The Adsorption and Desorption of Nitrogen Oxide by the Aqueous Dispersion of the Chelate Resin-Immobilized Iron(II) Complex

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Aqueous dispersions of the chelate resin-iron(II) complex were prepared by ion-exchange in water from iron(II) sulfate and a chelate resin containing iminodiacetic acid moieties. The resulting dispersions in water (50 cm^3) can adsorb 78% of the nitrogen oxide (NO) from 6 dm^3 of nitrogen gas containing 1000 ppm of nitrogen oxide at 25 °C. The adsorption rate of NO by the dispersions depends greatly on both the particle size of the chelate resin used and the concentration of iron(II) in the supernatant. A fast adsorption of nitrogen oxide can be achieved by using small particles of the chelate resin and by dissolving a large amount of iron(II) ions in the aqueous part of the dispersions. The adsorption and desorption of nitrogen oxide can be understood in terms of a 1 : 1 reversible coordination of NO to the iron(II) ion immobilized on the chelate resin. The equilibrium constant, enthalpy change, and entropy change for the above adsorbing reaction were 3.11×10^4 dm^3 mol^{-1}, −45.6 kJ mol^{-1}, and −68.2 J K^{-1} mol^{-1} respectively. Since the adsorbing reaction of NO in this system is reversible, the adsorbed NO can be released by heating the dispersions which have already adsorbed NO. The amount of the released NO can be predicted from the equilibrium constant at the releasing temperature. Moreover, a concentrated recovery of the NO can be achieved by the present aqueous dispersions system.

The concentration of NO in the atmosphere has never decreased in the past decade in spite of many efforts. Since NO is toxic for the human body and causes photochemical smog through nitrogen dioxide, advanced technology for the removal of NO is strongly desired. At the present time, the catalytic reduction of NO into innoxious nitrogen by using a gaseous reducing agent like ammonia or hydrogen is a well-known practical method for the removal of NO.[1-4] This method has, however, some disadvantages, such as a rapid deactivation of the catalyst by the contaminated gases (sulfur dioxide) or dust. On the other hand, aqueous absorbents for NO have been studied because of the relatively high durability against these contaminants. The typical solution systems involve: 1) an aqueous solution of sodium hydroxide, where NO is absorbed by the aqueous solution after the oxidation of NO to NO_2 by contact with O_3,[5] and 2) an aqeous solution of iron(II)-ethylenediaminetetraacetic acid (Fe(II)-EDTA), where NO can form a complex with Fe(II)-EDTA.[6-9] Among these methods, the aqueous solution of Fe(II)-EDTA is noteworthy for its high capability for the absorption of NO and its possible application for the simultaneous removal of NO and sulfur dioxide.[9] This solution, however, has disadvantages in the recovery of the Fe(II)-EDTA complex for the recyclic usage, since the complex is easily dissolved in water and the Fe(II) ions are easily oxidized into inactive Fe(III) ions.

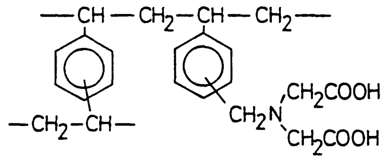

Fig. 1. Structure of the chelate resin.

In the present investigation, the immobilization of Fe(II) ions on the chelate resin involving iminodiacetic acid moieties (Fig. 1) instead of EDTA and the dispersion of the resulting Fe(II)-chelate resin complex (CR-Fe(II)) into water were examined for the purpose of establishing a method of ensuring easy handling, a concentrated recovery of NO, and an improvement in the durability against oxygen. In general, the immobilization of metal ions on the polymer resin gives rise to the following advantages:[10] 1) Easy recovery and repeated use of the metal complex; 2) the stabilization of the complex or protection of the active species by the polymer matrix against oxygen or water, and 3) an improvement in the activity by the polymer field. Many successful results supporting these advantages have been reported in the macromolecular metal complex catalyst system.[11] In the present paper, the preparation and characterization of aqueous dispersions of the chelate resin-immobilized Fe(II) complex, and its properties for the adsorption and desorption of NO will be described in detail.[12,13]

Experimental

Materials. The chelate resin (Diaion CR-10; mean diameter of the particles, 0.5 mm), purchased from Mitsubishi Chemical Industries, Ltd., was used without further purification. The commercial resin was swollen with water. One gram of the swollen substance was determined by the pH-titration method to contain 0.98 mmol of iminodiacetic acid moieties. One gram of the resin dried in vacuo, on the other hand, had 2.78 mmol of the moieties. A mass of the chelate resin in a dry or a swollen state containing 21.0 mmol of iminodiacetic acid moieties was used at one time for the preparation of each aqueous dispersion.

