

Gasification of Graphite with Steam below 900 K Catalyzed by a Mixture of Potassium Hydroxide and Transition Metal Oxide

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KOH coadsorbed with a transition metal oxide is able to catalyze the gasification of graphite with steam at temperatures as low as 860 K. Nine different KOH-transition metal oxide mixtures were studied. The most active co-catalysts found so far are KOH-NiO and KOH-Fe₂O₃. The reaction rate was monitored at 860 K for over 24 turnovers. The major products of the gasification process are H₂ and CO₂ with either catalysts. CH₄ and CO are also detectable in small concentrations.

INTRODUCTION

Gasification of carbonaceous solids with steam is an important route for the production of gaseous fuels. H₂, CO, CH₄, and CO₂ are the principal products in this process. Since various reactions with very different changes in free energy (ΔG_{298}) are involved (see Table 1), the product distribution at equilibrium is sensitive to temperature. The production of CH₄ and CO₂ is almost thermoneutral (Eq. (1) in Table 1) and methane may be produced at temperatures below 500 K. The reactions that produce H₂, CO, and CO₂, on the other hand, are endothermic (Eqs. (2) and (3) in Table 1) and therefore the formation of these gases from graphite and steam requires high temperatures (above 800 K). Secondary reactions involving these gas products can also occur: CH₄ can decompose, by reaction with water, to produce H₂, CO, and CO₂ (Eqs. (4) and (5) in Table 1), CO and CO₂ can interconvert by reaction with steam (Eq. (6) in Table 1), and CO can dispropor-

tionate to carbon and CO₂ (Eq. (7) in Table 1).

Even though thermodynamic considerations suggest that the gasification of graphite with steam is feasible below 1000 K, when steam is passed over a clean graphite sample, no significant gas evolution occurs until temperatures above 1400 K are reached (1). The presence of a catalyst, therefore, becomes indispensable to gasify graphite with steam at temperatures below 1000 K.

It is well accepted that alkali and alkali earth hydroxides and carbonates are effective catalysts for this process (2, 3). The catalytic action of alkali hydroxides in gasifying graphite with water vapor above 950 K has been well documented (4, 5). Our studies have shown that in the lower temperature range of 800-950 K, KOH is a reactant along with graphite to produce CH₄ and H₂ upon introduction of steam by a stoichiometric reaction. Gas production ceases after 0.5 moles of H₂ is produced per mole of KOH present (5, 6).

The results presented in this paper show that transition metal oxides coadsorbed with potassium hydroxide on graphite catalyze the gasification of graphite with steam

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TABLE 1

Change in Free Energy (ΔG_{298}) Involved in the Production of Several Gases from Graphite and Steam and for Several Possible Secondary Reactions

Equation number	Reaction	$\Delta G_{298 \text{ K}}$ (kcal/mol)
(1)	$\text{C}_{(\text{graphite})} + 2\text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CH}_4_{(\text{g})} + \text{CO}_2_{(\text{g})}$	2.89
(2)	$\text{C}_{(\text{graphite})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_{(\text{g})} + \text{H}_2_{(\text{g})}$	21.85
(3)	$\text{C}_{(\text{graphite})} + 2\text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_2_{(\text{g})} + 2\text{H}_2_{(\text{g})}$	15.02
(4)	$\text{CH}_4_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_{(\text{g})} + 3\text{H}_2_{(\text{g})}$	33.98
(5)	$\text{CH}_4_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_2_{(\text{g})} + 4\text{H}_2_{(\text{g})}$	27.15
(6)	$\text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_2_{(\text{g})} + \text{H}_2_{(\text{g})}$	-6.84
(7)	$2\text{CO}_{(\text{g})} \rightleftharpoons \text{CO}_2_{(\text{g})} + \text{C}_{(\text{graphite})}$	-28.69

at temperatures as low as 860 K. The most active co-catalyst mixtures for this reaction are NiO-KOH and Fe_2O_3 -KOH. The major products are H_2 and CO_2 and the overall reaction is given by Eq. (3) in Table 1. CH_4 and CO are present as minor products.

EXPERIMENTAL

Graphite powder of spectroscopic grade purity and a BET surface area of $30 \text{ m}^2/\text{g}$ was used in these experiments (Ultra Carbon Corp., Type UCP-2, 325 mesh). Graphite was chosen instead of coal to assure that H_2 is formed from the dissociation of water and not from the breaking of C-H bonds of the carbon source.

