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Combustion of Carbonaceous Deposits within Porous Catalyst Particles

III. The CO_2/CO Product Ratio

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In the combustion of carbonaceous deposits ("coke") on porous catalysts, a large spectrum of CO_2/CO product ratios is observed. It results from a definite initial ratio at the burning site dependent on temperature only, and subsequent oxidation of CO to CO_2 determined by a catalytic rate constant and the rate of diffusional escape of the carbon monoxide from the particle.

INTRODUCTION

The two preceding papers of this series (*1*, *2*) presented a systematic study defining the principal features of the kinetic behavior of carbon burning when carbonaceous deposits within various porous oxides are reacted with oxygen. That study dealt with both the intrinsic chemical kinetics and the diffusion effects in the burning of carbon to form volatile oxides. In burning under intrinsic combustion kinetics, the rate was shown to be quite independent of the origin and structure of the coke, and in fact was similar to that of graphite burning as studied by Gulbransen and Andrew (*3*, *4*).

When in our studies of carbon burning rates (*1*, *2*) the CO to CO_2 product ratios are examined, one appears to be confronted with a chaotic assembly of data, as shown in Fig. 1. On the other hand, in graphite burning, Arthur (*5*), and also Rossberg (*6*), reported unique CO_2/CO product ratios dependent on temperature alone.

In a brief communication [as a commentary on Rossberg's work (*6*)] Schmidt and Mossmann (*7*) observed that the CO_2/CO ratio generated during coke burning of amorphous silica-alumina cracking catalysts at low temperatures was surprisingly similar to the reported ratio in carbon burning, and commented that discrepancies observed for temperatures between 480° and 580°C were probably due to secondary conversion of carbon monoxide to carbon dioxide.

We have subjected the data used in our previous work on total burning rate to a careful analysis of the interaction of reaction kinetics and diffusion in determining the relative amounts of CO and CO_2 produced. This analysis shows that the ratio of CO_2 to CO produced *at the burning site* agrees exactly with Arthur's ratio at all temperatures tested. The ratio is then modified to different extents (dependent upon other conditions) by the conversion of CO to CO_2 as the CO molecules diffuse out of the catalyst particle.

METHODS

The experimental procedures have already been described (*1*, *2*). For this work, however, the combustion products were first passed through one barium hydroxide conductivity cell to measure cumulative CO_2 production. The effluent from this cell, together with excess air carrier gas, was then passed over a hot copper catalyst to convert CO to CO_2. The CO_2 was then absorbed by a second barium hydroxide cell to measure the cumulative CO production.

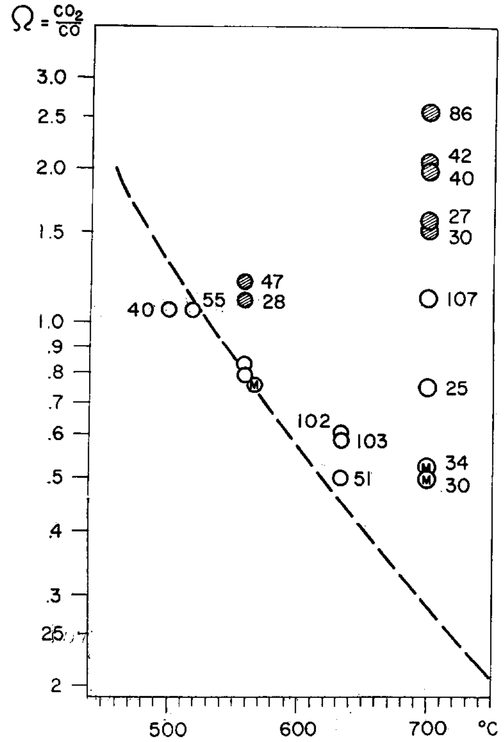

FIG. 1. The total cumulative CO_2/CO ratio for coke burnoff on spherical catalyst beads vs. combustion temperature in air: open circle, "white" amorphous silica-alumina; shaded circle, "green" Cr_2O_3-containing amorphous silica-alumina; M, macroporous "white" catalyst. Dashed line represents "intrinsic" ratios from carbon combustion research [J. R. Arthur, (*5*)].