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The iron(II) sulfate 7 hydrate, iron(II) perchlorate 6 hydrate, and iron(II) chloride *n* hydrate (*n* was determined to be 4.59 by the 1,10-phenanthroline method[14]) were used without further purification.

Mixed gases of NO and nitrogen of the designed NO concentration were purchased from Takachiho Shoji, Ltd., and were used without further purification.

The chelate resin in a small size was prepared by grinding the commercial chelate resin with an agate mortar and a pestle. Its mean particle size was proved to be 10 μm by measurement with an optical microscope. In order to avoid any differences in the particle size in the experimental lots, the chelate resin was previously ground on a large scale, and all the dispersion systems were prepared by using samples of the same lot.

Preparation of Absorbents or Adsorbents. (1) Aqueous Dispersions of the Chelate Resin-Immobilized Iron(II) Complex: Chelate resin containing 21.0 mmol of iminodiacetic acid moieties (21.4 g in the swollen state, or 7.53 g in the dry state) was added to 15 cm^3 of water in which a desired amount of Fe(II) sulfate had been dissolved under nitrogen. The resulting mixtures were shaken for 48 h with a mechanical shaker or magnetic stirrer to immobilize the Fe(II) ions on the chelate resin.

(2) An Aqueous Solution of the Iron(II)-EDTA Complex: An aqueous solution of the Fe(II)-EDTA complex, used as a conventional absorbent of NO, was prepared by dissolving 0.139 g (0.50 mmol) of $FeSO_4$ $7H_2O$ and 0.187 g (0.50 mmol) of EDTA 2Na $2H_2O$ in 50 cm^3 of water under oxygen-free conditions.

(3) An Aqueous Solution of Iron(II) Salt: Various kinds of Fe(II) solutions were prepared by dissolving 31.4 mmol of various Fe(II) salts in water under oxygen-free conditions, adjusting the total volume of the solution to 50 cm^3.

(4) Dispersions of the Chelate Resin-Immobilized Iron(II) Complex in an Aqueous Iron(II) Solution at a Designed Concentration: After the preparation of aqueous dispersions of the immobilized complex from 7.53 g of the ground chelate resin and 8.72 g (31.4 mmol) of Fe(II)SO_4 $7H_2O$, the supernatant of the dispersions was removed by use of a centrifuge. Adding 15 cm^3 of a fresh aqueous solution of $FeSO_4$ $7H_2O$ at a desired concentration provided dispersions of the immobilized Fe(II) complex in a Fe(II) solution. The exact concentration of the Fe(II) ions in the supernatant was determined by the 1,10-phenanthroline method.[14]

Characterization of Aqueous Dispersions of the Chelate Resin-Iron(II) Complex. (1) Electronic Spectra of the Complexes: The electronic spectra of the aqueous solutions of the complexes were measured with a Hitachi model 340 spectrophotometer. The electronic spectrum of the dry or wet chelate resin-immobilized Fe(II) complex was measured at room temperature with the same spectrophotometer equipped with an integrated reflection apparatus.

(2) Measurement of the Amount of the Iron(II) Ions Immobilized on the Chelate Resin: The amount of immobilized Fe(II) ions was measured by the following method. Fifty cm^3 of an aqueous solution of $FeSO_4$ with an exact, desired amount was added to 7.53 g of the dry chelate resin (containing 21.0 mmol of iminodiacetic acid moieties), after which the mixture was stirred for 48 h. After the immobilization of the Fe(II) ions on the chelate resin, the concentration of the Fe(II) ions in the supernatant was measured by the 1,10-phenanthroline method,[14] while the amount of immobilized Fe(II) ions was calculated from the decrease in the concentration of Fe(II) ions in the aqueous phase.

