fact that higher hydrocarbons up to C_6 are also formed is of interest [9]. The presence of the stoichiometric phenoxide compound was confirmed by XPS and was also established by NMR work reported by Mims and Pabst [3].

When a sample of potassium hydroxide impregnated graphite which has been reacted to completion of the stoichiometric reaction is heated to about 1025°C, the phenolate is decomposed with production of carbon monoxide. Following this, gasification at low temperature can again begin in line with regime 1 in Fig. 7.

b) <u>Binary Catalysts</u>

We have found that the overall reaction can be made truly catalytic by adding a co-catalyst to the potassium hydroxide. Suitable materials are metal oxides and particularly nickel and iron oxide as shown in Fig. 8. It appears that in the presence of the metal oxide the phenolate is decomposed as quickly as it is formed and gasification occurs at 525°C at a

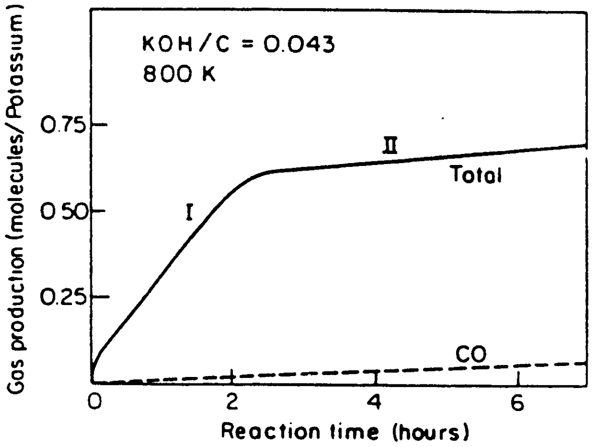

Fig. 7 Gas production in the flow reactor.

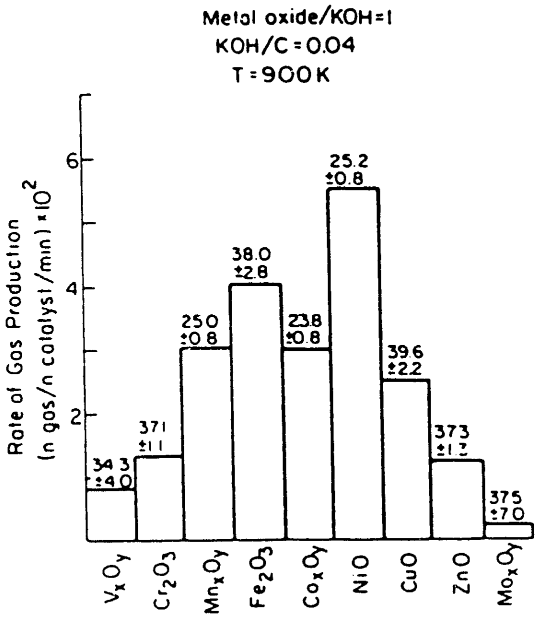

Fig. 8 Gas production and activation energy for various metal oxides

steady rate which has been followed up to 25% conversion of the graphite. This is illustrated in Fig. 9. The reaction proceeding can be simulated by the following equations:

$$4COK \xrightarrow{MeO_x} 2K_2O + 2C + 2CO$$
$$2K_2O + 2H_2O \rightarrow 4KOH$$

In the gasification with potassium hydroxide plus metal oxide the products are essentially hydrogen and carbon dioxide in a ratio of 2:1. Only traces of hydrocarbons are found. It was at first suspected that in these reactions methane might be a primary product which is then steam reformed to CO and hydrogen. Addition of methane to the water feed illustrated, however, that only minor amounts, if any, of steam-reforming take place. Decomposition of methane over the metal oxide may occur to a small extent and this may be the reason why only traces of hydrocarbons are found. The high hydrogen to CO_2 ratio and the absence of carbon monoxide are attributed to a watergas shift reaction proceeding simultaneously with the gasification. We have considered the possibility of a Boudouart reaction with subsequent gasification of the carbon from the disproportionation but believe it to be less likely than the watergas shift reaction. It is important to note that the production of hydrogen to carbon dioxide in the 2:1 molar ratio allows high hydrogen production directly from the gasification of carbonaceous material without a separate shift reaction and that the reaction proceeds at temperatures appreciably lower than those previously observed. One must also note that the reaction is carried out at essentially atmospheric pressure and that the kinetics might be improved by operating at higher water partial pressure.

It can be concluded that phenoxide type compounds are formed from the reaction of carbon, water and alkali hydroxide as intermediates in the production of hydrogen and/or of hydrocarbons from carbonaceous material and water in the presence of alkali hydroxides.

Isothermal experiments between 425°C and 725°C were performed to determine the product distribution for the gasification of graphite with steam using NiO-KOH as a catalyst. The rate of gas production was similar (within 10%) to those obtained from a temperature programmed experiment.

In the temperature range studied, the major products were H_2 and CO_2 with a molar ratio of 2.2 ± 0.5. Although some CO was produced above 625°C, the amount was one order of magnitude less than the amount of CO_2 produced. These results strongly contrasted with the CO/CO_2 molar ratio calculated at equilibrium conditions. Below 625°C, CH_4 was produced as a minor constituent and its fraction in the gaseous products decreased with time. At the beginning of the gasification process, the CH_4/H_2 molar ratio was $\approx 4 \times 10^{-2}$, but after 4% graphite conversion, it dropped to $\approx 10^{-3}$.

In order to prove that the gasification of graphite with steam was indeed catalyzed by KOH-NiO, the gas production was followed under isothermal conditions at 590°C up to a graphite conversion of 25%. The results are shown in Fig. 10 (curve A). Figure 10 (curve A) shows that the KOH-NiO catalyst was still active after 24 turnovers, while adsorbed KOH alone on graphite became inactive after 0.25 turnovers at the same temperature (see Fig. 9, curve C). When NiO only was present as a catalyst on graphite, no gas production was obtained at this temperature after an initial burst.

When KOH and Fe_2O_3 were codeposited on graphite, the results obtained were similar to the case when codeposited KOH and NiO were used. Isothermal experiments at 590°C with Fe_2O_3 and KOH coadsorbed on graphite showed that gasification was still occurring at a steady-state rate after 25% graphite conversion and 24 turnovers, although the rate of gas production was smaller than when the NiO-KOH catalyst was used. The major products were H_2 and CO_2 with a H_2/CO_2 molar ratio of 2.0 ± 0.5. When Fe_2O_3 is adsorbed alone, no gas production is obtained in a temperature-programmed experiment until temperatures above 825°C are employed.

The catalytic activity for the gasification of graphite with steam of K_2CO_3-NiO coadsorbed on graphite was studied in a temperature-programmed experiment. The rate of gas production and product distribution was identical, within experimental error, to the case of KOH/NiO.

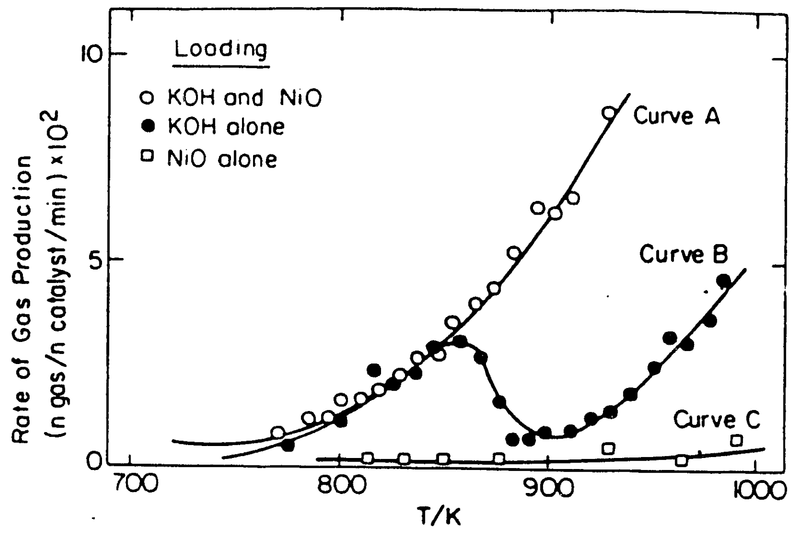

Fig. 9 Temperature controlled gas production for three catalysts.

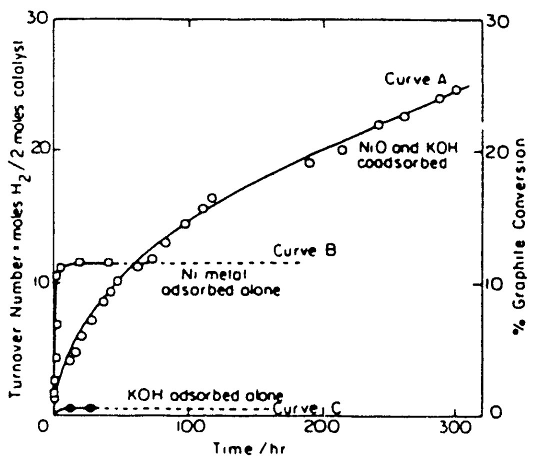

Fig. 10 Turnover number as a function of time for isothermal reactions at 590°C. The open circles (curve A) correspond to NiO-KOH codeposited on graphite, the open squares (curve B) to Ni metal deposited alone, and the full circles to KOH deposited alone on graphite. In curves A and B the ratio of Ni/C is 0.01. In curves A and C the ratio C/K is 0.01.

The activity of Ni metal adsorbed on graphite was also studied. A temperature-programmed experiment (Fig. 11) showed that Ni metal was active at much lower temperatures than when using NiO-KOH as a catalyst. Arrhenius plots (Fig. 12) showed that the activation energies in the two cases were similar (E_a = 25.2 ± 0.8 kcal/mol for KOH-NiO and E_a = 23.1 ± 2.6 kcal/mol for Ni metal) and much lower than in the case of KOH only deposited on graphite (E_a = 41.7 ± 1.3 kcal/mol). The Ni metal catalyst, however, deactivated rapidly. Figure 9 (curve B) shows that even though the initial rate of gas production at 859 K was much faster for Ni metal than for NiO-KOH (compare the slopes of curves A and B in Fig. 10), the rate of gas production stops after 10% graphite conversion in the first case (Ni metal), while gas was still being produced after 25% conversion when NiO-KOH was the catalyst.

The results presented show that a mixture of KOH and a transition metal oxide is able to catalyze the gasification of graphite with steam at a detectable rate at temperatures as low as 590°C. This temperature is 100° lower than the one needed to have a steady-state rate of reaction when KOH alone is used as a catalyst. The KOH-NiO mixture was the most active catalyst found, although other transition metal oxides (especially Fe_2O_3) were also effective when codeposited with KOH. The activity of these mixtures as catalyst for the gasification process below 625°C cannot be attributed to an additive effect, but rather to a cooperative effect. While the mixture of KOH and the transition metal oxide is a good catalyst for the steam gasification of graphite below 625°C, KOH adsorbed alone behaves as a reactant at this temperature range and the transition metal oxide adsorbed alone is inactive.

In the cases of nickel and iron, even though the oxide adsorbed alone is inactive, the metals are excellent catalysts. The results show that nickel converted to the metallic state when $Ni(NO_3)_2$ was decomposed on graphite in a H_2 stream at 800°C is an excellent catalyst for this process, while NiO produced from decomposition of the same salt at 400°C is completely inactive. Similar results have been found by other authors. McKee [10] found that iron is only effective for the gasification of graphite with steam if it is present in the metallic state. Walker et al. [11] found the same behavior for iron when CO_2 was used instead of H_2O. Yamada et al. [12] reported that the activity of nickel compounds in the gasification of char was related to their facility to decompose and produce nickel in the metallic state.

When KOH was added to nickel, the temperature at which the nickel nitrate was decomposed did not affect the catalytic activity of the mixture for the gasification of graphite with steam below 725°C. The same activity was found when $Ni(NO_3)_2$ was decomposed at either 400°C or 800°C in the presence of KOH. Since at 400°C the formation of Ni metal is not favored, these results suggest that KOH is stabilizing the presence of NiO at our reaction conditions. This does not exclude, however, that a small fraction of the nickel loading is in the metallic state. Figure 11 shows that the activation energies of the Ni metal and KOH-NiO catalysts are very similar, even though the activity of the first is higher. Also, both catalysts show the same product distribution. This is what we would expect if a small fraction of the Ni in the KOH-NiO catalyst were in the metallic state.

The most important difference between the KOH-NiO and the Ni metal catalysts is their total activity. Figure 10 shows that the Ni metal catalyst was completely inactive after 11 turnovers (11% graphite conversion) while the NiO/KOH catalyst was still active after 25 turnovers (25% graphite conversion). This higher total activity is also found in the case of the KOH-Fe_2O_3 catalyst.

