Reactivity of Coke. III. Effects of Some Metallic Additions on the Surface Area of Cokes from Humic Acid and on the Absolute Reaction Rates of the Coke-Carbon Dioxide System

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Introduction

It was recognized long ago that certain metallic impurities as well as added salts played an important role in catalyzing the reaction of carbon with carbon dioxide. Particularly, on the catalytic effects of inorganic additions on the reactivity of coke, a number of works have been written and briefly reviewed by M. A. Mayers.[1] The most effective catalysts to coke or pure graphite among them are the metals of the alkali group, usualy applied as the carbonates as well as the oxides and elemental iron or its carbide. Several other materials have been found to have slight or no effect. Though a great number of work have been published, these effects have hardly been treated quantitatively from the standpoint of chemical reaction rates.

In preceding papers[2,3] we have assumed that the catalytic effects of impurities of coke played an important part in the absolute reaction rates of the coke-carbon dioxide system.

In the present study, we have confirmed quantitatively the effects of some metallic additions on the specific surface area of cokes from humic acid and on the absolute reaction rates of the coke-carbon dioxide system. By the comparison between the cokes prepared from humic acid and metal-humates, the catalytic effects of the metallic constituents of the ash in coke have been examined; sodium, calcium, magnesium, iron and aluminium were used as metals which were most commonly found in the coke ash. The reason why humic acid was selected as the parent carbonaceous material was that the inherent mineral matter in coal might be considered to have partly entered into coal as metal-humates in the initial coalification process[4] and that it might be more important in the consideration of the catalytic

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[1] M. A. Mayers, "Chemistry of Coal Utilization", Editor, H. H. Lowry, John Wiley and Sons, Inc., New York, Vol. **1**, (1945), p.917.

[2] Y. Kawana, This Bulletin, **26**, 507 (1953).

[3] Y. Kawana, This Bulletin, **27**, 334 (1954).

[4] F. Fisher and W. Fuchs, *Brenn. Chem.*, **8**, 291 (1927). E. Biesalski and Berger, *Braunkohle*, **23**, 197 (1924/25).

effects of the ash in coke than the extraneous mineral matter.

Experimental

Preparation of Humic Acid and Metal-humates.—Humic acid was prepared from Takayama lignite. About 200 g. of dried Takayama lignite, bitumen of which had been previously eliminated by benzene-ethanol azeotropic mixture, was treated with ten-times one per cent sodium hydroxide solution for about five hours at the boiling temperature and after settling during about 15 hours, humic acid was precipitated by a little excess of hydrochloric acid from the upper parts of the solution. The precipitates of humic acid were purified by washing several times with distilled water and then by electrodialysis for about twenty days.

Metal-humates were prepared by treating the humic acid with metal chlorides or carbonate solution by the flow method. About 20 g. of humic acid crushed from 20 to 60 mesh was packed into a glass cylinder and 250 cc. of 1N salt solution passed through the humic acid column at a space velocity of about 0.5 and then the metal-humates were washed by distilled water until chlorine ion disappeared. These metal-humates were dried under reduced pressure. Extra-pure sodium carbonate and metal chlorides were used respectively for sodium-humate and the other metal-humates.

TABLE I

DESCRIPTION OF COKES

Cokes	Density g./cc.	Ash, % dry basis	Composition of ash in coke, %					
			$Na_2O+Na_2CO_3$	$CaCO_3$	MgO	Fe_2O_3	Al_2O_3	SiO_2
H-coke	1.630	2.63	—	1.10	0.55	11.46	31.07	51.15
Na- „	1.625	15.51	84.13	—	—	—	—	—
Ca- „	1.842	7.24	—	45.64	—	—	—	—
Mg- „	1.788	5.60	—	—	20.13	—	—	—
Fe- „	1.835	4.08	—	—	—	39.18	—	—
Al- „	1.862	3.40	—	—	—	—	43.20	—

Preparation of Cokes from Humic Acid and Metal-humates.—The experimental conditions for the preparation of cokes from humic acid and metal-humates were as follows. About 20 g. of humic acid or metal-humates packed in a graphite crucible were put into a silica cylinder and evacuated until about 5 mmHg at room temperature and then carbonized at a heating rate of about 5°C per minute until 1000°C under the reduced pressure of 6—8 mmHg and after maintenance at 1000°C for about one hour, the coke sample was cooled down to room temperature. The cokes carbonized from humic acid, sodium-, calcium-, magnesium-, iron-, and aluminium-humate are defined respectively as H-, Na-, Ca-, Mg-, Fe- and Al-coke.