Adsorption and Desorption Experiment on NO. (1) Adsorption of NO: Adsorption experiments on NO were carried out by using the closed-circulation system illustrated in Fig. 2. After removing the remaining gas in the system with a vacuum pump, 6 dm^3 of nitrogen containing 1000 ppm (or 980 ppm) of NO (the total amount of NO was 0.246 mmol) was introduced into this apparatus at room temperature and then circulated inside the apparatus, bubbling the aqueous dispersions through by means of a gas pump at the rate of 1.6 dm^3 min^{-1}. The adsorbent was kept at the desired temperature in a water bath with a thermostat.

Changes in the NO concentration in nitrogen were traced by sampling 23.8 cm^3 of the mixed gas in a 100 mm-cell and by measuring the absorbance at 226.5 nm.

(2) Dependence of the Amount of Adsorbed NO at Equilibrium on the Partial Pressure of NO: After placing the dispersions in contact with 6 dm^3 of nitrogen containing 980 ppm of NO until the equilibrium had been reached, the gas remaining in the system was removed and another 6 dm^3 of nitrogen with NO was introduced; the gas was then circulated again for the further adsorption of NO with the same dispersions. The amount of adsorbed NO was obtained from the sum of those NO values from the first and second runs. The concentration of NO in the second run corresponded to the partial pressure of NO at equilibrium. By repeating the above operation, the relationship between the amount of NO adsorbed and the partial pressure of NO was measured.

(3) Desorption of NO: The desorption of NO was carried out by the following two methods of heating and purging with pure nitrogen.

Heating: After the dispersions had been equilibrated with the mixed NO gas at 25 °C, the gas circulation was stopped and the system was left as it was. Then the temperature of the dispersions was raised to 80 °C, below which temperature the resin was known to be stable enough; the gas was then circulated again at the rate of 1.6 dm^3 min^{-1}. Repeated adsorption-desorption cycles were carried out by raising and dropping the temperature of the dispersions without exchanging the initially introduced mixed gas.

Purging with Pure Nitrogen: After the dispersions had been equilibrated with the mixed NO gas at 25 °C, the gas remaining in the circulation system was removed by the use

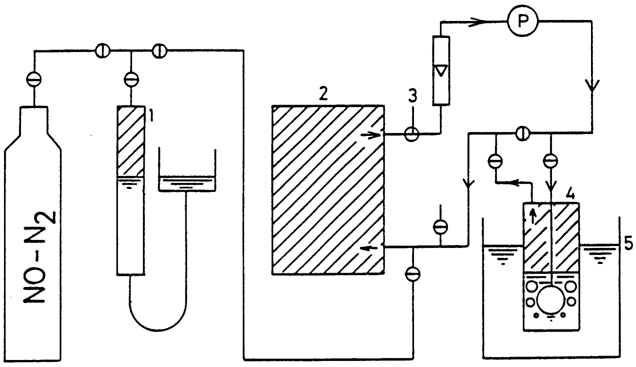

Fig. 2. Schematic diagram of gas adsorption apparatus.
1. Gas burette. 2. Gas holder. 3. Sampling outlet. 4. Adsorbing vessel. 5. Constant temperature water bath.

of a vacuum pump and 6 dm^3 of a pure nitrogen gas was freshly introduced into the system (except for the adsorbing vessel containing the dispersions). The nitrogen was then circulated through the dispersions at 25 °C. The error caused by the gas remaining in the adsorbing vessel was corrected in each run.