The formation of a stable compound by chemical reaction of the transition metal oxide with KOH could explain the cooperative effect found in this work. The production of K_2NiO_2 and $FeKO_2$ from the reaction of KOH, K_2CO_3, or K metal with NiO or Fe_2O_3, respectively, at temperatures around 750 K has been reported [13,14].

The cooperative effect and the high resistance to poisoning clearly show that there is interaction between KOH and the transition metal oxide as catalysts for the gasification of graphite with steam below 625°C. Adler and Hüttinger have studied the effect of combining K_2SO_4 and Fe_2SO_4 as catalysts for gasification of coke with steam plus hydrogen [15] and have found improvements over the performance of K_2SO_4 alone. A similar situation is found in the industrial steam reforming catalyst, where K_2CO_3 is added to

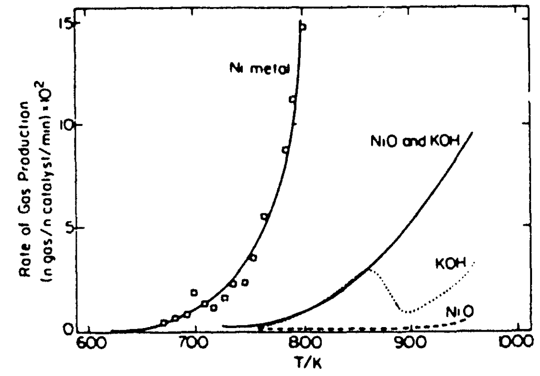

Fig. 11 Plot of the temperature dependence of the gas production rate during a temperature-programmed experiment at a heating rate of 5K min^{-1}. The open squares correspond to Ni metal deposited on the graphite surface. The ratio Ni/C is 0.04. The plots for KOH, KOH+NiO, and NiO shown in detail in Fig. 9 are included for comparison.

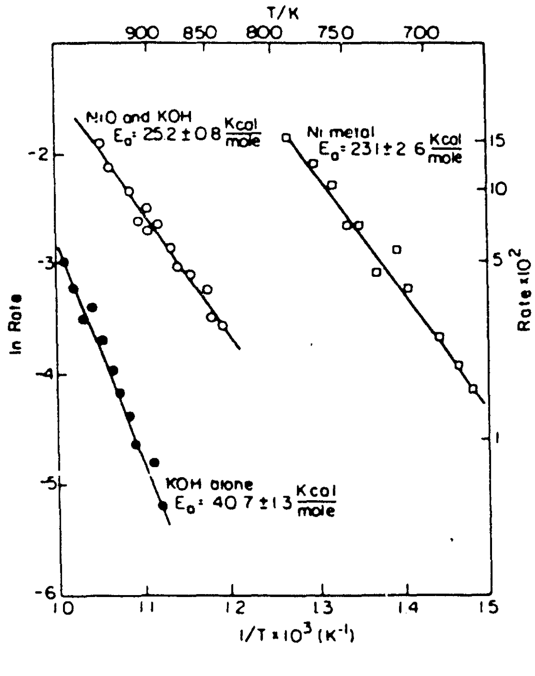

Fig. 12 Arrhenius plots of the temperature dependence of the gas production displayed in Fig. 9 (curves A and B) and in Fig. 11

nickel to avoid its poisoning from encapsulation by a carbon layer [16]. On the other hand, Wigmans and Moulijn [17] did not find evidence for interaction between K_2CO_3 and Ni metal for the gasification of carbon with steam at 800°C. All this suggests that the interaction between KOH and the transition metal oxide depends on the reaction conditions.

The product distribution obtained for the gasification of graphite with steam when either KOH-NiO or KOH-Fe_2O_3 were used as catalysts suggests that the kinetics of a surface reaction is controlling the process. The ratio of CO to CO_2 obtained when either KOH-NiO or KOH-Fe_2O_3 is adsorbed on graphite is far below the value expected at equilibrium. Also, the extremely low proportion of CH_4 in the gas products suggests that the process is kinetically controlled. The formation of CO_2 instead of CO has also been found by Wigmans et al. [18] when Ni metal is used as a catalyst.

The low proportion of CH_4 in the gas products might be due to steam reforming, particularly in the case of nickel, since Ni metal is used as an industrial catalyst for this reaction. Similar results are found, however, in the case of iron compounds which are widely used as a catalyst for the formation of hydrocarbons from H_2 and CO, even in the presence of large concentrations of steam. Another possibility for the low proportion of CH_4 in the gas products is that H_2 is preferentially formed over CH_4 in our reaction conditions. That is, the recombination of hydrogen atoms on the graphite surface is favored over the breaking of a carbon-carbon bond involved in the formation of CH_4 from graphite.

In experiments with K-Ni oxide catalysts, it was found that the catalysts were subject to potential poisoning by sulfur compounds. A search for a more poison resistant catalyst resulted in finding that calcium-potassium oxide catalysts are almost as active and more poison-resistant than K-NiO catalysts. The poisoning experiments will be described in the chapter on chars (chapter VI-2). Table 3 in chapter VI-2 gives a comparison of the activity of several catalysts.

A kinetic study was performed to enhance the comparison between the two most active bimetallic catalysts of those studied for the steam gasification of the various carbon samples investigated. The partial orders of reaction were determined with graphite samples containing a catalyst/carbon molar ratio equal to 0.01 with a mole of catalyst comprising 1 mol of K and 1 mol of Ca or of Ni. The same determination was also made with a K/graphite sample having a catalyst/carbon molar ratio equal to 0.01. One of the reactants (H_2O; H_2; CO_2) was diluted with inert gas (He), while keeping the partial pressure of the other gaseous reactants constant. Every system was kinetically tested after 30% of graphite conversion to ensure that a steady state was achieved (pseudo-zero order). Also, no tests were made after 70% conversion , so that major changes in catalyst/carbon ratio did not affect the final carbon conversion rates. These conditions required selection of different temperatures for each system: K-Ni/graphite, 933K; K-Ca /graphite, 941K; K/graphite, 953K.

The high activation energies found for all the carbonaceous and catalyst samples studied in our system along with the very small grain size and the high linear velocity of the gases used indicate that chemical reaction steps are controlling the rate of reaction and not diffusion.

Most of the kinetic studies reported in the literature have been carried out in gravimetric systems in which the carbon conversion is monitored by weight loss. Because of the characteristics of this reaction (solid-solid and solid-gas reaction), care must be taken to perform kinetic studies in our flow reactor system as shown by Holstein [24]. We therefore describe below in some detail how we analyzed our data.

During steady-state operation our reactor can be visualized as one in which a constant "flow" of carbon is passing through a stationary catalyst. If all other conditions are constant, including H_2O, H_2, and CO_2 partial pressures, the reaction rate should be constant. This state is experimentally observed with graphite and can be expressed because of our conditions (low water conversion levels, high space velocity) in a very simplified way as occurring in a differential reactor. Assuming that the number of moles of catalyst participating in the reaction is constant during the period of investigation one finds

$$R_c = (F_o/N_{cat})X \text{ or } R_c = SX,$$

where R_c is the rate of carbon conversion per mole of catalyst, F_o is the "molar flow of carbon," N_{cat} indicates moles of catalyst in the reactions, X indicates conversion, and S is the molar space velocity which under our conditions is approximately constant.

The rate expression can be generalized as

$$Rc = Kf[P^a(H_2O)P^b(H_2)...].$$

The partial orders of reaction can then be determined by varying the partial pressure of one component while keeping the partial pressures of the other components constant, using an inert gas to maintain the total pressure constant.

Under our conditions, CO_2 has been shown to have no effect on the reaction rate.

In the presence of a large excess of water or, alternatively, hydrogen, the expression becomes

$$Rc = K'P^a(H_2O) \quad \text{or} \quad Rc = K''P^b(H_2).$$

When the experimental data was plotted, good correlations were found, and the orders obtained for every system are presented in Table 1.

Table1

Steam Gasification of Graphite with Various Catalysts

Catalyst	After 700 min of reaction under STD conditions		Kinetic study			
	Conversion %	Rate (mol/mol/min)	E_a(KJ/mol)	H_2O partial order (a)	H_2 partial order (b)	Regression (a) - (b)
K-O	15	0.091	265	0.66±0.04	0.71±0.01	0.94-0.99
Ca-O	7	0.040	---	--	--	--
Ni-O	0	0.00	--	--	--	--
K-Ca-O	25	0.139	276	0.50±0.03	0.21±0.01	0.996-0.98
K-Ni-O	28	0.145	273	0.69±0.03	1.04±0.01	0.95±0.99

From these results it is apparent that the inhibiting effect of H_2 decreases in the order K-Ni > K > K-Ca. The close values of the activation energies indicate that the rate-controlling step may be independent of the catalysts. The high value found (about 60 Kcal/mol or 270 KJ/mol) indicates that the rate depends on a thermally activated step such as the surface complex decomposition suggested by Mims et al [3].

Water Dissociation with K-CaOx catalyst. When steam is passed over the K-Ca-O_x catalyst in the absence of carbon the dissociation of water is observed and the evolution of H_2 is readily detectable. The reaction stops after 2h at 625°C when using 0.3 g of catalyst and steam at 1 atm. If the temperature is raised, an additional H_2 release is observed, but this always stops after a few minutes at each temperature. No release of O_2 was observed at any time. Blank checks without catalyst showed no H_2 release. H_2 release was observed for one cycle of increasing temperatures only. This is most likely due to the oxidation of the catalyst to a form that is no longer active for water dissociation as indicated by the absence of oxygen evolution. In the presence of carbon the water dissociation becomes catalytic, as the carbon provides a sink for the oxygen produced from H_2O thereby preventing the catalyst deactivation.

c) Mechanism of the Graphite-Catalyst-Steam Interaction

In previous chapters 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°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°C (1.2ml H_2/min/g carbon) and a relative low activation energy (~30 kcal/mol).

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 two gas environments; H_2O vapor and N_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 on 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.

It has now been shown that the Ni/K catalyst has distinctive morphological and kinetic properties for carbon gasification.

A detailed description of the CAEM technique can be found elsewhere [13]. Ni and K are introduced onto transmission specimens of natural single crystal graphite (Ticonderoga, NY) as an atomized spray, using 0.1% solutions of $Ni(NO_3)_2$ and KOH. Samples were then dried in air and introduced into the environmental cell.

Before the sample was exposed 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 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_2 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 ~40/1 in the gas reaction cell.

After graphite samples loaded with KOH and $Ni(NO_3)_2$ were treated at 450°C in Ar, particle nucleation was observed on both the basal and the 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 nonwetting 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. Figures 13A and 13B show a two-picture sequence illustrating this mode of attack. The interval between A and B is 3 sec at 900°.

The edge recession involved the whole area and the various fronts of attack were separated by 60° angles, in the direction parallel to the 1120 crystallographic orientation of the graphite structure. The orientation was

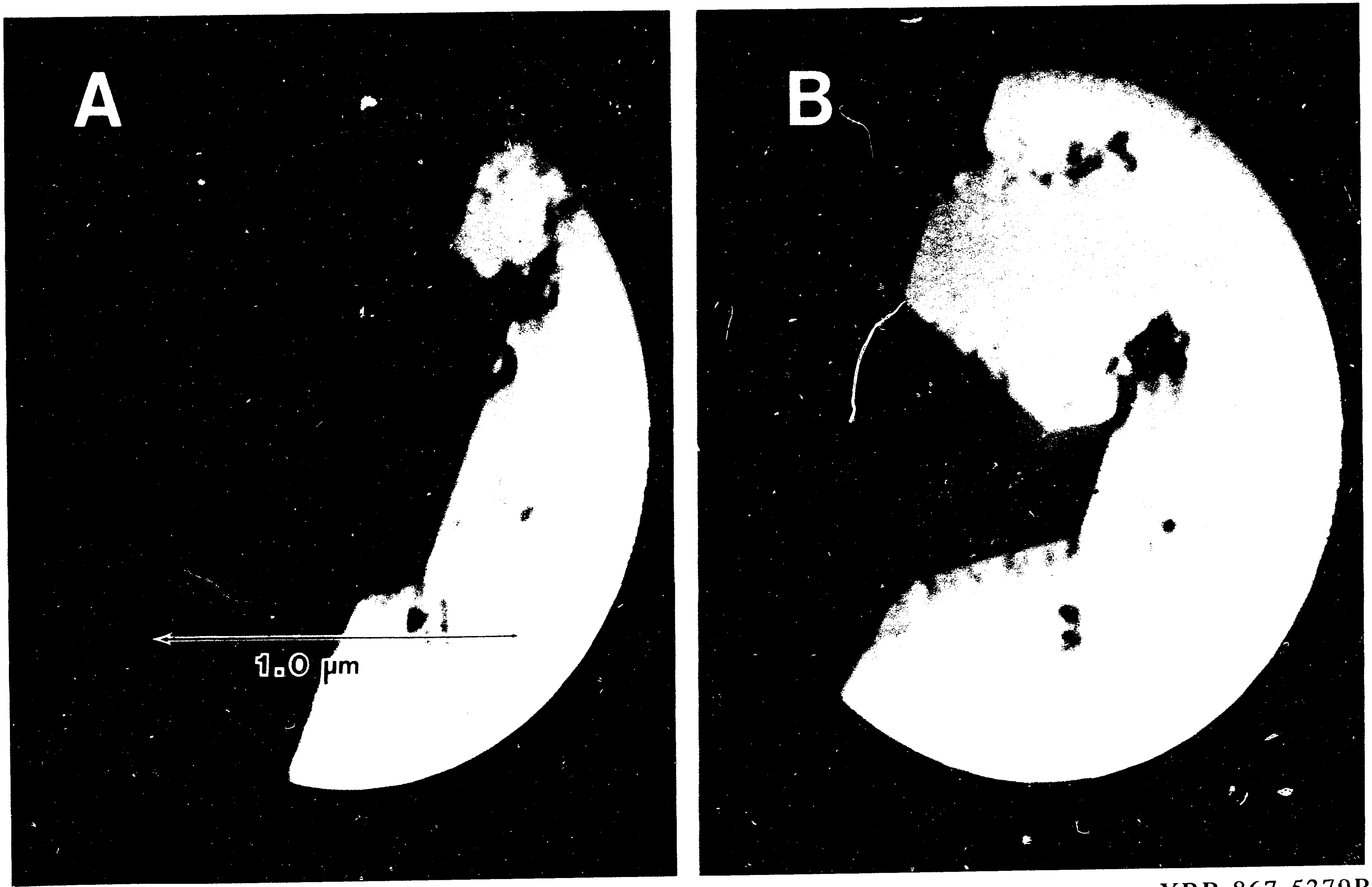

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Fig. 13 Sequence of photographs taken from the CAEM video display, showing the edge recession attack of carbon in H_2O vapor at 900°C. The time between (A) and (B) is 3 sec.

determined by referring the position of the fronts of attack to that of twin bands, which are always present in the graphite in the 1010 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. 14 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.

