Reactivity of Coke. II. Effects of Heat Treatment of Cokes on Their Specific Surface Areas and Absolute Specific Reaction Rates with Carbon Dioxide at 950°C

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Introduction

The reactivity of coke may be considered to depend mainly on its surface properties, crystallographic structure and the catalytic effects of ash in it. These properties are all changed considerably by heat treatment. Accordingly, knowledge on changes of physical and chemical properties of coke by heat treatment is very important for the consideration of the reactivity of coke. Since the conference on the ultra-fine structure of coals and cokes (London, 1943), the physical structure and surface chemical properties of coals and cokes have been actively studied.

The change of adsorption properties of coke or char by heat treatment has been obtained by Maggs⁽¹⁾ and Honda et al.⁽²⁾ Recently, Boyer and Foucault⁽³⁾ have obtained the variations of specific surface areas of cokes carbonized from four different coals below 1000°C. Walker et al,⁽⁴⁾ and Jolley and Poll⁽⁵⁾ discussed the surface area development of carbons during gasification reactions.

In our previous paper,⁽⁶⁾ surface areas of cokes were obtained by adsorption of ammonia at 0°C using the simple B.E.T. method, and by these surface area values together with kinetic data, the carbon dioxide-coke reaction was discussed from the standpoint of the absolute reaction rates theory. In this paper, the author obtained the effects of heat treatment of cokes from 1000° to 2000°C on specific surface areas of cokes and absolute specific reaction rates of cokes with carbon dioxide at 950°C.

Experimental

Preparation of Coke Samples.—As original coals, Nakayama lignite, Mitsui Bibai coal, Yatake coal and Hongei anthracite were selected, and after crushing from 20 to 60 mesh (Tyler), their ash contents were reduced by the float-and-sink test in benzene-carbon tetrachloride solution.

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1) F. A. P. Maggs, "Proc. Conf. Ultra-fine Structure of Coals and Cokes" B.C.U.R.A., London, 1944, p. 147.

2) H. Honda, Y. Kawana, K. Ōuchi and K. Nagata, *J. Chem. Soc. Japan* (Pure chemistry section, in Japanese), **74**, 887 (1953).

3) A. Boyer and G. Foucault, *Compt. rend.*, **257**, 895 (1953).

4) P. L. Walker, R. J. Foresti and C. C. Wright, *Ind. Eng. Chem.*, **45**, 1703 (1953).

5) L. J. Jolley and A. Poll, *J. Inst. Fuel*, **26**, 33 (1953).

6) Y. Kawana, This Bulletin, **26**, 507 (1953).

TABLE I

PROXIMATE AND ULTIMATE ANALYSES OF ORIGINAL COALS

Original coals	Proximate analyses (%) standard basis				Ultimate analyses (%) dry basis					Calorific value (cal./g.)	Fuel ratio	Caking property
	Moisture	Ash	V.M.	F.C.	C	N	H	S	O+errors			
Nakayama lignite	9.95	5.70	44.75	39.60	62.40	1.19	4.96	0.39	24.73	5330	0.884	Non-caking
Mitsui Bibai coal	1.57	8.95	35.27	54.19	77.61	1.79	5.46	0.11	5.95	7650	1.57	Weakly caking*
Yatake coal	0.70	5.82	19.63	73.76	84.15	1.88	4.71	0.59	2.80	8180	3.76	Strongly caking
Hongei anthracite	1.78	1.90	6.79	89.53	91.02	0.98	3.39	0.39	2.29	8250	13.2	Non-caking

* Although Mitsui Bibai coal is usually classified as non-caking, the present sample with the preliminary treatment of reducing ash contents of the coal indicates weakly caking property.

The results of analyses of original coals after this treatment are shown in Table I. These coals were primarily coked at 950°C by an electric furnace, and then both Mitsui Bibai and Yatake cokes were again crushed from 20 to 60 mesh because they solidified in larger blocks, while the other cokes remained as they were. The primary cokes were separately heated in a vacuum carbon resistance furnace at various temperatures from 1000° to 2000°C. The time of heating to desired temperatures and the maximum pressure during heat treatment were respectively about 10—30 minutes and 5—26 mm Hg.

The analytical results and the density of these coke samples are as shown in Table. II.

