JOURNAL OF CATALYSIS 6, 227–236 (1966)

Combustion of Carbonaceous Deposits within Porous Catalyst Particles

II. Intrinsic Burning Rate

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Received May 18, 1966

All observations concerning intrinsic burning rates of carbonaceous deposits on various porous oxide supports are consistent within a relatively simple mechanistic framework of behavior.

(1) For a given support, the rate of carbon burnoff is largely independent of the source and structure of the coke.

(2) The kinetics of coke burning in oxides of silica, alumina, and magnesia show both quantitative and qualitative resemblances to the combustion of pure graphite, and suggest the existence of a basic, uncatalyzed burning rate on such oxides.

(3) The presence of oxides of transition metals results in coke burning rates up to several orders of magnitude higher than the aforementioned uncatalyzed rate at any given temperature.

(4) An examination of the Arrhenius plots of catalyzed and uncatalyzed coke burning rates presents a challenge to mechanistic interpretation, particularly of the catalytic effect of metal additions.

INTRODUCTION

We have already described (*1*) the operating conditions under which the rate of combustion of carbonaceous deposits (coke) in porous catalyst particles is affected to varying degrees by the diffusion of oxygen to the reacting sites; the kinetics of coke burning under the conditions that lead to essentially *complete* diffusional control was then treated in detail. This paper reports studies of the *intrinsic* burning rate of carbonaceous deposits, i.e., the burning behavior in the *absence* of appreciable diffusion effects.

Haldeman and Botty (*2*) have examined catalyst coke with an electron microscope, and found it to be highly dispersed in the catalyst. Also, the carbon deposit exhibited considerable complexity of detail in structure and in burnoff behavior during the earliest portion of burnoff. One may hesitate to embark on a thorough kinetic study of combustion behavior of carbonaceous deposits because of the possibility of inherent complexity: The chemical and physical structure of the reactant "coke" may seem ill-defined, as well as elusively variable. However, our investigation demonstrates the existence of some general and well-defined underlying mechanistic features of combustion kinetics of carbonaceous deposits in porous solids.

EXPERIMENTAL

The experimental methods have already been described (*1, 3*). The cumulative amount of carbon oxidized (to CO plus

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CO_2) as a function of time was measured under differential reactor conditions: that is, by burning a small sample (50 to 200 mg) of coked catalyst in air flowing rapidly enough to keep the oxygen concentration essentially unchanged. Thus the measurement is made at a given temperature, and under the partial pressure of oxygen in air.

The solid material was pulverized until it could pass through a 200-mesh screen. A small sample was then spread evenly on a flat surface over an area approximately 3 cm^2 so that the bed depth would not impair the access of oxygen to the catalyst. Both measures were designed to ensure freedom of the rate process from the effects of diffusion both within particles and within the particle bed.

The primary data were obtained in terms of the total carbon burned as a function of time (*1*, *3*). In this procedure, structural detail about the course of the instantaneous rate during the earliest (and fastest) portion of burnoff may be lost to the observer. However, the gross overall rate of combustion during the major portion of burnoff is prominently displayed. When burning was measured at a temperature too low to achieve practically complete burnoff during a reasonably long period, the temperature of the combustion furnace was then raised to 700°C to rapidly obtain the total amount of carbon. The data were replotted as the logarithm of the fraction of coke remaining as a function of time. An example of this plot is given in Fig. 1.

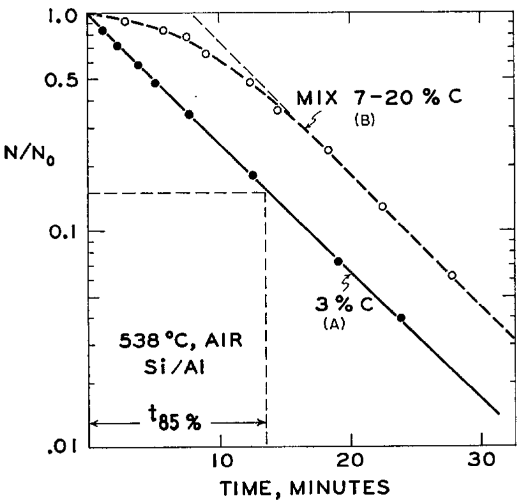

FIG. 1. Typical examples of rate plots of carbon remaining vs. burning time. Curve A: Normal sample. Curve B: Initial flattening due to carbon overload (partial inaccessibility).

