

CHAPTER II

LITERATURE SURVEY

2.1 Oxides of Nitrogen

The oxides of nitrogen include nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), nitrogen trioxide (NO₃), nitrogen sesquioxide (N₂O₃), nitrogen tetroxide (N₂O₄), and nitrogen pentoxide (N₂O₅). They and two of their hydrates, nitrous acid (HNO₂) and nitric acid (HNO₃), can exist in air. However, only three, nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O) are found in any appreciable quantities (Stern, 1976). In this work, nitric oxide and nitrous oxide were emphasized to study.

NO is a colorless, odorless, and tasteless gas. In presence of air, it is oxidized more slowly by oxygen to form brown fumes of NO₂, which is extremely reactive and a strong oxidizing agent.

N₂O is a colorless, slightly sweet, nontoxic gas present in the natural environment in relatively large amounts (0.25 ppm) when compared to the concentrations of the other trace gases except carbon dioxide, methane, and the noble gases. When mixed with air and inhaled it produces a loss of feeling. It is commonly called “laughing gas” because under some conditions it can cause those who inhale it to laugh violently (Stern, 1976).

2.2 NO, N₂O and the Environment

Both NO and N₂O are known to be involved in the greenhouse effect as well as in the destruction of Earth's protective ozone layer. These

phenomenon is represented schematically in Figure 2.1 (Wójtowicz *et al.*, 1993).

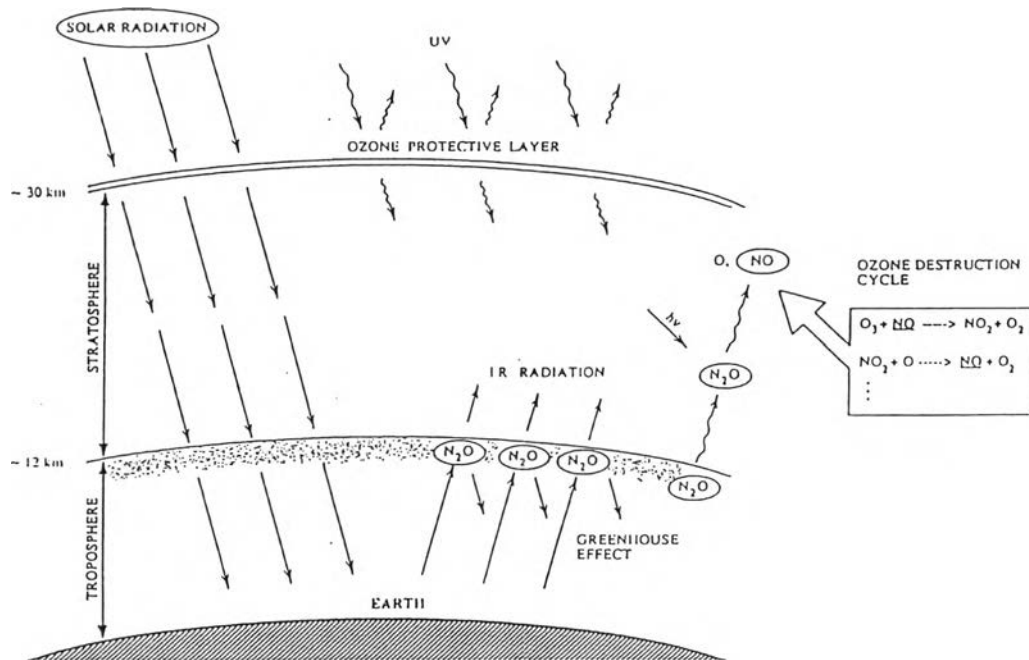


Figure 2.1 The role played by NO and N_2O in the greenhouse effect and in ozone layer depletion (Wójtowicz *et al.*, 1993).

The energy budget of our earth is governed by the balance between the amount of energy received from the sun and heat losses to outer space in the form of infrared radiation from the surface. The greenhouse effect, which consists in absorption of part of this radiation by some gases present in the atmosphere and subsequent re-radiation of heat back to the Earth, takes place in the troposphere and the main greenhouse gases are CO_2 , CH_4 , N_2O , chlorofluorocarbons (CFC's), ozone and water vapor. In turn, the greenhouse effect leads to an increase in the average temperature on the Earth, also known as global warming.