Results

Preparation and Characterization of an Aqueous Dispersion of the Chelate Resin-Immobilized Iron(II) Complex. The immobilization of Fe(II) ions on the chelate resin proceeds rapidly when the solution of Fe(II) ions is mixed with the chelate resin. The light green color of the solution gradually fades because of the decrease in the concentration of the Fe(II) ions in the supernatant. The immobilization was also observed in the electronic spectra. The chelate resin before the immobilization of the Fe(II) ions is white and has a peak at 280 nm in its electronic spectrum due to benzene chromophores in the matrices, as is shown by broken line in Fig. 3. The color of the resin changes from white to light green upon the immobilization of the Fe(II) ions, and a new peak appears at around 320 nm which does not exist in the electronic spectrum of an aqueous solution of $FeSO_4$ and the chelate resin. The exposure to NO gives new shoulder peaks around 450 and 600 nm, as is shown by the solid line in Fig. 3. A similar change has also been observed in the case of the adsorption by an aqueous solution of the Fe(II)-EDTA complex.[7,8] The release of NO by the heating of the adsorbed resin led to the disappearance of the two shoulder peaks and gave the same electronic spectrum as that of the original chelate resin-Fe(II) complex before the adsorption of NO.

Adsorption of NO by the Aqueous Dispersions of the Iron(II)-Chelate Resin Complex. Figure 4 shows the adsorption curves of various absorbents and adsorbents. An aqueous solution of Fe(II)-EDTA, a typical absorbent of NO, rapidly absorbs NO, even at a low concentration of NO. The absorption capacity, however, gradually decreases, probably because of the deterioration of the adsorbent by the trace amount of oxygen being contaminated by the leakage in air at the circulating pump. An aqueous solution of $FeSO_4$, the starting material of the dispersion system, absorbs only 3% of the initially charged amount of NO, as is shown by the open circles in Fig. 4. The mixture (the dispersions) prepared by adding the above aqueous solution of $FeSO_4$ to the chelate resin can adsorb enough NO, though its adsorption rate is not very fast. When these dispersions were separated into an aqueous part (the supernatant) and a solid part, however the aqueous part did not absorb NO, but the solid part did. This fact clearly indicates that Fe(II) ions immobilized on the chelate resin are the active species for the adsorption of NO.

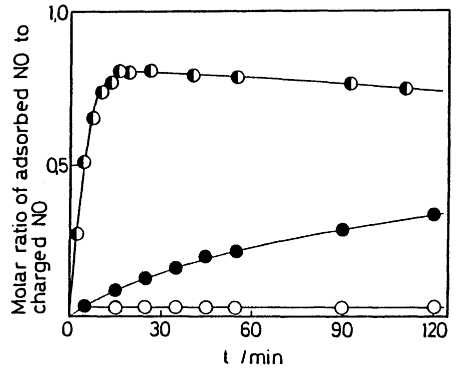

Fig. 4. Adsorption of NO at 25 °C by Fe(II)-EDTA solution (◐, 0.01 mol dm^{-3}), Fe(II)-SO_4 solution (○, 0.36 mol dm^{-3}), and resin-immobilized adsorbent dispersion prepared by mixing 18 mmol of Fe(II)SO_4 and 21.4 g of the chelate resin in water by using a shaker (●). The adsorbents were contacted with 6 dm^3 of nitrogen containing 1000 ppm of NO.

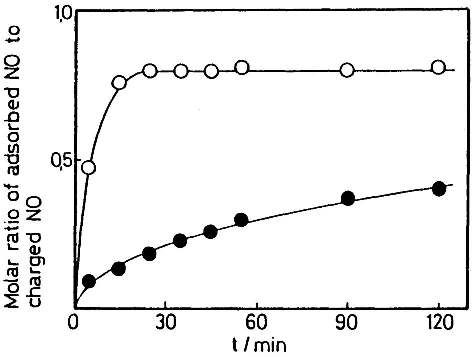

Fig. 5. Adsorption of NO at 25 °C by the resin-immobilized Fe(II) adsorbents prepared from commercial beads (●) and from fine beads ground with agate mortar and pestle (○). Adsorption of NO was carried out by the contact with 6 dm^3 of nitrogen containing 980 ppm of NO at the rate of 1.6 dm^3 min^{-1}.