Initially rapid transient burning rates were occasionally observed. They were believed to be caused by release of volatile hydrocarbon due either to thermal desorption or to cracking and product desorption at the temperature of the burning zone. This phenomenon was nearly always eliminated by exposing the sample to an oxygen-free atmosphere at 650°F (or, for burning rate measurements at higher temperatures, to a temperature equal to that of the intended burning reaction) for at least 15 min prior to making the burning rate measurements.

The Dependence of the Burning Kinetics on Carbon Concentration

The carbonaceous deposits obtained during cracking of hydrocarbons on catalysts such as silica-alumina have stoichiometric compositions varying from approximately $C_{1.0}H_{1.0}$ to $C_{1.0}H_{0.5}$. Materials relatively poorer in hydrogen may be present after the coked catalyst has been exposed to a high temperature for a long time. The term *coke* is generally applied to a combustible carbonaceous material that contains appreciable amounts of hydrogen. The burning rate measurements, however, concern and detect only the rates of oxidation of *carbon*.

A monomolecular layer of coke or carbon deposited on a porous solid of several hundred square meters per gram of internal specific surface area has an appreciable weight fraction of the solid. A simple calculation based on various sizes taken up by each atomic unit of carbon gives the following values:

Area of coke unit (Å^2)	Wt % Carbon on a catalyst with a surface area of 250 m^2/g
2	25.0
4	12.5
6	8.3

An atom of carbon in graphite takes up about $4 \times 10^{-16} \text{cm}^2 = 4 \text{Å}^2$. It follows, therefore, that a considerable weight fraction of coke can exist in a state of subdivision such that all portions are accessible to oxygen. Our experience confirms the applicability of this concept up to at least about 6 wt % coke on a porous catalyst with 250 sq. m/g of surface area: Within this limit the intrinsic burning rates are proportional to the total amount of coke present. Thus, the rate of coke removal is first-order in carbon, and the equation

$$d[\mathrm{C}]/dt = -k[\mathrm{C}] \qquad (1)$$

holds for a given temperature and oxygen partial pressure.

Figure 1(A) gives a burnoff graph for 3% carbon deposit on a 320 sq. m/g silica-alumina cracking catalyst, typical of more than a hundred burnoff experiments performed. It demonstrates normal first-order behavior [Eq. (1)]. The burning rate constant is given by the slope of the straight line. The curve in Fig. 1(B) was obtained from a sample of catalyst particles carrying from 7 to 20 wt % carbon. It demonstrates an initial apparent depression of the burning rate. However, after sufficient coke has burned off so that less than a monolayer is obtained, the slope of curve (B) approaches that of line (A).

When the burning rate is reasonably first order, it is convenient to use the observed time necessary to reach a particular fraction of burnoff as a measure of the rate constant, k. We have taken the burnoff time for 85% of the coke as a convenient quantity; it is related to the first order rate constant by

$$t_{85} = 1.9/k \qquad (2)$$

The Burning Kinetics of Coke on Silica-Alumina

The rate constant is independent both of the fraction of burnoff, and of the initial amount of coke—provided, as stated above, that the coke density is well below that calculated for a monolayer of completely accessible carbon. Figure 2 shows burning data on one sample of silica-alumina that had been loaded with various initial amounts of coke and subsequently burned at the same temperature (527°C). We have also made several hundred measurements of coke combustion rates on a number of silica-alumina cracking catalysts (containing 10% Al_2O_3) with surface areas varying from 100 to 450 sq. m/g. The methods used for production of these materials have been described by Weisz and Schwartz (*4*).