TABLE II

ANALYTICAL RESULTS(a) AND DENSITIES(b) OF COKES HEATED AT TEMPERATURES FROM 1,000° to 2,000°C

Cokes		Temperature of heat treatment, °C 1000	1200	1400	1600	1800	2000
Nakayama coke	Moisture, %	8.84	8.29	4.14	1.02	—	0.27
	Ash, %	11.18	11.60	12.40	11.00	—	6.36
	Density, g/cc	1.572	1.809	1.571	1.482	—	1.436
Mitsui Bibai coke	Moisture, %	2.42	0.60	0.42	0.20	0.16	0.20
	Ash, %	16.52	17.72	16.97	14.94	13.41	9.56
	Density, g/cc	1.780	1.852	1.894	1.976	2.039	1.917
Yatake coke	Moisture, %	0.72	0.44	0.20	0.20	0.18*	0.24
	Ash, %	8.84	9.46	8.38	6.88	6.70*	4.62
	Density, g/cc	1.809	1.904	2.041	1.959	1.994*	1.927
Hongei coke	Moisture, %	5.52	1.36	0.28	0.14	0.16	—
	Ash, %	4.73	6.16	5.90	6.06	5.78	—
	Density, g/cc	1.808	1.671	1.676	1.674	1.659	1.650

(*a*) Standard basis (*b*) The densities of cokes were obtained from the usual liquid displacement method using water at 25°C. The air in the coke sample was eliminated as thoroughly as possible by the rotary pump. (*) This coke was treated at 1780°C.

Apparatus and Procedure.—The apparatus and procedure for determination of the surface area of coke and for reaction rates study of the coke-carbon dioxide system are the same as already stated in the previous paper.6) The surface area of cokes was determined by the adsorption of ammonia at 0°C following the simple B. E. T. method.7)8)

After measurement, the sample was heated and the adsorbed ammonia was thoroughly desorbed and then the reaction rates of coke with carbon dioxide at 950°C under constant volume were obtained by measuring the increase of the total pressure of this system against time.

Absolute specific reaction rates, K_a, expressed as the number of molecules reacted per sq. cm per second at 950°C when p_{co_2}/p_{co} was equal to unity, were obtained by the kinetic data together with the surface area determination as explained in detail in the first paper.

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7) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

8) S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, ibid., **62**, 1723 (1940).

Results and Discussion

Variations of Specific Surface Areas of Cokes with Heat Treatment.—The B. E. T. plots of adsorption isotherms of ammonia at 0°C for various cokes heated at temperatures from 1000° to 2000° are shown in Fig. 1—Fig. 4. In lower temperatures of heat treatment, good straight lines are obtained, but above 1600°—1800°C, deviations from straight lines become larger and this may be ascribed to smaller adsorption volume. The errors in the surface area values coming from these deviations, however, may not be so large. Various values obtained from Fig. 1—Fig 4 by the usual procedures in the B.E.T. method are summarized in Table III.

