Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hsieh, Chien-To and Teng, Hsisheng(2001) 'STUDIES ON THE KINETICS OF NITROUS OXIDE ADSORPTION ON RESIN CHAR', Separation Science and Technology, 36: 1, 113 — 124
To link to this Article: DOI: 10.1081/SS-100000855
URL: http://dx.doi.org/10.1081/SS-100000855

SEPARATION SCIENCE AND TECHNOLOGY, 36(1), 113–124 (2001)

STUDIES ON THE KINETICS OF NITROUS OXIDE ADSORPTION ON RESIN CHAR

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ABSTRACT

Adsorption of nitrous oxide on resin char was investigated with a thermogravimetric system in this study. The char was prepared from pyrolysis of phenol-formaldehyde resins, followed by gasification of the resulting char in nitrous oxide to 18.5% burn-off. The temperature range used in the adsorption experiments was 35–80°C, and the partial pressure of nitrous oxide varied within 25–101 kPa. Experimental data showed that the adsorption isotherms were approximately linear in partial pressure of nitrous oxide. The adsorption was found to be reversible, based on the results of desorption experiments. Simulation of the adsorption kinetics with a modified Langmuir model has shown that the rate of adsorption had apparent orders of 4 and 5 with respect to the adsorptive sites and the nitrous oxide pressure, respectively. The rate constant of desorption was shown to increase with temperature, whereas that of the forward pathway of the reversible adsorption was less sensitive to temperature. According to the simulated results, the reversible adsorption was exothermic with an enthalpy change of -11.5 kcal/mol.

Key Words: Nitrous oxide; Adsorption kinetics; Char.

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INTRODUCTION

Nitrous oxide (N_2O) is a colorless gas with slightly sweet odor. This gas is one of the nitrogen oxides that are formed during combustion and has drawn attention during recent years. The mechanism of nitrous oxide formation during combustion is not known for certain. However, it is well known that nitrous oxide participates in reactions that may deplete stratospheric ozone, and it is also one of the greenhouse gases (1). Therefore, the efforts devoted to the reduction of nitrous oxide have gradually increased.

Many technologies, such as liquid absorption and membrane separation, can be used to separate contaminants from effluent gas streams. Efforts of the present research will be placed on the separation of nitrous oxide by adsorption. Several studies (2–4) have explored the heterogeneous reactions of gas adsorption on solids, such as carbon, and it has been concluded that the adsorption rate is related to the accessible surface area and the chemistry of the porous solids. However, the kinetics of nitrous oxide adsorption on carbons are rarely discussed. The present work investigates the process of nitrous oxide adsorption on a particular carbon, phenol formaldehyde resin char, at different temperatures. In order to characterize this system, both the temperature and pressure dependences of the adsorption rate and equilibrium capacity were extensively explored.

The well-known equilibrium adsorption isotherm, Langmuir, has been employed by previous studies for describing heterogeneous adsorption (5,6). This simple model of adsorption on solids is based on an assumption in which localized adsorption takes place on an energetically uniform surface without any interaction among adsorbed molecules. Here a modified Langmuir formulation was applied, and it gives the required rate expression and isotherm for the case of the homogeneous surface and localized adsorption. The majority of this paper is to elucidate the kinetics of nitrous oxide adsorption on carbons, based on a series of adsorption and desorption experiments occurring on a phenol-formaldehyde resin char. In developing the model of this adsorption system, it is desirable to obtain equations that can simultaneously describe both the forward and backward pathways of adsorption as well as the equilibrium surface coverage.

EXPERIMENTAL SECTION

Preparation of Adsorbent

In this study, phenol-formaldehyde resins were used as the starting material for the preparation of porous carbons. The resins were synthesized under an environment of nitrogen at 95°C, using an initial formaldehyde to phenol molar ratio of 1.33. In the synthesis, a base catalyzed method was used with ammonium hydroxide as the base. After synthesis, the resins were cured by heating in vacuum for 2 h at 60°C, followed by 12 h at 120°C. The samples were then carbonized in a horizontal cylindrical furnace (60 mm i.d.) in helium atmosphere. Carbonization was carried out by heating the samples from room temperature to 1050°C at 17.5°C/min followed by holding the samples at the carbonization temperature for 2 h before cooling under helium. Following the carbonization process, the resulting chars were gasified by N_2O to a burn-off level of ca. 18.5%. The gasification was performed at 700°C in a thermogravimetric analyzer (TGA, Perkin-Elmer TGA7). The gasified chars were ground and sieved to a desired particle size of 0.21–0.30 mm before being employed in adsorption.