At temperatures above 955°C 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 buildup of H_2 produced in the gas environment. This is in agreement with the results described in the following paragraphs.

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 at 2.0 Torr wet H_2O 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 Figs. 15A and 15B).

On raising the temperature to 675°C many of the previously inactive particles located on the graphite basal plane started to exhibit mobility. When

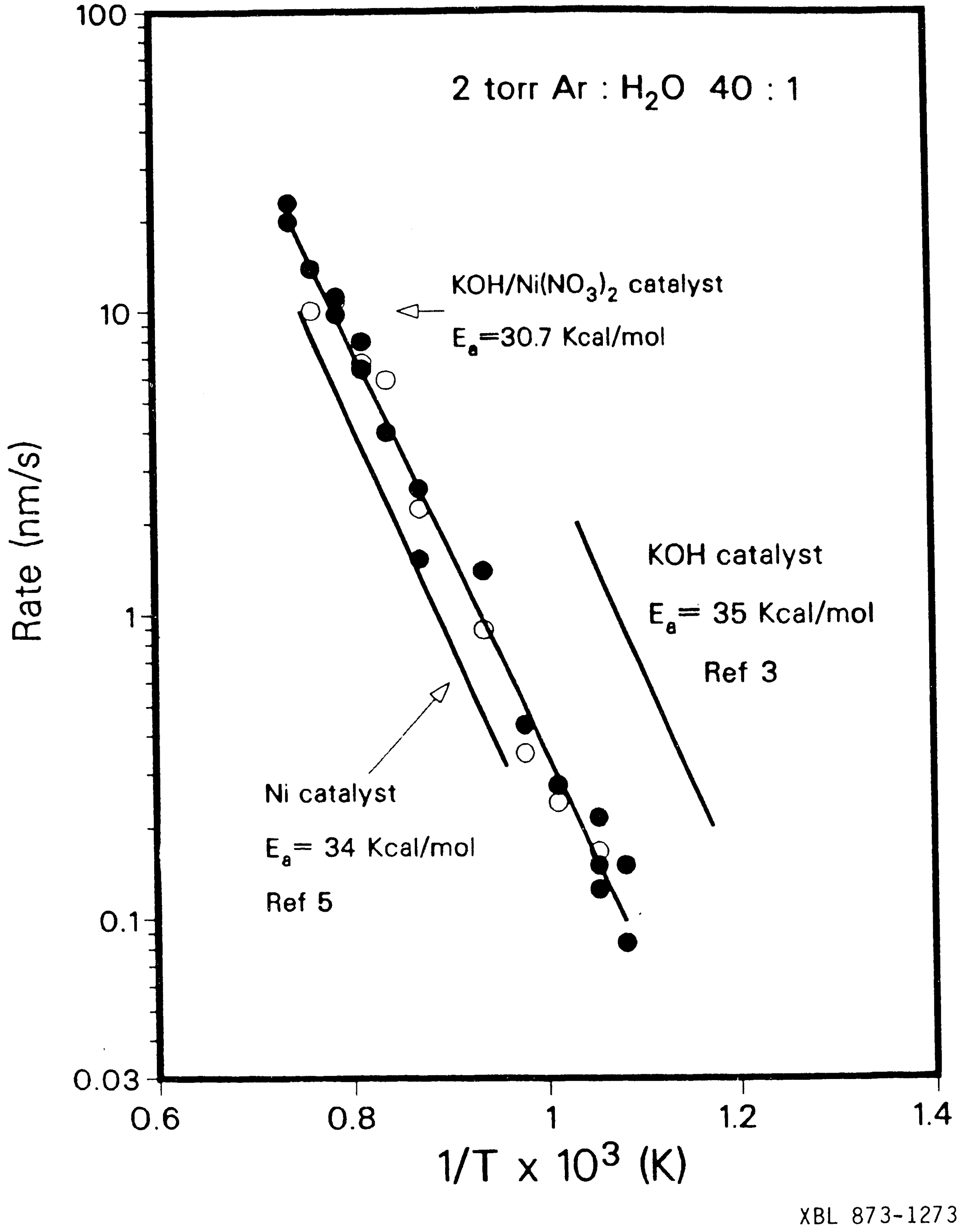

Fig. 14 Arrhenius plot of Ni/K catalyzed edge recession rates of graphite in 2 Torr of wet Ar. The filled circles represent the results obtained after heat treating the sample in Ar for 30 min at 450°C. The open circles represent the results obtained after treating the sample in 2 Torr of wet H_2 at 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.

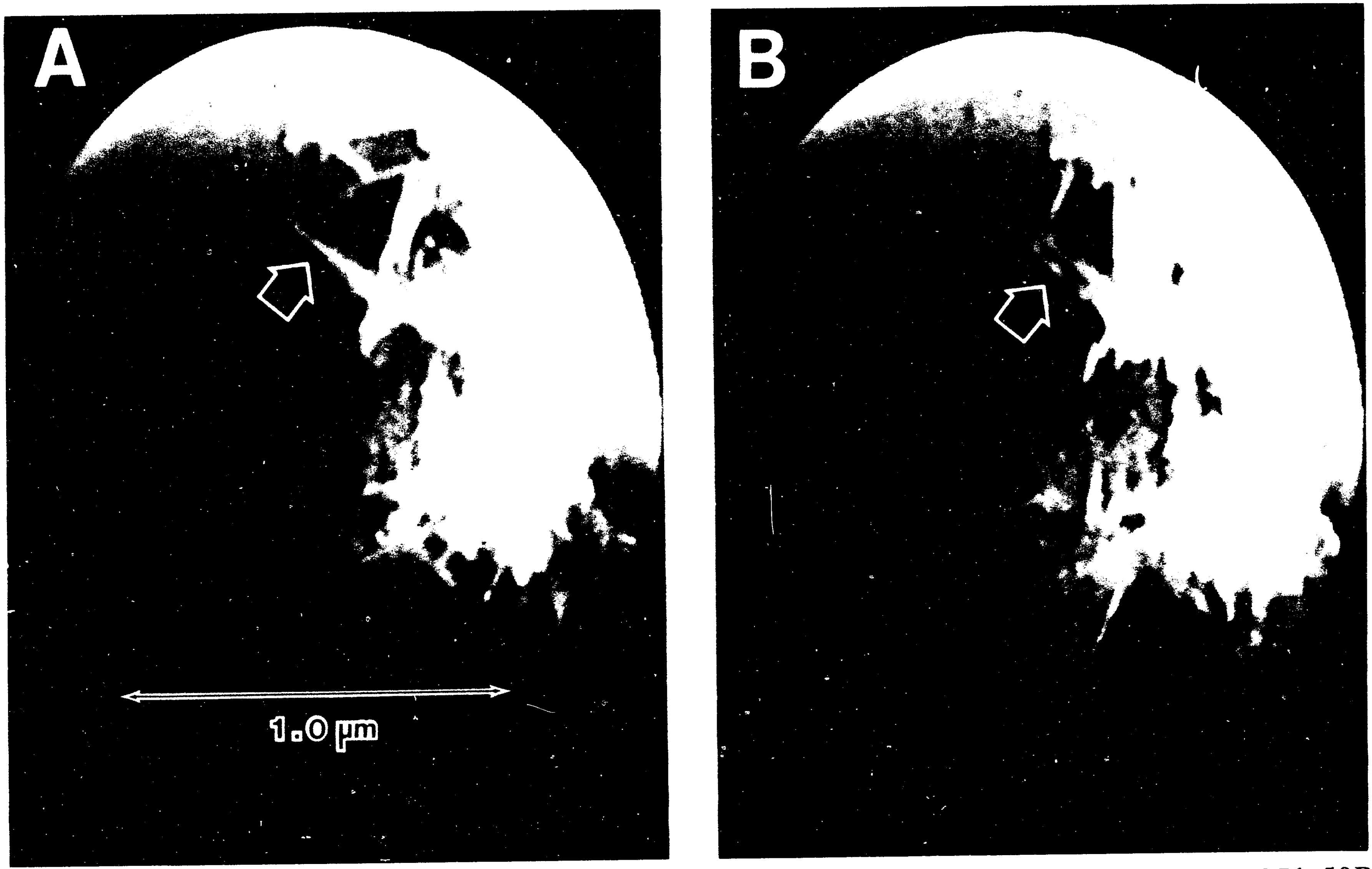

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Fig. 15 Sequence of photographs, showing the modes of attack in 2 Torr of wet H_2. The region indicated by the arrows shows the recession of the channel walls, as described in the text (see results). Also note the simultaneous carbon attack by edge recession and channeling in the lower part of the photographs. The time between (A) and (B) is 1 sec.

these particles encountered an edge they underwent a rapid spreading action and this resulted in a subsequent removal of carbon by edge recession in directions parallel to the 1120 crystallographic orientation. The variation in edge recession rate with temperature was determined and the data are presented in Fig. 16 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 to 1100°C the edge recession tended to slow down and in some regions it stopped completely, leaving channeling as the only mode of attack.

The edge recession activity could be regenerated by treating the sample in wet Ar at about 1000°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 14 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 (filled circles).

The Ni/K mixture catalyzes the gasification of graphite in both 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 the catalyst spreads and promotes the carbon attack by an edge recession mode. In wet H_2 the catalyst is present in both a wetting and a spreading condition, and the gasification occurs simultaneously by channeling and edge recession.

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

$$\gamma_{sg} > \gamma_{lg} + \gamma_{sl}.$$

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 rises 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.

CAEM experiments were also carried out during steam gasification of graphite impregnated with K-Ca oxide catalysts. The results, details of which are shown in reference [25] essentially confirm and duplicate the findings with K-Ni oxide catalysts.

It has previously been stated that the mechanism of steam gasification of carbonaceous materials involves a dissociation of water, with H_2 going into the gas phase and O_2 forming oxygenated compounds on the carbon surface. This is indicated in Fig. 17 which shows the H_2/CO_2 ratio produced during gasification. Initially this ratio is more than 2, while O_2 is adsorbed on the carbon. At the end of gasification the ratio drops below 2 as dissociation of oxygenated carbon accelerates.

Elucidation of the structure and stability of the various surface species formed after adsorption of O_2, CO_2, H_2, and H_2O on graphite is very important for the understanding of the chemistry of graphite and its connection with processes leading to the stabilization of high surface area carbons or to carbon gasification. Although numerous studies have focused on the kinetic properties and the nature of the surface species formed after O_2, H_2O, or CO_2 oxidation, only a limited understanding has yet been achieved, owing certainly to the complexity of the system.

TPD and XPS studies of O_2, CO_2 and H_2O adsorption of clean polycrystalline graphite were performed [20]. They showed the presence of semi-quinones and lactones on the graphite surface after CO_2 adsorption.

