

ALKALI CATALYZED CARBON GASIFICATION

I. NATURE OF THE CATALYTIC SITES

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INTRODUCTION

The published literature regarding the catalysis of gas-carbon reactions by alkali salts spans more than a century.¹ Diverse and sometimes conflicting mechanisms have been proposed to account for the catalytic activity. It is often difficult to make comparisons among the various studies because of differences in temperature range covered, carbon substrate used, and the gas atmospheres employed. The purpose of this study was to unify quantitatively the catalytic effect of potassium salts on the reactions of H₂O and CO₂ with microcrystalline or "amorphous" carbon. These poorly organized carbons are formed from a variety of precursors at temperatures greater than ~600°C. They consist largely of "graphitic" (or trigonally bonded) carbons in small microlayers.² The size of these layers is a function of heat treatment temperature, carbonaceous precursor, and the presence of impurities.

We show that potassium catalyst at one atmosphere and low conversions behaves reproducibly on many of these carbon substrates and in many modes of preparation. Because of this reproducibility and because the alkali dominates the effect of other impurities, this system is in some ways easier to understand than the "uncatalyzed" H₂O-carbon reaction.

EXPERIMENTAL

Most experiments here were performed in a small tube flow reactor at one atmosphere total pressure. The gasification rates were measured under gas compositions far from gas-carbon equilibrium. Most of the rate data are for the H₂O-carbon reaction. Unless stated otherwise, analogous behavior was observed in the CO₂-carbon reaction. Reactivity profiles (instantaneous gasification rates vs. fraction of carbon remaining) generally show constant activity which holds from ~20% to ~70% of total burnoff. We take this steady state rate to represent the characteristic rate of the alkali catalyzed reaction when the system is catalyst limited.

CATALYST LOADING RESPONSE

Fig. 1 shows the dependence of the "steady state" rate on the concentration of alkali catalyst. A wide variety of carbon types was examined with both K₂CO₃ and KOH applied. The K/C ratios for the coal chars are corrected for the loss of potassium in reactions with mineral constituents in the coal, principally to form aluminosilicates.

All the data fall near a linear correlation for this range of catalyst loadings. (The rate eventually saturates, as shown later.) The addition of an incremental amount of potassium produces an equivalent response on a wide variety of carbon

types. Equal numbers of reaction centers are formed for each mole of salt. The dispersion is independent of loading. The "activation" energy is independent of catalyst loading, thus supporting the idea that increasing the catalyst concentration simply increases the number of active sites. The linear correlation gives a turnover rate with respect to potassium atoms of 8.2 hr.^{-1} at these conditions (700°F , $(\text{H}_2\text{O})/(\text{H}_2) = 1$). It is also generally found that there is no major dependence of the reactivity on the methods by which the carbons are catalyzed. Provided there is adequate physical contact, a mixture of carbon and the dry powdered K_2CO_3 gives a sample of roughly equivalent activity to one which has been impregnated by a solution (see shaded points in Fig. 1). This has been noted by others.³ Alternatively, if one attempts to maximize dispersion by ion exchange of potassium onto an oxidized coal⁴, the response does not significantly differ (half shaded points in Fig. 1).

CATALYST SATURATION

The gasification rate saturates at a catalyst concentration which depends on the identity of the carbon substrate. Although the reactivity per site is insensitive to the method of impregnation, the number of catalytic sites on coal char can be controlled to some degree by pretreatment. Fig. 2 shows the rate saturation behavior for Illinois coal catalyzed in three different ways. Curve A resulted from carbonizing the Illinois coal first and then adding potassium catalyst (either KOH or K_2CO_3). Similar reactivity to the previous correlation was produced for samples with K/C loadings below 0.05. Above this loading additional alkali did not produce additional catalytic activity. Curve B in Fig. 2 shows rates for a set of K_2CO_3 solution impregnated Illinois coals. Note that the rate now saturates at a K/C ratio of ~ 0.1 . Curve C results from digesting the coal in concentrated KOH solution and then carbonizing. The hope was to stabilize more catalytic sites during carbonization by reaction of a strong base with the coal. As can be seen, higher rates were achieved than in the previous series. When alkali was washed off this char sample and its loading reduced below 0.1, the gasification rates fell on the linear correlation obtained for all the other carbons in Figs. 1 and 2. It is possible in case A that carbons with larger microlayers - and therefore fewer edge carbons - were able to form in the absence of the alkali salts. However, the saturation limit of a particular carbon can be limited by physical as well as chemical effects. We also show gasification rates for SP-1 graphite for comparison. Very few sites are available on this substrate.