Most important of all, the measurements were made either on *individual spherical beads* of coked amorphous silica-alumina catalyst of approximately 0.4 cm diameter (*1*), or on small samples of finely ground up catalyst (<200-mesh screen size) (*2*). The records of the values of the cumulative CO_2 and CO from a two-pen recorder were compared with one another, as shown by Figs. 2 and 3. The slopes $d(CO_2)/d(CO)$ represent the ratio of instantaneous rates of production of CO_2 and CO: $(d[CO_2]/dt)/(d(CO]/dt)$. Measurements were made on two types of bead cracking catalyst: a standard amorphous silica-alumina (10% Al_2O_3), which is white in appearance; and another of the same basic composition, which in addition contained 0.15 wt % of chromium (reported as Cr_2O_3). The second catalyst was steam-aged until green in appearance (*2*).

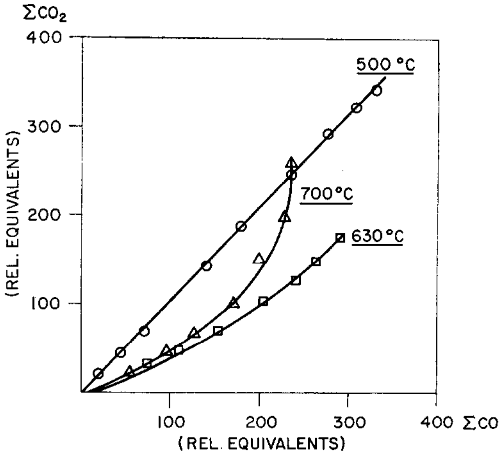

FIG. 2. Cumulative amounts of CO_2 vs. CO produced during burning of coke on white catalyst beads (open symbols), and on powdered catalyst (solid dots). Dashed lines correspond to powdered catalyst samples.

OBSERVATIONS

Figure 1 shows the final cumulative CO_2/CO ratios observed on a number of individual spherical beads, as a function of temperature of burnoff. The dashed line represents the ratios of products from intrinsic carbon burning as reported by Arthur (*5*). The spread of data is large; however, we note that the Arthur line

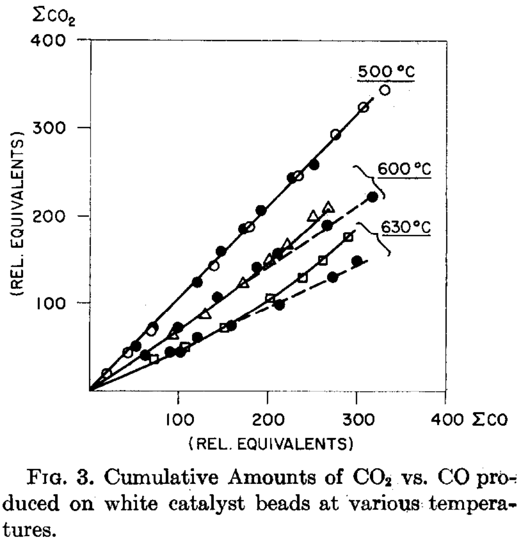

FIG. 3. Cumulative Amounts of CO_2 vs. CO produced on white catalyst beads at various temperatures.

appears to represent a lower bound to the data. The shaded circles appear to constitute a separate family lying generally higher in CO_2/CO ratio. These represent data from the amorphous silica-alumina beads containing chromia. The numbers marking individual data are the weights (in milligrams) of each bead tested. Within each family at any one temperature a correlation of higher CO_2/CO ratios with larger sphere size becomes apparent.

The open circles marked M represent white beads with a bimodal macroporous structure, which gave an effective diffusivity of 0.008 cm²/sec, as compared to 0.003 cm²/sec for the other white beads tested. The values of carbon monoxide diffusivity at 950°K were calculated by standard methods from measured values of hydrogen diffusivity obtained using a previously published technique (*8*). Qualitatively, these results are consistent with those of a mechanism that predicts an intrinsic CO_2/CO ratio, followed by a subsequent intraparticle conversion of carbon monoxide to carbon dioxide that increases with temperature and particle size (internal path length), and decreases with increasing diffusivity. The activity for such secondary conversion in the Cr_2O_3 is higher than that in the white beads.

Figure 2 shows the relative carbon dioxide and carbon monoxide production rates during burnoff in individual tests of white beads and of powdered catalyst. Figure 3 shows the course for bead burning at low, medium, and high temperatures. The bead vs. powder comparisons demonstrate the onset of "diffusion-constrained" secondary carbon monoxide conversion in beads as the temperature goes above about 540°C. We observe (Fig. 3) *a variable CO_2/Co ratio* during burnoff only for large particles (beads), and for high temperatures.

