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Effects of Heating Temperature and Irradiation on the Catalytic Activities of Active Carbons for Phosgene Synthesis

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The kinetic factors for phosgene synthesis over thermal and irradiated sucrose carbons were examined in particular regard to their dependences on the heating temperature and irradiation. Gamma-irradiation on carbons prepared at 900 or 1000°C produced new active sites with E_A of 11—12 kcal/mol. An explanation is suggested of the effects of heating temperature and irradiation on the catalysts; the catalytic activity is most reasonably related to the degree of growth of the network structure of carbons. In the case of carbons prepared by heating at 900 or 1000°C and having the structure grown to the largest extent, a high dose of gamma-rays presumedly destroys most efficiently the thermally generated active sites and forms sites with a high activation energy. Free radicals and peripheral atoms which also comprise characteristics of amorphous carbons seem to behave independently of catalytic activities and are supposed to have no direct relation to the activities.

The ionizing radiation has been known to affect the catalytic activity of metals, oxides and other salts.[1,2] None has been reported, however, about the irradiation effect on active carbon, which has a unique structural character among inorganic catalysts with its disorderly layered ring networks, peripheral atoms and free radicals. It is well known that carbons catalyze phosgene synthesis from carbon monoxide and chlorine as well as some other reactions.[3] No relation has yet been reported between the catalytic activity for this synthesis and other nautres of the catalysts.

We will report about catalytic activities of sucrose carbons prepared by evacuation within a range of temperatures, the effect of irradiation and some related behaviors of the carbons.

Experimental

Catalysts. Reagent grade sucrose was heated in air at around 350°C, crashed and heated twice, then ground to pass between 20 and 80 mesh (Primary Carbon, Pri. C.). Pri. C. was evacuated below 10^{-3} mmHg in a quartz tube for 20 hr at temperature (T) between 500 and 1000°C, at intervals of 100°C (C^T catalysts). Each C^T: catalyst was heated in an ampoule at 450°C for an hour in a helium stream and sealed while it was still hot. The ampoules were gamma-irradiated at room temperature with a ^{60}Co source at a dose rate of 1.0×10^6 R/hr to a total dose of 1.0×10^8 R (C^{T*} catalysts).

Catalytic Activity Measurements. The flows of tank chlorine (electrolytic) and of carbon monoxide (gas chromatographically pure) were mixed after being measured by flowmeters filled with concd. sulfuric acid and were introduced into a glass U-tube reactor of 6 mm I. D.; the tail gas was pulsed into a gas chromatographic system. A catalyst, 0.1—1 g, was placed on glass wool in the reactor, preheated to 450°C in the helium stream (about 20 m*l*/min) and kept for over an hour. Then the helium flow was stopped and chlorine flow (about 20 m*l*/min) was admitted for over 4 hr at the same temperature. The reactor was cooled to the reaction temperature (100—220°C) in the chlorine stream, then carbon monoxide was introduced in order to begin the reaction. The reaction products were analyzed over 100 min after the start of the reaction. The flow rates of both reactants were about 40 m*l*/min throughout the experiment. Such a pretreatment, without which no catalysis for the reaction was detectable, secured the constancy and reproducibility of the catalytic activity.

A fixed amount of the tail gas (2 m*l*), containing carbon monoxide, chlorine and the sole reaction product, phosgene, of less than 10% was analyzed by a gas chromatographic system after Runge[4] with a minor modification for convenience. The system was composed of a thermal conductivity cell with platinum filaments, a 4.5 m long glass tube analyzing column of 6 mm I. D. packed loosely with about 50 g of polytetrafluoroethylene powder[*2] on which trichlorinated diphenyl[*3] was carried in weight ratio of 1/20, and a

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1) E. H. Taylor, *Nucleonics*, **20**, 53 (1962); *J. Chem. Educ.*, **36**, 396 (1959).

2) R. Coekelbergs, A. Crucq and A. Frennet, *Advan. in Catalysis*, **13**, 55 (1962).

3) J. W. Hassler, "Active Carbon," Chemical Pub. Co., New York, N. Y. (1951).

4) H. Runge, *Z. anal. Chem.*, **189**, 111 (1962).

[*2] Polyflon M-11, 32—60 mesh, The Daikin Kogyo Co., Ltd.

[*3] Kanechlor-300, The Kanegafuchi Chemical Co., Ltd.

1 m long glass tube with Molecular Sieve 5A for desiccating helium carrier gas. All parts were connected with polyvinyl chloride tubes and set in a wooden case lined inside with aluminum plates. The analysis was done at a helium flow rate of 50 m*l*/min and a bridge current of 80 mA at room temperature. The retention times were 0, 2.0 and 6.6 min for carbon monoxide, chlorine and phosgene, respectively. The analytical accuracy and reproducibility were satisfactory. The system was operated without any trouble for one year.

