*Korean J. Chem. Eng.*, **15**(3), 336-340 (1998)
**SHORT COMMUNICATION**

# REACTION OF NO AND $N_2O$ GASES WITH GRAPHITE IN TGA

**Young-Cheol Bak**†

Department of Chemical Engineering/Research Institute of Industrial Technology,
Gyeongsang National University, Chinju, Korea
(*Received 28 October 1997 • accepted 13 March 1998*)

**Abstract** – Thermal analyses were conducted in a thermogravimetric analyzer by isothermal techniques in order to characterize the carbon-nitrogen oxide reaction. The carbon samples employed in the present study were SP-1 graphite and Micro 450 graphite. Carbon-NO and carbon-$N_2O$ reactions were carried out in a temperature range of 550-900 °C and 5-20 kPa of the partial pressure of reactant. In the NO reaction, reaction orders with respect to NO concentration and activation energy were 0.46-0.92 and 85-102 kJ/mol, respectively. The rate on the monolayer edge was higher than the rate on the multilayer edges. In the $N_2O$ reaction, reaction orders with respect to $N_2O$ concentration and activation energy were 0.55-1.35 and 167-190 kJ/mol, respectively.

Key words : Nitric Oxide, Nitrous Oxide, Graphite, TGA, Isothermal Reaction

## INTRODUCTION

Increasing environmental concern has led to numerous studies about removing nitrogen oxides from flue gases [Yaverbaum, 1979; Park et al., 1986; Sloss et al., 1992; Hong et al., 1997]. One such study involves the decomposition of nitrogen oxides to $N_2$ by reacting with carbon.

The reaction of carbon and nitrogen oxides has also attracted interest for the modelling of a coal combustor where the nitrogen oxides in the exhausted gas react with the uncombusted coal particles [Feng, 1996]. Especially, the NO content of flue gases in the fluidized bed combustor (FBC) is reduced by a reaction with entrained coal particles at freeboard conditions. But because the FBC is operated at a relatively low temperature compared with a pulverized coal combustor, the FBC has been identified as one of the major contributors to the anthropogenic emission of nitrous oxide. Nitrous oxide also contributes to deepening of the greenhouse effect and plays an important role in the depletion of the ozone layer [Rodriguez-Mirasol et al., 1994]. And the reaction of carbon and nitric oxide is also one of the basic reactions for the technology of nitric oxide reduction through reburning of exhaust gases in a fuel-rich environment [Burch et al., 1991; Chen and Ma, 1996].

Much research [Illan-Gomez et al., 1996; Furusawa et al., 1985; Chan et al., 1983; Suzuki et al., 1994] about the reaction mechanism of carbon and nitrogen oxide has been conducted by the measurement of gas conversion in a fixed bed, but little has resulted [Teng et al., 1992; Degroot and Richards, 1991] on the solid conversion of graphite in TGA. In the case of the fixed bed study, secondary reactions have positively contributed to the total conversion of nitric oxide according to the bed thickness. Actually, Aarna and Suuberg [1997] indicated that the reactivities derived from fixed bed results in the high temperature regime are consistently higher than those derived using the TGA technique.

The purpose of this paper is to present the results of intrinsic reaction rate of graphites with NO and $N_2O$ by use of TGA.

## EXPERIMENTAL

The apparatus used for measuring the reaction rate was a Chan 1000 thermogravimetric analyzer (TGA) which had a minimum sensitivity of 0.5 μg. Two graphite samples (SP-1 and Micro 450) were used to examine the effects of the surface area of a basal plane and an edge plane on the reaction rate. The impurities for these two graphite samples were <100 ppm and 0.95 %, respectively. The samples were disk-shaped. Chen and Yang [1993] measured the average particle size by using a scanning electron microscope (SEM) and BET apparatus by the standard $N_2$ adsorption method, as shown in Table 1.

The experimental conditions were as follows: The reaction temperature was isothermal in the range from 550 °C to 900 °C, and the partial pressures of nitric oxide or nitrous oxide were varied between 5 kPa and 20 kPa. The concentrations of the reaction gas were varied by mixing of pure nitric oxide or nitrous oxide (min 99.0 %) and ultra high purity helium gas (99.999 %). The water as impurity in the gas stream was removed by a trap of calcium sulfate anhydrate, and the residual oxygen was removed by a preheater quartz column packed with copper turnings maintained at 800 °C (initial oxidation temperature of copper turnings was 520 °C

**Table 1. Graphite samples**

| Sample | BET ($m^2/g$) | d (μm) | h (μm) | $A_1$ ($m^2/g$) | $A_2$ ($m^2/g$) |
|---|---|---|---|---|---|
| SP-1 | 2.01 | 33 | 0.46 | 1.95 | 0.054 |
| Micro 450 | 18.90 | 2.05 | 0.05 | 18.01 | 0.89 |

d=diameter, h=height, $A_1$=basal plane area, $A_2$=edge plane area

---

†To whom all correspondence should be addressed.
E-mail : ycbak@nongae.gsnu.ac.kr

from TGA measurements).