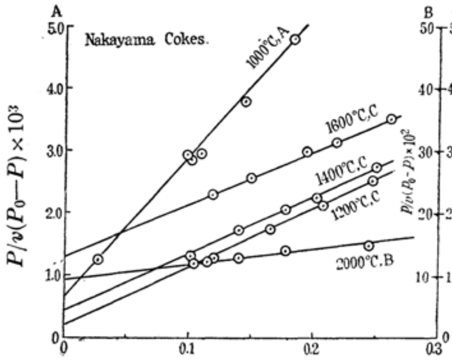


Fig. 1

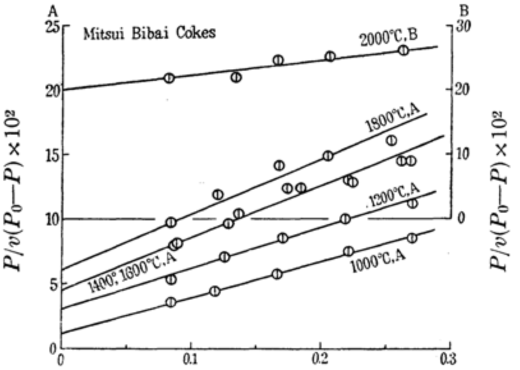


Fig. 2

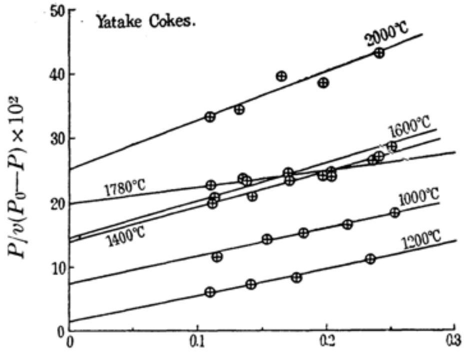


Fig. 3

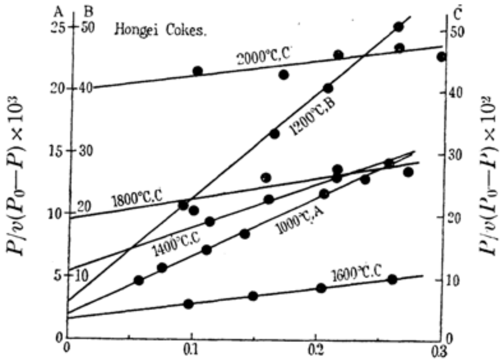


Fig. 4

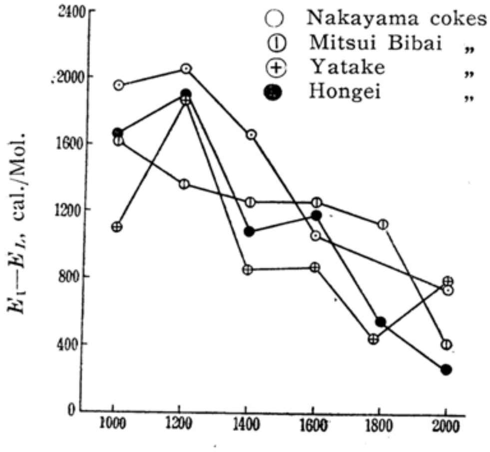
TABLE III. EFFECTS OF HEAT TREATMENT OF COKES ON THEIR SURFACE PROPERTIES AND ABSOLUTE SPECIFIC REACTION RATES OF COKES WITH CARBON DIOXIDE AT 950°C

Cokes	Temp. of heat treatment, °C	Vacuum pretreatment °C, hr (mmHg)	Sample weights	V_m	S	A	C	E_1-E_L	K	K_a molecules
			g	cc	m^2	m^2/g		cal/Mol		cm^{-2} sec^{-1}
Nakayama coke	1000	1000, 19 (10^{-4})	0.3924	43.1	149.4	381	36.3	1950	1.67	8.02×10^9
	1200	1100, 8 (10^{-5})	0.1566	10.5	36.4	232	43.2	2050	3.72	7.64×10^{10}
	1400	1100, 5 (10^{-4})	0.3179	10.5	36.4	115	21.2	1660	1.01	2.45×10^{10}
	1600	1100, 5 (10^{-4})	0.9002	10.9	37.8	42.0	7.09	1060	0.302	5.74×10^9
	2000	1100, 5 (10^{-4})	1.8291	2.80	9.71	5.31	3.89	740	1.75 1.61	1.28×10^{11} 1.17×10^{11}
Mitsui Bibai coke	1000	1000, 4.5 (10^{-3})	3.2387	3.63	12.6	3.89	19.7	1620	0.675	3.81×10^{10}
	1200	1100, 3.5 (10^{-3})	3.6872	2.86	9.92	2.69	12.3	1360	0.865	6.11×10^{10}
	1400	1100, 4 (10^{-3})	5.3936	2.20	7.63	1.41	10.1	1260	0.873	7.84×10^{10}
	1600	1100, 4.5 (10^{-4})	4.4478	2.20	7.63	1.72	10.1	1260	0.969	8.80×10^{10}
	1800	1100, 4.5 (10^{-4})	3.9977	2.03	7.04	1.76	8.02	1130	0.124	1.22×10^{10}
	2000	1100, 4.5 (10^{-4})	3.2879	2.29	7.94	2.41	2.18	420	1.05	9.20×10^{10}

Yatake coke	1000	1000,	$5(10^{-4})$	1.1308	1.92	6.66	5.89	7.57	1100	2.73	2.93×10^{11}
	1200	1100,	$2(10^{-3})$	2.3473	2.32	8.04	3.43	30.8	1860	1.39	1.23×10^{11}
	1400	1100,	$2(10^{-3})$	2.7940	1.49	5.17	1.85	4.81	850	1.67	2.27×10^{11}
	1600	1100,	$4(10^{-4})$	3.0608	1.38	4.78	1.56	4.98	870	0.722	1.06×10^{11}
	1780	1100,	$4(10^{-5})$	3.1939	2.20	7.63	2.39	2.27	450	0.925	8.45×10^{10}
	2000	1100,	$3(10^{-5})$	2.4947	0.96	3.33	1.33	4.25	790	0.310	6.57×10^{10}
Hongei coke	1000	1100,	$5(10^{-3})$	2.8936	21.4	74.2	25.6	21.2	1660	2.32	2.17×10^{10}
	1200	1100,	$5(10^{-3})$	1.7178	5.66	19.6	11.4	32.1	1890	2.76	1.00×10^{11}
	1400	1100,	$4(10^{-4})$	2.0311	1.24	4.30	2.11	7.37	1080	3.05	5.02×10^{11}
	1600	1100,	$4(10^{-4})$	6.1565	3.46	12.0	1.95	9.02	1190	2.92	1.60×10^{11}
	1800	1100,	$4(10^{-5})$	7.2682	1.90	6.59	0.91	2.75	550	1.35	1.36×10^{11}
	2000	1100,	$3(10^{-5})$	7.1644	1.53	5.30	0.74	1.65	270	0.0610	7.66×10^{9}