The catalysts studied in this work were mixtures of KOH and transition metal oxides. They were added to the graphite by impregnation to incipient wetness. Separate solutions of KOH and a water-soluble transition metal salt with the same molar concentration were used to deposit the desired loading of catalyst. Nickel, iron, copper, cobalt and chromium nitrate, zinc and manganese sulfate, ammonium metavanadate, and ammonium molybdate were used to deposit the respective metal oxide onto graphite.

A 0.5-g graphite sample was impregnated with 0.5 ml of the KOH and the metal salt solutions. The sample was then dried in an oven at 393 K for 10 min, placed in the reactor and heated under He for half an hour at a temperature high enough to de-

compose the metal salt and form the oxide. The gas flow over the sample was switched from He to steam and the rate of gas formation and product distribution for the gasification of graphite with steam was followed at different temperatures.

The activity of Ni metal as a catalyst was also studied. A catalyst preparation procedure similar to the one described previously was used. The only difference is that the salt used to load the nickel ($\text{Ni}(\text{NO}_3)_2$) was decomposed under He atmosphere at 1073 K in order to favor the formation of Ni in the metallic state by reaction with graphite (7).

Experiments were performed either by increasing the furnace temperature at a rate of 5 K/min and following the evolution of gas products (temperature-programmed experiment) or by setting the furnace temperature at a constant value and waiting until the rate of gas production became stable (isothermal experiment). The rate of gas production in a temperature-programmed experiment was obtained by measuring the total amount of gas collected in 2 min. This rate was then assigned to the highest temperature achieved during the collecting period. The rates of gas production obtained with either method agreed within 10%.

The apparatus used in these experiments has been described in detail in a previous publication (4). Briefly, it consisted of a steam generator, a tube furnace and a gas collection system, as shown in Fig. 1. Gas production rates were measured using a calibrated burette and gas products were analyzed by gas chromatography using a thermal conductivity detector and He as the gas carrier.

RESULTS

The catalytic activity of different KOH/metal oxide mixtures on the gasification of graphite with steam was evaluated as a fraction of temperature. The rate of gas production for samples with a KOH/C molar ratio of 0.04 and KOH/metal oxide molar ratio of 1.0 was studied in a tempera-

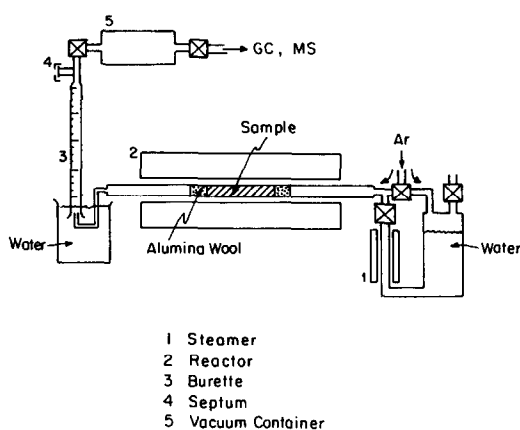


FIG. 1. Diagram of experimental apparatus.

ture-programmed experiment. Figure 2 (curve A) shows the results of gasification with steam using a mixture of KOH/NiO adsorbed on graphite. The rate of gas production increased steadily with temperature. No initial gas burst was observed, in contrast with the case of KOH only on graphite, where the reaction stops after 0.5 mol of H_2 is produced per mole of KOH deposited (6) (Fig. 2, curve B). Figure 2 (curve C) shows that the rate of gas production was very slow when only NiO was deposited on graphite.

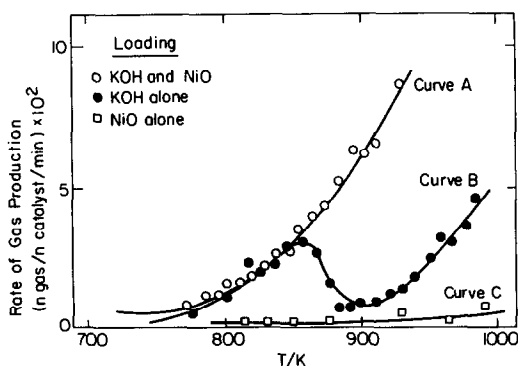


FIG. 2. Plot of the temperature dependence of the gas production rate during a temperature-programmed experiment at a heating rate of 5 K min^{-1} . The open circles (curve A) correspond to NiO and KOH codeposited on graphite, the full circles (curve B) to KOH deposited alone, and the open squares (curve C) to NiO deposited alone. In curves A and B the K/C ratio is 0.04. In curves A and C the Ni/C ratio is 0.04.