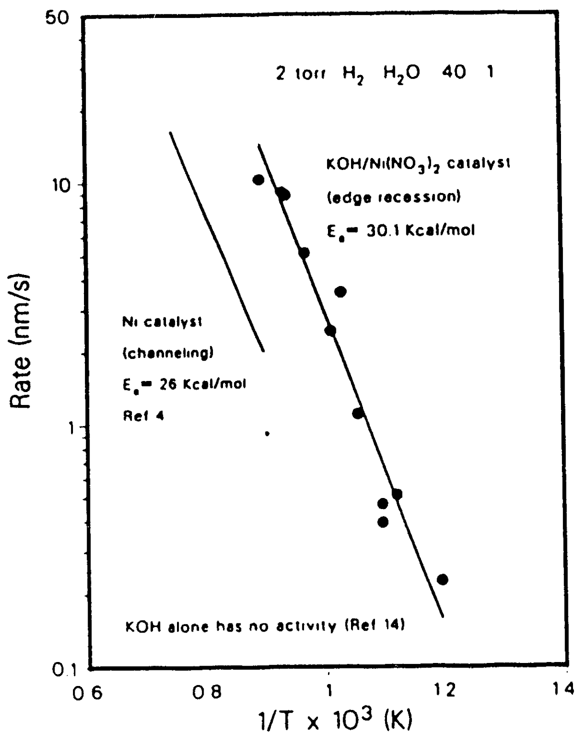

Fig. 16 Arrhenius plot of Ni/K catalyzed edge recession rates of graphite in 2 Torr of wet H_2. The results previously obtained for the channeling mode of attack of Ni metal are included for comparison. The length of the curves indicates the temperature range studied.

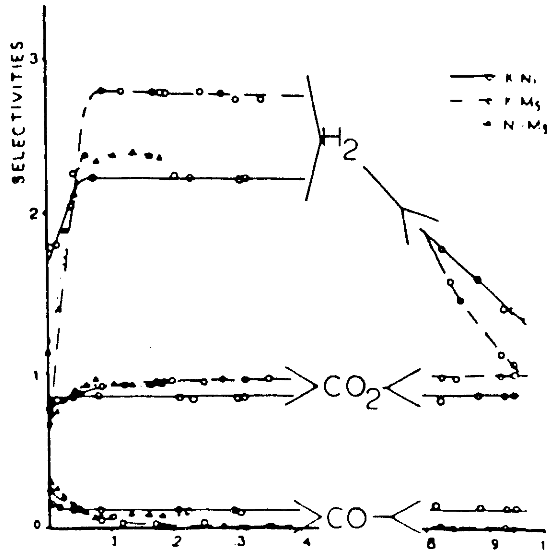

Fig. 17 H_2 and CO_2 selectivity during gasification

2) STEAM GASIFICATION OF CHARS

a) Potassium-Nickel Oxide Catalysts

The gasification rates of five different chars have been obtained. The chars' pretreatment, elemental composition and ASTM rank are summarized in Table 2. 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 publication [20] and in an earlier section of this report.

Table 2
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)	NV.B.Bit.	Unspecified	72.3	3.2	1.4	7.9	3.2	12
North Dakota Husky (NDHL)	Lignite	Partial Steam Gasification	71.2	1.1	0.37	13-17	2.0	8-12[c]
Montana (MS)	Subbituminous	Partial Steam Gasification: T = 1200K	66.0	1.1	0.20	-	0.92	-
Illinois #-6 High Temp. (I 6 HT)	HV.C.Bit.	Heated under He T = 1300K	-	-	-	-	-	-
Illinois #-6 Low Templ (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
Source of chars: I.G.T.

A detailed explanation of the equipment used in these studies is given in section V-1. 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 by 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 40eV. The position of the peaks was calibrated with respect to the position of the C_{1s} peak of graphite (binding energy - 284.6eV).

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 18a). This is reflected in a much higher carbon conversion after 6.0 hours (see Figure 18b) even though by then the char steam gasification rates have decreased to values similar to those of graphite.

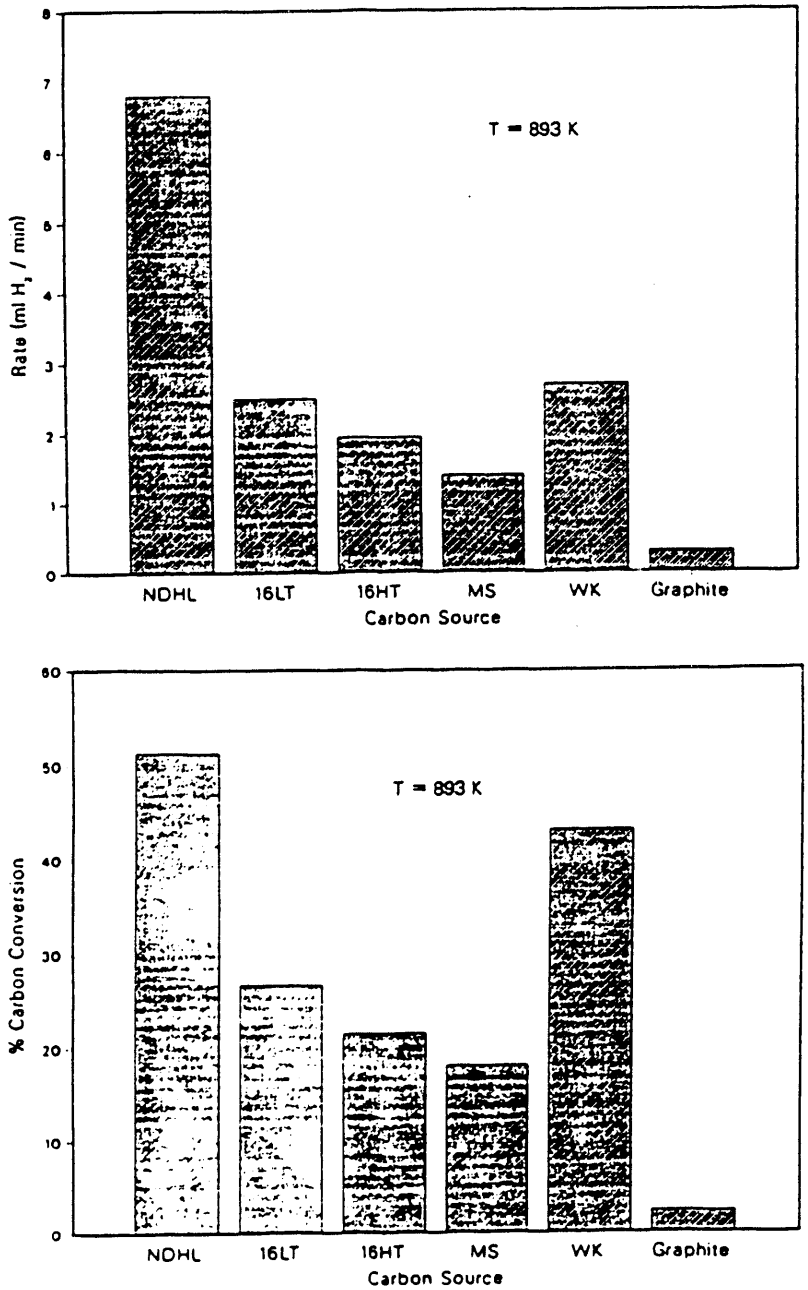

Fig. 18 (a) Steady state steam gasification rates of several carbonaceous solids after 1.0 hours when a mixture of nickel and potassium oxides is used as a catalyst.
(b) Percentage of carbon conversion obtained after 6.0 hours when the same catalyst is used.

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 19a and 19b 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 19a). 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 subbituminous char the rate of gasification of the mixture is similar to that of nickel alone and higher than that of potassium (see Figure 19b).

A surface science study of the interaction of potassium, nickel and carbon in the presence of water has been done. XPS of the $Ni_{2p3/2}$ 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 950K. The kinetic results show that at this temperature both systems are catalytically active. Figure 20 (Curve A) shows the spectrum corresponding to nickel deposited alone. There is a peak at 855.2 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 20) the binding energy of the $Ni_{2p3/2}$ 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 $Ni_{2p3/2}$ peak in the nickel-potassium mixture compared to NiO shows that there is an electronic interaction between nickel and potassium.

The kinetic results presented here 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 18 and 19) and the graphite gasification activity after 400 hours support this conclusion.

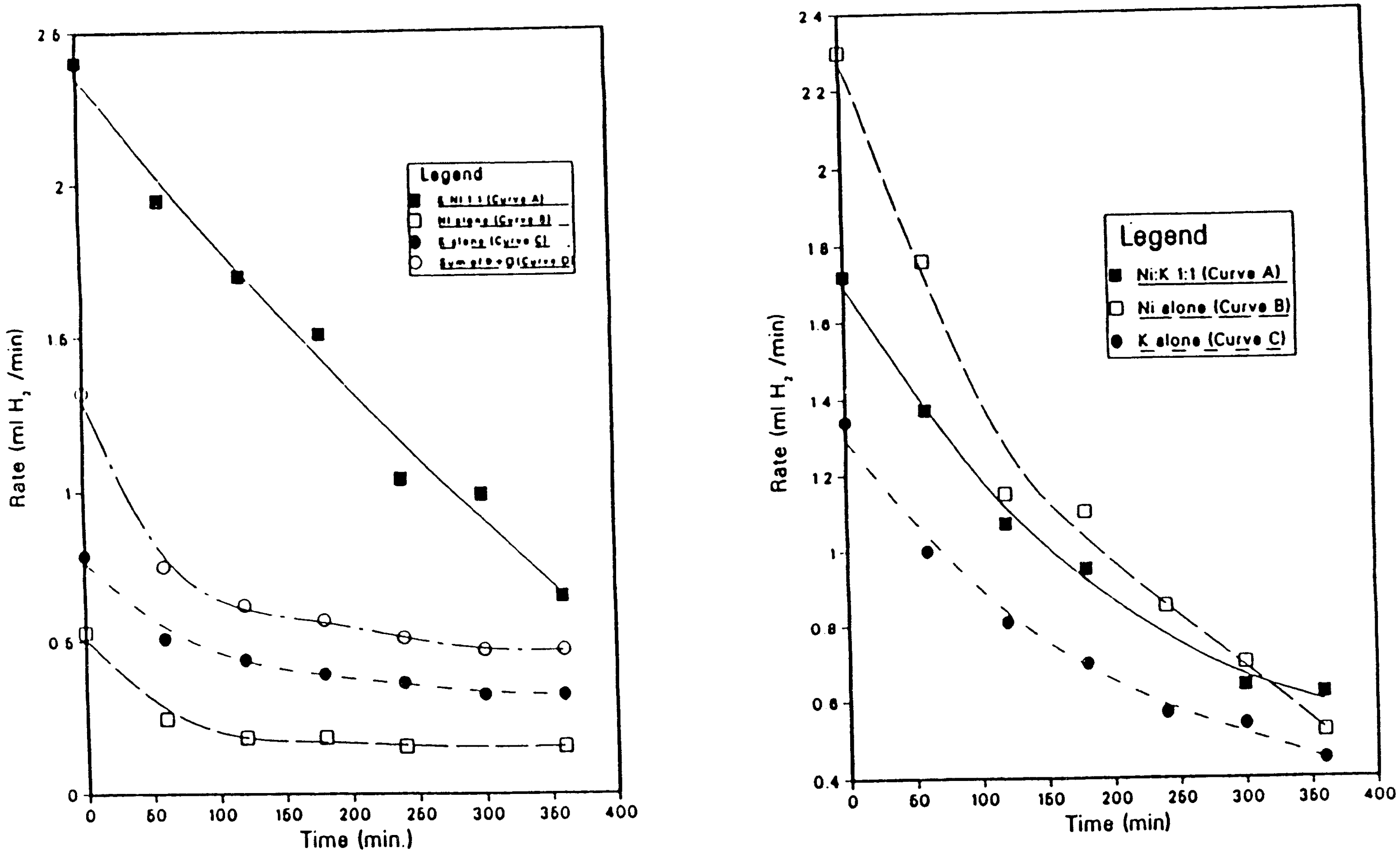

Fig. 19 Steam gasification rates at 893K for two chars, Illinois No. 6 High Temp.(a) and Montana (b) catalyzed by three different compounds, a 1:1 mixture of nickel and potassium (Curve A), nickel alone (Curve B) and potassium alone (Curve C). In Figure 19(a), Curve D is the mathematical sum of curves B and C.