Before the reaction rate was measured, the graphite samples (about 6-7 mg) were degassed at 120 °C in a flow of helium gas for several hours in order to remove the physically adsorbed gases. Then the furnace of TGA was heated at a constant heating rate (20 °C/min) to the final experiment temperature. At the final constant temperature the pre-mixed reaction gas flowed into the TGA, and graphites were isothermally reacted with reaction gas. To study the effect of the initial surface area of graphite on the reaction rate, we used only reaction rates from 0 % to 10 % burnoff.

## RESULTS AND DISCUSSION

### 1. Reaction Rate on the Different Bases

There are three other ways to express the NO-carbon reaction rate. They are based on (1) per unit mass, (2) per unit external (or geometric) surface area, and (3) per unit internal (total) surface area [Yang and Steinberg, 1977]. Also, there are many other ways to express the reactivities of NO (mass or molar) from a fixed bed experiment. These are based on (1) per unit volume of NO gas, (2) per unit reactor volume, (3) per unit mass of carbon, and (4) per unit carbon surface area [Aarna and Suuberg, 1997].

In the case of graphite, the valence electrons of carbon permit trigonal and $\pi$ bonding between each atom and its three neighbors. Such bonding results in the formation of a two-dimensional hexagonal lattice. The binding between carbon atoms in the same sheet is covalent, i.e., strong, whereas the binding between successive sheets is of van der Waals type and hence, weak. Therefore the reactivity of a basal plane formed by $\sigma$ bonding is different from the reactivity of an edge plane formed by $\pi$ bonding.

It is clear that vacancies and edge sites on graphite surfaces are active sites and that only these sites contribute to the gasification reaction. Therefore, Yang and Wong [1981] expressed the reaction rate data from the TEM experiments to the turnover frequency (TOF), i.e., rate per active site.

$$\mathrm{TOF}\left(\frac{\text{atoms gasified}}{\text{edge atom}\cdot\text{sec}}\right)=\frac{\text{atoms gasified/time}}{A_2\times\text{atoms C/edge plane surface areas}}$$

where atoms C/edge plane surface areas=0.120 C/Å$^2$

Mass reduction data from TGA experiments can be easily converted to TOF by Avogadro number.

$r_1$ for Micro 450 was 3-3.5 times greater than $r_1$ for SP-1, but $r_2$, $r_3$, and TOF for Micro 450 were smaller than those for SP-1. Especially $r_3$ and TOF for SP-1 were 3-5 times greater than those for Micro 450. The ratio of a basal plane surface area to an edge plane surface area ($A_1/A_2$) was 36.11 for SP-1 and 20.24 for Micro 450. Therefore SP-1 was more affected by the lattice faults of the basal plane than Micro 450.

The edge plane surface area of Micro 450 was 16 times greater than that of SP-1, but $r_1$ for Micro 450 was only 3-5 times faster than $r_1$ for SP-1.

If only the edge plane surface was used for the Micro 450 and NO reaction, it was expected that the maximum 6-12 % basal plane for SP-1 was composed of the lattice faults in order to the same $r_3$ or TOF for SP-1 and Micro 450.

For the C-$O_2$ reaction, the rate on the multilayer edge was reported to be about 100 times greater than that on the monolayer edge due to the cooperative effect. But for the C-$CO_2$ reaction, the TOF on the monolayer edge was about four orders of magnitude greater than the TOF on multilayer edges [Yang, 1984]. It can be predicted from the present studies that the rate on the monolayer edge was higher than that on the multilayer edges in the C-NO reaction, because the Micro 450 graphite containing more multilayer characteristics exhibited a lower TOF than the TOF for SP-1 graphite. This was opposite to Chu and Schmidt's [1993] result, in which a multilayer pit compared with the nearly monolayer pits revealed relatively greater reaction rate at low pressure (below 0.1 atm).