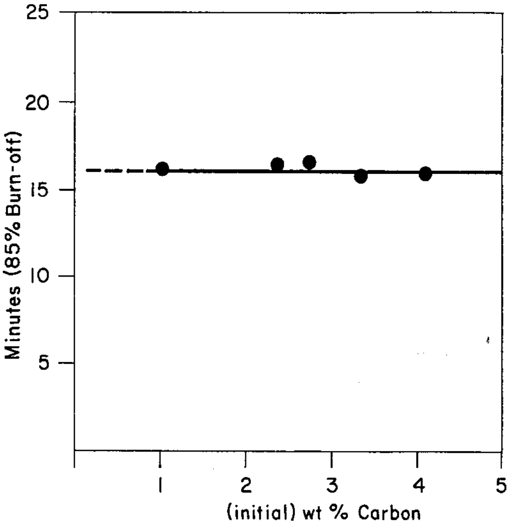

FIG. 2. Independence of the intrinsic burning rate from initial coke level (silica-alumina at 527°C).

We found, for any given temperature, a single and reproducible intrinsic rate constant. Moreover, the same temperature dependence of the rate constant was obtained for all catalyst samples. In Fig. 3 rate data are presented as a function of temperature for two different commercial silica-alumina catalysts. The open circle points represent results for a catalyst produced in 1951. The full circles give those for a Durabead catalyst produced in 1958. Chemically similar to the other catalyst, Durabead differs in the pore-size distribution, which is bimodal; the result is a higher diffusivity.

Lack of Dependence on the Nature of the Coke Deposit

The combustion behavior is remarkably independent of the nature or method of

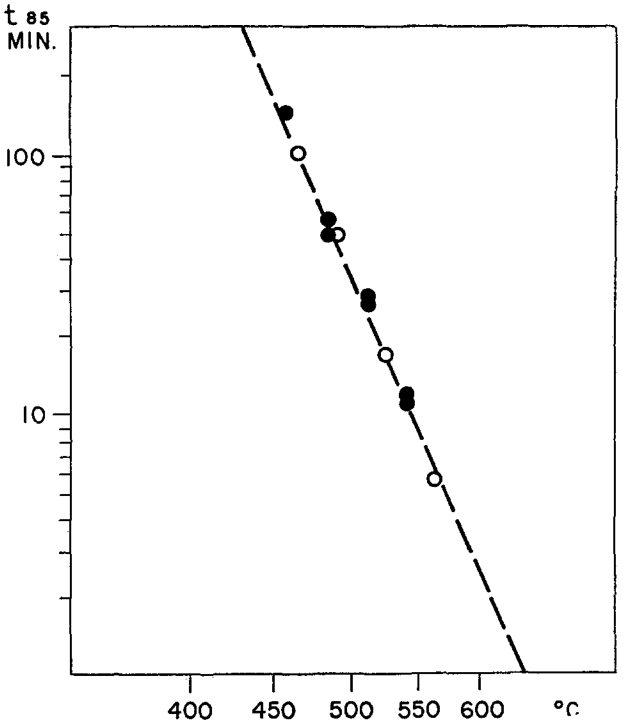

Fig. 3. Burning rate constant vs. temperature for two silica-alumina cracking catalysts: ○, 1951 silica-alumina; ●, 1958 "Durabead."