DISCUSSION

A change of product ratio during burnoff on a single bead will result—in spite of a fixed intrinsic CO_2/CO ratio at the burning site—if the average path length of escaping product molecules changes during burnoff. We have shown (*1*) that in these catalyst beads the coke combustion rate as a whole begins to be appreciably inhibited by oxygen diffusion above a temperature of about 500°C. It leads to local rates of coke removal that decrease toward the center, and therefore to a progressive lengthening of the average diffusion path during burnoff. At temperatures above about 540°C we have demonstrated that this gradient develops to its extreme form—the shell-progressive combustion mechanism—in which combustion takes place at a spherical shell surface that shrinks with progressive burnoff from its original radius, $r = R$, to $r = 0$.

We have been able to describe the burning rate behavior by our two limiting models, one on each side of all possible intermediate cases. These bounding models are (1) the intrinsic kinetic burning, and (2) the diffusion controlled (shell-progressive, or "fish-eye") burning. Similarly, we can analyze the CO to CO_2 conversion for these two analogous cases.

A. *CO to CO_2 Conversion in the Intrinsic Burning Region*

In this case we deal with a negligible radial oxygen gradient; and the CO to CO_2 conversion sources are therefore of uniform strength throughout the particle.

The concentration, C, of carbon monoxide must satisfy the equation

$$D\nabla^2 C + \alpha C_c - kC = 0 \qquad (1)$$

where C_c is the coke concentration, αC_c the rate of CO production, and k is the first order rate constant for the subsequent conversion of CO to CO_2. We need not consider the dependence on oxygen concentration because it must, by definition, be uniform throughout the particle for this case. We can solve Eq. (1) for spherical particle geometry to obtain the fraction, f, of CO that remains unconverted as it passes the particle boundary. We obtain, for the intrinsic burning rate-controlled kinetic region,

$$f_i = 3/\varphi)[(1/\varphi) - (1/\tanh \varphi)] \qquad (2)$$

wherein φ is of the familiar form $\varphi = R_0(k/D)^{1/2}$, and contains the particle radius, R_0; reactant (here carbon monoxide) diffusivity, D; and the conversion rate constant k.

We note that the solution has a form identical to that of the familiar Thiele utilization factor η, if $\eta \equiv f$. The quantity αC_c does not occur in the solution; i.e., the degree of secondary conversion of CO is independent of degree of burnoff, as was foreseen on the basis of physical reasoning, since no change in the average path length for CO diffusion is involved.

B. CO to CO_2 Conversion in the Shell-Progressive Kinetic Region

For the region between the burning shell at R_b and the outer particle radius R_0, we have

$$D\nabla^2 C - kC = 0 \qquad (3)$$

We will be interested, again, in the fraction, f, remaining, i.e., in the flux ratio

$$f = \left[R_0 \Big/ \left(\frac{dC}{dr}\right)_{R_0}\right] \Big/ \left[R_b \Big/ \left(\frac{dC}{dr}\right)_{R_b}\right] \qquad (4)$$

The solution of (3) for spherical geometry has the form

$$C = (a/r) \exp mr + (b/r) \exp(-mr)$$

where $m = (k/D)^{1/2}$, and we have

$$r^2(dC/dr) = a(mr - 1) \exp(mr) - b(mr + 1) \exp(-mr)$$

With the boundary condition, $C = 0$, at $r = R_0$, we have, for a single particle burning under differential reactor conditions

$$r^2(dC/dr) = a\{(mr - 1) \exp(mR) + (mR + 1) \exp(-mr) \exp(2mR_0)\} \qquad (5)$$

From (5) we can form the ratio (4), and by introducing the familiar form $\varphi = R_0(k/D)^{1/2} = R_0 m$, and the amount of coke remaining at any time, $y = (R_b/R_0)^3$, we obtain f in the diffusion-controlled burning region as

$$f_D = \{y^{1/3} \cosh(1 - y^{1/3})\varphi + (1/\varphi) \sinh(1 - y^{1/3})\varphi\}^{-1} \qquad (6)$$

In Fig. 4 we have plotted f_D vs. y for $\varphi = 1, 2, 3, 4, 5$.