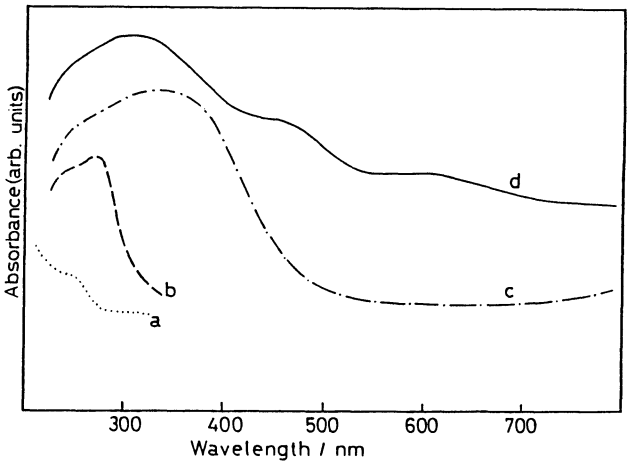

Fig. 3. Electronic spectra of the NO adsorbent and the related materials. a(······): $FeSO_4$ solution in water, b(— —): chelate resin, c(·—·—): NO adsorbent before adsorption of NO, d(——): NO adsorbent after adsorption of NO.

Figure 5 shows the NO adsorption curves of the dispersions of the adsorbents prepared by using the resin in a small size (10 μm) as well as in a commercial size (0.5 mm). The equilibrium is achieved within 25 min in the case of the small size resin by adsorbing 78% of NO at 25 °C, as Fig. 5 shows. Moreover, no deterioration by the contaminated oxygen as is seen in the case of an aqueous solution of Fe(II)-EDTA is observed in this system.

Figure 6 shows the dependence of the amount of adsorbed NO at equilibrium on the charged amount of Fe(II). The capital letter R in the figure shows the molar ratio of the initially charged amount of Fe(II) ions to the IDA moieties in the resin. The amount of NO adsorbed at equilibrium increases with the increase in the amount of charged Fe(II) ions and reaches saturation at the point where the amount of Fe(II) is half as much as the molar amount of IDA moieties in the resin by adsorbing 68% of the NO at 30 °C. The amount of immobilized Fe(II) ions, which are the active species for the adsorption of NO, reaches saturation over R=0.7, no further immobilization of the Fe(II) ions on the chelate resin was observed beyond this point.

The aqueous dispersions prepared from various Fe(II) salts with the different counter anions listed in Table 1 have almost the same activity for the adsorption of NO, while the aqueous solution of each Fe(II) salt absorbs only 6% of the NO. Thus, no significant difference in the adsorbing capability caused by the Fe(II) salts used was observed.

The adsorption rate of NO increased with the increase in the amount of charged Fe(II), as is shown in Fig. 7. The increase in the rate was observed after the saturation of Fe(II) immobilization, while the amount of adsorbed NO was at the saturation point.

The amount of NO adsorbed at equilibrium depends strongly on both the partial pressure of NO and the temperature. Figure 8 shows the relationship between the partial pressure of NO at equilibrium and the amount of NO adsorbed. As this figure shows, the

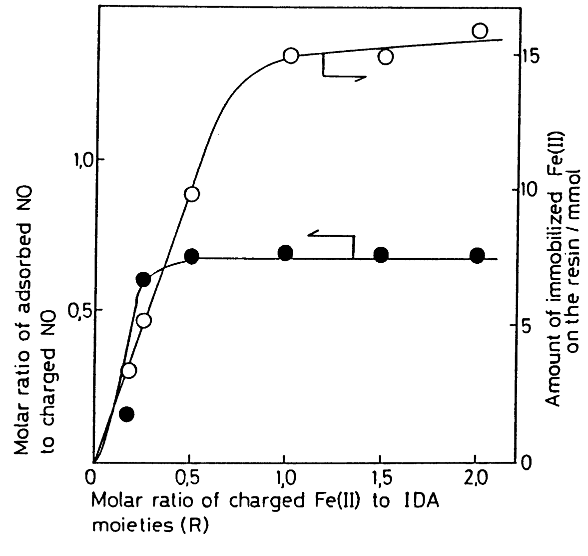

Fig. 6. Relationship between the amount of adsorbed NO at equilibrium (●) and the amount of immobilized Fe(II) on the resin (○) at various amount of Fe(II) charged. Initially charged amount of chelate resin was 7.53 g containing 21.0 mmol of IDA moieties.