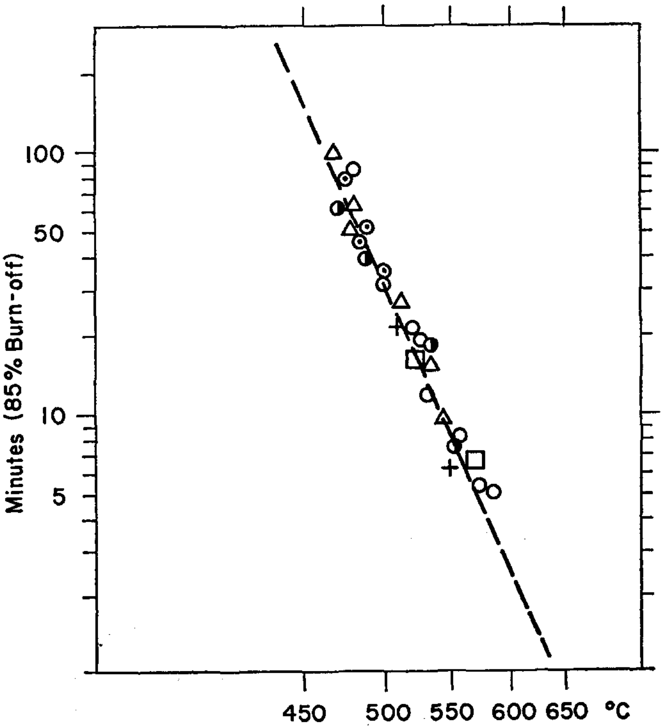

Fig. 4. Burning rate constant is independent of origin of coke. Five different modes of coking are represented by different symbols.

deposition of coke, as shown by the data (Fig. 4) obtained for carbonaceous deposits on silica-alumina that were produced by five distinctly different methods: (a) laboratory cracking of a (Light East Texas) Gas Oil at 470°C (○) and (⊙); (b) commercial refinery cracking in adiabatic TCC moving-bed reactor (◑); (c) cracking of cumene in a differential reactor at 420°C (□); (d) Cracking of a C_6 to C_{10} naphtha mixture at 535°C (△); (e) Reaction of, and exposure to, propylene at 420°C (+).

Evidence for a Basic Uncatalyzed Combustion Kinetics

Since oxidation catalysis usually requires the action of transition metal elements, we may assume that the observed coke burning kinetics on silica-alumina represent an uncatalyzed burning reaction. This is confirmed by the data (Fig. 5) for the observed burning rates for carbonaceous deposits on a variety of other solid oxides: (a) *Silica-magnesia cracking catalyst,* bearing carbon deposits from gas oil cracking (□); (b) *natural clay-derived cracking catalyst* (Filtrol 110), bearing carbonaceous deposits from gas oil cracking (×); (c) *Fuller's Earth adsorbent clay,* bearing carbonaceous deposits derived from chromatographic decolorizing of a heavy oil (percolation); it was purged at 430°C with nitrogen to remove residual liquid (●).

The coke content of these three samples was approximately 2.5 wt %, and their surface areas exceeded 150 m^2/g in all cases: All of the measurements support our concept of a generally applicable noncatalyzed burning kinetics, represented by the dashed lines in Figs. 3, 4, and 5. The slopes of these lines correspond to an apparent activation energy of $37.6 + 1.6$ kcal/mole. Expressed as a rate constant according to Eqs. (1) and (2), the equation for the rate constant for uncatalyzed, monolayer coke burning is given by

$$k = (1/C)(dC/dt = 4 \times 10^7 \times \exp[-(37{,}600 \pm 1{,}600)/RT] \quad (3)$$