Depletion of the stratospheric ozone layer is likewise the result of a man-induced imbalance among the sources and sinks of ozone, Stratospheric ozone constitutes a natural shield protecting us from excess ultraviolet (UV)

radiation. UV rays are believed to cause an increased risk of skin cancer and possibly also suppression of the human immune system. Removal of ozone from the stratosphere may also affect the distribution of solar heating and thus contribute to global warming. N_2O is a source of NO molecules in the stratosphere where they play a important role in the destruction of ozone as indicted in Figure 2.1.

2.3 Sources of Atmospheric NO and N_2O

Sources of atmospheric NO and N_2O can be divided into two sources.

2.3.1 Natural Sources

They involve emission from soil, ocean and freshwater as well as lightning.

2.3.2 Anthropogenic Sources

The largest sources from which both NO and N_2O are produced come from burning fossil fuel, either in oil-, gas-, or coal-fired power stations (stationary sources), or in the internal combustion engines of cars, lorries, etc. (mobile sources), which can be noticed in Table 2.1 and 2.2. In addition, both NO and N_2O released into the atmosphere due to human activities also come from land cultivation and are associated mainly with the use of fertilizers. Biomass burning and the manufacture of adipic acid (used in nylon protection) play a important role the significant amount of N_2O in atmosphere(Wójtowicz *et al.*, 1993).

Table 2.1 Estimated anthropogenic NO_x emissions in the United States in 1976, expressed as NO₂ (Flagan and Seinfeld, 1982).

Source	10 ⁶ metric tons/yr.
Transportation	10.1
Highway vehicles	7.8
Nonhighway vehicles	2.3
Stationary fuel combustion	11.8
Electric utilities	6.6
Industrial	4.5
Residential, commercial, and institutional	0.7
Industrial processes	0.7
Chemicals	0.3
Petroleum refining	0.3
Metals	0*
Mineral products	0.1
Oil and gas production and marketing	0
Industrial organic solvent use	0
Other processes	0
Solid waste disposal	0.1
Miscellaneous	0.3
Forest wildfires and managed burning	0.2
Agricultural burning	0
Coal refuse burning	0.1
Structural fires	0
Miscellaneous organic solvent use	0
Total	23

* A zero entry indicates emissions of less than 50,000 metric tons/yr.

Table 2.2 Estimated amounts of N₂O emitted by various human activities (Kapteijn *et al.*, 1996).

Source	Kton/year	% Man made
Adipic acid production	545	5-8
Nitric acid production	280-370	4-8
Land cultivation, fertilizers	1000-2200	14-45
Fossil fuels (stationary)	190-520	4-10
Fossil fuels (mobile)	200,400-850	4-15
Biomass burning	500-1000	10-20

2.4 The Formation and Reduction of NO and N₂O during Combustion of Coal

As described previously, the combustion of fossil fuels is the largest sources due to human activities, from which both nitric oxide and nitrous oxide are released. Emission of NO and N₂O during the combustion process are believed to be derived from both the nitrogen present in the coal and the nitrogen in the air used in the combustion process. Referring to Figure 2.2, Coal-N transformation during combustion can be divided into three stages: coal devolatilisation and pyrolysis, N₂O/NO formation (both in the gas phase and at the surface of char), followed by N₂O/NO destruction (mainly reduction to N₂). The latter process can again be either homo- or heterogeneous. The amount of nitrogen oxide that survives the last stage is carried out of the system with flue gases. Devolatilisation can be viewed as a physicochemical process governing the relative amounts of original coal-N that will react along

