FUEL

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On the high reactivity of American lignite chars

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(Received 18 April 1977)
(Revised 19 September 1977)

Previous studies in this laboratory have shown that there is a wide range of reactivities of coal chars to air and CO_2, depending upon the rank of the precursor coal[1,2]. The most reactive char, produced from a Montana lignite, gasified at a rate roughly 200 times as great as that of a char produced from a low-volatile (Pennsylvania) bituminous coal.

It is instructive now to back off and consider the prime factors promoting high carbon gasification rates — that is, high concentration of active carbon sites, good accessibility of the sites to the reactive gas, and substantial catalysis of the gasification reaction by inorganic impurities[3,4]. Each of these factors can be considered briefly.

Coals are composed of aromatic and hydroaromatic building blocks, containing more or less crosslinks between the building blocks and functional groups at their periphery. Upon their heating to gasification temperatures, functional groups are removed as volatile matter, some crosslinks are broken, and hydroaromatic building blocks are converted first to additional aromatic building blocks and then to small carbon crystallites. Breakage of crosslinks permits improved alignment of the building blocks. Whether the char particles remaining have a more open or less open pore structure than that in the coal precursor depends upon a balance between additional pore volume created by volatile matter release and loss of pore volume caused by enhanced alignment of the planar building blocks. The balance is a function of the rank of the starting coal, maximum heat-treatment temperature, and heating rate to maximum temperature.

The concept of *active sites* on the small carbon crystallites, or those sites most reactive to gasification, is understandable from extensive studies on the reactivity of graphitic carbon[3]. The carbon atoms which are reactive are those located at the edges of the basal planes. The ratio of such sites to the total number of carbon sites in the structure obviously increases as the crystallite (or building block) size decreases.

Once the concentration of active sites in a char is established by the choice of starting coal and heating conditions, it is then of concern as to how well the sites will be utilized in gasification. The concept of *active site utilization* in heterogeneous reactions has been well developed by a number of workers and particularly considered for the gasification of porous particles of carbonaceous solids by Walker and co-workers[3]. The utilization factor, η, varies from zero to one (complete utilization, all active sites are then 'bathed' in the same concentration of reactive gas as that which exists in the main gas stream outside of the particles). It is obviously desirable for η to approach one as closely as is possible and economically feasible. Its value is a balance between the resistance to the inherent chemical rate of the gasification reaction and the resistance to the mass transport rate of the reacting gas into the pores of the carbonaceous particle. The larger the ratio of these two resistances, the larger will be the value of η.

The third factor which has a pronounced effect on gasifi-cation rates is the presence of inorganic impurities in the carbonaceous matrix. Many inorganic impurities are effective *catalysts for dissociating molecular species* into atomic or free-radical species and, thereby, enhancing gasification rates. That is, the rate of gasification of an active carbon site is much more rapid in the presence of atomic oxygen or hydrogen than in the presence of molecular species containing these elements.

Considering the three prime factors affecting carbon gasification, it is now understandable why reactivities of lignite chars are much greater than those of chars produced from high-rank coals. *First*, it has been shown that as the rank of coal decreases the average layer-plane size decreases[5]. For the same heat-treatment temperature, we would expect, then, the average crystallite size of the char to be smaller the lower the rank of the precursor coal. This is also con-sistent with crystallite growth being less the more cross-linking there is between planar regions; low-rank coals have a high density of cross-linking. As a result, the active site concentration should be a maximum in lignite chars.

Second, as the rank of coal decreases, the amount of volatile matter released upon heat treatment generally increases. This results in a progressive increase in porosity within the chars and enhanced accessibility of the reactive gas to active sites. Thus, the utilization of active sites (η) is increased. Increased accessibility to the internal porosity of chars with decreasing rank of coal from which the char is produced is shown dramatically in *Figure 1*, where specific surface areas as measured by N_2 adsorption at 77 K and CO_2 adsorption at 298 K are given. These chars were produced by heating 40 x 100 mesh fractions of the coals to 1000°C in N_2 at a heating rate of 10°C/min. Samples were held at 1000°C for 2 h. The fact that the CO_2 surface areas are much higher than the N_2 surface areas is indicative of molecular sieving, the predominant aperture size in the chars being in the range 4.9 to 5.2 Å in thickness[6].