### 2. Rate Parameter for NO Reaction

The effect of reaction temperature on the NO and graphite reaction at 9.5 kPa NO is shown in Fig. 1. TOF can be expressed as the following equation.

$$\mathrm{TOF}=k_0\exp(-E/RT)\,C_{NO}$$

where $k_0$ is a frequency factor and $C_{NO}$ is the partial pressure of NO (concentration of NO).

The activation energy of SP-1 graphite was 102 kJ/mol and that of Micro 450 was 85 kJ/mol. The frequency factor was $2.623\times10^6(\mathrm{sec}\cdot\mathrm{atm})^{-1}$ for SP-1, and $1.063\times10^5(\mathrm{sec}\cdot\mathrm{atm})^{-1}$

**Table 2. Reaction rate on the different bases**

| Temperature (°C) | $r_1\times100$ (min$^{-1}$) | | $r_2\times100$ (g/m$^2\cdot$hr) | | $r_3\times100$ (g/m$^2\cdot$hr) | | TOF (sec$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | SP-1 | Micro 450 | SP-1 | Micro 450 | SP-1 | Micro 450 | SP-1 | Micro 450 |
| 550 | | 0.051 | | 0.16 | | 3.44 | | 0.04 |
| 600 | 0.024 | 0.127 | 0.72 | 0.40 | 26.7 | 8.56 | 0.31 | 0.10 |
| 650 | 0.051 | 0.169 | 1.52 | 0.54 | 56.7 | 11.39 | 0.66 | 0.13 |
| 700 | 0.102 | 0.313 | 3.03 | 0.99 | 112.8 | 21.07 | 1.31 | 0.25 |
| 750 | 0.149 | 0.568 | 4.45 | 1.80 | 165.6 | 38.29 | 1.92 | 0.45 |
| 800 | 0.218 | 1.137 | 6.51 | 3.61 | 242.2 | 76.62 | 2.81 | 0.89 |
| 850 | 0.410 | 1.389 | 12.24 | 4.41 | 455.6 | 93.61 | 5.29 | 1.09 |
| 900 | 1.220 | | 36.27 | | 1350.0 | | 15.67 | |

where $r_1$ : reaction rate based on weight (g carbon/g carbon·min)
$r_2$ : reaction rate on total surface area (g carbon/m$^2\cdot$hr)
$r_3$ : reaction rate based on edge surface area (g carbon/m$^2\cdot$hr)

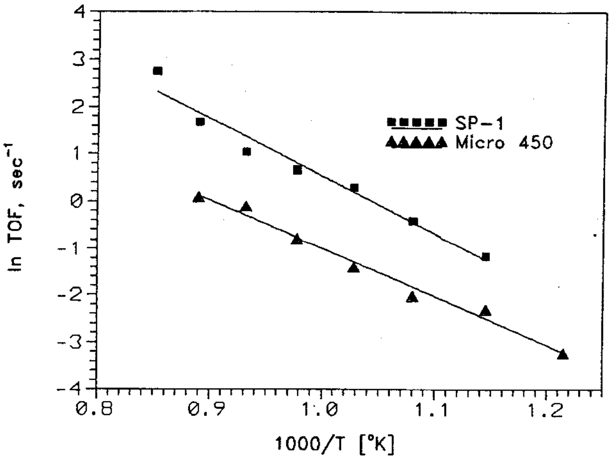

**Fig. 1. Effect of reaction temperature on the rate of NO and graphite reaction.**

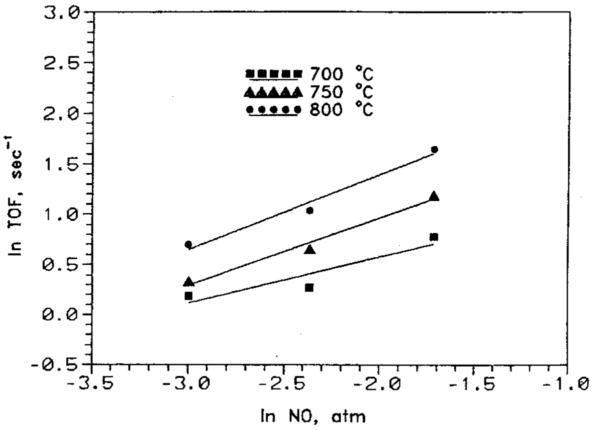

**Fig. 2. Effect of NO partial pressure on the rate of NO and SP-1 graphite reaction.**

for Micro 450. In Aarna and Suuberg's [1997] results, the kinetics of the NO-carbon reaction was found to be a two-regime Arrhenius behavior, with the activation energy of the low temperature regime being typically less than 100 kJ/mol, and the activation energy of the high temperature regime generally being considerably in excess of this value.