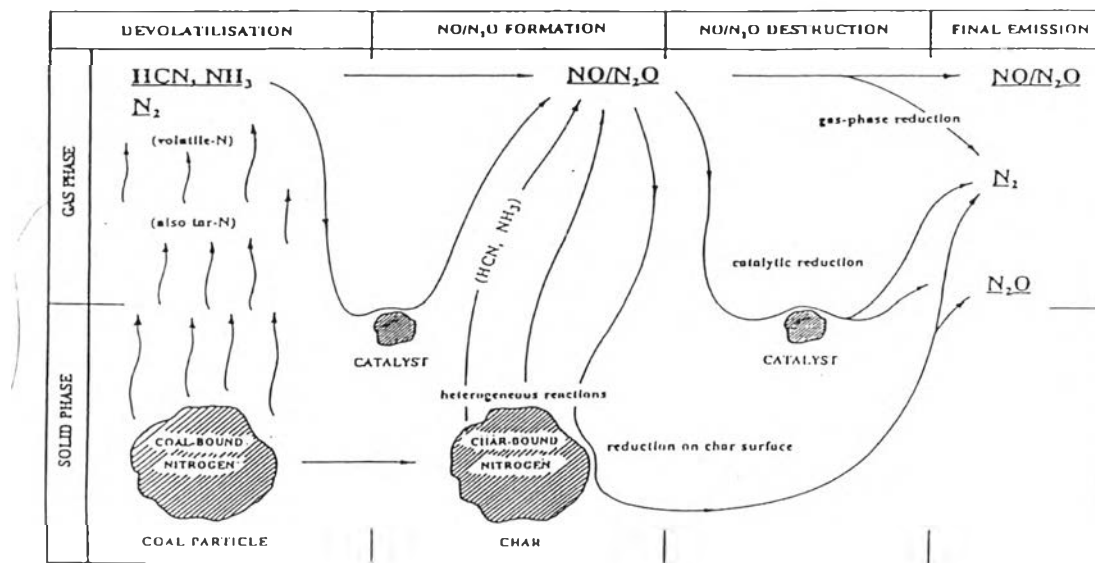


Figure 2.2 Formation and reduction of NO and N₂O during combustion of coal (Wójtowicz *et al.*, 1993).

the gas-phase versus heterogeneous routes. The main nitrogen-containing process of coal devolatilization and pyrolysis are hydrogen cyanide (HCN), ammonia (NH₃), N₂ as well as tar- and char-bound nitrogen. Hydrogen cyanide and NH₃ play an important role acting as gas-phase precursors for both N₂O and NO reactions of nitrogenous species can be substantially accelerated, in some cases also modified, by catalytic effects associated with the presence of solid particles in the reacting mixture. In the fluidised-bed combustion, these solid particles usually include ash, limestone or dolomite particles.

Combustion of char is another source of nitrogen oxides. The relative contribution of NO_x/N₂O formed via gas-phase versus heterogeneous routes depend on the type of fuel combusted, reaction temperature, excess oxygen level, etc. Apart from NO and N₂O resulting from combustion of char, HCN

and NH_3 may also be formed from char-N. subsequently reacting in the gas phase to yield NO and N_2O .

Reduction of NO and N_2O to molecular nitrogen involves chemical processes of great practical interest as they constitute a powerful mechanism of $\text{NO}_x/\text{N}_2\text{O}$ destruction. The reduction may be either heterogeneous, solid-catalyzed or occurring on char surface, or it may take place in the gas phase. In the latter case, H and OH radicals present in the combustion zone are particularly strong reducing agents for NO and N_2O .

2.5 NO and N_2O Abatement Strategies

There are three main approaches to lower NO and N_2O emission (Wójtowicz *et al.*, 1993).

2.5.1 Minimization of Pollutant Emissions through Improvements in Operating Conditions and Process Control of Boilers

These following techniques are used to abate emissions of NO and N_2O (Johnsson , 1994):

- a) Increasing the devolatilization temperature of the char increases NO formation and decreases N_2O formation.
- b) Increasing the combustion temperature increases NO formation and decreases N_2O formation.
- c) N_2O formation increases with coal rank, but NO formation has been found to be almost independent of rank or to decrease with increasing rank.
- d) With increasing nitrogen content of the char, conversion to NO decreases, but conversion to N_2O increases.
- e) Air or fuel staging and excess air are one of the technique used to reduce NO level but its effect on N_2O emissions is unclear.