Third, as seen in *Figure 2*, the calcium content of chars (expressed as CaO) increases sharply as the rank of the pre-cursor coal decreases. Although there is considerable spread of data around the line, the low-rank coals tend to have much more calcium because of ion exchange on carboxyl groups. This fact appears to be generally true for American coals. This results in enhanced reactivity for chars produced from low-rank coals as was previously shown[1,2]. Since the first step in the carbon—steam reaction is the oxygen transfer step, as it also is in the $C—O_2$ and $C—CO_2$ reactions, it is to be expected that calcium also catalyses this reaction. Recent work by Hippo[7] shows this to be the case. The magnesium content of chars also increases sharply as the rank of the precursor coal decreases[8], but studies have shown no correla-tion between magnesium content of chars and char reactivity[1,2]. Recent studies[7], where varying amounts of magnesium were added to a lignite by ion exchange (prior to charring), showed that MgO is a poor catalyst for char gasification in steam and presumably in air and CO_2.
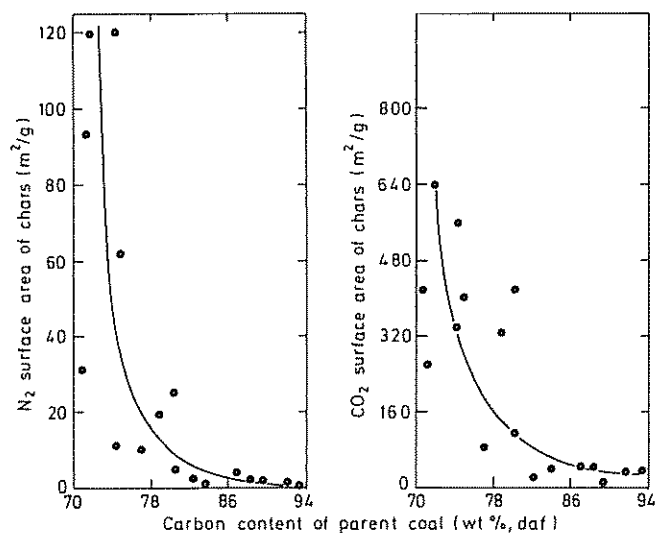
Figure 1 Correlation between the N_2 (77 K) and CO_2 (298 K) surface areas of chars and the carbon content of the parent coals

Figure 2 Correlation between the calcium content of chars and the carbon content of the parent coals

ACKNOWLEDGEMENT

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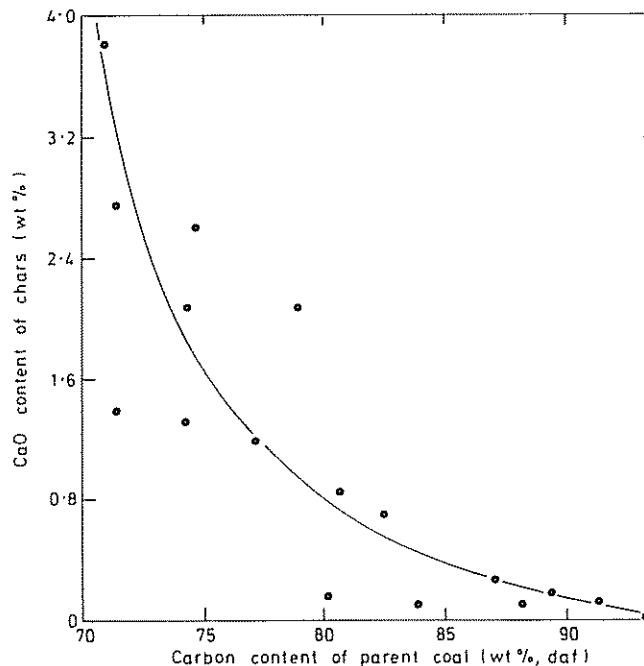4 Walker, P. L. Jr, Shelef, M. and Anderson, R. A., in *Chemistry and Physics of Carbon*, Vol.4 (Ed. P. L. Walker Jr), Marcel Dekker, New York, 1968, p 287
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Catalytic hydrogenation of aromatic compounds, coal, and asphaltenes with Meutterties catalyst (η^3-$C_3H_5Co[P(OCH_3)_3]_3$)

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*(Received 14 March 1977)*

A number of very active homogeneous hydrogenation catalysts have been developed[1]. These might prove useful in the hydrogenation of coal, coal derivatives, or other heavy ends. A recent paper in this journal reported the failure of several of these catalysts to bring about the hydrogenation of coal[2]. We wish to report that the Muertterties catalyst,[1b,c,d] probably the most active hydrogenation catalyst for benzene yet developed, is not capable of catalysing the hydrogenation of coal or asphaltenes.

EXPERIMENTAL

All the organic compounds studied are commercially available. Bruceton coal was kindly supplied by PERC. It was ground (ball mill) to a particle size below 300 mesh U.S., dried in nitrogen at 110°C, and stored under dry N_2. Petroleum asphaltenes were kindly supplied by Exxon

Research and the coal asphaltene was a gift from Mobil.

Since very dry, pure tetrahydrofuran (THF) is critical to the preparation of the catalyst, we list here the steps in its preparation. After drying over anhydrous $MgSO_4$, it was refluxed over $LiAlH_4$ for 48 h. After distillation into a flask containing sodium metal, it was deoxygenated with dry argon and stored in a dry box.

η^3-$C_3H_5Co[P(OCH_3)_3]_3$
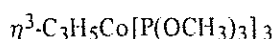
Muetterties procedure[3] was used with a few modifications which are listed below. The hydrido complex, $HCo[P(OCH_3)_3]_4$, was purified using a neutral alumina column (activity IV) before recrystallization from hexane. It was eluted with hexane, and an additional 20% could be obtained by subsequent elution with 20% ether–hexane. The potassium salt $KCo[P(OCH_3)_3]_4$ was prepared in a round-bottom flask equipped with a magnetic stirrer and