

THE ADSORPTION AND CATALYZED REACTIONS OF CO AND CO₂ ON GRAPHITE SURFACES

By W. T. Tysoe, J. Carrazza and G. A. Somorjai

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

1. Introduction

The use of ultra-high vacuum (10^{-10} - 10^{-11} torr) in conjunction with various electron spectroscopies has, over the past twenty years, provided considerable insight into adsorption on well-characterized transition metal surfaces. The incorporation of a high-pressure cell into the vacuum chamber has allowed surface species to be related to the mechanism of catalytic reactions (1).

A similar approach is adopted in this work in the study of catalytic reactions of graphite with CO and CO₂. Prior to studying catalytic reactions, results are presented in this paper on the interaction of these molecules with a clean graphite surface.

The experimental probes that are brought to bear on this problem are Auger electron spectroscopy (AES) for elemental analysis of the surface, temperature programmed desorption (TPD) to examine thermal decomposition of adsorbate species and, finally, x-ray photoelectron spectroscopy (XPS) in order to identify surface entities.

2. Experimental

The experimental apparatus is shown in Figure 1, and has been described in detail elsewhere (2). Briefly, it consists of a UHV chamber which contains a high-pressure cell, a double-pass cylindrical mirror analyzer with co-axial electron gun for Auger spectroscopy, and an X-ray source with a magnesium anode for XPS. The chamber is also equipped with a quadrupole mass spectrometer for residual gas analysis and TPD experiments. Two types of carbon were used in these experiments: a polycrystalline carbon for high pressure reactions and TPD, and a piece of oriented graphite from the Carbon Products Division of Union Carbide for XPS.

3. Results

Oxygen was the major contaminant of both graphite samples as revealed by AES. This could be effectively removed by extensive outgassing at 1500K in UHV. Hydrogen, another possible contaminant is not detectable by AES, but since C-O bond strengths are likely to be greater than for C-H, thermal removal of oxygen implies that all hydrogen has also been removed.

3.1 CO and CO₂ Adsorption and Reaction

Shown in Figure 2 are 28 amu (CO) and 44 amu (CO₂) desorption spectra after high exposures ($>10^8$ L) of CO and CO₂ onto clean polycrystalline graphite at room temperature. No other desorption species were detected. The large exposures required to saturate the surface imply very low sticking probabilities.

Surprisingly, both CO and CO₂ give rise to identical 28 and 44amu spectra above 600K, exhibiting a CO₂ peak at 740K and a CO peak at 1230K. Features below 600K may originate from "physisorbed" molecules (3) or from desorption from supports. (Platinum, the support material, has a CO desorption peak at ~ 500 K).

The number of adsorption sites on the polycrystalline sample may be estimated at $\sim 5 \times 10^{14} \text{ cm}^{-2}$ from a comparison of these data with a desorption spectrum from a CO saturated Pt foil. The reaction between CO or CO₂ and polycrystalline graphite was investigated as a function of sample temperature in the high pressure reactor. The results for the reaction $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$, using a gas pressure of 230 torr, are shown in Figure 3a. These results were obtained by measuring the gas production rate, and the turnover frequencies calculated assuming the active site concentration obtained from TPD experiments ($\sim 5 \times 10^{14} \text{ cm}^{-2}$). Measurement of the slope of this curve yields an activation energy for CO production of $67 \pm 3 \text{ kcal/mole}$. This is in good agreement with values of 59 kcal/mole obtained in a flow reaction (4).

Figure 3b shows a similar plot for the reverse reaction ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$). An activation energy may be extracted from the linear region and yields a value of $24 \pm 2 \text{ kcal/mole}$. The difference between these activation energies, i.e. the enthalpy for reaction is $-43 \pm 5 \text{ kcal/mole}$, which is in good agreement with the literature value of -41.2 kcal/mole (5).

Oriented graphite was used for X-ray photoelectron experiments since polycrystalline samples exhibited a broad feature on the high binding energy side of the Cls peak due to excitation of a plasmon (6). This peak is sufficiently intense to effectively obscure any adsorbate induced features. However, the plasmon satellite is strongly attenuated with the X-ray beam impinges at grazing incidence onto an edge plane which allows chemically shifted species to be observed. This sample orientation is also likely to lead to increase in number of adsorbate sites.