The nine different KOH-transition metal oxide mixtures showed the same behavior, although the rate of gas production changed from system to system. Figure 3 shows the rate of gas production at 900 K and the activation energy for the gasification of graphite with steam of all the mixtures studied. NiO-KOH and Fe_2O_3 -KOH coadsorbed on graphite showed the highest activity. For this reason, these mixtures were studied in greater detail.

Isothermal experiments between 700 and 1000 K 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 were 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 . The overall reaction is then given by Eq. (3) in Table 1. Although some CO was produced above 900 K, the amount was one order of magnitude less the amount of CO_2 produced. These results strongly contrasted with the CO/CO_2 molar ratio calculated at equilibrium conditions

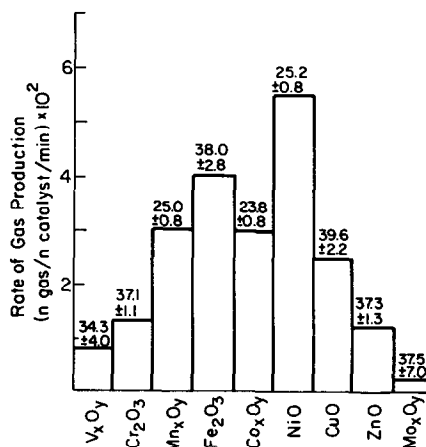


FIG. 3. Rate of gas production at 900 K obtained for the nine transition metal oxide-KOH catalysts studied. The numbers above each column are the activation energies (in kcal/mol) obtained from temperature-programmed experiments. The transition metal oxide mixed with KOH appears below the corresponding column. Metal oxide/KOH = 1; KOH/C = 0.04.

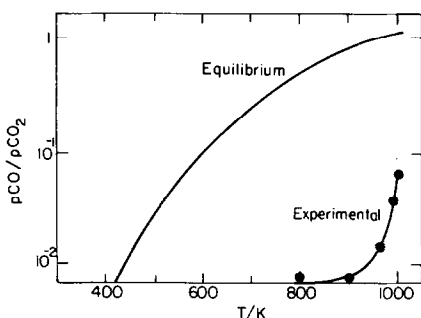


FIG. 4. Ratio of pressure of CO to pressure of CO₂ as a function of temperature. Top: ratio expected at equilibrium conditions when Eqs. (2) and (3) in Table 1 are considered. Bottom: full circles correspond to the values obtained in a temperature-programmed experiment using KOH–NiO as a catalyst.

when reactions (2) and (3) were considered (see Fig. 4). Below 900 K, CH₄ was produced as a minor constituent and its fraction in the gaseous products decreased with time. At the beginning of the gasification process, the CH₄/H₂ 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 859 K up to a graphite conversion of 25%. The results are shown in Fig. 5 (curve A). Assuming that the overall reaction was given by Eq. (3) in Table 1, a turnover number was defined as moles of H₂ produced (or two times the moles of CO₂) divided by two times the moles of catalyst. In the case of KOH–transition metal oxide catalysts, 1 mol of catalyst is defined as 1 mol of KOH plus 1 mol of transition metal oxide. A discussion about the criteria used for choosing this definition of turnover number will be given later (see Discussion). Figure 5 (curve A) shows, then, 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. 5, curve C). It should be recalled from Fig. 2, that when NiO only was present as a catalyst on

graphite, no gas production was obtained at this temperature.

When KOH and Fe₂O₃ were codeposited on graphite, the results obtained were similar to the case when codeposited KOH and NiO was used. Isothermal experiments at 859 K with Fe₂O₃ 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. (For comparison of the rates, see Fig. 3.) The major products were H₂ and CO₂ with a H₂/CO₂ molar ratio of 2.0 ± 0.5 . As in the case of NiO–KOH, the net reaction was given by Eq. (3) in Table 1. When Fe₂O₃ is adsorbed alone, no gas production is obtained in a temperature-programmed experiment until temperatures above 1100 K were employed.

The catalytic activity for the gasification of graphite with steam of K₂CO₃–NiO coadsorbed on graphite was studied in a temperature-programmed experiment. The rate of gas production and product distribu-

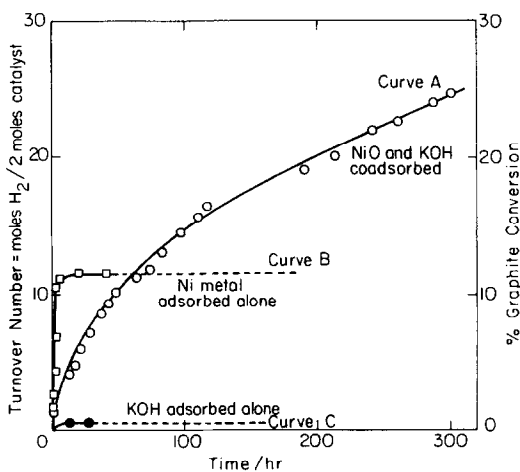


FIG. 5. Turnover number as a function of time for isothermal reactions at 860 K. The open circles (curve A) correspond to NiO–KOH codeposited on graphite, the open squares (curve B) to Ni metal deposited alone, and the full circles to KOH deposited alone on graphite. In curves A and B the ratio of Ni/C is 0.01. In curves A and C the ratio C/K is 0.01.

tion was identical, within experimental error, to the case of KOH/NiO.

