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USE OF OXYGEN ISOTOPE EXCHANGE IN CO₂ TO CHARACTERIZE ACTIVE SITES

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Abstract—The characterization of carbon surface activity in the absence of gasification was attempted using oxygen isotope exchange in CO₂ over spectroscopically pure natural graphite, the surface activity being characterized by the rate of approach to isotopic equilibrium. The probable mechanism of exchange is via the first step in the carbon-CO₂ reaction, the dissociation of CO₂ over a carbon free site: $\text{CO}_2 + \text{C}_f \xrightleftharpoons[k_1]{k_2} \text{C}(\text{O}) + \text{CO}$. Assuming this mechanism to hold for isotopic exchange, the theoretical rate equation was derived. The rate constants k_1 and k_2 were obtained from previous studies. Theoretical calculations show that the exchange rate is negligible over natural graphite at temperatures much below gasification conditions. Experimental verification of the theoretical analysis was not possible due to the activity of the quartz boat, holding the graphite, for catalyzing the exchange reaction. The exchange reaction was successfully followed over the Pt and CaO supported on a graphitized carbon black, in which case the activity was much, much greater than that over the empty quartz boat.

1. INTRODUCTION

It is well known that only a fraction of the total surface area (TSA) of carbons is active surface area (ASA) and that this fraction varies from carbon to carbon [1, 2]. Active area is thought to reside primarily at prismatic planes at crystallite boundaries but also can reside at defects within the basal planes of trigonally bonded carbon crystallites [3, 4]. The activity of sites will vary depending upon their geometric configuration, that is whether they are located in the (101) or (100) plane or are dangling carbon sites. Site activity may be enhanced momentarily in the presence of carbon gasification. The newly formed active site may have an unpaired σ electron associated with it until it is joined by an electron jumping from the π -band into the σ -state, forming a spin pair at the crystallite edge (5). The number and activity of carbon active sites are of supreme importance in affecting virtually all properties of carbon; and, therefore, their characterization is a prime goal of carbon science.

One technique which we have used in this laboratory to determine the number of carbon active sites is to measure the dissociative chemisorption of oxygen in the essential absence of carbon gasification (1) or the chemisorption of olefins in the essential absence of carbon deposition (6). Knowledge of ASA enabled us to determine meaningful rate constants for both carbon gasification by O₂ and carbon deposition from propylene (2).

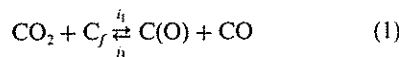
Some years ago oxygen-18 tracer studies allowed us to determine that CO and CO₂ are both primary products of carbon gasification in O₂ (7). To use O¹⁸ to study the possible reactions leading to the formation of CO₂, it was first necessary to show that CO₂ was formed more rapidly than oxygen was exchanged in the CO₂ molecule. This was found to be the case, despite the fact that exchange occurred at a mea-

surable rate over burned-off Graphon held in a quartz sample holder at 773 K. Starting with a non-equilibrium mixture of 92.0% CO₂¹⁶⁻¹⁶, 5.7% CO₂¹⁸⁻¹⁸, and 2.3% CO₂¹⁶⁻¹⁸, an equilibrium mixture containing 12.8% CO₂¹⁶⁻¹⁸ was attained within 40 min. No detectable CO was found during the exchange period.

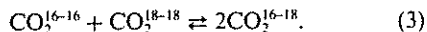
It recently occurred to us that this exchange reaction would be a useful approach for measuring the activity of carbon ASA, particularly as we will see, since the coverage of ASA by stable oxygen complex during the exchange at 773 K should be negligible. This paper is primarily concerned with our efforts in this direction.