Fig. 2 shows the effect of NO partial pressure on the reaction rate of NO with SP-1 graphite for different reaction temperatures. The reaction orders with respect to NO were 0.75 (800 °C), 0.67 (750 °C), and 0.46 (700 °C). Also the reaction orders with respect to NO for Micro 450 graphite were in the range from 0.67-0.92.

Reaction orders of 1 and below 1 with respect to NO have been reported by many researchers. In the review of Aarna and Suuberg [1997], the reaction orders with respect to NO in the condition of NO partial pressure from 0.001 kPa to 10.1 kPa were in the range from 0.22-1. The range of NO partial pressure for this study was between 5 kPa and 20 kPa, and the reaction order with respect to NO was below 1.

### 3. Rate Parameter for $N_2O$ Reaction

Fig. 3 shows the effect of reaction temperature on the reaction rate of $N_2O$ and graphites at 11.5 kPa $N_2O$. The activation energy of SP-1 graphite was 190 kJ/mol and that of

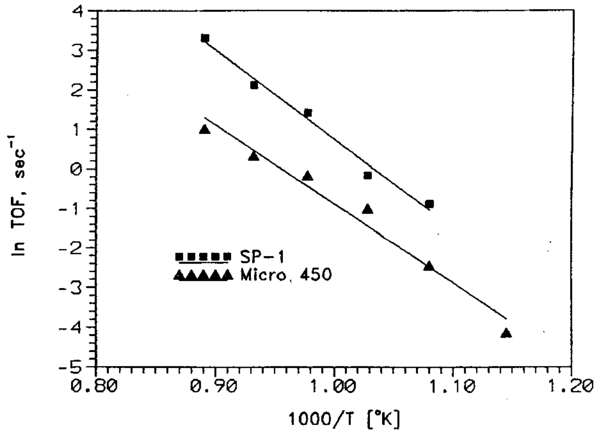

**Fig. 3. Effect of reaction temperature on the rate of $N_2O$ and graphite reaction.**

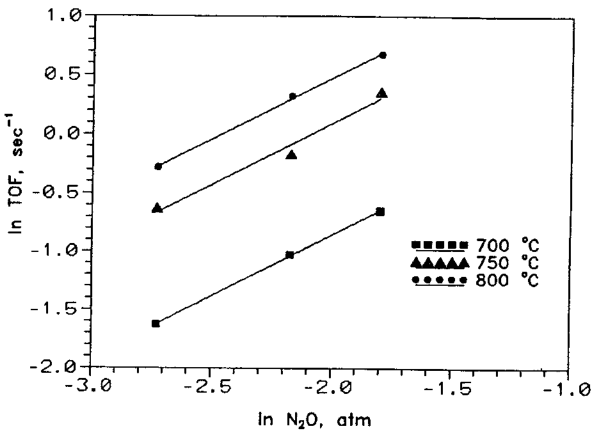

**Fig. 4. Effect of $N_2O$ partial pressure on the rate of $N_2O$ and Micro 450 graphite reaction.**

Micro 450 is 167 kJ/mol. The activation energy of Micro 450 graphite is lower than that of SP-1 as shown in the case of NO reaction. The reported activation energies vary between 40 and 280 kJ/mol [Teng et al., 1997]. The frequency factor was $1.52\times10^{11}$ $(sec\cdot atm)^{-1}$ for SP-1, and $1.93\times10^{9}$ $(sec\cdot atm)^{-1}$ for Micro 450. The activation energy and the frequency factor revealed characteristics of the compensation effect.

Fig. 4 shows the reaction rate of Micro 450 with $N_2O$ gas in the partial pressure range between 6.6 kPa and 16.7 kPa. The reaction orders with respect to $N_2O$ are 1.35 (800 °C), 1.04 (750 °C), and 1.06 (700 °C). Also the reaction orders for SP-1 graphite are in the range between 0.55 and 1.03. The reaction order with respect to $N_2O$ pressure for $N_2O$-carbon reaction was reported to be between zero and unity [Teng et al., 1997].