The analytical results and the densities of coke samples are shown in Table I. All cokes, except for Na-coke treated in high vacuum at lower temperature of 500°C, were subjected to vacuum treatment ($10^{-1}-10^{-3}$ mmHg) at 1100°C for half an hour. H-coke is unfortunately not pure and its ash content is 2.63 per cent. The density and ash contents of metal-cokes are remarkably increased as compared with those of H-coke, and the increase of ash contents of metal-cokes is respectively due to metal ions inserted as metal-humates. The chemical analysis of the ash of metal-cokes was made only on the metal ion inserted.

Apparatus and Procedure.—The apparatus and procedure for determination of the surface area of cokes and for absolute reaction rates of the coke-carbon dioxide system at various temperatures were the same as already described in the first paper.[2)] The surface area of cokes was determined by the adsorption of ammonia at 0°C using the B.E.T. method. After that, the reaction of this coke and carbon dioxide at the constant temperature ranging from 730°C to 970°C under constant volume was obtained by measuring the increase in the total pressure of this system against time.

The specific reaction rates per unit area of the coke surface *Ka* expressed as the number of molecules reacted per sq. cm per second when

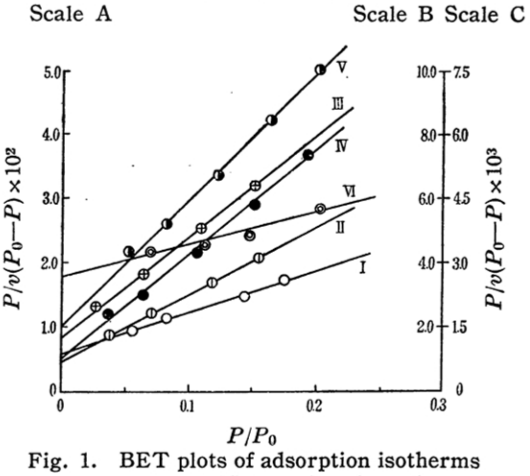

Fig. 1. BET plots of adsorption isotherms of ammonia at 0°C by cokes from humic acid and metal-humates.

	Cokes	Scale
I	H-coke	A
II	Ca-coke	B
III	Mg-coke	„
IV	Fe-coke	C
V	Al-coke	„
VI	Na-coke	A

$P_{co_2}P/_{co}$ was equal to unity, were obtained at various temperatures by the surface area determination together with the reaction rates measurement as already explained in the first paper.

Results and Discussion

Specific Surface Areas of Cokes from Humic Acid and Metal-humates.—The B.E.T. plots of ammonia adsorption at 0°C by cokes from humic acid and metal-humates are shown in Fig. 1 and good straight lines are obtained for a series of relative pressure from about 0.05 to 0.3. According to the usual procedures in the B.E.T. method various values obtained from Fig. 1 are summarized in Table II.

TABLE II

SUMMARY OF SURFACE AREA DATA OF COKES

Cokes	*Pre-treatment in* vacua °C, hr(mmHg)	*Sample* weights (g.)	S (m^2)	A (m^2/g.)	A_M/A_H	E_1-E_L (cal./mol.)
H-coke	1100,7 (10^{-4})	0.6306	50.8	80.6	1.00	1295
Na- „	500,2 (10^{-5})	0.3188	53.3	170	2.11	698
Ca- „	1100,1 (5×10^{-3})	0.4262	184.0	433	5.37	1650
Mg- „	1100,1 (10^{-4})	0.2817	100.2	356	4.42	1678
Fe- „	1100,1 (10^{-3})	0.3439	139.4	405	5.02	1900
Al- „	1100,1 (10^{-3})	0.3618	112.0	310	3.84	1660

Before the surface area determination, the coke sample was evacuated at higher temperatures to eliminate the surface oxide and also residual volatile matters; "Pre-treatment in vacua" in Table II shows the conditions of this treatment and the treatment for Na-coke was made at 500°C lest metallic sodium should vaporize by the probable reaction of carbon with sodium oxide.

The specific surface area of metal-coke was about two or five times larger than that of H-coke, and the value of A_M/A_H in Table II is the specific surface area ratio of metal-coke to H-coke. The large specific surface areas of metal-coke compared with H-coke can be expected, as metallic ion exists in highly dispersed state in metal-humate and it is well known that when carbonaceous materials are carbonized with inorganic salts an increase in the surface area is obtained. T.D. Smith[5] had already obtained the similar results with barium mellitate. The values of A_M/A_H must probably depend on not only the valency of the metallic ions, but also their contents in the parent metal-humates.