2. THEORY

The accepted mechanism for the gasification of carbon by CO₂ is [8, 9]



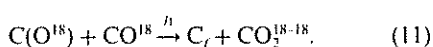
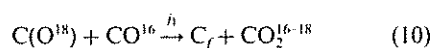
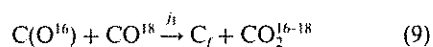
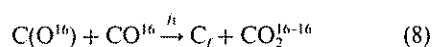
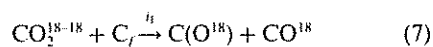
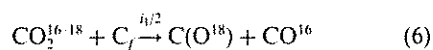
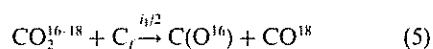
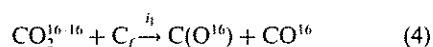
where C_f is a free carbon active site and C(O) is an active site covered by a chemisorbed oxygen atom. The isotopic exchange reaction of oxygen in CO₂ is as follows



When a mixture of CO₂¹⁶⁻¹⁶, CO₂¹⁶⁻¹⁸, and CO₂¹⁸⁻¹⁸ is exposed to a "clean" carbon surface at 773 K (a surface which has been first heated to 1223 K for 3 hr to remove oxygen surface complex), two parallel reactions take place: (1) the isotopic exchange reaction where statistical mixing of the oxygen species in CO₂ is

occurring and (2) the gas–solid equilibrium reaction [reaction (1)] where there is a net build up of oxygen surface complex to some equilibrium value. The rate of carbon gasification is negligible [10]. After the second reaction has equilibrated, a steady-state concentration of CO₂, oxygen complex, and free carbon active sites exists. The atomic fraction of oxygen-18 in the surface complex should be the same as in the gas phase, assuming no kinetic isotope effect.

As we will see, if the exchange reaction proceeds via the first step in the carbon gasification mechanism, the reaction rate can be predicted from the rate constants of Strange and Walker [10]. Neglecting the kinetic isotope effect, the following reactions occur during isotope exchange:



The rate of the exchange reaction can be given by

$$d[\text{CO}_2^{16-16}]/dt = -i_1[C_f][\text{CO}_2^{16-16}] + j_1[\text{C(O}^{16})][\text{CO}^{16}] \quad (12)$$

The equilibrium constant for reaction (1) is

$$K = i_1/j_1 = [\text{C(O)}][\text{CO}]/[\text{CO}_2][C_f] \quad (13)$$

The concentrations denoted in eqn (13) refer to the total concentration of each species, i.e.

$$[\text{CO}_2] = [\text{CO}_2^{16-16}] + [\text{CO}_2^{16-18}] + [\text{CO}_2^{18-18}] \quad (14)$$

$$[\text{CO}] = [\text{CO}^{16}] + [\text{CO}^{18}] \quad (15)$$

$$[\text{C(O)}] = [\text{C(O}^{16})] + [\text{C(O}^{18})] \quad (16)$$

From eqn (13),

$$[\text{C(O)}][\text{CO}] = K[\text{CO}_2][C_f] \quad (17)$$

If we expose a given concentration of CO₂ to a clean carbon surface, then after the attainment of gas–solid equilibrium,

$$[\text{CO}_2] = [\text{CO}_2]_i - X \quad (18)$$

$$[C_f] = [C_f]_i - X \quad (19)$$

where X is the amount of CO₂ reacted to form complex and the subscript i represents the initial concentration. By the stoichiometry of reaction (1),

$$X = [\text{CO}] = [\text{C(O)}] \quad (20)$$

Equation (17) then becomes

$$X^2 = K[\text{CO}_2][C_f] \quad (21)$$

From eqns (15) and (20),

$$X = [\text{CO}^{16}] + [\text{CO}^{18}] \quad (22)$$

and

$$X = [\text{C(O}^{16})] + [\text{C(O}^{18})] \quad (23)$$

Assuming the isotopic distribution on the surface is equal to the isotopic distribution in the gas phase, that is no kinetic isotope effect, we can write

$$X = [\text{CO}^{16}] + [1/\alpha][\text{CO}^{16}] \quad (24)$$

where α is the ratio of the atomic fraction of oxygen-16 to oxygen-18 in the gas phase. Then,