### 4. Variation of the Reaction Rate with Oxidant

The combustion reaction of graphites in the oxygen partial pressure of 9.6 kPa was conducted to compare with the NO and $N_2O$ reactions. Fig. 5 shows the reaction rate for Micro 450 graphite with several gases normalized to a partial pressure of 10.1 kPa. In the case of the combustion reaction, the reaction region is converted from a chemical reaction region to a gas diffusion control region at 700 °C. But

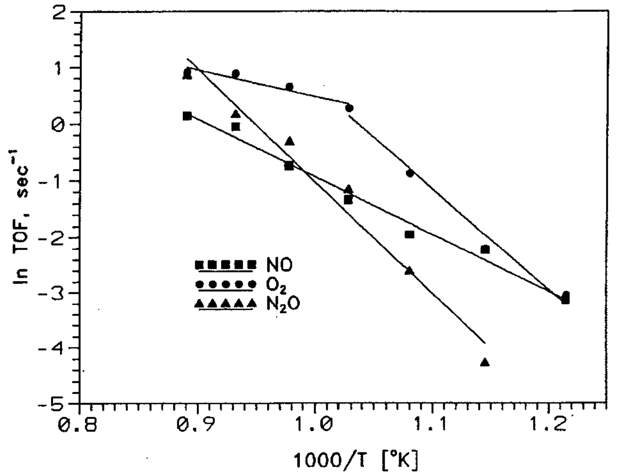

**Fig. 5. Variation of the reaction rate with oxidant for Micro 450 graphite.**

in the case of the $N_2O$ and NO reactions, the variation of control region did not appear.

The activation energy and the frequency factor for combustion reaction below 700 °C were found to be 149.2 kJ/mol and $1.16\times10^9$ (atm·sec)$^{-1}$, respectively. The activation energy for the combustion reaction is higher than that of the NO reaction (85 kJ/mol), but is lower than that of the $N_2O$ reaction (167 kJ/mol). The results show that the reaction rate in the combustion below 700 °C decreases in the order $O_2$>NO>$N_2O$. But above 700 °C, the reaction rate of $N_2O$ is faster than that of NO.

DeGroot and Richards [1991] determined the rates of gasification of cellulose char (HTT 1,000 °C) in the temperature range 400-600 °C in 0.1 atm of oxygen, $N_2O$, and NO, respectively. The results showed that the overall reactivity in gasification decreases in the order $O_2$>NO>$N_2O$. Chu and Schmit [1993] studied by STM to obtain the noncatalytic reactivities of $NO_2$, NO, $N_2O$, and $O_2$ with graphite between 400 °C and 700 °C. The rate of basal plane abstraction decreased in the order $N_2O$>NO>$O_2$. Moulijn and Kapteijn [1995] reviewed the gasification of peat char by oxygen-containing reactant molecules between 450 °C and 650 °C. $O_2$ was most reactive followed by $N_2O$ which is about as reactive at low temperature, and NO was less reactive.

## CONCLUSIONS

1. The rate on the monolayer edge was higher than the rate on the multilayer edges in the C-NO reaction.

2. The activation energy for the SP-1 graphite and NO gas reaction was 102 kJ/mol, and that for Micro 450 was 85 kJ/mol. The frequency factor was $2.623\times10^6$(sec·atm)$^{-1}$ for SP-1, and $1.063\times10^5$(sec·atm)$^{-1}$ for Micro 450. The reaction orders with respect to NO for SP-1 graphite were in the range of 0.46-0.75, and that for Micro 450 graphite were in the range from 0.67-0.92.

3. The activation energy for SP-1 graphite and $N_2O$ reaction was 190 kJ/mol, and that for Micro 450 was 167 kJ/mol. The frequency factor was $1.52\times10^{11}$(sec·atm)$^{-1}$ for SP-1, and $1.93\times10^9$(sec·atm)$^{-1}$ for Micro 450. The reaction orders with respect to $N_2O$ were in the range of 1.04-1.35 for Micro 450. Also, those for SP-1 graphite were in the range between 0.55 and 1.03.

4. The gasification reaction rate below 700 °C decreased in the order $O_2$>NO>$N_2O$. But above 700 °C, the reaction rate of $N_2O$ was faster than that of NO.

## ACKNOWLEDGEMENT

This research was financially supported by Korea Science and Engineering Foundation in the '96 Post-doc. program, and was conducted in the facilities of The University of Michigan.

## REFERENCES

Aarna, I. and Suuberg, M., "A Review of the Kinetics of the Nitric Oxide-Carbon Reaction", *Fuel,* **76**, 475 (1997).

Burch, T. E., Tillman, F. R., Chen, W., Lester, T. W., Conway, R. B. and Sterling, A. M., "Partitioning of Nitrogenous Species in the Fuel-Rich Stage of Reburning", *Energy & Fuels,* **5**, 231 (1991).