Figure 4a shows a $\text{MgK}\alpha$ Cls x-ray photoelectron spectrum from the edge plane of an oriented graphite sample after exposure to $\sim 10^8$ L CO₂ and flashing to 450K to remove "physisorbed" species. The solid line depicts the spectrum of clean graphite taken under identical conditions. The graphite Cls peak has a binding energy of 285.0 eV, and the adsorbate induced peaks occur at 281.7 eV and 280.6 eV constituting chemical shifts of 3.3 ± 0.2 and 4.4 ± 0.1 eV) remains. This peak may be removed by heating to ~ 1400 K corresponding to the desorption of CO.

4. Discussion

The use of single crystal graphite aligned so that the x-ray source impinges onto the edge plane atoms allows adsorbate induced C1s features to be observed. It is well established (7) that these shifts may be due to carbon species that can be categorized as follows: ether and hydroxyl groups ~ 1.6 eV, carbonyl groups ~ 3 eV and carboxyl groups, ~ 4.2 eV. The trend in O1s binding energies is less clear cut. On this basis, the peaks that arise after CO₂ exposure may be identified as being due to carboxyl (280.6 eV) and carbonyl (281.7 eV) species. The XPS data indicates that the carboxyl species disappears on heating to above 850K. CO₂ is desorbed at this temperature in TPD so that carboxyl species thermally decomposes to yield CO₂. The $\pi \rightarrow \pi^*$ shake-up satellite also disappears. Such behavior has been observed by Schlogel after similar treatments of graphite samples (6). Further heating to 1400K evolves CO in TPD and the remaining adsorbate induced peak due to a carbonyl species disappears. High pressure reactions on a polycrystalline graphite sample result in the formation of CO₂ from CO in the temperature range 800-900K and CO from CO₂ in the range 1000-1100K. These temperatures correspond to those at which CO₂(740K) and CO(1230K) are evolved, so that the rate limiting step for CO₂ formation may be the decomposition of carboxyl species. Similarly, the reaction to form CO may take place via carbonyl decomposition.

Further work is required to identify the exact nature of the surface carbonyl and carboxyl species so that their interconversion mechanism may be elucidated in greater detail.

5. Conclusion

The interaction of clean graphite surfaces with CO and CO₂ is amenable to investigation using conventional surface science techniques such as AES, TPD and XPS. Preliminary studies indicate that carboxyl and carbonyl species may be identified and appear to arise from exposure to either CO or CO₂. CO₂ production at similar temperatures in both high pressure reactions and in TPD suggests that carboxyl decomposition may be the rate limiting step to CO₂ formation. Analogously, carbonyl decomposition appears to be rate limiting for the formation of CO.

6. Acknowledgements

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7. References

1. G. A. Somorjai and S. M. Davis, *Platinum Metals Review*, 27, 54(1983).
2. A. L. Cabrera, Heinz Heinemann and G. A. Somorjai, *J. Catalysis*, 75, 7(1982).
3. T. Wigmans, J. van Doorn, and J. A. Moulyn, *Fuel*, 62, 190(1983).
4. S. Ergun, *J. Phys. Chem.*, 60, 480(1956).
5. *Handbook of Chemistry and Physics*, 61st ed., R. C. Weast, ed., CRC Press, 1980-81.
6. Schlogel and H. P. Boehm, *Carbon*, 12, 345(1983).
7. D. T. Clark and H. R. Thomas, *J. Polymer Science (Polymer Chem Ed.)*, 16, 791(1978).