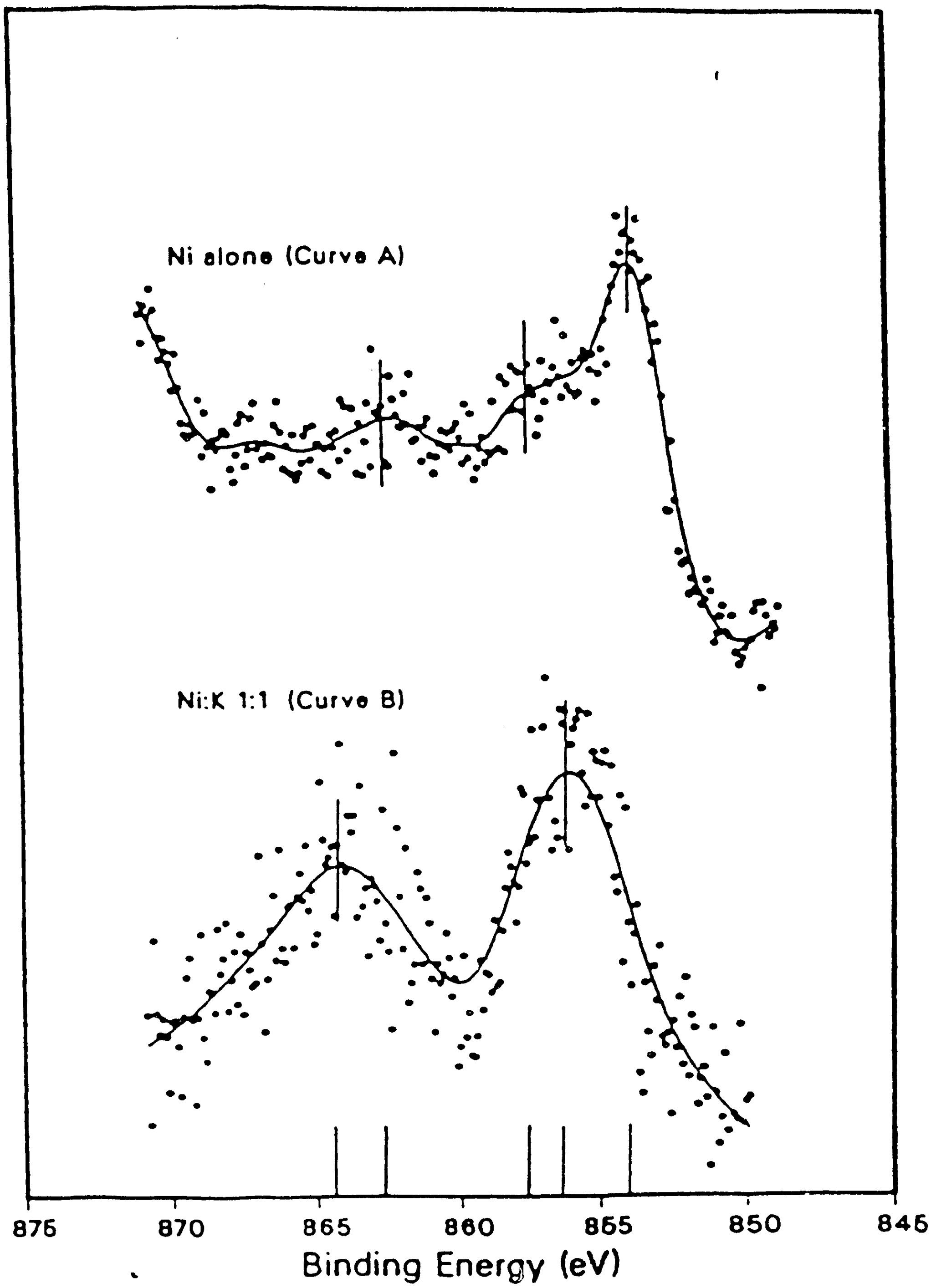

Fig 20 $Ni_{2p3/2}$ XPS of nickel (Curve A) and a 1:1 Ni:K mixture (Curve B) deposited on graphite. The spectra was taken after exposing the samples to 24 torr of water at 923K for 15 min.

We previously concluded that there is a cooperative effect between potassium and nickel in this catalyst. The results shown here present the clearest evidence obtained so far for this effect. In Figure 19a the gasification rate of Illinois #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 20 show that nickel deposited alone is active as a gasification catalyst when it is present in this 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 $Ni_{2p3/2}$ 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 (<725°C). There is evidence in the literature for the presence of several nickel-potassium mixed oxides [22], but we do not have enough information to decide which of them is present in our system.

Mixtures of transition metals and alkaline metals as catalysts for steam gasification of various carbon sources have been reported previously. Wigmans and Moulijn [17] reported that there was no interaction between nickel and K_2CO_3 for the steam gasification of chars at 750°C. Similar results were obtained in our laboratory when the gasification of graphite was studied above 725°C. Also, XPS data obtained in our laboratory show that at 725°C 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 Wigmans and Moulijn , a cooperative effect between a transition metal and an alkaline metal has been reported by two other authors. Adler and Hüttinger [15] found that mixtures of $FeSO_4$ and K_2SO_4 deposited on PVC coke were better catalysts than the salts deposited alone. Also, Suzuki et al [23] 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.

b) Potassium-Calcium Oxide Catalysts

We have earlier described research using only potassium oxide as a catalyst for gasification. We also found that potassium-nickel oxide mixtures exhibited markedly higher activity than that of either K_2O or NiO [13]. In the following we describe the behavior of a superior poison-resistant catalyst mixture, potassium-calcium oxide, for the steam gasification of carbon solids. This catalyst exhibits high activity at relatively low temperatures (575-625°C) and it produces primarily H_2 and CO_2. The activity is at least partially attributable to the excellent wetting of carbon by the catalyst precursors in their molten state prior to their decomposition.

Electron microscopy studies indicate that a homogeneous binary catalyst is formed after decomposition of the nitrate precursor salts and that gasification occurs by edge recession of the graphite prismatic planes while the basal plane is unreactive. This is similar to findings with K-Ni-O_x catalysts. Water dissociation by the K-Ca-O_x catalyst was found to be an important reaction step. Hydrogen is released and oxygen forms compounds with the carbon. The rate-limiting step appears to be the breaking of C-C bonds releasing carbon oxides.

Chars contain C-H bonds in addition to C-C bonds and have much higher surface areas than graphite. Since both the H/C ratio and the surface area (as well as mineral impurities content) vary from char to char several different char types were investigated to establish the catalyst performance for their steam gasification. In Table 3, data for the K-Ca-O_x catalyzed gasification of various chars are compared. The activation energies are similar to that of graphite, indicating that the much higher conversion and rates compared to those of graphite must be due to the char composition. The rate of gasification proceeds in the order lignite > subbituminous > bituminous > graphite. It should be noted that K-Ni-O_x exhibited identical trends when different chars were compared with graphite. Thus, the observed rate data is not a unique property of the K-Ca-O_x catalyst. The chars contain hydrocarbons that appear to gasify more rapidly than graphite. The reaction of steam with C-H bonds is more facile than the reaction with C-C bonds. In no case were hydrocarbons observed in the reaction products.

It was found that the K-Ca-O_x catalyst is highly resistant to poisoning by the sulfur content in the char. When K-Ni-O_x catalyst was used for steam gasification, it was rapidly poisoned in the presence of sulfur.

Figure 21 compares the rates of steam gasification under the standard conditions of a demineralized char loaded with either K-Ca-O_x or K-Ni-O_x in the presence or absence of 3% sulfur (obtained by the decomposition of dibenzothiophene) to demonstrate the poison-resistant behavior exhibited by the K-Ca-O_x catalyst.

The K-Ca-O_x catalyst is much more active than potassium oxide or calcium oxide alone as shown in Table 3. Its reaction rate is twice that of K-O_x and fivefold that of Ca-O_x at a temperature of 893K and 750 torr of steam. This high activity is probably due to the inhibition of a stable calcium carbonate formation that results in the case of calcium alone as a catalyst. In addition the formation of a molten eutectic phase which is observed during the catalyst preparation and prior to decomposition of the nitrate salts provides good wetting of the carbon solids.

Table 3
Steam Gasification of Graphite
with Various Catalysts

Catalyst	After 700 min of reaction under STD conditions	
	Conversion %	Rate (mol/mol/min)
K-O	15	0.091
Ca-O	7	0.040
Ni-O	0	0.00
K-Ca-O	25	0.139
K-Ni-O	28	0.145

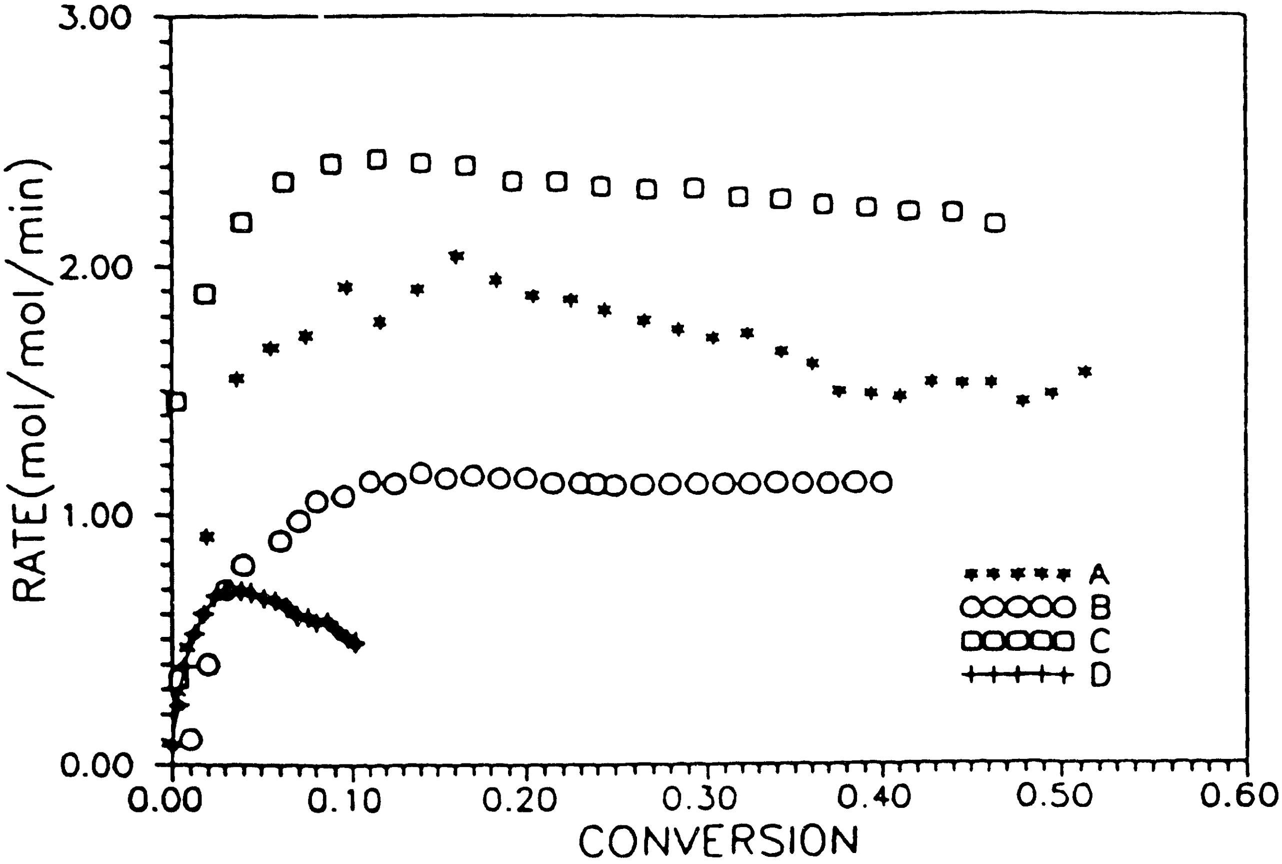

Fig. 21 Sulfur poisoning of demineralized K-Ni/KY 13 char and K-Ca/KY 13 char systems. Rate vs conversion plots. (A) K-Ca/KY 13 char; (B) K-Ca/KY 13 char + 3% S (ex DBT); (C) K-Ni/KY 13 char; (D) K-Ni/KY 13 char + 3% S (ex DBT).

Much of the work carried out with chars was with three chars, a subbituminous (Rosebud) and two bituminous chars (OH Pitt #8 and KY 13) supplied by IGT. Analysis of these is shown in Table 4

The rate equation for the gasification reaction and the activation energies for gasifying the various carbon solids (graphite and different chars) are very similar for different catalysts although the hydrogen inhibition effect varies somewhat from catalyst to catalyst, being the smallest for the K-Ca-O_x catalyst. Several oxygenated carbon species can coexist at the temperature range used in this work. However, the decomposition temperature for each of these species is different and the type of carbon oxide released can be different. Phenolic species decompose at temperatures higher than those used here and produce predominantly CO rather than CO_2. Under our conditions carboxylates and lactone species are decomposed, producing CO_2 [20].

It appears that the mechanism of gasification is very similar for the three catalysts. As suggested by earlier studies [8,12], the C-C bond breaking next to a surface carbon-oxygen complex to produce CO_2 (or CO at higher temperatures) is the likely rate-determining step for carbon gasification. There is a great deal of supporting evidence for this model, including oxygen- and carbon-labeled isotope studies and temperature-programmed thermal desorption [8,12]. The formation of stable oxygenated surface species has been identified by spectroscopic techniques such as EPR, FTIR, and XPS [26]. Also, the change in H_2/CO_2 ratio during steam gasification clearly indicates oxygen uptake by carbon in the beginning of the reaction [19].