Absolute Reaction Rates of Cokes from Humic Acid and Metal-humates with Carbon Dioxide.—The reaction rates of the present cokes having the known surface area and carbon dioxide at constant temperature and volume can similarly be expressed by the following equation as already stated in the first paper,

$$dP/dt=KP_{co_2}/P_{co} \tag{1}$$

where K is a rate constant, P, the total pressure, t, the time, and P_{co_2} and P_{co} denote the partial pressure of carbon dioxide and carbon monoxide respectively.

The specific reaction rates per unit area of the coke surface K_a, expressed as the number of molecules reacted per sq. cm per second at $P_{co_2}/P_{co}=1$, can be calculated by the following equation (Eq. (8) in Ref. (2)) from the rate constant K and the total surface area of the coke S.

$$K_a=a\cdot K\cdot\frac{273}{760}\cdot\frac{1}{60}\cdot\frac{6.02\times10^{23}}{22400}\cdot\frac{1}{S\cdot10^4} \tag{2}$$

The relations between K_a and $1/T$ for various cokes are shown in Fig. 2 and K_a may be expressed as:

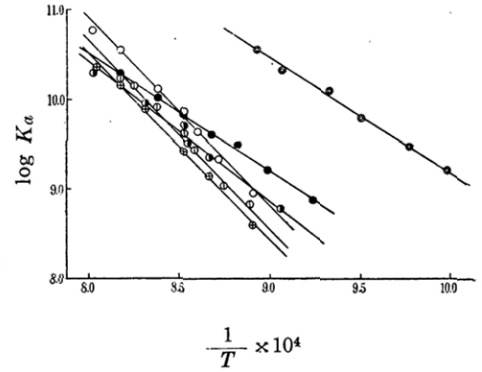

Fig. 2. Relations between log K_a and $1/T$
○ H-Coke, ⊕ Mg-Coke ◑ Al-Coke
① Ca-Coke, ● Fe-Coke ◎ Na-Coke

$$K_a=A\ \exp.\ (-E/RT), \tag{3}$$

where A is a constant and E, the experimental activation energy. The values of A and E determined by the least squares are summarized in Table III. Although the large difference in A and E among H-, Ca- and

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[5] T. D. Smith, *J. Chem. Soc.*, **1952**, 923.

TABLE III

THE VALUES OF A AND THE ACTIVATION ENERGIES E

Cokes	$A_{obs.}$ molecules (cm^{-2} sec^{-1})	$A_{calcd.}$ molecules (cm^{-2} sec^{-1})	E (kcal./mol.)
H-coke	4.46×10^{27}	5.57×10^{27} (1173°K)	96.0
Na- „	7.75×10^{21}	4.98×10^{27} (1050°K)	58.3
Ca- „	1.12×10^{27}	5.57×10^{27} (1173°K)	94.0
Mg- „	1.29×10^{27}	„	95.1
Fe- „	1.00×10^{21}	„	60.1
Al- „	8.91×10^{22}	„	71.8

Mg-coke can not be seen, those of Fe-, Al- and Na-coke are much smaller than H-coke.

Provided that the reaction mechanism presented in the first paper may be applicable, the quantity A must be calculated from the following equation applying the absolute reaction rates theory (Eq. (14) in Ref. (2)),

$$A=kT/h\cdot L\cdot f_{co}/f_{co_2}\cdot f_a^{\neq}/f_s \tag{4}$$

The calculated values of A are also given in Table III, using $L=10^{15}$, $f_a^{\neq}/f_s=1$, $T=1050$°K for Na-coke and $T=1173$°K for the other cokes. The difference between the observed and calculated values for H-, Ca- and Mg-coke is very small, but for Fe-, Al- and Na-coke, it is much greater than expected from the theory. Accordingly, it is concluded that the simple reaction mechanism presented in the first paper may be applicable for H-, Ca- and Mg-coke, but for the other cokes, a more complicated reaction may probably be occurring.

The specific reaction rates per unit area of the coke surface, K_{aM} for metal-cokes and K_{aH} for H-coke at various temperatures, can be calculated from Eq. (3) using the experimental values of A and E, and the ratio, K_{aM}/K_{aH}, is given in Table IV. From these values of K_{aM}/K_{aH}, we can clearly see the effects of metallic impurities on the absolute reaction rates of the coke-carbon dioxide system.

These values for Na-, and Fe-coke at lower temperatures are of the order of 10^1 or 10^2 and under the present experimental conditions it may be considered that metallic sodium for Na-coke and metallic iron or its carbide for Fe-coke would most probably take part in the reaction. These results agree well with those of earlier[1] and recent studies[6] that the most effective catalysts of inorganic additions to coke or pure graphite are the metals of the alkali group and metallic iron or its carbide.