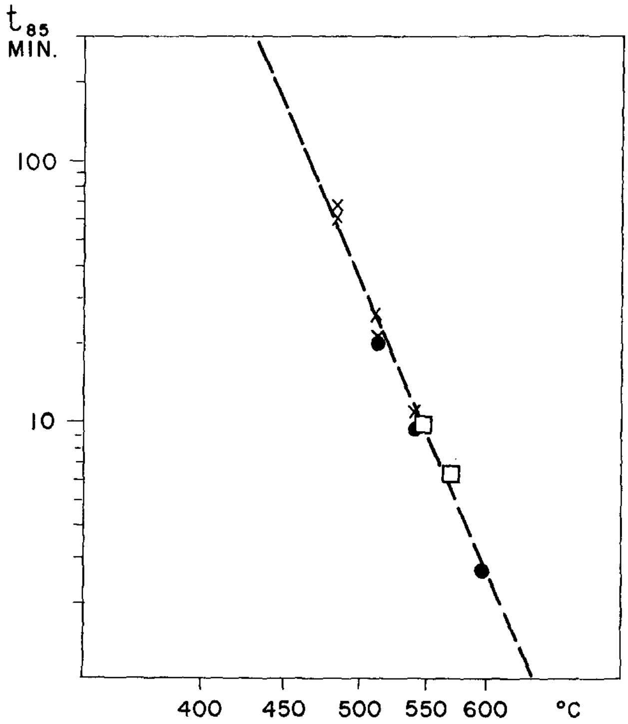

FIG. 5. Comparison of intrinsic combustion rate constant on various noncatalyzing oxide bases: ×, Filtrol 110; □, silica-magnesia; ●, Fuller's earth. Dashed line is standard noncatalyzed kinetics.

The dashed line represents the "standard" behavior observed for silica-alumina. All data coincide well with the standard behavior pattern, including that for the Fuller's Earth support, in spite of the complete departure from the catalytic method of coke deposition.

In preliminary burnoff experiments a somewhat faster burnoff rate was observed during the early stage; this was shown to be related to the evaporation of residual oils: Prepurging at ever-increasing temperature tends to eliminate such early "fast" behavior.

We conclude that the attack of the carbon atoms by oxygen apparently is not appreciably altered by variations in the mode and source of coke formation: The hydrogen atoms may be removed from the coke structures by a rapid initial attack, leaving the remaining carbon structure subject to the standard burning kinetics.

Comparison of Coke and Graphite Burning Rates

It is interesting to compare the observed combustion kinetics with that of a high-purity graphite surface, as observed by Gulbransen and Andrew (*5*). Their results are believed to be free from effects of mass transport and thermal gradients.

Gulbransen reports a combustion rate in terms of atoms of carbon burned per sec per centimeter square of graphite surface:

$$dC/dt = 1.7 \times 10^{23} \exp(-36\,700/RT)$$

at a partial pressure of oxygen of 0.1 atm. This rate may be recalculated using, as the unit of area, the area of a graphite atom, 4.10^{-16} cm², at a partial pressure of oxygen of 0.21 atm; we then obtain

$$k = (1/C)(dC/dt) = 3 \times 10^{7} \times \exp[-36\,700/RT] \quad (4)$$

The agreement between the numerical values in Eqs. (3) and (4) is remarkable.

The comparison we have just made logically extends our demonstration (that the carbon oxidation rate for uncatalyzed burning is independent of the carbon structure) to include the graphite surface. In addition, this result supports the contention that the silica-alumina carrier does not catalyze the rate of carbon burning.

Catalyzed Coke Combustion

Incorporating chromia in silica-alumina causes much faster coke burning rates. During production of such a catalyst a chromic salt (such as chromic sulfate) was added to the solution used to form the hydrogel. When fresh, the catalyst containing chromium has a distinctly yellow color. Figure 6 shows the result of adding 0.15 wt % chromium, analyzed as Cr_2O_3, to a silica-alumina cracking catalyst (□).

The burning rates follow a simple first order relation in coke; but the rate constants are greater by a factor of 4, and show the same apparent activation energy as does uncatalyzed burning. The catalytic effect of the chromium is lost, however, if the sample is treated with high-temperature steam, or after cyclic cracking; that is, whenever hydrocarbon contact alternates with oxygen regeneration: Figure 6 shows this loss of catalyzed burning rate of the fresh catalyst (□) within 3 days after being placed into a commercial cracking installation (⧄). Similarly, treating the catalyst with atmospheric steam for 3 hr at 710°C caused a loss of the catalyzed rate. Both steam and cyclic treatments are accompanied by a change in the color of the chromium species from bright yellow to dark green. This alteration is believed due to an irreversible change from a Cr^{6+} ion complex to a Cr^{3+} structure. It is interesting to note that the green chromium continues to catalyze the conversion of CO to CO_2.