Nitrous Oxide Adsorption and Desorption

The TGA apparatus was also applied for studying the kinetics of nitrous oxide adsorption on the char. Experiments were conducted in a steady flow of N_2O/He at 101 kPa total pressure. Char samples (10–30 mg) were held in a platinum pan suspended in the heated zone of a quartz tube. A thermocouple placed within a few millimeters of the pan served to indicate its temperature. The surface of char was cleaned of oxides prior to nitrous oxide adsorption experiments by heating the sample at 900°C in extra purity helium for 1 h.

The N_2O adsorption experiments were performed after surface cleaning by lowering the temperature of the sample from 900°C to the desired adsorption temperature and then quickly introducing the desired N_2O/He mixture. The adsorption experiments were carried out at partial pressures of nitrous oxide ranging from 25 to 101 kPa and at temperatures ranging from 35 to 80°C. Mass uptake of nitrous oxide during adsorption was continuously monitored for at least 24 h, during which the rate of mass gain became negligible. Following the saturation of N_2O uptake, the desorption of N_2O was sequentially performed at the same temperature. Desorption was monitored for at least 24 h with only helium flowing through the TGA.

Char Characterization

The specific surface area and pore volume of the char were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2010) was employed for these measurements. Adsorption of N_2, as a probe species, was performed at -196°C. Before any such analysis, the sample was degassed at 300°C in a vacuum at about 10^{-3} Torr. Surface area and micropore volume were determined from the application of the Brunauer-Emmett-Teller (BET) and Dubinin-Radushkevich (D-R) equations, respectively, from the N_2 adsorption isotherms at relative pressures between 0.06 and 0.2. In Type I isotherms, the amount of N_2 adsorbed at relative pressures near unity corresponds to the total amount adsorbed at both micropores (filled at low relative pressures) and mesopores (filled by capillary condensation at relative pressures above 0.2); consequently, the subtraction of the micropore volume (determined from the D-R equation) from the total amount of N_2 adsorbed (determined at $P/P_0 = 0.98$ in this case) would provide the volume of the mesopore (7). The adsorption isotherms were employed to deduce the BET surface area as well as the micropore and mesopore volumes. The average pore diameter can be determined according to the surface area and total pore volume (the sum of the micropore and mesopore volumes) if the pores are assumed to be cylindrical and have no intersection.

RESULTS AND DISCUSSION

In an effort to avoid any experimental artifacts due to differences in the nature or concentration of active sites caused by differing extents of burn-off, all the resin chars used in the N_2O adsorption experiments have similar extents of burn-off in nitrous oxide (about 18.5%). It has been shown that the adsorption behaviors can be sensitive to the burn-off level (8). The nitrogen adsorption isotherm for the resin char is shown in Figure 1. The isotherm is typical of microporous carbons (Type I); that is, the knee of the isotherm is sharp and the plateau is fairly horizontal (9).

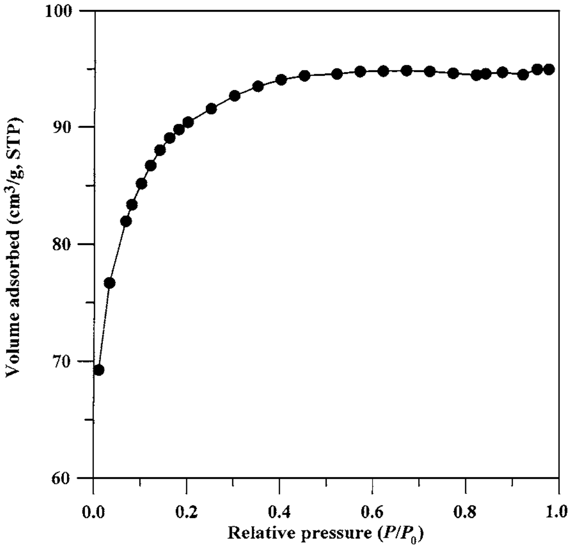

Figure 1. Adsorption isotherm of N_2 on the resin char with 18.5% of burn-off in N_2O.