2.5.2 Innovative Combustion Design to Produce Low-Emission Systems

2.5.3 Sacrificing Emissions of One Pollutant for the Sake of Low Emissions of the Others, Combined with Adopting Special Measures to Reduce Excessive Levels of the Selected Pollutant

An example of these approaches is suggested by Wójtowicz *et al.* (1993). It would be to minimize NO_x and SO_x emissions and then to deal with relatively high N_2O levels. The treatment of the combustion product gases can be performed as follows: addition of limestone, injection of an additive such as ammonia, urea and cyanuric acid in selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) processes. In general SNCR involves NO_x reduction to N_2 and H_2O and the process is usually carried out in the temperature range of 1173-1373 K (Wójtowicz *et al.*, 1993). For the SCR process, It concerns with ammonia injection into the flue gas combined with the use of a solid catalyst (typically V_2O_5 and TiO_2). The SCR process is normally utilized in the temperature range of 573-673 K. In addition to feed such additives, The use of carbon is another way to reduce the releases of NO and N_2O . The advantages of the utilization of carbon as a reducing agent include:

a) From the fact that sufficient catalytic activity for decomposition of NO and N_2O in oxygen-rich atmosphere has not been realized because of the deactivation of catalyst oxygen, The use of carbon would be another candidate which is able to scavenge oxygen efficiently.

b) The utilization of carbon as a reducing agent, instead of the other reducing agent such as ammonia can eliminate the poison of ammonia.

Furusawa *et al.* (1985) pointed out NO produced during combustion can be heterogeneously reduced in-situ by the carbonaceous solid

intermediates of compensation. Chan *et al.* (1983) studied the reduction of NO by carbonaceous solid in a packed bed reactor and also observed that N₂, CO and CO₂ formed were the dominant products.

Åmand and Leckner (1994) studied the reduction of N₂O in a circulating fluidized-bed combustor during combustion of fuels of different volatiles matter: coke, bituminous coal and wood. Their results showed that the reduction of the N₂O injected into the lower part of the combustion chamber was >80%, but also, especially in wood combustion, at the top of the combustion chamber a certain degree of reduction occurred, which is interpreted as being caused by volatiles combustion.

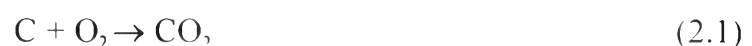
2.6 Carbon Gasification

Carbon gasification is defined as a heterogeneous reaction between a gas and a solid phase, the latter being consumed continuously.

The followings are the global chemistry of important gasification reactions (Figueiredo and Moulijn, 1986).

2.6.1 C-O₂ Reaction

Arguably, the combustion of carbon to produce heat is the most important chemical reaction available to mankind. However, as we will see shortly, carbon gasification by O₂ is most undesirable when carbon is used as a material. It has been shown that upon the reaction of carbon with O₂, two primary gasification products, CO and CO₂, are formed.



Following these reactions, secondary reactions can occur, as follows



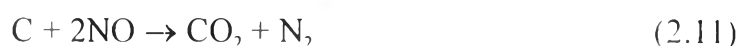
2.6.2 C-H₂O Reaction

Carbon gasification by steam is most important reaction. Like the C-O₂ reaction, there are instances where the reaction is desirable; there are other instances where it is undesirable. Following the gasification of carbon by steam, other reactions can occur which can be of great importance. Some are listed.



2.6.3 C-NO and C-N₂O Reaction

In addition to O₂, H₂O, CO₂, and H₂ being important molecular reactants for the gasification of carbon, other reactants should be mentioned. Interaction of several of these reactants with carbon has considerable significance to the air pollution field. For example, oxides of nitrogen formed during the combustion of coal can subsequently react with carbon to produce N₂, a highly desirable reaction.



2.7 Carbon

The element carbon C, atomic number six, atomic weight 12.01115, is the first of five elements located in Group IVA of the Periodic Table. It exists in three allotropic forms, namely, diamond, graphite, and amorphous carbon. Diamond and graphite are naturally occurring crystalline solids possessing widely divergent properties, whereas amorphous carbon is a term applied to a comparatively large variety of carbonaceous substances not classified as either diamond or graphite.