$$[\text{CO}^{16}] = [\alpha/(\alpha + 1)]X \quad (25)$$

and similarly

$$[\text{C(O}^{16})] = [\alpha/(\alpha + 1)]X \quad (26)$$

If the attainment of equilibrium in the gas–solid reaction is much faster than that for isotopic exchange, we can substitute eqns (25) and (26) into eqn (12) and get

$$d[\text{CO}_2^{16-16}]/dt = -i_1[\text{CO}_2^{16-16}][C_f] + j_1[\alpha/(\alpha + 1)]^2 X^2 \quad (27)$$

We can now substitute eqn (21) into eqn (27)

$$d[\text{CO}_2^{16-16}]/dt = -i_1[\text{CO}_2^{16-16}][C_f] + j_1[\alpha/(\alpha + 1)]^2 K[\text{CO}_2][C_f] \quad (28)$$

Substituting the definition of K

$$d[\text{CO}_2^{16-16}]/dt = -i_1[\text{CO}_2^{16-16}][C_f] + i_1[\alpha/(\alpha + 1)]^2 [\text{CO}_2][C_f] \quad (29)$$

If the atomic fractions of oxygen-16 and oxygen-18

are y_{16} and y_{18} , respectively, then, from statistical considerations, the isotopic equilibrium fractions of the three CO₂ species must be

$$\text{CO}_2^{16-16}, y_{16}^2 \quad (30)$$

$$\text{CO}_2^{16-18}, 2(y_{16})(y_{18}) \quad (31)$$

$$\text{CO}_2^{18-18}, y_{18}^2 \quad (32)$$

Since there are only two oxygen species,

$$y_{16} + y_{18} = 1 \quad (33)$$

or

$$y_{16} + [1/\alpha]y_{16} = 1 \quad (34)$$

or

$$y_{16} = [\alpha/(\alpha + 1)]. \quad (35)$$

The equilibrium fraction of CO₂¹⁶⁻¹⁶ from eqn (30) is

$$[\alpha/(\alpha + 1)]^2 \quad (36)$$

and thus the equilibrium concentration of CO₂¹⁶⁻¹⁶ is

$$[\text{CO}_2^{16-16}]_e = [\alpha/(\alpha + 1)]^2 [\text{CO}_2]. \quad (37)$$

Substituting eqn (37) into (29),

$$d[\text{CO}_2^{16-16}]/dt = -i_1[C_f][(\text{CO}_2^{16-16}) - (\text{CO}_2^{16-16})_e]. \quad (38)$$

Equation (38) shows that the rate of isotopic exchange is first order when the atomic fraction of each species in the gas phase remains constant.

Two conditions are necessary for the above derivation to be valid: (1) the kinetic isotope effect is negligible, and (2) the gas-solid reaction reaches equilibrium much more quickly than does the isotope exchange reaction. It can be shown that the kinetic isotope effect for the dissociation of CO₂ over a carbon free site is only ~2.5% [11]. It can further be shown, for spectroscopically pure natural graphite, that the half-life for gas-solid equilibrium is at least two orders of magnitude less than the half-life for isotopic exchange equilibrium at temperatures between 773 and 1173 K [11].

As can be shown [11], the equation to be used in the analysis of the experimental data on isotope exchange is

$$dP_{16-16}/dt = -k_a[P_{16-16} - P_{16-16,e}] \quad (39)$$

where k_a is the apparent rate constant for the exchange, and P_{16-16} and $P_{16-16,e}$ are the pressures of CO₂¹⁶⁻¹⁶ at time, t , and equilibrium, respectively. Since a constant volume reactor was used in which only a small fraction (65 cm³) of the total volume (1290 cm³)

was heated to the reaction temperature, k_a was normalized by multiplying by the ratio of reaction temperature (T_R) to room temperature (T_N) in degrees absolute [12], to yield k'_a .