Table 1. Surface Characteristics of Phenol-Formaldehyde Resin Char with 18.5% Burn-Off in Nitrous Oxide

BET SA (m^2/g)	Total Pore Vol. (cm^3/g)	Micropore Vol. (cm^3/g)	Mesopore Vol. (cm^3/g)	Average Pore Diameter (Å).
320	0.156	0.117	0.039	20.3

The physical properties of the resin char are shown in Table 1. The data show that the porosity of the char is mainly contributed by micropores. The average pore diameter of the resin char is larger than molecular size of nitrous oxide, indicating that there is no problem of restricted diffusion of N_2O at higher temperatures.

The results of nitrous oxide adsorption at 50.5 kPa and at temperatures ranging from 35 to 80°C are shown in Figure 2. It can be seen that the amount of mass uptake increases with the decrease in the adsorption temperature. The adsorption of nitrous oxide is rapid initially and slows down markedly with increasing surface coverage. Almost over 90% of total mass uptake was completed by 4 h. After 4 h of adsorption, the rate of adsorption becomes very slow, and the amount of mass uptake varies little with time, although there is never a distinct "endpoint" of adsorption for a much longer time. Here the total amount of nitrous oxide uptake was determined after a long period (24 h). The results of the total amount of nitrous oxide uptake are plotted in terms of adsorption isotherms in Figure 3. In the

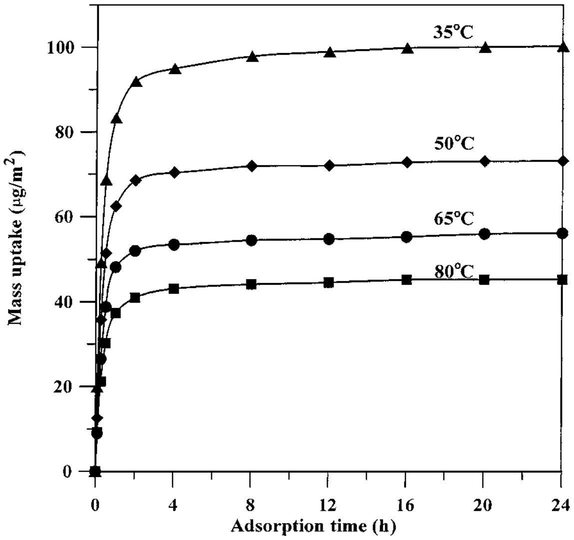

Figure 2. Mass uptake during the course of nitrous oxide adsorption on resin char at N_2O partial prassure of 50.5 kPa.

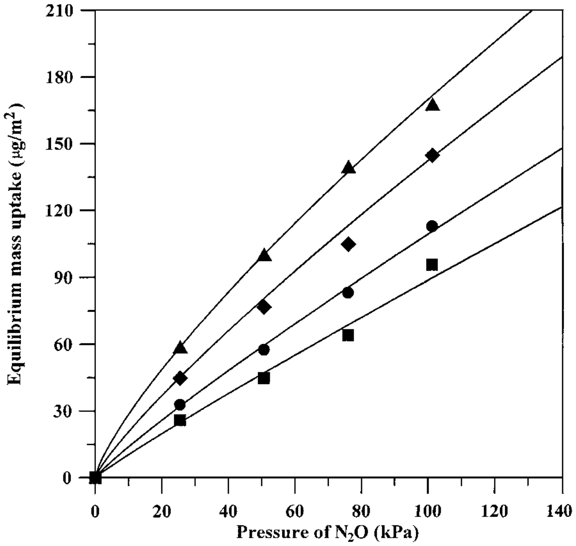

Figure 3. Adsorption isotherms of nitrous oxide on the resin char at different temperatures: 35°C (▲); 50°C (◆); 65°(●); 80°C (■). Solid lines represent simulated data from the modified Langmuir model using the parameters determined from the present study.

isotherms obtained, the relation between mass uptake and N_2O partial pressure is found to be approximately linear.