In Ca-, and Mg-coke, calcium and magnesium impurities would exist as the oxides, which intend to inhibit the specific reaction rates per unit surface area to cabron dioxide as seen in Fig. 2 and Table IV. The behavior of Al-coke resembles very much to that of Fe-coke. The ratio of the maximum value of K_a to the minimum at one temperature for various cokes is in the range from 1.74×10^1 at 1000°C to 1.10×10^3 at 700°C evaluated from Table IV. It was already stated that these ratios were about 16 or 20 for various cokes investigated in the first paper and that K_a at 950°C in the second paper[3] changed irregularly with these ratios of 10^1 or 10^2 by the heat treatment of cokes from 1000° to 2000°C, and these experimental facts have been considered as the catalytic effects of the ash in coke. The present results of strong effects of metallic impurities would confirm that these considerations might be most reasonable.

Metallic impurities introduced as metal-humates have strong effects on the specific surface area of cokes from humic acid and on the absolute reaction rates of the coke with carbon dioxide, and the products of A_M/A_H in Table II and K_{aM}/K_{aH} in Table IV represent the effects of metal impurities on the apparent or relative reactivity of the coke. These values of the product are in the range from 1.08 to 1.01×10^3 for all metallic impurities investigated at 700° to 1000°C. That is, all metallic impurities investigated

TABLE IV

THE RATIOS OF THE SPECIFIC REACTION RATES OF METAL-COKES TO THAT OF H-COKE AT VARIOUS TEMPERATURES

Cokes	K_{aM}/K_{aH}			
	700°C	800°C	900°C	1000°C
H-coke	1	1	1	1
Na- „	4.78×10^2	7.75×10^1	1.74×10^1	4.89
Ca- „	8.7×10^{-1}	7.9×10^{-1}	7.4×10^{-1}	6.9×10^{-1}
Mg- „	4.36×10^{-1}	4.26×10^{-1}	4.07×10^{-1}	3.98×10^{-1}
Fe- „	2.45×10^1	4.36	1.05	3.09×10^{-1}
Al- „	5.36	1.66	6.30×10^{-1}	2.81×10^{-1}

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[6] E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.*, **44**, 1048 (1952); W. F. K. Wynne-Jones, H. E. Blayden and H. Marsh, *Brenn. Chem.*, **33**, 238 (1952).

in the present study increase the relative reactivity of the coke.

Summary

The surface area of cokes from humic acid and metal-humates and the absolute reaction rates of these cokes to carbon dioxide at various temperatures have been determined by the same method and procedure as those described in the first paper.

The specific surface area of cokes from metal-humates are about two or five times larger than the coke from humic acid, and this increase is expected from the well-known fact that when carbonaceous materials are carbonized with inorganic salt an increase in the surface area is obtained.

The specific reaction rates per unit surface area K_a of these cokes and carbon dioxide can be expressed by an equation

$$K_a = A \text{ exp. } (-E/RT),$$

and the values of A and activation energies E have been determined. The activation energies of cokes from humic acid, Ca- and Mg-humates are about 95 kcal./mol. and a large difference is not seen among them, but those of cokes from Fe-, Al- and Na-humates are about 25–40 kcal./mol. smaller than H-coke. The experimental values of A for cokes from humic acid, Ca- and Mg-humate are in satisfactory agreement with those expected from the application of the absolute reaction rates theory to the reaction mechanism already presented in the first paper, but those of A for cokes from Fe-, Al- and Na-humate are much smaller than expected from the theory. These results may be considered to indicate that the more complicated reaction must be occurring for cokes from Fe-, Al- and Na-humates. Calcium and magnesium impurities have effects of decreasing the specific reaction rates per unit surface area of the coke from humic acid to carbon dioxide and on the other hand, aluminium, especially iron and sodium impurities at lower temperatures have great effects of increasing the specific reaction rates. The effects of these sodium and iron impurities agree well with the earlier results and the present results also confirm that the catalytic effects of impurities in coke play an important role in the absolute reaction rates of the coke-carbon dioxide system, which was assumed in previous papers.

By considering the effects of metallic impurities on both the specific surface area of cokes from humic acid and the specific reaction rates per unit surface area of the coke with carbon dioxide, all metallic impurities investigated increase the relative reactivity of the coke from humic acid and for example, sodium impurities increase the apparent reactivity of the coke about 10^3 times at 700°C.

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