The dissociation of water into hydrogen and oxygen by the catalyst has also been identified as an important reaction step. Surface science studies [27,28] have shown the ability of potassium to dissociate water to produce K-O_x. It appears that the evolution of hydrogen derives from this process, as does the oxidation of carbon at the catalyst interface. Our results show that water dissociates by a stoichiometric reaction over the K-Ca-O_x catalyst. In the presence of carbon this reaction becomes catalytic and is an important step in the gasification although its activation energy is relatively low (138 KJ/mol or 33 Kcal/mol of H_2) [21].

Table 4. PROXIMATE, ULTIMATE, AND INORGANIC CHEMICAL ANALYSES OF COALS USED IN GASIFICATION TESTS

Data supplied by I.G.T.

Seam Mine	Rosebud	OH Pitt No. 8 Franklin 125	KY No. 13
Proximate Analysis, wt%			
Moisture	23.1	2.5	9.8
Volatile Matter	28.5	38.6	32.2
Ash	11.3	7.5	7.3
Fixed Carbon	37.1	51.4	50.7
Total	100.0	100.0	100.0
Ultimate Analysis, wt% (dry basis)			
Ash	14.66	7.68	8.08
Carbon	62.78	74.47	73.74
Hydrogen	4.40	5.24	4.82
Sulfur	1.29	3.21	1.40
Nitrogen	0.99	1.50	1.85
Oxygen (by difference)	15.88	7.90	10.11
Total	100.00	100.00	100.00
Ash Composition, wt%			
SiO_2	48.8	41.6	58.5
Al_2O_3	23.55	20.9	26.9
Fe_2O_3	7.02	31.7	8.1
TiO_2	0.12	1.02	0.87
P_2O_5	0.25	0.07	0.16
CaO	7.16	1.14	0.90
MgO	2.57	0.36	1.21
Na_2O	0.09	0.35	0.24
K_2O	0.36	0.98	2.94
SO_3	9.91	1.00	0.80
Total	99.78	99.2	100.62
Ash Content (as ashed for analysis of ash, dry basis)	11.1	7.7	8.2
Basic Ash Constituents, wt%	19.22	35.2	13.4
Dolomite Ratio, wt%	56.6	4.3	15.8
SiO_2/Al_2O_3 Ratio	2.1	2.0	2.2
Forms of Sulfur, wt% (dry basis)			
Pyritic	0.76	2.37	0.40
Sulfate	0.015	0.21	0.10
Organic	0.52	0.97	1.03
Total	1.28	3.56	1.53

Forms of Iron (dry basis)	Rosebud wt%	Rosebud % of Fe	OH Pitt No. 8 wt%	OH Pitt No. 8 % of Fe	KY No. 13 wt%	KY No. 13 % of Fe
Pyritic	1.32	62*	2.07	96	0.35	70
HCl-Soluble	0.12	6	0.08	4	0.15	30
Total of HCl Sol + Pyritic	2.13*	100	2.15	100	0.50	100
Acid-Insoluble	0.69	--	<0.10	--	<0.1	
Pyritic, % of total Fe**		--	97		54	

*Based on total iron including 0.69 wt% HCl-insoluble
**Of 1/4-inch-top-size coal after storage

Chars gasify at much higher rates than graphite (over tenfold increase, Table 5). It is clear that gasification of the carbons that contain many C-H bonds in addition to C-C bonds is more facile. This has the effect of increasing the rate without change in the activation energy for the process. Thus, it appears that the rate of gasification is the same for graphite and for chars but that the preexponential factor is greatly increased for chars. This could be related to the much higher edge density of chars. These are the sites from which gasification proceeds.

The K-Ca-O_x catalyst exhibits superior poison resistance compared to that of the K-Ni-O_x catalyst, which has similar steam gasification activity. This property should be of importance in the technology as it permits the use of carbon feedstocks that have not been demineralized or contain sulfur.

Table 5
Steam Gasification of Three Chars and of Graphite With K-Ca-O Catalysts

Char (rank)	Activation energy (KJ/mol)	% Conversion after 120 min reaction	Reaction rate (mol/mol/min) 120 min
Graphite	260	10	0.6
North Dakota (lignite)	234	45	15.6
Rosebud (subbituminous)	240	30	2.75
KY 13 Frank. (bituminous)	269	15	0.82

A comparison of the K-Ca oxide and K-Ni oxide catalysts is shown in Figure 22 for the subbituminous Rosebud char. It shows higher activity for the K-Ca oxide catalyst. When the chars were first demineralized by HCl-HF treatment, the K-Ni oxide performed better than the K-Ca oxide and better than the non-demineralized char with K-Ni oxide. The demineralization

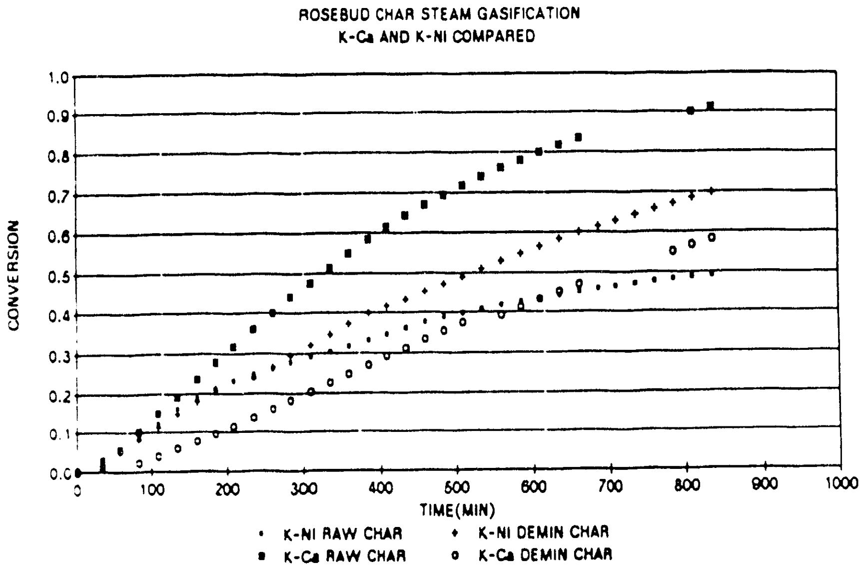

Fig. 22 Comparison of calcium-potassium oxide and nickel-potassium oxide catalysts for steam gasification of subbituminous (Rosebud) char.

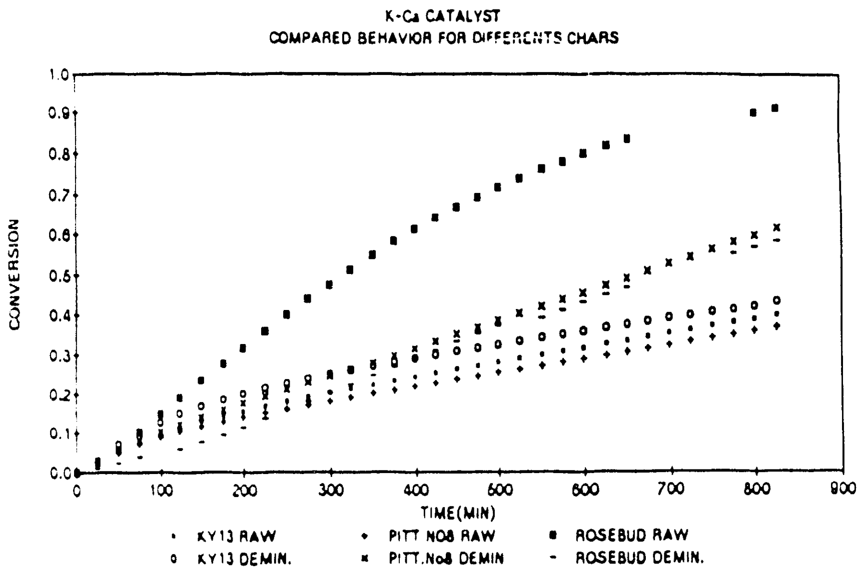

Fig. 23 Comparison of behavior of two bituminous (KY 13; Pitt #8) and one subbituminous (Rosebud) chars before and after dimineralization for steam gasification in the presence of K-Ca-O_X catalyst.

apparently removed components in the ash which promoted the K-Ca oxide. It also removed components in the ash which promoted the K-Ca oxide.

Using the K-Ca oxide catalyst for different chars, it is apparent that the subbituminous Rosebud char gasifies better than the two bituminous chars tested (Figure 23). The bituminous chars after demineralization performed somewhat better than the raw chars, while the reverse was true for the subbituminous char.

A similar picture evolves from the activation energies of the K-Ni oxide and K-Ca oxide impregnated bituminous and subbituminous chars (Table 6). The K-Ca oxide on raw Rosebud char has the lowest activation energy.

Table 6
Arrhenius Analysis for Different Catalysts and Chars

Catalyst + Char	Activation Energy KJ/mol Kcal/mol	Frequency Factor	Min Squares Reg. Factor (No. Values)
K-Ca + Pitt No. 8 Franklyn Char	268.7 64.4	$2.11\ 10^{10}$	0.996 (5)
K-Ca + Pitt No. 8 Franklyn Demineralized	263.2 63.1	$2.22\ 10^{10}$	0.986 (5)
K-Ni + Pitt No. 8 Franklyn Char	225.6 54.1	$4.90\ 10^{9}$	0.9098 (4)
K-Ca + Rosebud Char Demineralized	240.9 57.8	$2.22\ 10^{9}$	0.977 (6)
K-Ca + Rosebud Char	202.2 48.6	$3.61\ 10^{9}$	

3) STEAM GASIFICATION OF COALS

a) Kinetics

Samples of three coals were obtained from IGT. These are the parent coals of the chars which have been used in earlier work. They comprise a subbituminous (Rosebud) and two bituminous coals (Ohio Pitt #8 and Kentucky #13). An analysis of these coals is given in Table 7.

The three coals were subjected to steam gasification at 640°C both in the absence of and in the presence of K-Ca-O catalyst. When the catalyst was used, it was impregnated on the coal by an aqueous nitrate solution containing equimolecular amounts of K and Ca. The procedure used and the nitrate decomposition treatment were the same as previously described for chars and graphite.

In the absence of catalysts no gasification occurred except for an evolution of light hydrocarbons (devolatilization) during the heat-up period. This was most pronounced for the subbituminous Rosebud coal.

In the presence of catalysts, gasification of all three coals was quite rapid and much faster than that of the corresponding chars, which in turn gasified better than graphite. Complete (100%) gasification of all coals was achieved at 640°C. The subbituminous Rosebud coal gasified better than the bituminous coals.

Figure 24 plots the catalytic gasification of Rosebud coal at two temperatures, 580 and 640°C. The gasification occurring at the lower temperature is essentially only a devolatilization. However, while in the absence of catalysts the products of this devolatilization were mostly light paraffins and aromatics, in the presence of catalyst a majority of the products consisted of H_2 and CO_2, indicating that the catalyst has steam reforming activity at this low temperature.

For all the coals there is some devolatilization while heating up and before actual carbon gasification occurs. This explains why carbon

Table 7. Proximate, Ultimate, and Inorganic Chemical Analyses of Coals Used in Gasification Tests (Data supplied by I.G.T.)

Seam Mine	OH Pitt #8 Franklin 125	KY #13 Ken #13	Rosebud Rosebud
Proximate Analysis, wt%			
Moisture	2.5	9.8	23.1
Volatile Matter	38.6	32.2	28.5
Ash	7.5	7.3	11.3
Fixed Carbon	51.4	50.7	37.1
Total	100.0	100.0	100.0
Ultimate Analysis, wt% (dry basis)			
Ash	7.68	8.08	14.66
Carbon	74.47	73.74	62.76
Hydrogen	5.24	4.82	4.40
Sulfur	3.21	1.40	1.29
Nitrogen	1.50	1.8	0.99
Oxygen (by difference)	7.90	10.11	15.88
Total	100.0	100.0	100.0
Ash Composition, wt%			
SiO_2	41.6	58.5	48.8
Al_2O_3	20.9	26.9	23.5
Fe_2O_3	31.7	8.1	7.02
TiO_2	1.02	0.87	0.12
P_2O_5	0.07	0.16	0.25
CaO	1.14	0.90	7.16
MgO	0.36	1.21	2.57
Na_2O	0.35	0.24	0.09
K_2O	0.98	2.94	0.36
SO_3	1.00	0.80	9.91
Total	99.2	100.6	99.78
Ash Content (as ashed for analysis of ash, dry basis)	7.7	8.2	--
Basic Ash Constituents, wt%	35.2	13.4	19.2
Dolomite Ratio, wt%	4.3	15.8	56.6
SiO_2/Al_2O_3 Ratio	2.0	2.2	2.1
Forms of Sulfur, wt% (dry basis)			
Pyritic	2.37	0.40	0.76
Sulfate	0.21	0.10	F0.015
Organic	0.97	1.03	0.52
Total	3.56	1.53	1.28

Forms of Iron (dry basis)	wt%	%Fe	wt%	%Fe	wt%	%Fe
Pyritic	2.07	96	0.35	70	1.32	62[a]
HCl-Soluble	0.08	4	0.15	30	0.12	6
Total	2.15	100	0.50	100	2.13[a]	100
Acid-Insoluble	<0.10	--	<0.10	--	0.69	--
Pyritic, % of total Fe[b]	97		54		--	

[a] Based on total iron including 0.69 wt% HCl-insoluble

[b] Of 1/4-inch-top-size coal after storage.