The adsorption behavior of nitrous oxide onto the particular char surface can be regarded as the process of reversible adsorption. Here the main reaction of interests can be represented in thermodynamic terms as

$$n\,C^* + mN_2O \leftrightarrow n\,[C^*(N_2O)_x] \qquad \text{(R1)}$$

In the above reaction, C^* represents the adsorptive sites for nitrous oxide adsorption, N_2O represents the nitrous oxide molecule, and the complex $C^*(N_2O)_x$ represents the sites that were occupied by nitrous oxide. The stoichiometry of reaction (R1) indicates that the value of x is the ratio of m to n. To simplify the adsorption model, the following assumptions were made:

1. Monolayer adsorption and all adsorptive sites were localized.
2. The surface of the resin char was energetically homogeneous.
3. There was no dissociation of molecules on the surface.
4. There were no lateral adsorbate–adsorbate interactions at higher coverage in the surface phase.
5. Each adsorptive site could be occupied by one or more nitrous oxide molecules, forming as intermediate complex, $C^*(N_2O)_x$, on the char surface.

The precise nature of the pathways to final surface complexes in the present analysis assumes that there is no net creation or destruction of the rate-determining adsorptive sites during intermediate steps. Under these circumstances, the global rate expression of N_2O-char adsorption can be written as

$$r_a = d\theta/dt = k_a(1-\theta)^n P^m - k_d\theta^n \tag{1}$$

where r_a is the global adsorption rate, θ the fraction of adsorptive sites occupied by nitrous oxide, $1-\theta$ is the fraction of sites that were empty and available for nitrous oxide adsorption, P is the partial pressure of nitrous oxide, k_a and k_d are the rate constants for adsorption and desorption respectively, and n and m are the apparent reaction orders with respect to adsorptive site and N_2O partial pressure respectively. This adsorption model, a modified Langmuir (ML) model, was used and expected to shed some light on the details of the kinetics of nitrous oxide adsorption on carbon.

In order to give a complete description of this adsorption kinetics, the parameters shown in Equation (1) have to be determined. However, it is difficult to find these parameters directly from the adsorption data, as both the adsorption and desorption occur during the course of mass uptake. Therefore, the desorption data were employed first to determine the parameters for desorption, which was a single step. The reaction in the desorption of nitrous oxide from the adsorptive sites under a helium flow can be expressed as

$$n[C^*(N_2O)_x] \rightarrow n\,C^* + m\,N_2O \tag{R2}$$

where the desorption rate, r_d, can be written as

$$r_d = -d\theta/dt = k_d\theta^n \tag{2}$$

In Equation (2), the values of k_d and n are the same as those in Equation (1). Integration of Equation (2) yields

$$\theta_t^{1-n} - \theta_e^{1-n} = -(1-n)\,k_d\,t \tag{3}$$

where θ_e is the coverage at the beginning of desorption and θ_t is the coverage at any desorption time t. The value of θ_e was equivalent to the coverage at the final stage of adsorption prior to the desorption.

As mentioned previously, the value of θ represents the occupied fraction of surface that is capable of adsorbing N_2O molecules at monolayer coverage. Assuming that the nitrous oxide molecules have a close-packed hexagonal arrangement on the char surface (10), the cross-sectional area of a nitrous oxide molecule was estimated to be 26.4 Å^2 (11). Under this assumption, the area occupied by nitrous oxide can be determined, and θ can be evaluated by dividing the occupied area with the BET surface area of the carbon.