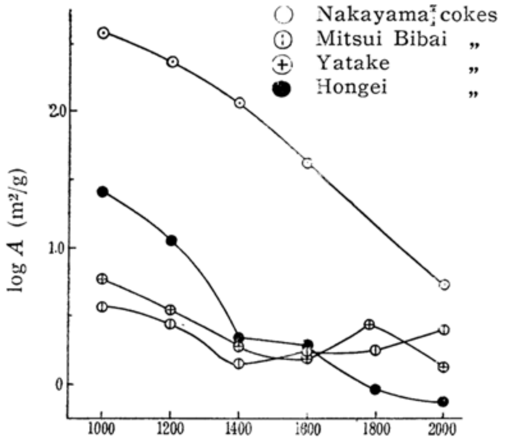
Before adsorption, coke samples were evacuated at higher temperatures to eliminate the surface oxide and residual volatile matters; "Vacuum pretreatment" in Table III shows the conditions of this preliminary treatment. The quantities of V_m, S, A and C in Table III are respectively monomolecular adsorption volume, total surface area, specific surface area and the B. E. T. constant. The quantity of $(E_1—E_L)$ can be evaluated from C as usual.

The variations of (E_1-E_L) with heat treatment are also indicated in Fig. 5. For all kinds of cokes, generally speaking, (E_1-E_L) decreases with the increase of heat treatment temperature and the difference due to the rank of original coals can not be clearly seen in Fig. 5. Except for Mitsui Bibai cokes, there seem to be maximum points of (E_1-E_L) at about 1000° – 1200°C.



Temperature of heat treatment, °C
Fig. 5. Variations of $E_1—E_L$ with heat treatment.

The variations with heat treatment of the specific surface area of cokes are illustrated in Fig. 6. The area of cokes carbonized from non-caking coals such as Nakayama lignite and Hongei anthracite in lower temperature of heat treatment is much larger than that of cokes from other caking coals such as Mitsui Bibai and Yatake coals, but the values of the former cokes decrease rapidly with heat treatment temperature, while those of the latter cokes do not change so much by heat treatment and there may be minimum points at about 1400° – 1600°C. The ratios of the area of coke heated at 2000°C to that at 1000°C are respectively about 1.4×10^{-2} for Nakayama, 6.2×10^{-1} for Mitsui Bibai, 2.3×10^{-1} for Yatake and 2.9×10^{-2} for Hongei cokes. It is very interesting to notice that there is a close relationship between the manner of decrease of the area of coke by heat treatment and the caking property of the original coal.



Temperature of heat treatment, °C
Fig. 6. Effects of heat treatment of cokes on their specific surface areas.

Recently, the views that amorphous carbon consists not only of the so-called "turbostratic structure"[9] but also of a third "three-dimensional covalent cross-linked structure", which plays a great role in the structure of chars and cokes, have been justified by X-ray studies[10] on carbonization products from

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[9] J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

[10] J. Gibson, M. Holohan and H. L. Riley, *J. Chem. Soc.*, **1946**, 458.

hexaiodobenzene and hexachlorobenzene and by the wet oxidation rates studies[11] of various kinds of amorphous carbons containing cokes. According to the magnetochemical studies[12] of coals and their related substances, the structure of chars and cokes depends much on both the carbonization temperature and the structure of starting substances; moreover the structure of coke carbonized at about 1100°C may be considered to consist mainly of the three-dimensional covalent cross-linked structure, the change of which to the turbostratic structure or to the graphite one may occur at temperatures higher than 1100°C.

The higher the temperature of heat treatment is, the more the three-dimensional covalent cross-linked structure of cokes is decomposed and the nearer it is to that of graphite; hence, in general, the surface area of cokes decreases with heat treatment temperatures. However, the structure of cokes depends on the kind or rank of original coals as well as the heat treatment temperature, so the specific surface area of cokes heated even at the same temperature may differ a great deal from each other.