A dramatic demonstration of catalysis of carbon combustion may be made with oxides of the transition metals themselves, such as on chromia-alumina catalyst designed for dehydrogenation, aromatization, and naphtha reforming. It was prepared by procedures already cited (*4*). The coke burning rates observed were so high that they had to be measured at a much lower temperature to remove the effects of diffusion and thermal transport. In Fig. 7 the observed rate behavior is shown in relation

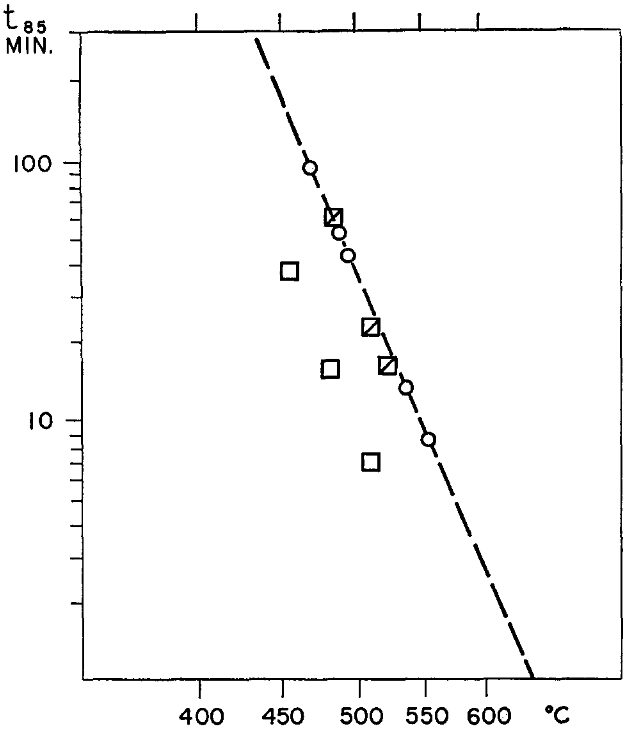

FIG. 6. Effect of Cr incorporation into silica-alumina: □, fresh yellow catalyst; ⧄, same after 3 days in commercial cracker installation; ○, same fresh catalyst after steam treatment. Dashed line is standard noncatalyzed kinetics.

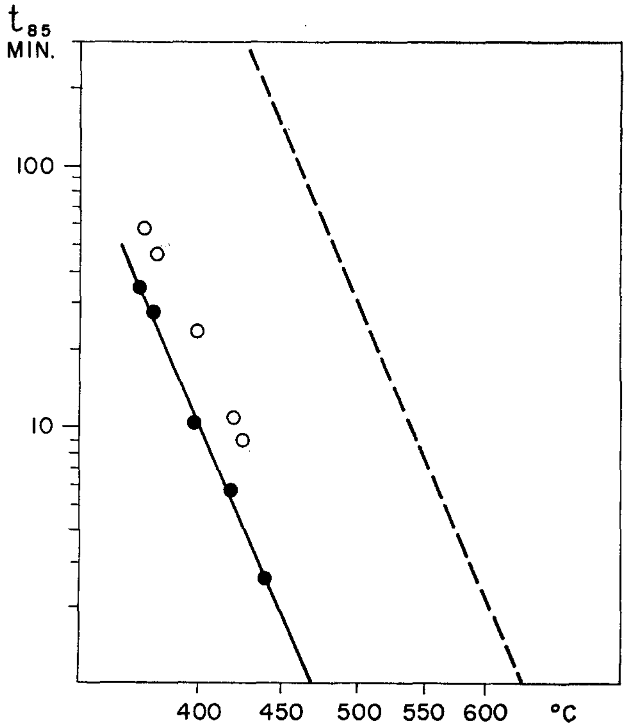

FIG. 7. Combustion rate constant for coke on chromia-alumina catalysts: ●, fresh sample; ○, pilot plant operating sample.

to the uncatalyzed rate. While the rates are two orders of magnitude higher than for the corresponding uncatalyzed rate, the new rate plot is again characterized by an apparent activation energy similar to that encountered in all previous cases. We have found that the activity level depends on the severity of oxidative, reductive, and cyclic exposure. This parallels qualitatively the effects seen in silica-aluminas containing chromium.