The progression curves of nitrous oxide desorption from the resin char are given in Figure 4. It clearly shows that the desorption kinetics are similar

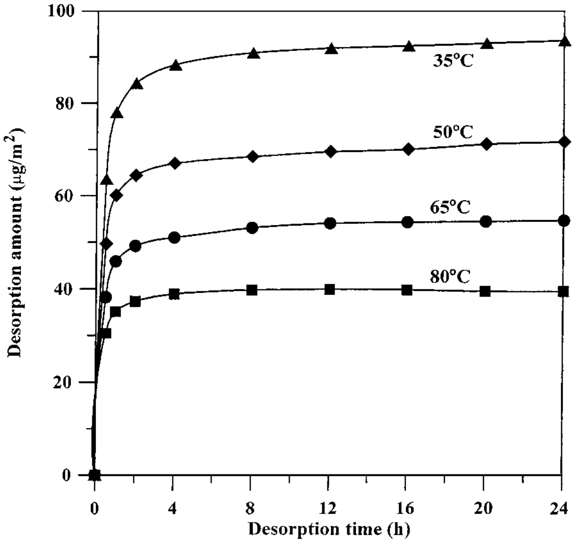

Figure 4. Mass loss during the course of nitrous oxide desorption from the N_2O-saturated resin chars shown in Figure 2.

to the adsorption process. The desorption of nitrous oxide is very fast initially, but decreases markedly after 4 h. The desorption data shown in Figure 4 were simulated with Equation (3), and a value of 4 for parameter n was found to give the best linearity of $(\theta_t^{1-n} - \theta_e^{1-n})$ against t at the temperatures studied. These linear fits are fairly good, having correlation coefficients (r^2) around 0.99. The high value of n indicates that the desorption rate is highly dependent on the surface coverage and would thus decline sharply with the decreasing number of the complexes, as reflected in Figure 4. The other parameters of this adsorption model, including the reaction orders and the energetics, will subsequently be determined in the following discussion, and the results are summarized in Table 2.

The values of k_d for different temperatures were determined from the slopes of the linear fits, and the results are plotted in Figure 5. As expected, the k_d value is an increasing function of the desorption temperature. To explore the

Table 2. Parameters of the Modified Langmuir Model for the Adsorption of Nitrous Oxide on Resin Char

n	m	x	E_d (kcal/mol)	ΔH_L (kcal/mol)	E_a (kcal/mol)
4	5	1.25	10.4	11.5	1.1

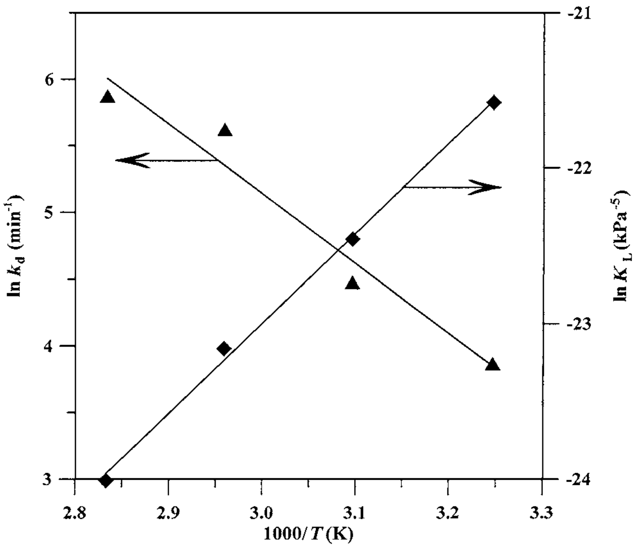

Figure 5. Temperature dependence of the desorption rate constant, k_d, and the equilibrium constant, K_L.

energetic of the process, the heat of desorption should follow the van't Hoff equation (12).

$$d(\ln k_d)/d(1/T) = -E_d/R \tag{4}$$

where T is the desorption temperature, and E_d represents the apparent activation energy of desorption. The linear plot of ln k_d versus $1/T$ in Figure 5 would result in the value of E_d from the slope, and its result is listed in Table 2. Because of the physical nature of the interaction between N_2O and char the activation energy obtained is smaller than those for chemical reactions.