K_2CO_3 is predicted to be the thermodynamically stable salt under gasification atmospheres.⁵ We heated Illinois coal with K_2CO_3 in which the carbonate carbon was labelled with ^{14}C . The evolution of $^{14}\text{CO}_2$ proceeds essentially to completion in 10 minutes at temperatures above $\sim 500^\circ\text{C}$. No ^{14}C was detected in the form of CO or hydrocarbon products. The reaction temperature of 500°C is far below the decomposition or melting temperature of K_2CO_3 . Fig. 3^a shows that the amount of K_2CO_3 which can react with Illinois coal at 700°C is limited. When approximately one potassium atom is present for every 10 carbon atoms in the resultant char, no further CO_2 is liberated from the carbonate. The saturation behavior seen in the K_2CO_3 -carbon reaction is reflected in the gasification rate, shown in Fig. 2^b and 3^b. The parallelism strongly suggests that the complex formed in the K_2CO_3 -carbon reaction is the site of gasification chemistry. Finally, panel 3^c shows that an important reaction step in gasification, the transfer of oxygen to and from the carbon surface, is catalyzed in an identical manner to the gasification rate. The reaction rate was monitored by the appearance of ^{14}CO in $^{14}\text{CO}_2/\text{CO}$ gas mixtures. A similar set of experiments performed in $\text{H}_2\text{O}/\text{D}_2$ and $\text{D}_2\text{O}/\text{H}_2$ mixtures gave similar results. Oxygen exchange rates on catalyzed activated charcoal are included in panel 3^c to show that the oxygen exchange rates are independent of carbon substrate. We will discuss the relative rates of the various elementary steps and their mechanistic implications in the following paper.

The above indicates a unique, reproducible degree of catalyst dispersion in this system. We obtained evidence that the dispersion is very high from poisoning studies of the H₂O-D₂ oxygen exchange reaction. In the absence of CO₂ this reaction proceeds with measurable rates at 300°C. The loading dependence of this reaction rate is analogous to that of oxygen exchange in ¹⁴CO₂/CO mixtures and gasification. We may therefore suppose that the catalyst is in the same state of dispersion upon cooling to 300°C as at 700°C. At 300°C the exchange reaction between H₂O and D₂ can be poisoned by addition of HCl. Figure 4 shows the "titration" of reactivity by HCl on a catalyzed Illinois char sample. The reaction is quantitative - no HCl breakthrough is seen until the exchange activity has been poisoned. At the end point, one HCl molecule is adsorbed for every two potassium atoms. The stoichiometry of the poisoning reaction is independent of loading unless the sample has been saturated with catalyst.

If the poisoned system is heated to temperatures >450°C the species can rearrange to form KCl, which can be seen by X-ray diffraction, and liberate the remainder of the potassium for catalysis. The gasification rate at 700°C is then roughly one-half that of the original sample. When subsequently cooled to 300°C the H₂O-D₂ exchange rate is also one-half the original value. This activity can again be titrated in a similar manner (see Figure 4). Thus the catalyst dispersion based on HCl chemisorption is approximately one-half. The high degree of dispersion achieved by K₂CO₃ accounts for the reproducibility seen here.

Alkali salts of strong acids are much less effective catalysts than the carbonate and other salts of weak acids.^{1b,d} In a thermochemical sense stable anions of strong acids provide a more attractive environment than the carbon surface for the alkali ion. Thus KCl remains as KCl on the carbon surface at K/C ratios below saturation values. This is confirmed by X-ray diffraction of KCl catalyzed samples. Much of the previous work in the literature can be explained in this framework.

CONCLUSION

Active potassium gasification catalysts are highly dispersed on the carbon substrate. We believe that K₂CO₃ reacts with the carbonaceous material to form groups at the edges of the carbon microlayers. These are the sites of the dominant gasification chemistry on amorphous carbons. This self-dispersion explains the reproducibility seen in this system. The relative catalytic activities of other alkali salts can also be rationalized by their propensity to react with the carbon surface. In the following paper, we will discuss the kinetics of the individual gasification reactions in terms of the discrete site picture presented here.

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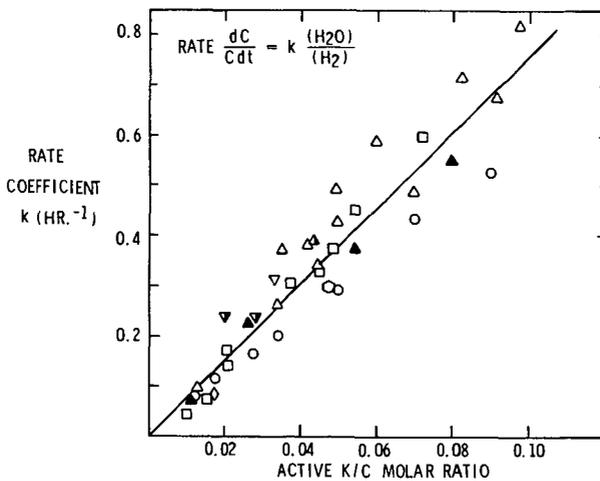