B. E. T. Surface Areas. Specific surface areas of C^T catalysts were measured by the B. E. T. method with nitrogen.

Infrared Spectra of Catalysts. The infrared spectra of the carbon catalysts, ground into fine powder, were observed by the KBr pellet method in the wavelength range, 650—4000 cm^{-1}.

Results and Discussions

Surface Area. Specific surface areas of C^T catalysts are shown in Table 1. The data show a drastic change of the catalyst structures by heating.

Elementary Analysis. It was reasonably expected that the contact of the carbon with chlorine at 450°C and perhaps with phosgene up to 220°C may cause considerable change in its structure and elementary composition. Carbon blacks[5] were reported to react with chlorine with the maximum uptake at 400—500°C, nearly total content of hydrogen being substituted. However, our results of the elementary analysis of the carbons before and after use, does not exhibit any general relationship among components. Atomic ratios of the components, hydrogen, oxygen and chlorine (C=1.000) are shown in Table 1.

The increase of the specific surface area as the heating temperature of carbons was raised from 500 to 700°C corresponds to a loss of hydrogen and oxygen. The decrease of the surface area at higher heating temperature (800—1000°C) is accompanied with a loss of hydrogen but not with that of oxygen.

After use as the catalyst, the carbons were hydrogenated, deoxygenated and chlorinated. The dehyderogenation was severe for low temperature carbons. A remarkable deoxygenation was however, limited to occur to C^{500} alone, and beyond C^{600} the oxygen content with regard to carbon remains almost unchanged. The degree of chlorination is not associated with that of dehydrogenation, though the chlorine content is comparable to the hydrogen content before reaction for higher temperature carbons. Considering that conditions of the pretreatment and the reaction were common to all samples, the rather small divergence of the amount of the chlorine introduction into carbons, which is in remarkable contrast to a large change in the B. E. T. surface areas, suggests that chlorine does not necessarily combine with or substitute peripheral atoms but rather attacks peripheral and even inner carbon atoms with equal probability; one chlorine atom corresponds with 13—19 carbon atoms. That is, chlorine may react with carbon atoms to the same extent although they are present in a variety of imperfect polycondensed system.

Infrared Spectra. IR spectra of chars and coals have been observed and several assignments[6-8] have been made for characteristic absorption.

The spectra of some of our samples were examined in order to find any relation between the catalytic activities and the structures of the catalysts.

The low temperature carbon C^{500} did not show perceptible absorption before and after reaction in the wave number range 550—800 cm^{-1} ($\nu_{\phi-Cl}$= 702 cm^{-1}) or at around 950 and 1100 cm^{-1} (ν_{C-Cl} in RCOCl), in spite of the large uptake of chlorine by the catalyst. The appearance of the

Table 1. B.E.T. surface areas and elementary compositions of C^T catalysts

Catalyst	Surface area m²/g*	Elementary composition**	
		Before use	After use***
Pri. C.	—	$C_1H_{0.604}O_{0.245}$	—
C^{500}	121	$C_1H_{0.430}O_{0.076}$	$C_1H_{0.248}O_{0.043}Cl_{0.063}$
C^{600}	378	$C_1H_{0.373}O_{0.044}$	$C_1H_{0.186}O_{0.037}Cl_{0.053}$
C^{700}	418	$C_1H_{0.194}O_{0.043}$	$C_1H_{0.089}O_{0.030}Cl_{0.080}$
C^{800}	384	$C_1H_{0.129}O_{0.029}$	$C_1H_{0.043}O_{0.023}Cl_{0.081}$
C^{900}	195	$C_1H_{0.093}O_{0.026}$	$C_1H_{0.061}O_{0.041}Cl_{0.062}$
C^{1000}	90.3	$C_1H_{0.067}O_{0.025}$	$C_1H_{0.052}O_{0.027}Cl_{0.063}$

* For catalysts before use.

** Oxygen content was given by subtraction.

*** Catalysts were kept in a desiccator after use over a month.

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[5] H. P. Boehm, U. Hofmann and A. Clauss, "Proc. 3rd. Conf. on Carbon," 1957, Pergamon Press, New York, N. Y. (Pub. 1959), p. 241.

[6] R. A. Friedel, "Proc. 4th. Conf. on Carbon," 1959, Pergamon Press, New York, N. Y. (Pub. 1960), p. 321.

[7] R. A. Friedel and J. A. Queiser, *Anal. Chem.*, **28**, 22 (1956).