It cannot be clearly explained why the specific surface area tends to increase above 1600°C for caking coals, but not for non-caking coals. As the temperature of 1600°C coincides with that of rapid graphitization of cokes,[13] there may be some special relation between the increase of the specific surface area and the graphitization of cokes from caking coals.

Variations with Heat Treatment of Absolute Specific Reaction Rates of Cokes with Carbon Dioxide at 950°C.—The values K and K_a in Table III are respectively rate constants and absolute specific reaction rates, expressed as the number of molecules reacting per sq. cm per second at 950°C when P_{co2}/P_{co} equals unity in the reaction of coke with carbon dioxide, as defined in the first paper. The relations between K_a and the heat treatment temperature are also indicated in Fig. 7. Generally, a regular relation between K_a and the heat treatment temperature is neither seen for all kinds of cokes, nor is there a clear relation between K_a and the rank of original coals for all temperatures of heat treatment. Although the higher the temperature of heat treatment is, the more regular becomes the crystallographic structure of cokes, which approaches to that of graphite, there is not a general tendency of the decrease of K_a with the heat treatment temperature. The irregular changes of K_a by heat treatment may be due to the catalytic effects of the ash which coexists on the surface of coke, and the magnitudes of the changes are comparable with or are larger than those of the specific surface area decrease by heat treatment. According to this result, it may be said that the impurities in coke have stronger effects on the reactivity of coke than the surface area of coke has.

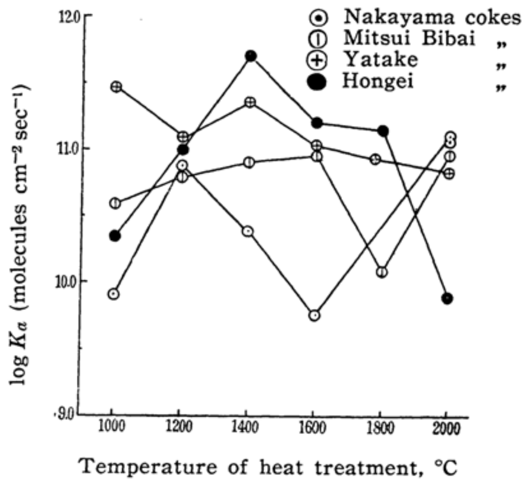

Fig. 7. Effects of heat treatment of cokes on absolute specific reaction rates of cokes with carbon dioxide at 950°C.

On the other hand, in our first paper, it has been concluded that the difference of K_a between pure amorphous carbon and pure graphite at the same temperature will be small, and that for carbons containing some impurities, the catalytic effects of the ash in carbons on the absolute specific reaction rates may be much greater than those of the difference of the crystallographic structure of carbons, that is, the degree of graphitization of carbon, from the absolute reaction rates study of various carbons with carbon dioxide. The same conclusion could again be derived from the above-mentioned results. That is, there are some effects which are much greater than those of the difference of the degree of graphitization of cokes, and these effects have been assumed to be the catalytic effects of the ash in coke.

Summary

The effects of heat treatment of cokes on their specific surface areas and absolute

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[11] H. E. Blayden and H. L. Riley, *J. Soc. Chem. Ind.*, **54**, 159T (1935); A. F. Balfour, H. E. Blayden, A. H. Carter and H. L. Riley, *J. Soc. Chem. Ind.*, **57**, 1 (1938); H. L. Riley, *J. Chim. Phys.*, **47**, 565 (1950).

[12] H. Honda and K. Ouchi, *Reports of the Resources Research Institute* (in Japanese) No. 1 (1952).

[13] H. Honda and K. Ouchi, *Sci. Rep.*, Tohoku Univ. Series 1, **37**, 55 (1953).

specific reaction rates of cokes with carbon dioxide at 950°C have been obtained by the same procedure as stated in the first paper.

Generally, the specific surface area of cokes decreases with heat treatment temperature, and the values for cokes from non-caking coals are much greater than those for cokes from caking coals in lower heat treatment temperatures, and there is a close relationship between the manner of decrease of the specific surface area of coke by heat treatment and the caking property of the original coal.

The changes by heat treatment of absolute specific reaction rates of cokes with carbon dioxide at 950°C are very irregular for all the temperatures. There are some effects, which are much greater than those of the difference of the crystallographic structure of cokes, on the absolute specific reaction rates of cokes with carbon dioxide. These effects have been assumed as the catalytic effects of the ash in coke, which may also be larger than those of the surface area of coke on the reactivity of coke.

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