GENERAL CONCLUSION AND DISCUSSION

The kinetics of combustion of carbonaceous deposits on porous solids (catalysts or adsorbents) is consistent with a simple model. When measurements are conducted under conditions that avoid disturbing phenomena such as mass and thermal transport effects, presence of vaporizable carbonaceous deposits, etc., we find that the burning kinetics is (a) largely independent of the source or method of coke deposition; (b) similar to the burning behavior of graphite in uncatalyzed burning (for coke on solid oxide supports that do *not* contain transition metals); (c) catalytically enhanced on supports containing oxides of transition metals. On chromia-alumina supports, for example, rates two to three orders of magnitude above uncatalyzed rates can be attained.

The carbon oxidation rates of catalyzed cokes are normally proportional to the amount of carbon present, which indicates that the degree of dispersion is high enough to make the carbon atoms fully accessible to oxygen. This finding is consistent with the electron microscope observations made by Haldeman and Botty (*2*). Their work also showed that initial burning rates varied with the method of purging before combustion. Nevertheless, with time the rates approached orderly first-order behavior. Our results indicate rates in agreement with their stabilized rates. Also, our observed temperature dependence of 37.6 ± 1.6 kcal/mole is in fair agreement with their proposed value of 34.5 kcal/mole.

Deviations from the described general behavior can occur: Higher initial rates can be caused by thermal release of sorbed hydrocarbons. Lower initial rates (per amount of carbon present) are caused by inaccessibility of a portion of the carbonaceous material, which results from overloading of the pore surface with coke. Experience shows that such slowing occurs if the initial carbon content approaches or exceeds about 2 wt % carbon per 100 m^2/g of specific surface area of the support.

Interpretation of the Mechanism of Combustion Kinetics

In attempting to formulate a mechanistic interpretation of the burning kinetics of carbonaceous deposits, we must apparently meet two challenges:

(a) If the frequency factor of the uncatalyzed rate constant given by Eq. (3) is expressed on the basis of the unit surface area of coke, using 4×10^{-16} cm^2/C atom, it has a magnitude of $10^{23}/cm^2$ sec. The collision rate alone of oxygen molecules at 500°C and 0.21-atm partial pressure is $0.3 \times 10^{23}/cm^2$ sec. It is therefore tempting to propose a simple reaction mechanism such that every oxygen molecule with a Boltzmann energy of at least 37.6 kcal/mole reacts when it collides with a carbon atom. This is consistent with the rate law given by Eq. (3).

(b) The second problem arises in connection with the nearly fivefold increase in the rate of carbon oxidation on silica-alumina caused by addition of only 0.15 wt % of chromium (as Cr_2O_3). Here, on 1 g of solid, the rate of combustion of some 10^{-3} moles of surface carbon atoms is decisively influenced by only 10^{-5} moles of chromium atoms. Furthermore, a large portion of the chromium atoms must be located within the solid structure. Thus, apparently, a mechanism is needed by which the catalytic action of chromium that increases the burning rate of coke can proceed without contact.

One may try to resolve the first of these problems by assuming that the similarity between the apparent activation energies of the catalyzed and uncatalyzed processes is purely coincidental. He could then propose some more complex catalytic mechanism wherein the frequency factor no longer bears any direct relation to the oxygen collision frequency. However, an added difficulty arises because large variations in catalytic effectiveness among the cases of catalyzed burning have no apparent effect on the temperature coefficient. Any conclusion as to how a change in the rate constant can result from a variation in the number of active sites in the *solid* runs into difficulty because there is no reason to assume that contact between the carbon atoms and the active sites does occur.