[8] J. K. Brown, *J. Chem. Soc.*, **1955**, 744; *ibid.*, 752.

absorption due to R-Cl group was neither observed for the high temperature carbon C^{1000} after its use as the catalyst.

The pile irradiation was reported to have an effect on the IR spectra of carbons simply to make them diffuse.[6] In our case, gamma-rays were likewise proved to have the similar effect on the spectrum of the carbon C^{1000}.

Dependences of Kinetic Constants on Heating Temperature and Irradiation. A rate equation was reported for phosgene synthesis over a commercial carbon catalyst by Potter and Barron.[9] Their results were found to obey either the mechanism of the surface reaction of molecular carbon monoxide with molecular chlorine or that with atomic chlorine, but they rejected the atomic chlorine mechanism because of the reaction temperature (31—99°C) and some other factors. However, a re-examination[10] of their data showed that rates could be expressed simply in the form;

$$\text{Rate} = k p_{CO} p_{Cl_2}{}^{1/2} \tag{1}$$

where k is the rate constant per unit catalyst weight.

In our work, the almost constant partial pressures of the reactants made no significant difference in quality of the kinetic canstants whichever nearly linear[9] or square root[10] dependence of the rate on chlorine pressure might be adopted. Considering our higher reaction temperatures employed, we adopted the expression of reaction rate given in Eq. (1).

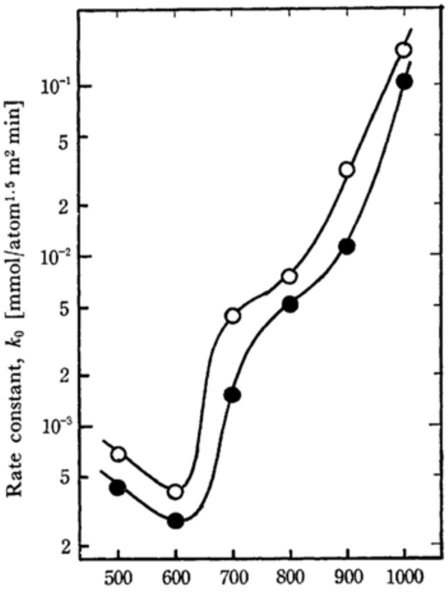

Fig. 1. Rate constants per unit area.
○ Unirradiated catalysts (C^{T})
● Irradiated catalysts (C^{T}*)

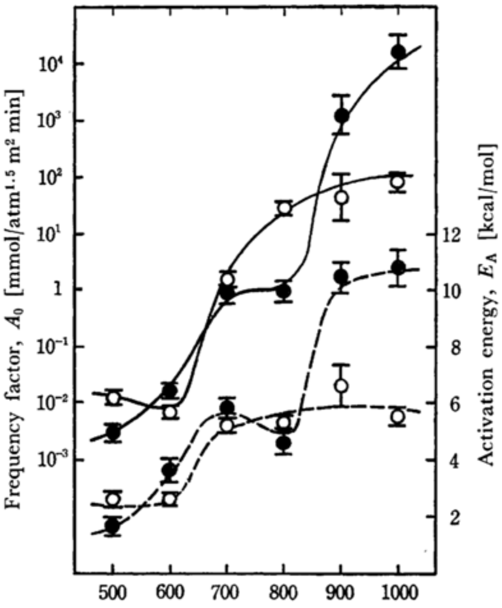

Fig. 2. Frequency factors and activation energies.
○ Unirradiated catalysts
● Irradiated catalysts
Full line Frequency factors
Broken line Activation energies

Rate constants per unit area, k_0, at 180°C are plotted against the heating temperature, T, in Fig. 1, where k_0 is k/S, and S is the specific area. The rate constant, k, at 180°C increases monotonously as the heating temperature is raised, while k_0 exhibits a slight decrease with T from 500°C to 600°C. Since C^{600} has the surface area three times as large as that of C^{500}, it is shown that the newly developed surface on C^{600} may have a smaller catalytic activity. With the heating temperature increased from 600°C to 700°C, both k and k_0 increase about tenfold, whereas the surface area is scarcely changed.

Gamma-irradiated carbons (C^{T}*) have always lower k and k_0 than the corresponding catalysts (C^{T}), as shown in Fig. 1. But an apparent parallelism of temperature dependences of the rate constants of the two catalyst groups may not have any significance. Analyses of k_0 values by separating them into frequency factors, A_0, and activation energies, E_A, reveal a definite dissimilarity between the two groups.

The A_0 values of C^{T} catalysts (Fig. 2) increase with the increasing heating temperature, but at higher heating temperatures they seem to be saturated. Those of C^{T}* catalysts do not show such a saturation, and A_0 of C^{1000}* exceeds that of C^{1000} by more than two orders of magnitude.