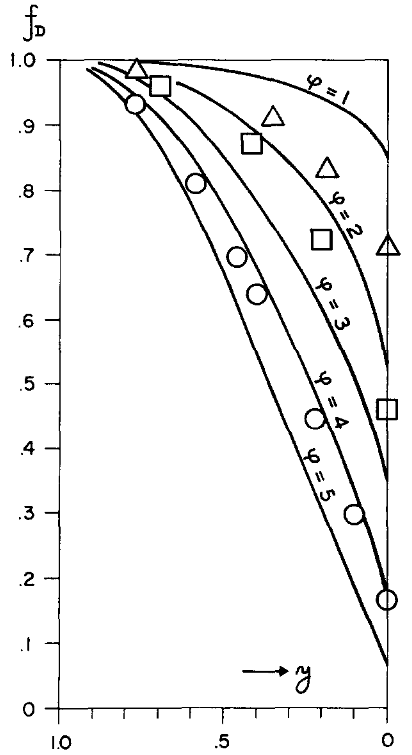

FIG. 4. Course of the fraction (f) of originally produced CO emerging unconverted vs. degree of burnoff (y, relative amount of carbon remaining), at various φ of the secondary CO reaction.

The relation of f (f_i or f_D) to the two ratios, (1) the relative rate of production of CO and of CO_2 at the burning site, $\delta_0 = d[CO_2]_0/d[CO]_0$, and (2), the corresponding one actually leaving the particle, $\delta = d[CO_2]/d[CO]$, is

$$f = (\delta_0 + 1)/(\delta + 1) \qquad (7)$$

The total cumulative ratio of CO_2 to CO produced during burnoff,

$$\Omega = \Sigma[CO_2]/\Sigma[CO],$$

is experimentally more accurately, and often more conveniently, obtainable than is accurate instantaneous rate information. We can derive a dependence on φ and y analogous to (6), based on total cumulative product information as follows: We have

$$\frac{d[CO]}{dt} = \frac{dN/dt}{\delta + 1},$$

$$\frac{d[CO_2]}{dt} = \left(\frac{dN}{dt}\right)\left(1 - \frac{1}{\delta + 1}\right),$$

wherein dN/dt is the total burning rate of carbon.

With $dN/dt = N_0(dy/dt)$, and with (7), we have

$$d[CO_2] = N_0\,dy\{1 - [f/(\delta_0 + 1)]\}$$
$$d[CO] = N_0\,dy[f/(\delta_0 + 1)]$$

and

$$\Omega = (\delta_0 + 1)[\textstyle\int dy/\int f(y,\varphi)dy] - 1$$

or, in analogy with (7),

$$F = (\delta_0 + 1)/(\Omega + 1) \qquad (8)$$

where

$$F = \textstyle\int f(y,\varphi)dy.$$

In Fig. 5 we have plotted the machine-calculated values of the integral F for use in the interpretation of the final cumulative CO_2/CO production observed.

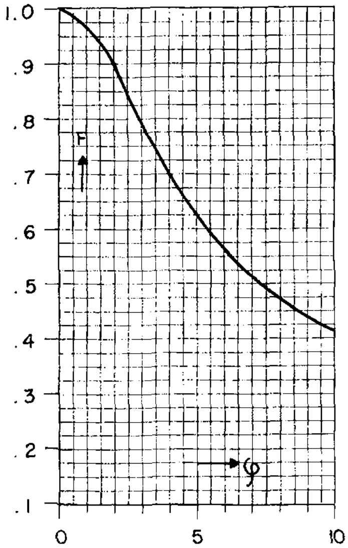

Fig. 5. The function (F) for the total cumulative CO_2/CO ratio for various φ of the secondary CO reaction.

INTERPRETATIONS OF OBSERVATIONS

At the temperatures at which the white catalyst beads show appreciable deviation from Arthur's CO_2/CO values (i.e., above about 600°C [see Fig. 1]), we have shown (1) that the burning kinetics for these catalysts follow the shell-progressive mechanism. We can, therefore, expect the relation (6) (Fig. 4) to be followed during burnoff. If, for the 107-mg white catalyst bead burning at 700°C (see Fig. 1), we assume that the original CO_2/CO ratio is that given by Arthur's curve, and calculate the resulting f_D values that must have been operative to give the observed variation and values, we obtain the points ○ entered in Fig. 4. These points are entirely consistent with a value of $\varphi = 4.4 \pm 0.6$. We have assigned a generous error in our estimation of the instantaneous slopes of the cumulative $[CO_2]$ vs. [CO] plots.

The white catalyst sphere of 25-mg weight burned at the same temperature should differ from the 107-mg particle only in that φ is scaled by a factor of $(25/107)^{1/3}$; this gives a value of $\varphi = 2.7$. The observed values are entered as □ and agree well with the predictions.