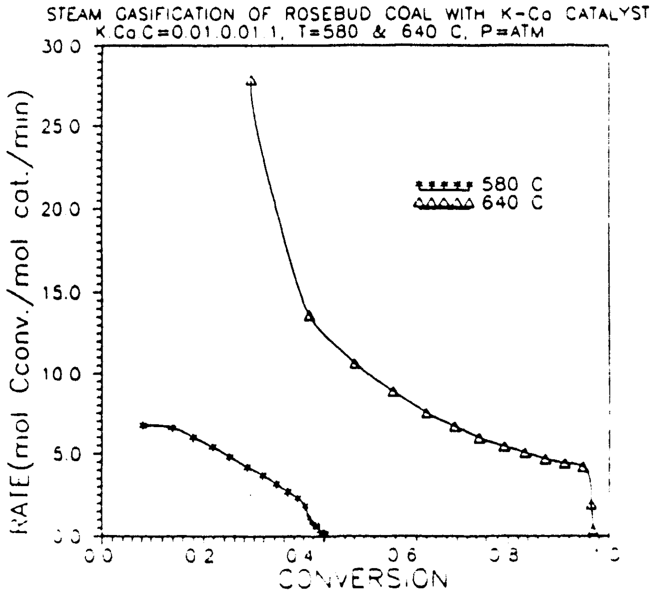

Fig. 24 Catalyzed steam gasification of subbituminous (Rosebud) coal at two temperatures.

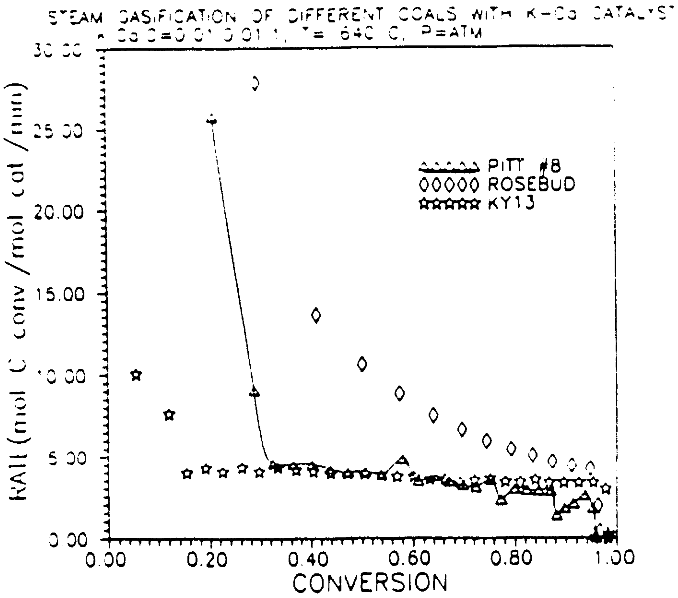

Fig. 25 Comparison of the rate of catalyzed steam gasification of bituminous and subbituminous coals.

gasification starts only after 10-25% conversion. Figure 25 presents a comparison of the three coals investigated. The two bituminous coals have the same steady gasification rate except for the devolatilization part. The Ohio Pitt #8 has more volatiles in the presence of steam and catalyst than Kentucky #13. This is somewhat different than the volatile matter content given in Table 6 determined in the absence of steam. The subbituminous Rosebud coal shows a better gasification rate than the bituminous coal.

Figure 26 presents percent conversion of the three coals as a function of time. It shows that the Rosebud subbituminous coal is fully gasified in about one-half the time required for the bituminous coals. Figure 27 demonstrates the advantage of a K-Ca catalyst over K alone for the Rosebud coal. Complete gasification is achieved with K-Ca in about 16% of the time required for K.

A comparison of the Rosebud coal with the Rosebud char (gasification of this was reported in an earlier section of this report) is shown in Figures 28 and 29. The coal gasifies at a much higher rate than the char. Complete carbon conversion occurs in 450 min for the coal, 900 min for the char (Figure 28).

The distribution of gases produced from the coals in the presence of K-Ca is illustrated in Figure 29, plotting conversion vs. molar fractions of gases on a logarithmic scale. Hydrogen and carbon dioxide production is steady at a 2:1 ratio over the whole range of conversions while CO, CH_4 and C_2 production gradually decline. CO production amounts to about 2%, CH_4 to 0.5% and C_2 to less than 0.01%. Rosebud coal gives slightly higher yields of CO, CH_4, and C_2 than the other coals.

While Figure 29 shows gas distribution after devolatilization, Figure 30 includes the devolatilization period. During this period (first 30% of conversion) larger amounts of CH_4 and C_2 hydrocarbons (and somewhat higher amounts of CO) are produced. It is remarkable, however, that the major products are again H_2 and CO_2, indicating that steam reforming of paraffins and aromatics must occur.

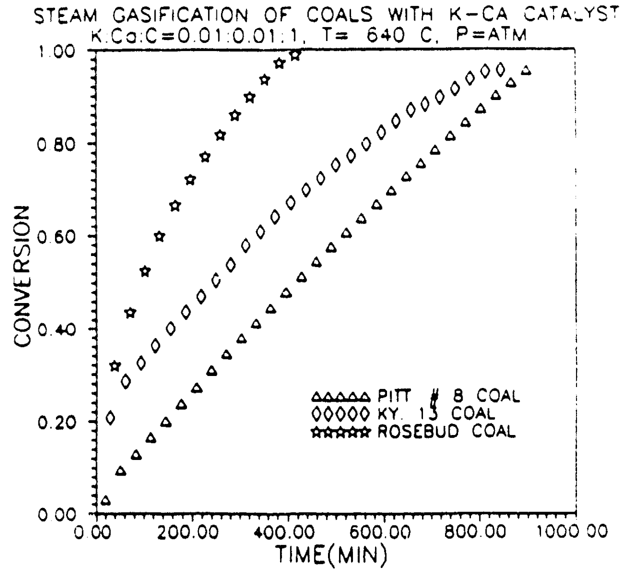

Fig. 26 Comparison of the conversion of bituminous and subbituminous coals during catlyzed steam gasification.

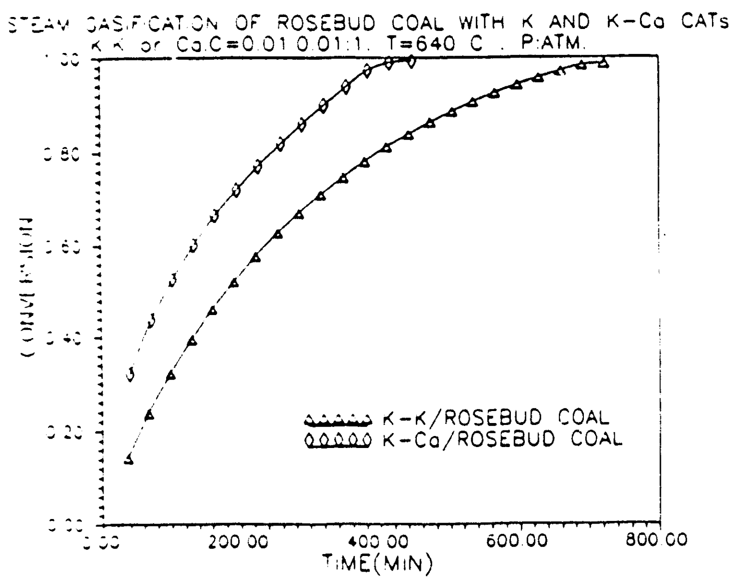

Fig. 27 Comparison of K-Ca-O catalyst with potassium alone for the steam gasification of subbituminous coals.

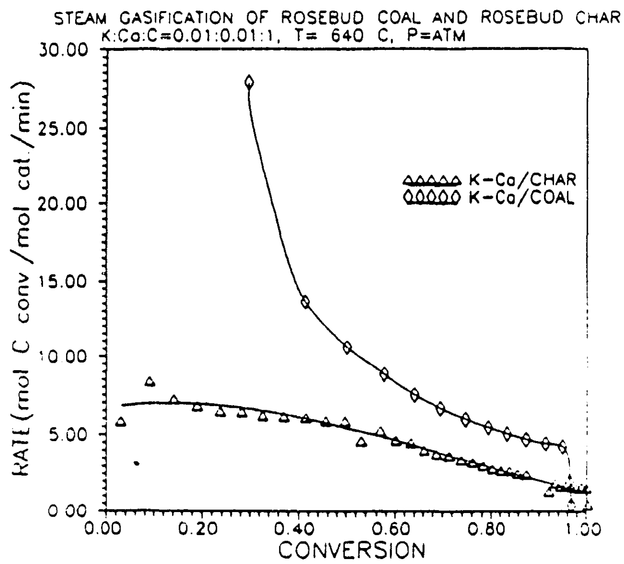

Fig. 28 Comparison of the rates of catalyzed steam gasification of a subbituminous coal and of the char derived from it.

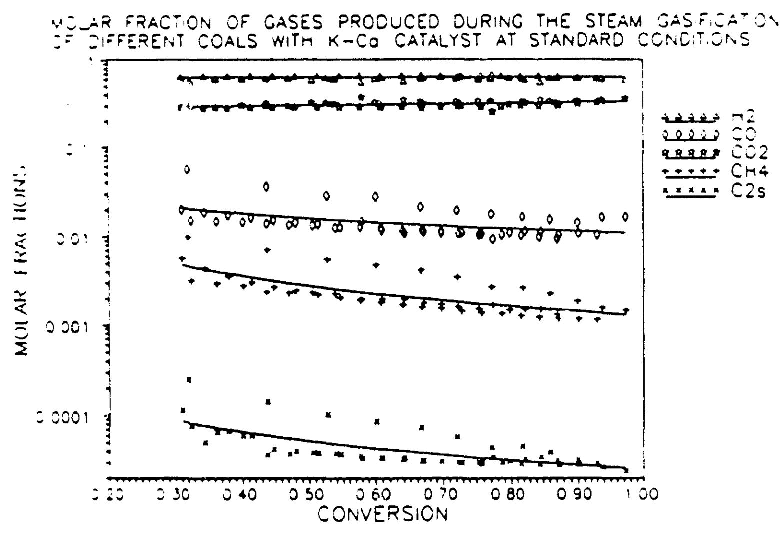

Fig. 29 Gas distribution during catalytic steam gasification of coals, excluding volatilization period.

b) Catalyst Modifications.

In order to test the necessity of using relatively expensive potassium as a catalyst component, gasification of the Ohio Pitt #8 coal was undertaken employing a Na-Ca catalyst. The proportions of Na in the catalyst were the same as in the case of K-Ca. As shown in Figure 31, the Na-Ca catalyst was at least as active as K-Ca, increasing the likelihood that the catalyst may be used on a throw-away basis.

A catalyst comprising cesium-calcium was also tested. It exhibited almost no gasification activity. The reason for this may lie in the large atomic size of the Cs relative to Ca.

Negative results were obtained when it was attempted to improve the K-CaOx catalyst by incorporating a third oxide component. A standard $KCaO_x$ impregnated Rosebud coal was further impregnated with $Ni(NO_3)_2$ solution (Ni=1/2 of molar K-Ca content) and then dried and decomposed by stadard procedure. The thus prepared coal was less active than the $K\text{-}CaO_x$ impregnated coal, perhaps because the Ni blocked access to some of the $KCaO_x$ sites.

Figure 32 extends earlier work comparing the relative activity of $KNiO_x$ and $KCaO_x$ catalysts from chars to coals. Ohio Franklin Pitt #8 coal was impregnated with $KCaO_x$ and with $KNiO_x$. Just as in the case of chars, $KCaO_x$ was more active in gasifying the coal than was $KNiO_x$. This result further confirms earlier conclusions that $KCaO_x$ is more active than $KNiO_x$ for high rank coals.

Impregnation of Franklin Pitt #8 coal with other alkali and/or earth alkali oxides was undertaken. It was previously shown that Na could be substituted for K without adverse effects. Using a cesium-barium nitrate aqueous solution for impregnation and following the standard drying and decomposition procedure, the $CsBaO_x$ catalyst behaves similarly to $KCaO_x$.