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[9] C. Potter and S. Barron, *Chem. Eng. Progr.*, **47**, 473 (1951).
[10] S. Weller, *Am. Inst. Chem. Eng. J.*, **2**, 59 (1956).

The A_0 values of lower temperature carbons are less affected by irradiation.

The activation energies of C^T group can be classified into two groups. Both C^{500} and C^{600} have activation energies of about 2—3 kcal/mol and higher temperature catalysts about 5—6 kcal/mol. The general feature of C^{T*} carbons is similar to C^T ones for heating temperatures lower than 800°C, however C^{900*} and C^{1000*} have activation energies nearly doubled.

Changes in A_0 and E_A by the irradiation indicate that to lower (T=500 and 600°C) and middle (T=700 and 800°C) temperature carbons the gamma-dose of 1.0×10^8 R gives only a vague effect, the quality and the quantity of catalytic sites being not greatly affected.

The disappearance of the saturation of A_0 and the remarkable increase of E_A upon irradiation for higher heating temperature (900 and 1000°C) carbons will be associated with the destruction of some of the thermally generated sites and with the creation, by gamma-irradiation, of new sites of different nature which may not be produced by any thermal treatment of the carbons.

Conclusions

Characteristics of structure of amorphous carbons are peripheral atomic groups, free radicals and π-electron systems. Free radicals do not disappear but are indeed produced by pile-irradiation in 90% carbon coals which behave much alike the carbons from carbohydrates.[6] If the catalytic activity is to be related with free radicals, irradiation should enhance the activities of carbons. Moreover, succrose carbons have a maximum concentration of free spins when heated around 600°C,[11] although C^{600} is not active as shown in Fig. 1. It is clear from the results of elementary analyses that the increasing tendency of the catalytic activity with increasing heating temperature can not be related to the content of any component nor to the change in the content of C^T carbons. The measurement of the IR spectra could not point out any special bonding in carbons, which is positively responsible for the catalytic activity. The only remaining possible explanation for the effect of structure for the catalysis seems to be the correlation of the catalytic activity to the growth of the condensed ring system.

The radiation is able to destroy the π-electron system through bond ruptures, resulting certainly in an activity decrease. Atomic displacements of 0.35—0.7 per 10^4 atoms occurred in the graphite sample pile-irradiated to about 10^8 rad.[12] This leads to the radiation yield of the atomic displacement, G_d=0.03—0.05. For polystyrene, the most stable polymer to radiation, the G-value of C–C splitting by electron irradiation[13] could be estimated to about 0.04. Also C–H splitting yield in carbons could be assumed from some reported radiolytic yields; for n-hexane, $G(C_6H_{13})=5.5$,[14] for cyclohexane, $G(C_6H_{11})=7.2$,[15] and for benzene, twice of $G(H_2)$ is about 0.08.[16]

There would be a possibility to explain the radiation effect by correlating the varied activity directly with the radiation induced point defects. The broken bonds might be associated with the irradiation effect. But the radiolytic yield is too low. For carbon with a surface area of 100 m²/g, about 8% of the total carbon atoms exist on the surface, if only the (001) planes were exposed on particles of graphite structure. If any speculative mechanism allowed radiation damage to occur preferentially on surface atoms, 1.6% of the surface atoms (0.13% of the total atoms) could be damaged by doses of 10^8 R through a process with $G=1$.

This value is not recognized as sufficient so long as the catalytic action of the carbons is related simply to atomic lattice points. However, when a considerably developed carbon network as a whole is thought effective for the catalysis, the damaged several tenths percents of the total carbon atoms may suffice the observed radiation effect on the reaction rate.

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[11] L. S. Singer, W. J. Spry and W. H. Smith, "Prod. 3rd. Conf. on Carbon," 1957, Pergamon Press, New York, N. Y. (Pub. 1959), p. 121.

[12] G. R. Hennig, "The Effects of Radiation on Materials," ed. by J. J. Harwood, H. H. Hausner, J. G. Morse and W. G. Rauch, Reinhold Pub. Corp., New York, N. Y. (1958), p. 226.

[13] A. R. Schulz, R. I. Roth and G. B. Rathmann, *J. Polymer Sci.*, **22**, 495 (1956).

[14] H. A. Dewhurst, *J. Phys. Chem.*, **61**, 1466 (1957); **62**, 15 (1958).

[15] H. A. Dewhurst, *ibid.*, **63**, 813 (1959).

[16] R. H. Schuler, *ibid.*, **60**, 381 (1956).