2.7.1 Diamond

The diamond crystal structure as shown in Figure 2.3 is face-centered cubic with interatomic distances of 0.154 nm. Each atom is covalently bonded to four other carbon atoms in the form of a tetrahedron.

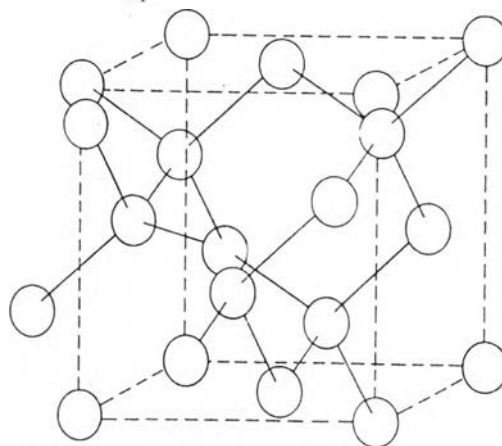


Figure 2.3 Crystal structure of diamond.

2.7.2 Graphite

Graphite or graphitic carbons are all varieties of substances consisting of the element carbon in the allotropic form of graphite irrespective of the presence of structural defects.

The accepted ideal structure for graphite is described as infinite layers of atoms of carbon which are arranged in the form of hexagons lying in planes as shown in Figure 2.4 (Figueiredo and Moulijn, 1986). The stacking arrangement is ABAB so that the atoms in alternate planes align with each other. The unit cell was 0.670 nm high and 0.246 nm on each side. The spacing between layers is 0.3354 nm, the interatomic distance within the planes 0.1415 nm, and the crystal density 2.266 g/cm³.

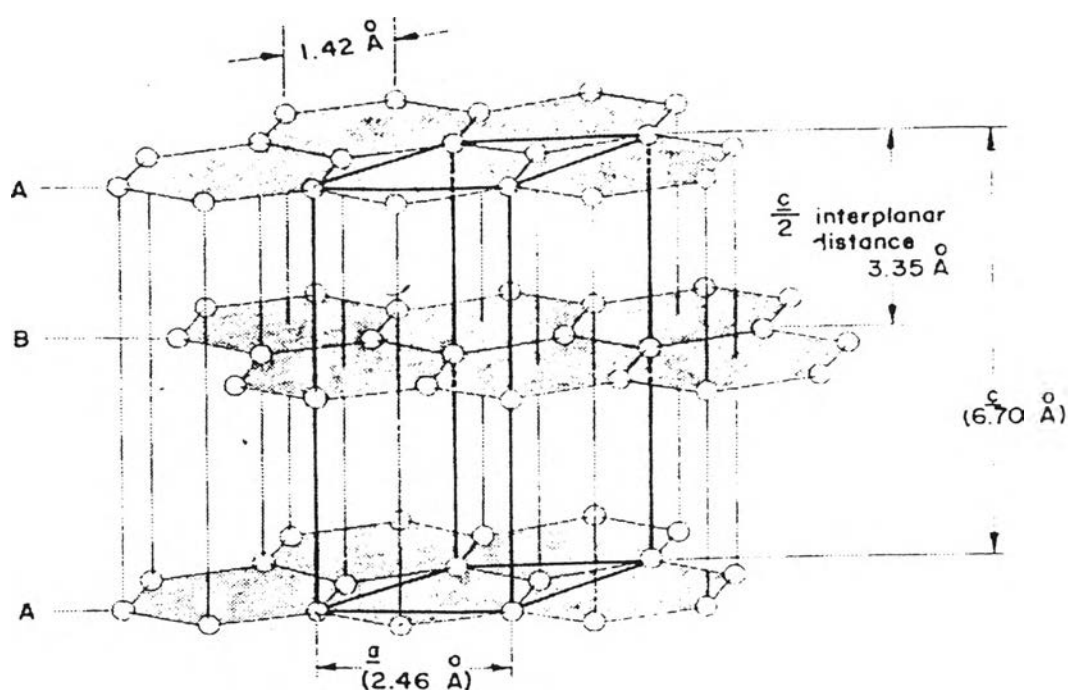


Figure 2.4 Hexagonal form of graphite.