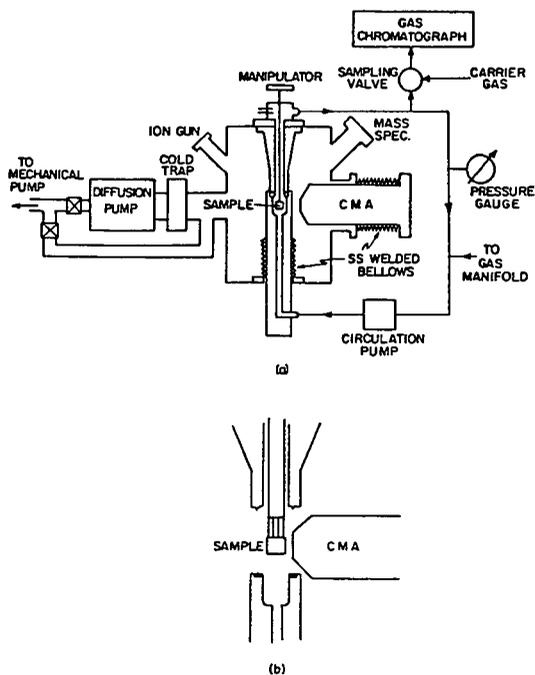


Fig. 1 (a) Schematic diagram of apparatus with high pressure cell closed; (b) detail with high pressure cell open.

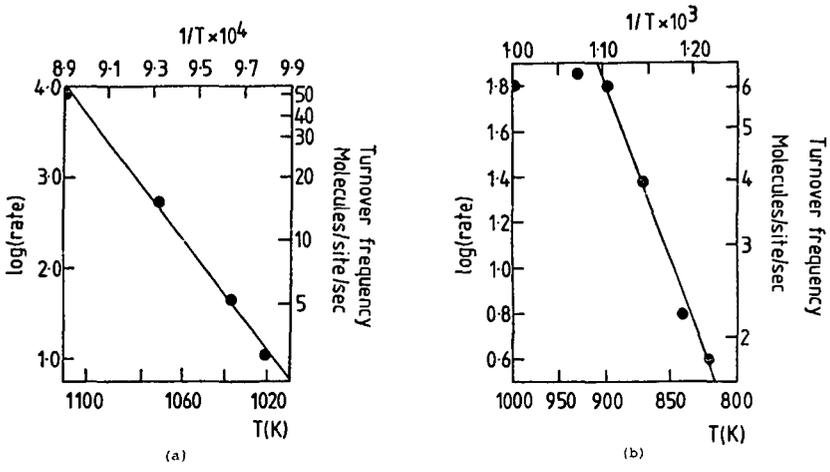


Fig. 3 (a) Arrhenius plot for the reaction, $\text{CO}_2 + \text{C} + 2\text{CO}$; (b) Arrhenius plot for the reaction $2\text{CO} + \text{CO}_2 + \text{C}$.

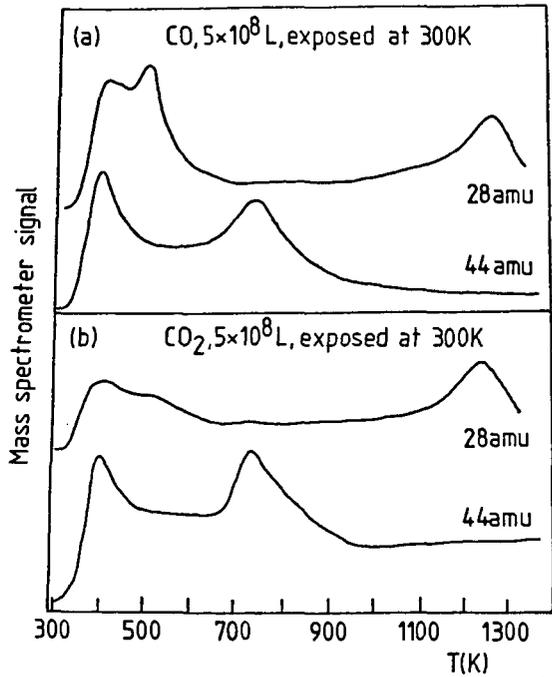


Fig. 2 28 and 44 amu desorption spectra obtained after (a) $5 \times 10^8 \text{ L}$ exposure of CO and (b) $5 \times 10^8 \text{ L}$ exposure of CO_2 onto polycrystalline.