Chan, L. K., Sarofim, A. F. and Beer, J. M., "Kinetics of the NO-Carbon Reaction at Fluidized-Bed Combustor Conditions", *Combustion and Flame,* **52**, 37 (1983).

Chen, S. G. and Yang, R. T., "Titration for Basal Plane versus Edge Plane Surface on Graphite Carbons by Adsorption", *Langmuir,* **9**, 3259 (1993).

Chen, W. and Ma, L., "Effect of Heterogeneous Mechanisms during Reburning of NO", *AIChE,* **42**, 1968 (1996).

Chu, X. and Schmidt, L. D., "Intrinsic Rates of $NO_x$-Carbon Reactions", *Ind. Eng. Chem. Res.,* **32**, 1359 (1993).

DeGroot, W. F. and Richards, G. N., "Gasification of Cellulosic Chars in Oxygen and in NO", *Carbon,* **29**(2), 179 (1991).

Feng, B., Liu, H., Yuan, J., Lin, Z. and Liu, D., "Mechanisms of $N_2O$ Formation from Char Combustion", *Energy & Fuel,* **10**, 203 (1996).

Furusawa, T., Tsunoda, M., Tsujimura, M. and Adschri, T., "Nitric Oxide Reduction by Char and Carbon Monoxide", *Fuel,* **64**, 1306 (1985).

Hong, S. S., Lee, G. D., Park, J. W., Park, D. W., Cho, K. M. and Oh, K. J., "Catalytic Reduction of NO over Perovskite-Type Catalysts", *Korean J. Chem. Eng.,* **14**, 491 (1997).

Illan-Gomez, M. J., Linares-Solano, A., Radovic, L. R. and Salinas-Martinez de Lecea, C., "NO Reductions by Activated Carbons. 7. Some Mechanistic Aspects of Uncatalyzed and Catalyzed Reaction", *Energy & Fuels,* **10**, 158 (1996).

Moulijn, J. A. and Kapteijn, F., "Towards a Unified Theory of Reactions of Carbon with Oxygen-Containing Molecules", *Carbon,* **33**(8), 1155 (1995).

Park, Y. S., Lee, W. Y., Rhee, H. K., Sung, B. P. and Lee, H. I., "The Effects of Carbon Monoxide on the Adsorption of Nitric Oxide on Polycrystalline Platinum", *Korean J. Chem. Eng.,* **3**, 165 (1986).

Rodriguez-Mirasol, J., OOMS, A. C., Pels, J. R., Kapteijn, F. and Moulijn, J. A., "NO and $N_2O$ Decomposition over

Coal Char at Fluidized-Bed Combustion Conditions", *Combustion and Flame,* **99**, 499 (1994).

Sloss, L. L. et al., "Nitrogen Oxides Control Technology Fact Book", Noyes Data Corporation, N. J. (1992).

Suzuki, T., Kyotani, T. and Tomita, A., "Study on the Carbon-Nitric Oxide Reaction in the Presence of Oxygen", *Ind. Eng. Chem. Res.,* **33**, 2840 (1994).

Teng, H., Suuberg, E. M. and Calo, J. M., "Studies on the Reduction of Nitric Oxide by Carbon: the NO-Carbon Gasification Reaction", *Energy & Fuels,* **6**, 398 (1992).

Teng, H., Lin, H. and Hsieh, Y., "Thermogravimetric Studies on the Global Kinetics of Carbon Gasification in Nitrous Oxide", *Ind. Eng. Chem. Res.,* **36**, 523 (1997).

Yang, R. T. and Steinberg, M., "A Diffusion Cell Method for Studying Heterogeneous Kinetics in the Chemical Reaction/Diffusion Controlled Region. Kinetics of $C+CO_2 \longrightarrow 2CO$ at 1,200-1,600°C", *Ind. Eng. Chem. Fundam.,* **16**, 235 (1977).

Yang, R. T. and Wong, C., "Kinetics and Mechanism of Oxidation of Basal Plane on Graphite", *J. Chem. Phys.,* **75**, 4471 (1981).

Yang, R. T., "Etch-Decoration Electron Microscopy Studies of the Gas-Carbon Reactions", in 'Chemistry and Physics of Carbon', ed. by P. A. Thrower, Vol. 19, Marcel Dekker Inc., N.Y., p.163 (1984).

Yaverbaum, L. H., "Nitrogen Oxides Control and Removal-Recent Developments", Noyes Data Corporation, N. J. (1979).