There may be a close mechanistic relation between the difficulties presented by (a) and (b). In trying to design a single mechanistic model consistent with both, observations (a) and (b), we appear to be forced (1) to propose that the observed temperature coefficient does not reflect an activation energy of a simple kinetic process (making the similarity of the apparent frequency factor and gas–surface collision frequency fortuitous), and (2) to invoke the role of a mobile, and therefore probably gas-phase, species to provide a coupling mechanism between catalyst sites and carbon sites. We can point to two types of mechanisms that would possess the required characteristics.

FIRST EXAMPLE:

Let

$$C + O \underset{k'_1}{\overset{k_1}{\rightleftarrows}} [X] \xrightarrow{k_2} P$$

where an uncatalyzed reaction of C and O can occur very rapidly to produce an intermediate, X, that exists in the gaseous phase. Let the free energy change that leads to X be sufficiently unfavorable so that X occurs in very small concentration, that is $k_1/k'_1 = K \lll 1$. (The identity of X may therefore have remained obscure for that reason alone.) The intermediate product, X, then undergoes a catalytic or thermal conversion to the final product, P. We then have

$$\begin{aligned} \text{Rate} &= k_2[X] \qquad & k_2 &= a \exp[-Q/RT] \\ [X] &= Kf(O,C) \qquad & K &= \exp[-\Delta F/RT] \end{aligned}$$

and the overall rate will have the general form

$$\text{Rate} = af(O,C) \exp[-Q + \Delta F)/RT$$

The apparent activation energy will then appear approximately invariant if, in all cases, $\Delta F \gg Q$, i.e., if the major portion of the observed 37.6 kcal/mole is the *thermodynamic* free energy of formation of the intermediate X, and the kinetic activation energy Q is relatively small. The change in catalytic effectiveness for oxidation can then be attributed to changes in the frequency factor, a.

SECOND EXAMPLE:

Let the reaction lead to a side product Y, also represented in the gaseous and therefore mobile phase: A product that strongly *inhibits* the carbon oxidation reaction by competing for carbon sites. Then, the result of such competition would be a kinetic dependence of the form

$$\text{Rate} = \frac{a \exp(-Q_1/RT)}{1 + b \exp(-Q_2/RT)},$$

where Q_2 would characterize the activation energy for sorption of the competing species Y to a nonreactive carbon complex and b would be proportional to the gas-phase concentration of the species Y. A metal catalytic component added to the system is then presumed to be actively destroying the species Y (by catalytic decomposition or further oxidation, with an activation energy small compared to Q_2).

In a temperature range where $b \exp(-Q_2/RT) \gg 1$, we obtain

$$\text{Rate} \approx (a/b) \exp[-(Q_1 - Q_2)/RT]$$

the quantities Q_1, Q_2, and therefore $(Q_1 - Q_2)$, being characteristic of the carbon sites alone, would not be affected by the addition of metal catalyst. However, such addition will lead to the rise of the apparent frequency factor by reduction of b.

The general role of a mobile species appears in both examples to provide the influence of catalytic centers without direct chemical contact with carbon. The effectiveness of this coupling, however, will be somewhat dependent on long-range physical proximity in a manner analogous to what one encounters in polyfunctional catalysis (*6*).

The present observations do not warrant speculations concerning more specific mechanistic aspects of the carbon combustion process.

SUMMARY AND CONCLUSIONS

(1) For a given support, the rate of carbon burnoff is largely independent of the source and structure of the coke.

(2) Coke deposited on supports made of oxides of silica, alumina, and magnesia gives a minimum rate of burning at any given temperature and exhibits similar burning kinetics. The kinetics of coke burning on these supports show both quantitative and qualitative resemblances to the combustion of pure graphite, and suggest the existence of *a basic, uncatalyzed burning rate* on such oxides.

(3) On the other hand, oxides of transition metals give coke burning rates up to several orders of magnitude higher than the aforementioned uncatalyzed rate at any given temperature.

(4) An examination of the Arrhenius plots of catalyzed and uncatalyzed coke burning rates presents the investigator with a challenge to a mechanistic interpretation of the carbon combustion process, and, in particular, of the catalytic effect of metal additions.

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