At the equilibrium stage of the adsorption reaction (R1), the global rate of N_2O adsorption diminishes, and Equation (1) can be rewritten as

$$K_L = \theta_e^n/[(1-\theta_e)^n P^m] \tag{5}$$

where K_L is the equilibrium constant for the ML model and its value is equal to the ratio of k_a:k_d. Rearranging Equation 5, a linear from of the equation can be obtained

$$n\ln(\theta_e/1-\theta_e) = m\ln P + \ln K_L \tag{6}$$

A plot of $[n\ln(\theta_e/1-\theta_e)]$ versus ln P would give m and ln K_L from the slope and intercept. The mass uptake data in Figure 2 can be used to calculate the values of m and K_L for each temperature. The values of m were found to be ca. 5 for different temperatures, and the temperature dependence of K_L is shown in Figure 5. The value of x is thus determined to be 1.25, which is the ratio of m to n.

The data in Figure 5 show that the value of K_L decreases with the adsorption temperature, indicating an exothermic process for the formation of $C^*(N_2O)_x$ complexes. The exothermic feature of reaction (R1) is expected, as the affinity due to the dispersion force, which accounts for major part of the adsorbate-adsorbent potential (10,12), will decrease with temperature.

The enthalpy of adsorption, ΔH_L, for reaction (R1) can be calculated according to

$$d(\ln K_L)/d(1/T) = -\Delta H_L/R \tag{7}$$

The value of ΔH_L was determined from the slope of the linear plot of ln K_L against $1/T$ in Figure 5. The value was found to be −11.5 kcal/mol. The negative value of ΔH_L reflected the exothermic nature of the adsorption process. The heat of adsorption provides a direct measure of the strength of the binding forces between the adsorbate molecule and adsorbent surface (13). In general, physisorption is an exothermic process and enthalpy changes for various types of physisorption were summarized at −2 to −12 kcal/mol (14). In the present study, the ΔH_L value for the adsorption of nitrous oxide on char falls in this range corresponding to a physisorption process.

Because of the relation of $K_L = k_a/k_d$ for the adsorption reaction (R1), the energetic relationship can be given as

$$\Delta H_L = E_a - E_d \tag{8}$$

with

$$E_a = -R[d(\ln k_a)/d(1/T)] \tag{9}$$

where E_a represents apparent activation energy for the forward reaction of reaction (R1). The value of E_a can be determined from Equation (8), and the result was found to be −1.1 kcal/mol. It is interesting to note the small activation energy for the adsorption pathway. The small value is expected, as the adsorption rate is mainly affected by the collision frequency, which is less sensitive to temperature variation than desorption.

The parameters determined for the ML model have been summarized in Table 2, and these determined values were used to simulate the equilibrium adsorption of nitrous oxide on char. The comparison of the simulation results with the experimental data is shown in Figure 3. It can be seen that the model gives fairly good fit over the entire temperature and pressure ranges. This indicates that the ML model can provide a simple way to estimate to the equilibrium adsorption of nitrous oxide on char.

CONCLUSIONS

It has been shown on the basis of the present study that the adsorption of N_2O on resin char is an exothermic process, and the equilibrium amount of mass uptake increases linearly with the N_2O pressure within the temperature range studied. The kinetic data from the adsorption and desorption experiments have shown that the N_2O uptake on char is totally reversible, and both the adsorption and desorption rates are high at the initial stage and slow down markedly with the progress of the process.

The kinetic data were fitted to a modified Langmuir model, and the results have reflected that this reversible adsorption process had apparent reaction orders of 4 and 5 with respect to the adsorptive sites and the N_2O pressure, respectively. The rate constant of N_2O desorption from char was found to increase with temperature, associated with an apparent activation energy of 10.4 kcal/mol, whereas the uptake of N_2O molecules onto char surface was less sensitive to temperature. An enthalpy of -11.5 kcal/mol was determined from the Langmuir model for this adsorption system. The derived kinetic parameters were employed to simulate the adsorption data, and it has been demonstrated that the Langmuir model is capable of providing good fits to the isotherms of N_2O adsorption on char.

ACKNOWLEDGMENTS

This research was supported by National Science Council in Taiwan, through project NSC 89-EPA-Z-006-004.

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Received August 30, 1999
Revised April 2000

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