Some of the data are reported on the basis of the half-life of the isotopic equilibrium reaction,

$$t_{1/2} = \ln 2/k'_a \quad (40)$$

3. EXPERIMENTAL

3.1 Materials

The carbon used in this investigation was SP-1 spectroscopically pure natural graphite obtained from the Carbon Products Division of Union Carbide Corp. Previous workers [13] have shown that this material consists of nonporous graphite flakes about 0.3–0.5 μm in thickness and about 30 μm in dia. The BET surface area of this material is 1.8 m²/g and the He density is 2.25 g/cm³. The geometric edge (active) area of these flakes is about 3.3% of the BET area. The total impurity content is guaranteed to be < 1 ppm, with the major impurities being Fe, Mg and Si. The samples were burned off to 10% in 0.1 MPa of air at 723 K for use in this study.

The effect of catalysts on the exchange rate was investigated using graphitized Cabot Corp carbon black Vulcan 3G (V3G) to which Pt and CaO were added. The V3G particles are polyhedral in shape, nonporous, and have a BET surface area of 63 m²/g. The ASA is estimated from oxygen chemisorption as < 0.2% of the TSA. Total impurity content is < ~125 ppm, with B content being ~100 ppm. The Pt catalyst was prepared following the impregnation technique described elsewhere [14]. Ultimately, the sample was reduced in H₂ at 773 K. The Pt content was 1.07 wt%. The platinum dispersion, as measured by CO-titration [15], was 18.9%; and, therefore, the Pt TSA is estimated at 49 m²/g of Pt, if one takes the area of a Pt atom as 0.084 nm².

Samples containing calcium were prepared in the following manner. Carboxyl groups were added to the carbon by twice treating 5 g of carbon black with 250 cm³ of concentrated HNO₃ and evaporating to dryness under agitation. The carbon was then immersed in a 250-cm³ solution of 0.5 M calcium acetate; the solution was heated to 333 K and stirred for 8 hr to effect ion exchange of calcium with hydrogen on the carboxyl groups. It was then cooled to room temperature and stirred for 12 hr. The solution was decanted, the carbon was washed with distilled water, and dried in a vacuum oven. The carbon was then heated to 1273 K at a heating rate of 10 K/min and held for 1 hr. The sample had a total calcium content of ~1 wt%. The crystallite (particle) size of the CaO could not be determined from X-ray diffraction because of the very low loading. The particle size of CaO would not be expected to be larger than the average particle diameter of V3G (23.5 nm). Using 23.5 nm as the particle size for CaO particles on V3G, dispersion is estimated to have a minimum value of

5.3% [11]. If one takes the molecular area of CaO as 0.115 nm^2 , the CaO TSA is estimated at $66 \text{ m}^2/\text{g}$ of CaO.

3.2 Apparatus

A schematic diagram of the apparatus is shown in Fig. 1; the total system volume is 1290 cm^3 . The system was constructed of Pyrex except for the reactor. The double-walled reactor was made of quartz (>99% SiO_2 from Quartz Scientific Inc); the annular space was continuously evacuated to prevent permeation of external gases at high temperature. The surface area of the heated zone in the reactor was 0.021 m^2 .

The system was evacuated to $\sim 10^{-4} \text{ Pa}$ with a mechanical pump and an oil diffusion pump connected in series. An 8 l/sec Vacion pump was then used to reduce the pressure to $\sim 10^{-6} \text{ Pa}$. The system pressure during the reaction was monitored by an M.K.S. Baritron electronic manometer.

A General Electric Analytical mass spectrometer was used to monitor the composition of the reacting gases. The gases were leaked into the mass spectrometer through a molecular flow (Knudsen) leak. The leak rate was first order in pressure. The mass spectrometer was interfaced with a mini-computer to provide rapid data acquisition.