The white catalyst sphere of 103-mg weight burned at 630°C should follow behavior corresponding to a φ smaller than that for the 107-mg bead burned at 700°C by the ratio $(k_{630}/k_{710})^{1/2}$. The points (Δ) in Fig. 4 show that $\varphi = 1.5$. As we know the diffusivity to be $D = 0.003$ cm²/sec, we can derive the CO to CO_2 conversion constant from $\varphi = R_0(k/D)^{1/2}$. We obtain, with $R_0 = 0.275$ cm (for the large 107-mg beads), the values placed in Fig. 6 for "white" catalyst, corresponding to an apparent activation energy of 28 kcal/mole for the CO to CO_2 conversion.

At still lower temperatures k, and therefore φ, rapidly become small enough to yield insignificant CO conversion. It is thus interesting to note that *the shell-progressive model is wholly satisfactory to deal with this intraparticle product conversion problem*; the intraparticle product conversion problem fades out at lower temperature, before inadequacy of the shell model becomes important.

We can devise the constants necessary to explain the behavior of the chromia-containing (green) catalyst beads most simply by making use of the cumulative final CO_2/CO data of Fig. 1 (Ω), combining them with δ_0 (the appropriate intrinsic Arthur value), and using Fig. 5, to obtain the values of φ. Figure 7 shows the φ values thus obtained for burning at 700°C, where they are recorded as a function of the particle radius in each case. The excellent agreement of the

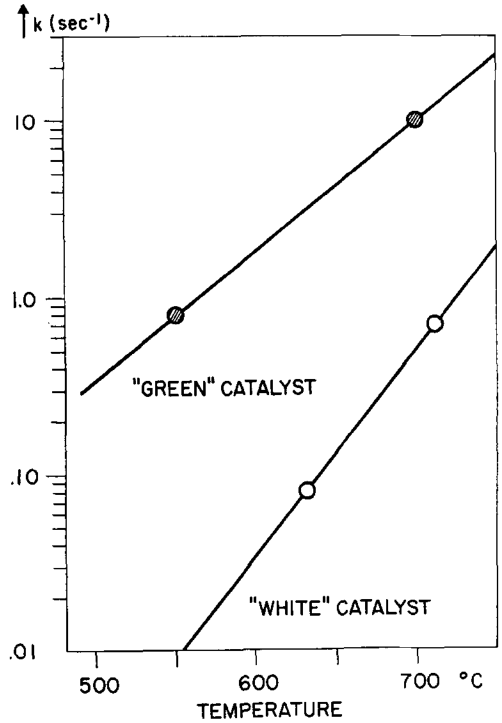

FIG. 6. Rate constants for the CO → CO_2 conversion in white amorphous silica-alumina, and in "green" amorphous silica-alumina (containing 0.15 wt % chromia), derived from the diffusional CO_2/CO kinetics.

results with the theoretically expected linear relation between φ and R, which passes through the origin, supports the soundness and all-around consistency of the mechanism.

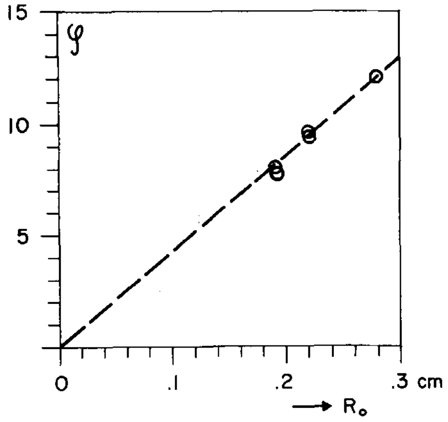

FIG. 7. Diffusional modulus φ derived from CO_2/CO data for various "green" amorphous silica-aluminas plotted against bead size.

From the effective diffusivity for carbon monoxide of these beads, $D = 0.005$ cm²/sec we obtain the CO to CO_2 conversion rate constants plotted in Fig. 6 for "green" catalyst. The effect of the 0.15 wt % "green" chromia is seen to enhance the CO conversion rate constants by a factor of between 100 and 10 in the usual range of temperatures. This catalytic oxidation activity of "green chromia" is found to be stable and reproducible through several thousand hours of catalyst operation.

SUMMARY

All observations concerning the observed ratios of CO_2 and CO in combustion of coke from porous oxide catalyst are shown to be fully consistent with the generation of a definite CO_2/CO ratio determined by temperature, and the subsequent intraparticle conversion of CO to CO_2. The ratio of the initial desorbing species is identical to that observed in the oxidation of carbon as described by the Arthur relation (*5*). It has been possible above to give this mechanism full quantitative substance and description. This broadens further the extent of similarities between the kinetics of carbon burning and of coke-on-catalyst combustion discovered and described in a recent publication by Weisz and Goodwin (*2*).

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