The surfaces of a graphitic carbon consist of two types: the basal plane surface and the edge plane surface. The surface areas of the graphites are quite low, and dominated by basal plane area. It is the edge sites and other imperfections in the planar aromatic structure that are commonly thought to be the main locus of the C-NO and C-N₂O reactions.

It has been well demonstrated by the use of electron microscopy and optical microscopy that vacancies and the edge sites on carbon surfaces are

active sites and that only these sites contribute to gasification reactions (Yang and Chen, 1986). The defect-free basal plane has only negligible reactivity that make no or little contribution to gasification reaction. Therefore, the edge surface area is responsible for gasification.

2.8 Overall Reaction Schemes

2.8.1 Carbon-Nitric Oxide Reaction

The products of NO-carbon reaction are generally found to be N₂, CO and CO₂. The overall reactions can be expressed as follows:



Reaction (2.16) is a catalytic reaction (catalyzed by carbon), based upon the observation that NO reduction by carbon is enhanced in the presence of CO.

Furusawa *et al.* (1985) studied the relative importance of carbon consuming reactions (2.14) and (2.15) and the catalytic reaction (2.16) and also measured the material balances over the temperature range prevailing in FBC. Their results showed that, at low temperatures (994 and 1078 K), the amount of CO formed was stoichiometrically equal to the molar amount of NO reduced and to the molar amount of CO₂ consumed. The overall reaction scheme can be represented by reaction (2.15). At higher temperatures (1120 and 1994 K), the molar amount of CO₂ was less than that represented by the stoichiometry of reaction (2.15), indicating that the carbon consuming reactions became significant. The contribution of the carbon consuming

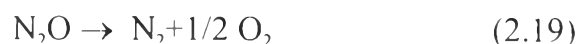
reactions to the total reduction of NO is enhanced with increasing temperature and with a decrease in the ratio of CO/NO. The catalytic reduction of NO was found to be dominant even at higher temperatures, if the partial pressure of CO was sufficiently higher than that of NO.

2.8.2 Carbon-Nitrous Oxide Reaction

The products of N₂O-carbon reaction are generally thought to be N₂, CO₂ and CO over the complete temperature range studied. The possible overall reaction could be expressed as



At low temperatures, only N₂ and CO₂ were found (Rodriguez-Mirasol *et al.*, 1994) as the products; reaction (2.17) is predominant in contributing to the overall reduction. At high temperatures, emission of CO increases with increasing temperature, and reaction (2.18) becomes important. With further increases in temperature N₂O is unstable and decomposed over a number of solid materials, such as limestone, bed material, ash, and even the reactor wall. The decomposition reaction is



The temperature range required for N₂O reduction is much lower than that for NO reduction.

2.9 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique for measuring the amount and rate of change in sample mass as a function of temperature and time. It is used to characterize only material that exhibits weight loss or phase change as a result of decomposition, dehydration, and oxidation. Two modes are commonly used for investigating thermal stability behavior in controlled atmospheres; (1) dynamic, in which the temperature is increased at a linear rate, and (2) isothermal, in which the temperature is kept constant.

2.10 Kinetic Studies

2.10.1 Turnover Frequency

In the case of graphite, it is clear that vacancies and edge sites on graphite surfaces are active sites and that only these sites contribute to the gasification reaction. Yang and Wong (1981) expressed that the reaction rate data from the TEM experiments to the turnover frequency (TOF), that is, rate per active site is given as,

$$\text{TOF} \left(\frac{\text{atoms gasified}}{\text{edge atom sec}} \right) = \frac{\text{atoms gasified/time}}{\rho_{1120} \cdot A_2} \quad (2.20)$$

where ρ_{1120} is the number of active sites per edge surface area

$$= 0.120 \text{ carbon atoms/}^\circ\text{A}^2$$

A_2 is the edge surface area

2.10.2 Reaction Order

2.10.2.1 Carbon-Nitric Oxide Reaction

The reaction of NO with carbon is generally reported to be of first order with respect of NO partial pressure (Furusawa *et al.*, 1980; Chan *et al.*, 1983; Suuberg *et al.*, 1990; Teng *et al.*, 1992). Fractional orders between 0.2 and 0.8 have also been found (Johnsson, 1994; Rodrigues-Mirasol *et al.*, 1994).