The carbon sample was placed in a cylindrical quartz boat (surface area 0.006 m^2 , >99.99% SiO_2 from Wales Apparatus Co.). The boat rested on top of a quartz thermocouple well in the heated zone of the reactor. The sample temperature was monitored through this thermocouple well. The control thermocouple was placed between the outside wall of the reactor and the furnace. A West Guardsman temperature controller was used to control the reactor temperature to $\pm 1 \text{ K}$.

3.3 Gases

The CO_2^{16-18} (99.95% purity) used was obtained from the Matheson Co. CO_2^{18-18} was produced by burning a Saran char at 673 K in 0.11 kPa of O_2^{18-18}

and freezing out CO_2^{18-18} in a liquid nitrogen trap. The oxygen-18 was obtained from the Yeda Research and Development Co., Rehovoth, Israel; the gas was 98.2 atomic % 0-18, 0.364 atomic % 0-17, and 1.436% 0-16. The CO_2^{18-18} produced was purified by thrice freezing out the gas in a liquid nitrogen trap and then evacuating the residual gas. Trace amounts of water which may have desorbed from the Saran during combustion were removed by condensing it in a dry ice-acetone trap.

3.4 Procedure

A 0.1-g sample of SP-1 graphite was placed in the quartz sample boat and covered by a small quartz wool plug. The sample was heated to 1223 K under vacuum to remove the oxygen chemisorbed on the carbon prior to lowering the temperature to reaction conditions. A CO_2 gas mixture of known isotopic distribution was exposed to the sample of 773 K; the total pressure of gas was 3.1 Pa. The isotopic distribution was continually monitored during the reaction with the mass spectrometer. Generally, the reaction was allowed to proceed to at least 80% completion.

For Pt and CaO supported on graphitized V3G, $\sim 0.1 \text{ g}$ of sample was used. The empty quartz boat was first heated in air in the reactor to 1173 K for 2 hr. To minimize handling of the boat, a known weight of sample was placed in a sample vial, the boat was raised out of the reactor, and the sample placed in the boat by dumping the contents of the vial into the boat. The boat was quickly lowered back into the reactor and the system was evacuated. This entire procedure took less than 30 sec. The weight of sample introduced into the system was determined by measuring the weight of the sample vial before and after the sample was transferred.

Samples of Pt on carbon were not given any pretreatment before performing the first exchange reaction. Exchange was measured in the temperature range of 648–723 K and a total pressure of 3.1 Pa. At these temperatures the rate of exchange over Pt was at least 50 times that of the reactor containing the

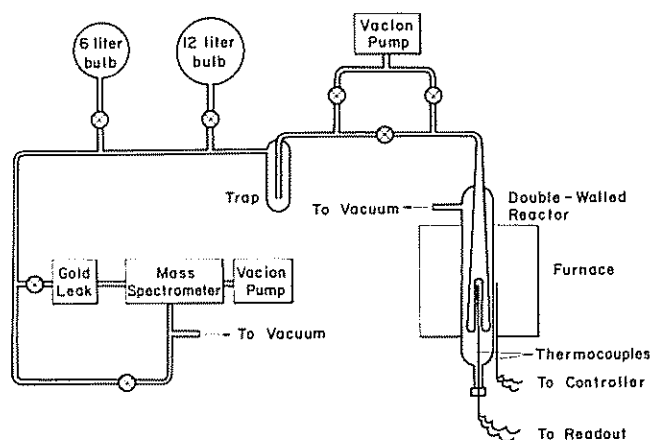


Fig. 1. Schematic diagram of experimental apparatus.

empty quartz boat. After a series of runs at these temperatures the sample was heated to 873 K and held under vacuum for 4 hr. The Tammann temperature of Pt is approx. 923 K[16]; therefore, presumably negligible change in catalyst dispersion occurred during this heat treatment. A series of exchange reactions was run over the same temperature range as with the fresh sample. Finally, the sample was cooled to room temperature, and the oxygen remaining on the surface was titrated with CO, following the procedure described elsewhere[15]. The chemisorbed CO was removed by heating, in vacuum, to 623 K[17]. The exchange was again measured on the sample in the same temperature range.