FIGURE 1. DEPENDENCE OF GASIFICATION RATE ON CATALYST LOADING FOR DIFFERENT CARBONS. K/C RATIOS ARE CORRECTED FOR REACTIONS WITH COAL MINERALS. METHOD OF CATALYST IMPREGNATION: OPEN SYMBOLS-SOLUTION-INCIPIENT WETNESS, HALF-SHADED SYMBOLS-ION EXCHANGED, SHADED SYMBOLS-DRY MIXED. Δ ILLINOIS, ∇ WYODAK (WASHED), \square ACTIVATED CHARCOAL, \circ SPHEROCARB, \diamond SPHERON 6, \diamond POLYFURFURYL ALCOHOL COKE

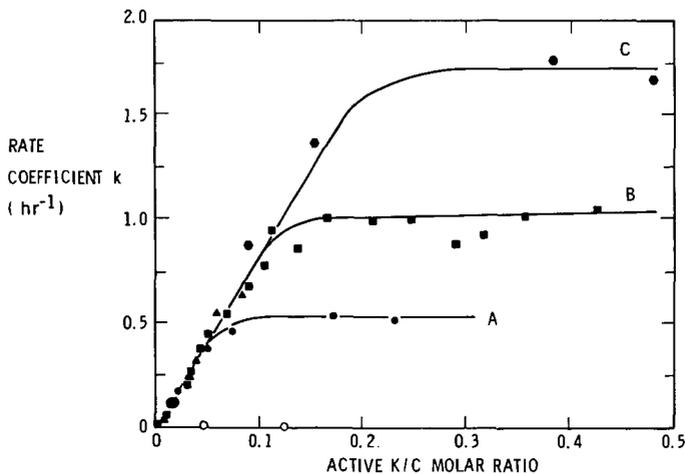


FIGURE 2. GASIFICATION RATE SATURATION CURVES. CURVES A, B, AND C ARE FOR CATALYZED ILLINOIS SAMPLES PREPARED USING DIFFERENT PRETREATMENT TECHNIQUES (SEE TEXT FOR DETAILS). \circ - SP-1 GRAPHITE.

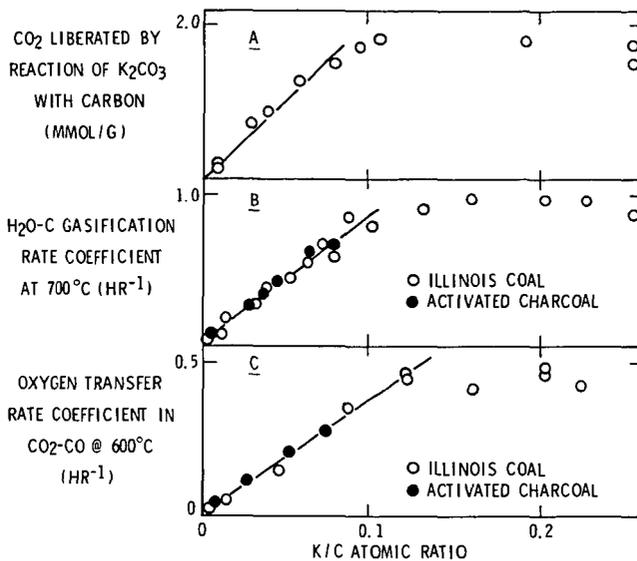


FIGURE 3. COMPARISON OF GASIFICATION RATES WITH K₂CO₃-CARBON REACTION YIELD. ○ ILLINOIS COAL, ● ACTIVATED CHARCOAL

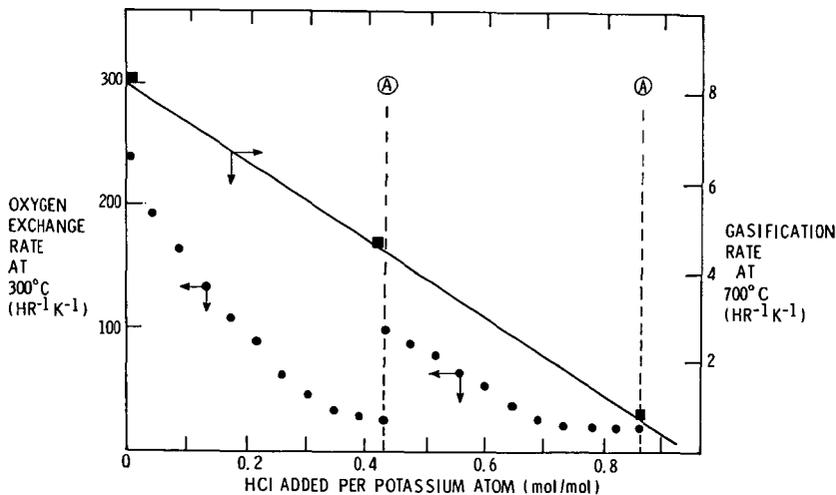


FIGURE 4. HCl POISONING OF POTASSIUM CATALYZED ILLINOIS CHAR. OXYGEN EXCHANGE AT 300°C IS SHOWN AS A FUNCTION OF HCl ADDED. AT POINTS LABELLED (A) THE SAMPLE WAS HEATED TO 700°C AND THE GASIFICATION RATE MEASURED. FOR BOTH RATE MEASUREMENTS, (H₂O)/(H₂, D₂) = 1.