The activity of Ni metal adsorbed on graphite was also studied. A temperature-programmed experiment (Fig. 6) showed that Ni metal was active at much lower temperatures than when using NiO-KOH as a catalyst. Arrhenius plots (Fig. 7) showed that the activation energies in the two cases were similar ($E_a = 25.2 \pm 0.8$ kcal/mol for KOH-NiO and $E_a = 23.1 \pm 2.6$ kcal/mol for Ni metal) and much lower than in the case of KOH only deposited on graphite ($E_a = 41.7 \pm 1.3$ kcal/mol). The Ni metal catalyst, however, deactivated rapidly. Figure 5 (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. 5), 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. In both cases the overall reaction was given by Eq. (3) in Table 1.

As was mentioned before, the Ni metal catalyst was prepared by decomposing $\text{Ni}(\text{NO}_3)_2$ over graphite at 1073 K under a

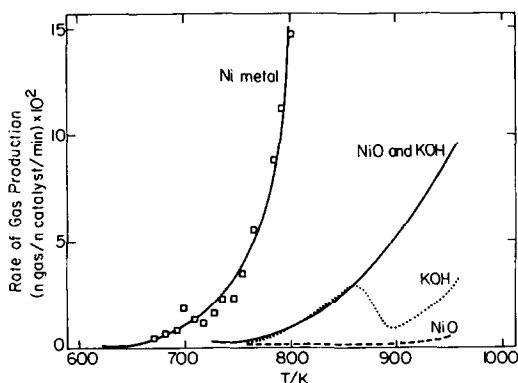


Fig. 6. Plot of the temperature dependence of the gas production rate during a temperature-programmed experiment at a heating rate of 5 K min^{-1} . The open squares correspond to Ni metal deposited on the graphite surface. The ratio Ni/C is 0.04. The plots for KOH, KOH + NiO, and NiO shown in detail in Fig. 2 are included for comparison.

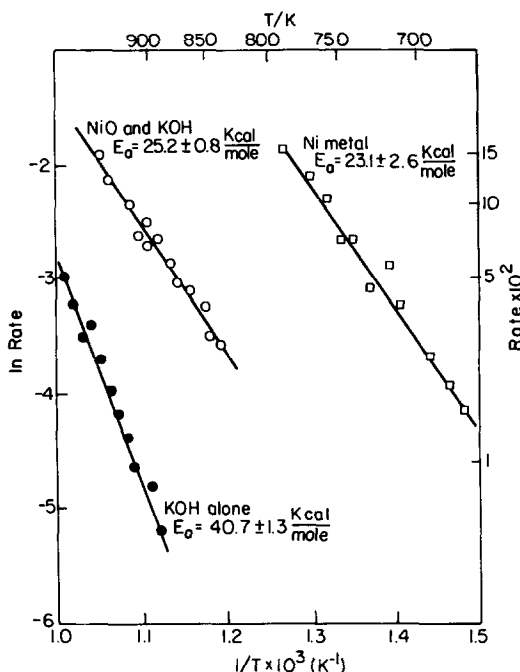


Fig. 7. Arrhenius plots of the temperature dependence of the gas production displayed in Fig. 2 (curves A and B) and in Fig. 6.

He atmosphere. Several authors have reported that Ni catalysts prepared under those conditions remain in the metallic state, even in the presence of steam, due to a redox reaction with graphite (7). When the $\text{Ni}(\text{NO}_3)_2$ was decomposed at 1073 K in the presence of KOH, a temperature-programmed experiment gave similar results to those obtained with KOH-NiO ($\text{Ni}(\text{NO}_3)_2$ decomposed at 673 K in the presence of KOH).

Blank experiments were carried out adsorbing KOH-NiO on silica and passing steam through the sample in a temperature-programmed experiment. No gases were collected up to 1273 K.