Samples of CaO on carbon were pretreated at 1173 K for 1 hr under vacuum to remove oxygen chemisorbed on the carbon, prior to performing the exchange reaction. The exchange rate on the CaO sample was measured in the temperature range 300–773 K at a total pressure of 3.1 Pa.

It is to be emphasized that for all runs, no CO was detected, indicating both negligible carbon gasification by CO₂ and negligible formation of oxygen complex on the carbon. The latter result was expected because of the low value for the equilibrium constant for reaction (1) at temperatures below 773 K[8].

4. RESULTS AND DISCUSSION

4.1 Exchange over empty quartz boat and SP-1 graphite

Table 1 presents a number of results for half-lives for isotopic exchange in CO₂ at 773 K and 3.1 Pa

pressure. The rate of exchange reaction in the empty quartz reactor (run 1) was negligible. However, the empty quartz sample boat (run 3) showed a significant activity to the exchange reaction (an exchange half-life some 120-fold less than that in the empty reactor), despite the fact that the area of the boat was 3.5-fold less than the heated quartz reactor area. The exchange rate in the presence of the empty sample boat was within an order of magnitude of the exchange observed in the presence of SP-1 graphite (run 2), indeed in some cases being higher. The sample boat was subjected to many treatments in an attempt to deactivate it. Table 1 lists the various treatments used and the half-life of the isotopic equilibrium.

The only means by which the activity of the boat could be reduced was heat treatment in atmospheric air at 1173 K for 2 hr (run 12). The exchange rate on the boat was within an order of magnitude of the empty reactor. After the boat had been deactivated in the manner described, it was removed from the reactor, handled with Nylon gloves and Nylon forceps, placed on the pan of a microbalance, weighed, and put back into the reactor. This procedure increased the activity by two orders of magnitude, indicating that handling affected the activity of the boat. The work of Hochstrasser and Antonini[18] shows that freshly cleaved silica surfaces can chemisorb CO₂ at "E-centers" forming a CO₂-radical. The "E-centers" are surface silicon atoms containing unpaired electrons. It was thought that the sample boat may have become abraded during handling, resulting in the formation of "E-centers". Deactivation of the

Table 1. Half-lives for isotopic exchange in CO₂ at 773 K and 3.1 Pa pressure

Run	Exchange Half-Life, s
1. Empty reactor	9.5×10^4
2. 0.1 g of SP-1 graphite in quartz boat	596
3. Empty quartz boat	755
4. Empty boat washed with conc. HF	1460
5. Empty boat heated to 1123 K for 4 h under vacuum	3252
6. Empty boat washed with conc. HF and heated to 1273 K in muffle furnace	4471
7. Empty boat as treated in 6, removed and placed on the pan of a microbalance and placed back in reactor	86
8. Oxidation of empty boat in 6 Pa of O ₂ at 875 K for 1 h	341
9. Oxidation of empty boat in 107 Pa of O ₂ at 873 K for 18 h	373
10. Empty boat placed in steam autoclave at 393 K and 202 kPa for 4 h and dried in a vacuum oven at 353 K for 2 h	113
11. Empty boat treated as in 10, but heat treated to 1173 K in vacuum for 3 h	746
12. Empty boat burned out in atmospheric air at 1173 K for 3 h in reactor and cooled under vacuum	3.7×10^4

"E-centers" can be accomplished by adding hydroxyl groups to these sites [19]. This was attempted in run 10, but the activity of the boat for isotopic exchange was not significantly affected. A subsequent 1173 K heat treatment of the hydroxylated boat under vacuum (run 11) did not sufficiently reduce its activity.