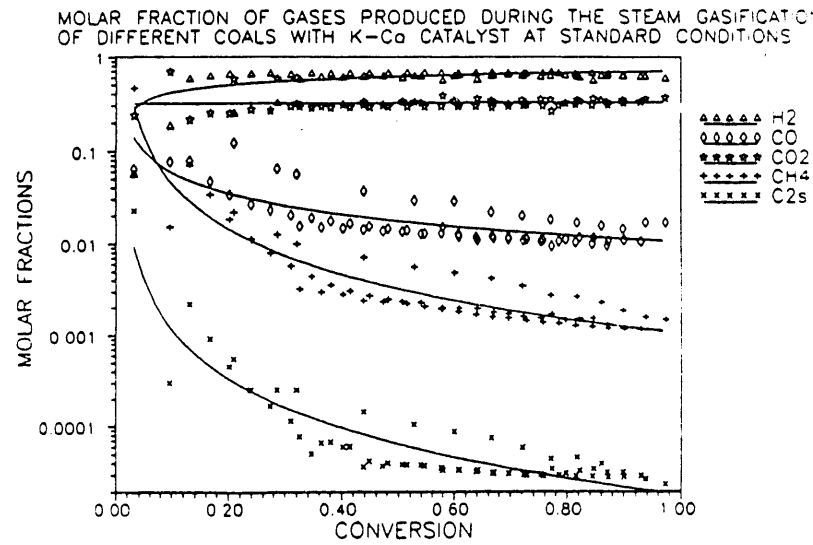

Fig. 30 Gas distribution during catalytic steam gasification of coals, including volatilization period.

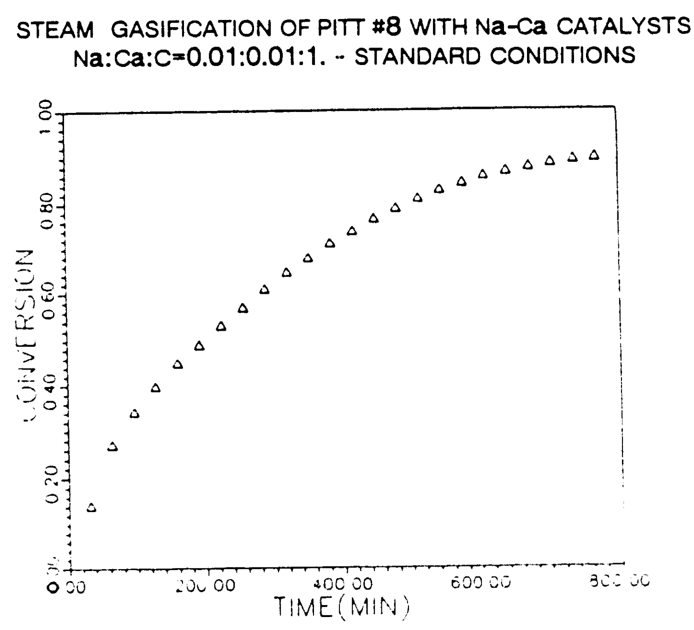

Fig. 31 Conversion of a bituminous coal in the catalytic steam gasification using a sodium-calcium oxide rather than the potasssium equivalent.

Coal samples previously used in this work had been obtained from IGT and had been stored there and in our laboratory under conditions which may have led to a surface oxidation of the coal. Samples of "Premium" coals were obtained from the coal bank at Argonne National Laboratory which were mined, crushed and stored under atmosphere controlled conditions and which can be assumed not to have been contaminated by atmospheric oxygen. The Pitt #8 Franklin "Premium" coal has been gasified under our standard conditions and compared with the gasification of the same coal which had been stored without precautions. Figure 33 presents a time vs. conversion plot for the "Premium" coal in the absence of catalyst and for both coals in the presence of $KCaO_x$ catalyst. The "Premium" coal in the absence of catalyst showed only very minor gasification characteristics at standard conditions. The two coal samples impregnated with 1% $KCaO_x$ behaved very similarly with a slight advantage for the air exposed coal. It is concluded that exposure to air is not detrimental to the gasification of coals and that no special precautions have to be taken in preparing the coals for gasification.

4) STEAM GASIFICATION OF PETROLEUM COKES

In an attempt to determine the effect of metals in the substrate on catalytic gasification, a series of petroleum cokes with different compositions and metal contents were gasified. The approximate composition of the cokes is shown in Table 8. It is apparent that there are wide variations of sulfur content (0.6-8%), in metal content (116-4011ppm), and metal distribution between Ni, V, and Fe. Coke samples were supplied by Mobil Research and Development Corporation.

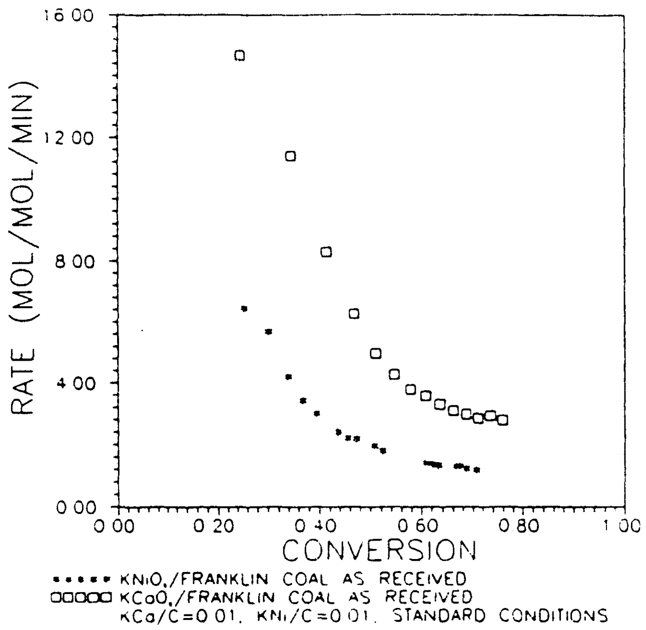

Fig. 32 Comparison of Ni-K-O_x and Ca-K-O_x catalysts for the steam gasification of a bituminous coal.

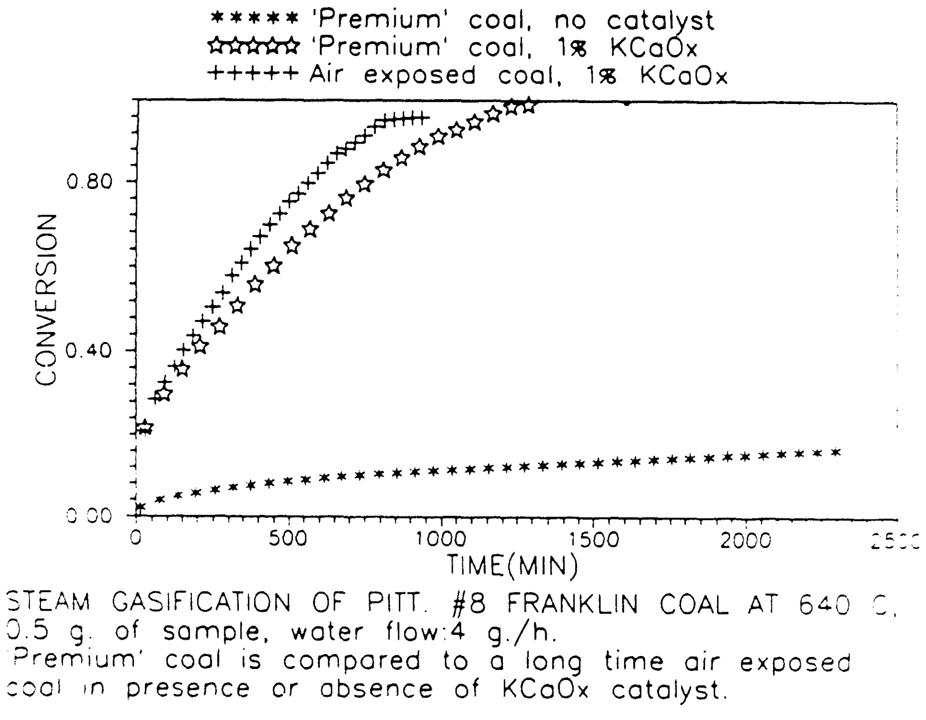

Fig. 33 Comparison of steam gasification of a fresh bituminous coal with a surface oxidized coal.

Table 8
Analytical Data for Petroleum Coke Samples

Number	%C	%H	%O	%S	ppmNi	ppmV	ppmFe	ppm Total Metals
1	87.6	3.55	2.39	2.55	707	1090	832	2629
2	86.1	3.61	1.48	6.12	422	1919	1166	3507
3	92.8	3.90	1.41	0.55	147	20	3844	4011
4	88.6	3.76	0.97	5.13	223	657	209	1089
5	87.7	3.18	1.07	5.62	334	809	536	1679
6	90.9	4.0	0.42	4.45	12	5	99	116
7	86.6	3.35	0.93	7.96	175	509	178	862

The cokes were impregnated with 1 mol% of a catalyst comprised of equimolar calcium and potassium oxides for a Ca+K/C atomic ratio of 0.04. Gasification was at 600° C using 8cc water per gram of carbon per hour at atmospheric pressure. Results of the gasification of several of the cokes are shown in Figure 34.

It is apparent from Figure 34 that all but one of the cokes tested were easily gasified in the presence of catalyst and that their gasification rate was somewhere between those of subbituminous and bituminous coals. The relatively poor performance of coke #1 is unexplained and cannot be attributed to metals, sulfur or high carbon content, since these (as shown in Table 7) are not essentially different from some of the other cokes. This particular coke behaves more like graphite. It is also the most aromatic coke.

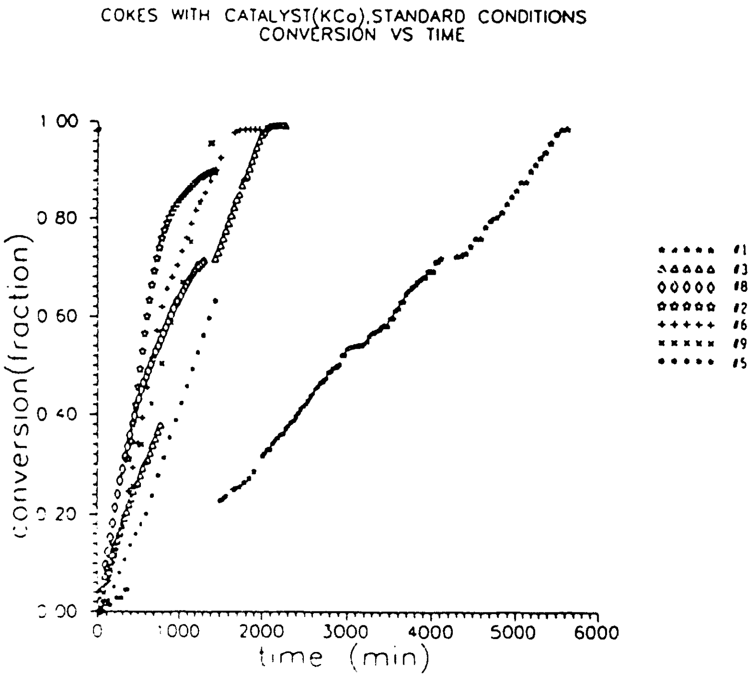

Fig. 34 Catalytic steam gasification of petroleum cokes. Dissociate water at reaction temperature

VII CONCLUSIONS

- Good steam gasification catalysts must:
  - Wet the carbonaceous material
  - Attack by edge recession
  - Dissociate water at reaction temperature
- The catalytic gasification mechanism involves water dissociation forming H_2 and carbon surface oxygenates (lactones; quinones) and C-CO bond breakage, forming CO_2. The carbon-carbon bond breakage is the rate limiting step..
- The mechanism of catalytic gasification of graphite, chars and coals is the same as evidenced by their same activation energy.
- Gasification products are hydrogen and CO_2.
- K-CaO_X (or NaO_X-CaO_X) catalysts equal KO_X-NiO_X catalysts.

- K-CaO_x catalysts are not poisoned by S, while K-NiO_x is poisoned by organic sulfur.
- K-CaO_x catalysts have good gasification rates at 800-900K (527-630°C) giving H_2 and CO_2 from lignite > subbituminous > bituminous chars or coals.
- Coals gasify at better rates than their chars which gasify better than graphite.
- Petroleum cokes can be catalytically gasified at rates very similar to those of coals.
- The catalysts may be used on a throw-away basis.

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IX FUTURE WORK

1. Investigate ternary compounds as catalysts for steam gasification. In particular, calcium-nickel-potassium oxide should be interesting.

2. Determine the effect of pressure on steam gasification with binary or ternary catalysts.

3. Determine the role of transition metals in the dissociation of C-C bonds as a rate determining step. Search for superior catalysts for dissociation of aromatic C=C bonds using model aromatic compounds. Study the role of valence in C-C dissociation and the process conditions which can stabilize the transition metal (or oxide) in the active state.

4. Study the reaction mechanism of the interaction between water, -OH groups and the K-O-C complex. Is there a liquid insertion step?

X APPENDIX

Publications of work performed under this contract

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