DISCUSSION

The results presented in this paper 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 860 K. This temperature is 100 K 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 (specially Fe_2O_3) were also effective when codeposited with KOH. The activity of these mixtures as catalysts for the gasification process below 900 K can not 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 900 K, 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. Our results show that nickel converted to the metallic state when $\text{Ni}(\text{NO}_3)_2$ was decomposed on graphite in a He stream at 1073 K (see Experimental) is an excellent catalyst for this process, while NiO, produced from decomposition of the same salt at 673 K, is completely inactive. Similar results have been found by other authors. McKee (8) found that iron is only effective for the gasification of graphite with steam if it is present in the metallic state. Walker *et al.* (9) found the same behavior for iron when CO_2 was used instead of H_2O . Yamada *et al.* (10) 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 1000 K. The same activity was found when $\text{Ni}(\text{NO}_3)_2$ was decomposed at either 673 or 1073 K in the presence of KOH. Since at 673 K 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 7 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 5 shows that the Ni metal catalysts 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.

In this reaction, both the reactant and the catalyst are solid. It is difficult, then, to decide what active site concentration should be used in the definition of the turnover number. Since there is no activity for the gasification of graphite with steam at 900 K in the absence of a catalyst, and the percentage of graphite conversion studied was always below 25%, it was decided that the concentration of catalyst sites was the important factor in the rate of reaction. From our results, it is not clear what is the nature of this site. For this reason, it was considered that each molecule of catalyst was equally active in the process. One turnover number was then defined as the moles of H_2 produced divided by two times the moles of catalyst loaded. In the case of the KOH–transition metal oxide mixture, 1 mol of catalyst was considered as 1 mol of KOH plus 1 mol of transition metal oxide. This definition of one turnover number gives a lower limit for the efficiency of a given catalyst, since it is considering that all the molecules adsorbed on the surface are equally active for the reaction, which is not likely to be the case.

The formation of a stable compound by chemical reaction of the transition metal oxide with KOH could also explain the co-

operative 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 (11, 12).

When the total activity of the KOH–NiO and Ni metal catalysts were compared, the higher turnover number obtained with the first catalyst can be due to one of two factors. Either the number of active sites in the KOH–NiO catalyst is larger and therefore by dividing by the total loading in both cases, we obtain an artificial higher turnover, or the number of active sites is the same in both cases but the resistance to poisoning of the KOH–NiO catalyst is higher. Since the initial activity of the Ni metal is higher, we do not expect the number of active sites of the KOH–NiO catalyst to be higher. Therefore, we propose that the higher total activity of the KOH–NiO catalyst is due to its higher resistance to poisoning.

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 900 K. 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 (13) and have found improvements over the performance of K_2SO_4 alone. A similar situation is found in the industrial stream reforming catalyst, where K_2CO_3 is added to nickel to avoid its poisoning from encapsulation by a carbon layer (14). On the other hand, Wigmans and Moulijn (15) did not find evidence for interaction between K_2CO_3 and Ni metal for the gasification of carbon with steam at 1075 K. All this suggests that the interaction between KOH and the transition metal oxide depends on the reaction conditions. Further work is being carried out, using surface science techniques, to determine how different reaction conditions affect the oxidation state of the transition metal and its in-

teraction with KOH. Also, even though the high resistance to poisoning of the KOH–transition metal oxide catalyst is gratifying, the reasons for it are not well understood. Work is being carried out to study this effect.

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 were adsorbed on graphite was 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 Moulijn *et al.* (16) when Ni metal was used as a catalyst. They proposed that the CO formed in the gasification reaction disproportionates to form CO_2 and C (Eq. (7) in Table 1) in the presence of Ni metal. Also, CO adsorption and thermal desorption experiments under ultrahigh vacuum conditions carried out in our laboratory (17) indicate that the disproportionation reaction can occur even over a clean graphite surface. The low proportion of CO in the gas products can also be due to the water-gas shift reaction (Eq. (6) in Table 1). This reaction is specially important in the case of iron. The industrial catalyst for water-gas shift reaction is based on Fe_3O_4 , which could also be present in our reaction conditions.

The low proportion of CH_4 in the gas products might be due to steam reforming (Eq. (4) in Table 1), 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 is 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. Our results at present do not give enough information to decide what reaction path is responsible for the product distribution obtained. Surface science studies are being carried out to elucidate this problem.

CONCLUSIONS

The results presented in this work clearly show that KOH and transition metal oxides coadsorbed on graphite are good catalysts for the gasification of graphite with steam at temperatures as low as 860 K. This is due to a cooperative effect between the two catalyst components. Under our conditions of preparation, KOH-NiO and KOH- Fe_2O_3 are the most active catalysts. H_2 and CO_2 are the major products for this reaction. The product distribution is far from equilibrium and thus the kinetics of a surface reaction controls the process.

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