As discussed, the theoretical rate of the isotopic exchange reaction for oxygen in CO_2 over carbon is given by eqn (38), provided that the rate of gas-solid equilibration is much faster than the rate of equilibration in the isotopic exchange reaction. Exchange half-life is given by

$$t_{1/2} = \frac{\ln 2}{i_1 [C_r]} \quad (41)$$

Taking values for i_1 and C_r from the data of Strange and Walker for SP-1 graphite (10), the half-life of the exchange reaction at 773 K is estimated to be about 10^{16} sec. If the mechanism postulated for the exchange reaction is correct, the much more rapid exchange rate observed in the presence of SP-1 graphite was the result of some catalytic effect. Catalysis seems likely since in some cases observed exchange rates over the empty quartz boat were higher than in the presence of carbon. These rates are comparable to the exchange rates measured by Walker *et al.* [7]. It is not likely that the intrinsic rate constants for the carbon- CO_2 reaction for the graphitized carbon black used in their investigation are very much different than those reported by Strange and Walker for SP-1 graphite [10]. We can, therefore, conclude that the exchange reaction observed by Walker *et al.* [7] was catalyzed by either some impurity on the sample boat or some impurity on the carbon black. Walker *et al.* [7] report that the total impurity content of the Graphon used was < 11 ppm. Beiderman *et al.* [20] have shown that even this apparently low impurity content can still affect the rate of carbon gasification in CO_2 . They have shown that the gasification rate of Graphon in CO_2 at 1123 K and 13.3 Pa is approx. 700 times higher than that of SP-1 graphite. The ratio of active surface areas for Graphon to SP-1 (as measured by oxygen chemisorption at 573 K and 6.67 Pa) was only 34, suggesting that the observed higher gasification rate on Graphon was the result of the presence of catalytic impurities.

Since oxygen isotopic exchange in CO_2 appears to be catalyzed by traces of impurities on the carbon and/or on the boat holding the carbon, it was concluded that use of the exchange reaction to characterize active sites is best suited to the study of catalysts supported on carbon. The activity of the catalyst at significant loadings should be much higher than background.

4.2 Exchange over carbon-supported catalysts

The half-life of the exchange reaction (pressure of 3.1 Pa) over 0.1 g unloaded V3G held in the quartz boat at 773 K was 590 sec. Thus, the exchange rate

was similar to that found for SP-1 graphite held in the quartz boat and not significantly different than that found for the empty quartz boat.

4.2.1 *Exchange over Pt.* The exchange reaction was measured over two samples of Pt on carbon obtained from the same batch. Above about 650 K exchange rates were much, much more rapid than those found over the empty quartz boat. As discussed previously, values of k'_a , the apparent rate constant, could then be calculated. In turn, specific rate constants, k , could be calculated as follows

$$k = k'_a (V_s / \text{ASA}) \quad (42)$$

where V_s is the total system volume (1290 cm^3) and ASA is the active surface area of the catalyst. For both Pt and CaO, their ASA was taken as equal to their TSA. If one knows k , the rate of disappearance of CO_2^{16-16} or CO_2^{18-18} as a result of exchange to CO_2^{16-18} can be calculated at any time in the exchange reaction, R_t , as follows

$$R_t = [k][\text{ASA}][C_t - C_e] \quad (43)$$

where C_t and C_e are concentrations of the particular CO_2 species at time, t , and equilibrium.

Figure 2 shows data on an Arrhenius plot for the specific rate constants for the fresh samples, samples heat treated to 873 K for 3 hr, and samples titrated with CO followed by heat treatment at 623 K for 3 hr. The temperature range ($\sim 100 \text{ K}$) over which exchange could be followed was limited. Below $\sim 623 \text{ K}$, exchange rates were slow, approaching background rates too closely. Above 723 K,