2.10.2.2 Carbon-Nitrous Oxide Reaction

Rodriguez-Mirasol *et al.* (1994) showed an apparent reaction order of 0.6 for all chars, except for D53 char under their experimental conditions. This char exhibited almost zero order at 723 K. This was claimed that this phenomenon is probably due to the saturation effect of oxygen complexes on the char surface at low temperatures. However, the reaction order for this char changed when the reaction temperature increased to 823 K.

Teng *et al.* (1997) investigated the global kinetics of carbon gasification in nitrous oxide. The carbon material used in their study was phenol-formaldehyde resin char. Their results showed the global reaction order with respect to the N_2O partial pressure was not constant.

2.10.3 Activation Energy

2.10.3.1 Carbon-Nitric Oxide Reaction

Two temperature regimes for the reactivity of NO-carbon reaction have been observed by many workers (Furusawa *et al.*, 1980; Chan *et al.*, 1983; Suuberg *et al.*, 1990; Teng *et al.*, 1992; Illán-Gómez *et al.*, 1996; Rodrigues-Mirasol *et al.*, 1994). A distinctive break in the apparent activation energy has been found to occur in the temperature range of 873-953 K. At higher temperatures, the activation energy was found to have a higher value than that in a lower temperature regime.

This behavior conflicts with what might be expected if this were simply a case of transition from chemical reaction rate control to mass transfer control. The transition temperature indicates a change in mechanism and reflects the transition from a slow desorption of surface complexes at low temperature, to a process that is dominated by the release of products from the actives at high temperatures (Teng *et al.*, 1997). Both of these two competing processes contribute significantly to overall rate, even in the temperature regime where they do not apparently control the rate. There is no precious change in mechanism, but rather a gradual transition. Below this transition temperature, the apparent activation energy increases continuously with temperature from 60 to 90 kJ/mol due to the activation energy distribution for desorption of surface complexes (Suuberg *et al.*, 1990). In the high temperature regime, the apparent activation energy exhibits a relatively constant value of 180 kJ/mol, which is controlled by NO attack and perhaps by the N-O bond energy. The activation energy over the higher temperature regime also varies in some cases. It was explained that this is due to the catalytic effect of impurities in the carbonaceous materials (Chan *et al.*, 1983; Illán-Gómez *et al.*, 1996). The catalytic effect has the potential to reduce the activation energy. For example, in the work of Chan *et al.* (1983), the activation energy obtained for a deashed char was higher than that of the same char without deashing. Similar results were obtained in the studies of Illán-Gómez *et al.* (1996) and Rodriguez-Mirasol *et al.* (1994).

The transition temperature observed by different studies also varies, depending probably on the carbonaceous materials used.

2.10.3.2 Carbon-Nitrous Oxide Reaction

Teng *et al.* (1997) used a phenol- formaldehyde resin char as a carbon material with low impurity levels. Their results showed a break

temperature was at around 748 K. The low-temperature regime (< 748 K) was characterized by an activation energy, which increased slightly with the extent of carbon burn-off, ranging from 57 to 66 kJ/mol. The high-temperature regime (> 748 K) was exhibited by an activation energy, which was also an increasing function of the burn-off level, ranging from 170 to 230 kJ/mol.

Rodrigues-Mirasol *et al.* (1994) studied the decomposition of N_2O by char under a fixed bed reactor. The reactions were studied at temperatures from 673 to 1223 K and at partial N_2O pressures in the range of 0.19-1.92 mbar. Four coals with different ranks were used in this study as char precursors: lignite coal (DE53), subbituminous coal (Gardanne), high-volatile bituminous coal (Daw-mill), and anthracite (Blanzy). Their results showed apparent activation energies in the range of 66-104 kJ/mol were obtained for N_2O decomposition.