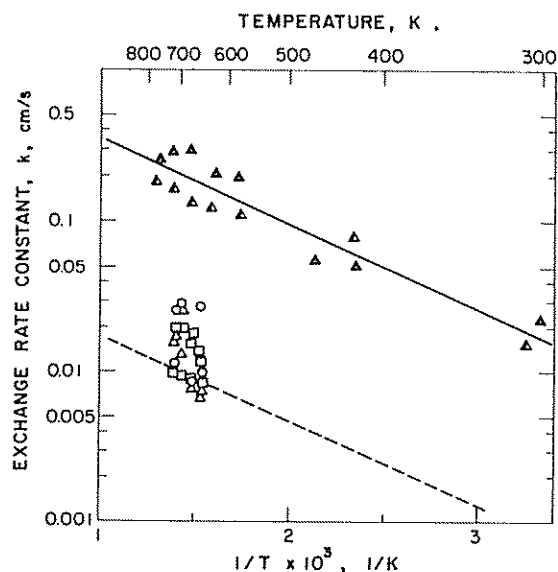


Fig. 2. Arrhenius plots of specific rate constants for oxygen isotope exchange in CO_2 over 1% Pt on V3G (18.9% dispersion) and 1% CaO on V3G (estimated dispersion, 5.3%); Δ , Pt on V3G, untreated samples; \circ , Pt on V3G, heat treated samples; \square , Pt on V3G, CO-titrated samples; Δ , CaO on V3G; ----, CaO results, assuming 100% dispersion.

gasification of carbon, as catalyzed by Pt, became significant. Rate constants for the three pretreatments used fall within an order of magnitude at any given temperature, indicating that, within the temperature range used in this study, exchange does not change significantly with sample pretreatment. Linear regression was used to determine the slope and standard deviation of the slope for the Arrhenius plots. The large standard deviation of the slope of the Arrhenius plots precludes estimation of the activation energy for this exchange.

A common feature of exchange for Pt samples studied under all pretreatments is that there was: (i) no detectable CO produced, (ii) no net loss of CO₂ during exchange, and (iii) no transfer of oxygen-18 to the Pt surface. The sensitivity of the mass spectrometer was sufficient to detect coverages of the Pt surface greater than ~3%. The first finding is consistent with negligible carbon gasification or build-up of oxygen complex on the Pt from CO₂. The second finding is consistent with negligible carbon gasification or chemisorption of CO₂ on the Pt. The third finding indicates that any oxygen chemisorbed on the fresh Pt, as a result of exposure to atmospheric air at room temperature and still present during reaction, does not participate in the exchange reaction.

4.2.2 Exchange over CaO. Exchange was measured over two samples of CaO from the same batch. Agreement between the two runs was reasonable, as seen in Fig. 2. The activation energy for exchange was 13 kJ/mol, with a standard deviation of 2 J/mol. These results are based on a CaO dispersion of 5.3% which, as previously discussed, is considered to be a lower limit for dispersion. The dashed line shows results if CaO dispersion were 100%, which is highly unlikely.

Comparison of exchange results over Pt and CaO is interesting. Clearly the activation energy for exchange over Pt is higher than over CaO. Also the exchange reaction could be followed over a much broader temperature range over CaO than over Pt, for an equal loading weight (1%). The lower limit is somewhere below room temperature over CaO, compared to ~623 K for Pt. The upper limit, above which significant carbon gasification occurs, is ~773 K over CaO compared to ~723 K over Pt. As with Pt, no exchange of oxygen-18 to the CaO surface was detected. That is, the oxygen derived from the dissociation of CO₂ at the CaO surface did not exchange with the oxygen in CaO to any measurable extent.

5. CONCLUSIONS

It appears that oxygen exchange in CO₂ does not have utility to characterize the activity of carbon

sites, due to the much higher specific activity of traces of inorganic impurities for the reaction. These impurities can be associated both with the carbon and the quartz container holding the carbon. Even exposure of the container to an ambient air atmosphere for a brief period appears to add sufficient impurities to catalyze a measurable rate of exchange at 773 K. Oxygen exchange in CO₂ is found to be a convenient reaction to characterize the activity of catalysts supported on carbon substrates, if the amounts of catalyst added are sufficient to result in background activity being negligible.

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