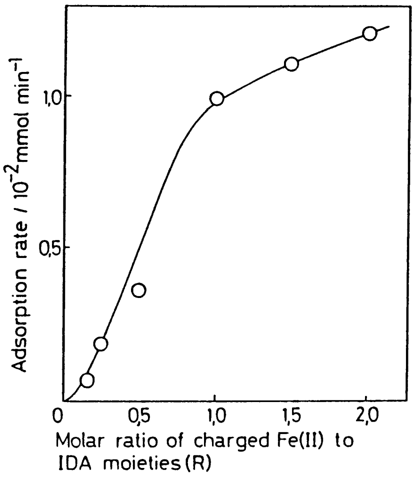

Fig. 7. Dependence of initial adsorption rate of NO on molar ratio (R) of the charged amount of Fe(II) to the amount of iminodiacetic acid moieties in the chelate resin by the contact with 6 dm^3 of nitrogen containing 980 ppm of NO at the rate of 1.6 dm^3 min^{-1} with the adsorbent dispersions prepared from 7.53 g of chelate resin containing 21.0 mmol of IDA moieties and designed amount of $FeSO_4$.

Table 1. Adsorption of NO with Fe(II) Complexes from Various Salts[a)]

Fe(II) complex			Molar ratio of adsorbed NO to charged NO
Fe(II) salt		IDA[b)] of chelate resin/mmol	
Formula	Amount/mmol		
$FeSO_4$	18	0	0.033
$FeSO_4$	31	21	0.776
$Fe(ClO_4)_2$	31	0	0.061
$Fe(ClO_4)_2$	31	21	0.700
$FeCl_2$	30	0	0.067
$FeCl_2$	30	21	0.767

a) Initial amount of NO=0.246 mmol. b) 21.0 mmol of the iminodiacetic acid (IDA) moieties were included by 21.4 g of the chelate resin.

amount of adsorbed NO increases linearly with the increase in the partial pressure of NO. As for the temperature-dependence, the increase in the temperature decreases the amount of NO adsorbed. Thus, the dispersions adsorbed 78% of NO at 25 °C; this figure decreased to 11% at 80 °C.

Desorption and Recyclic Use. Figure 9 shows the adsorption and desorption cycles of NO upon treatment with heat. The concentration of NO rapidly decreases to 220 ppm in 90 min when it is in contact with the dispersions at 25 °C. By elevating the temperature of the dispersions to 80 °C, the NO is smoothly released from the dispersions and the concentration of NO recovers to 876 ppm. In other words, 85% of the NO adsorbed is released, while only 12% of the NO charged remains in the dispersions at 80 °C. The adsorption-desorption cycles were repeated for 5 times without any deterioration.

The desorption of NO is also possible by letting pure nitrogen flow through the dispersions. Twenty-three percent (0.041 mmol) of the adsorbed NO was recovered at the concentration of 167 ppm by circulating 6 dm^3 of bubbling pure nitrogen through the dispersions, which had previously adsorbed NO (0.18 mmol) from 6 dm^3 of the mixed gas at 25 °C.

From the viewpoint of the recovery of NO as chemical resources, the recovery of NO at a higher concentra-

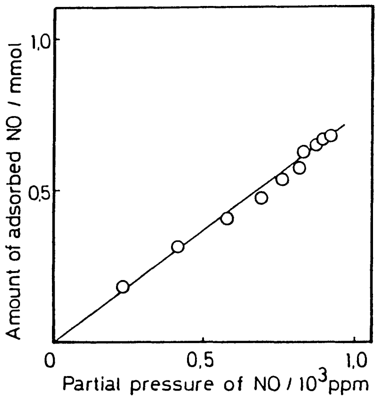

Fig. 8. Dependence of the amount of adsorbed NO at equilibrium on the concentration of NO. Adsorption experiment was carried out by the contact with 6 dm^3 of nitrogen containing 980 ppm of NO at 30 °C by the adsorbent dispersions prepared from 7.53 g of chelate resin containing 21.0 mmol of IDA moieties and 8.72 g of $FeSO_4$.

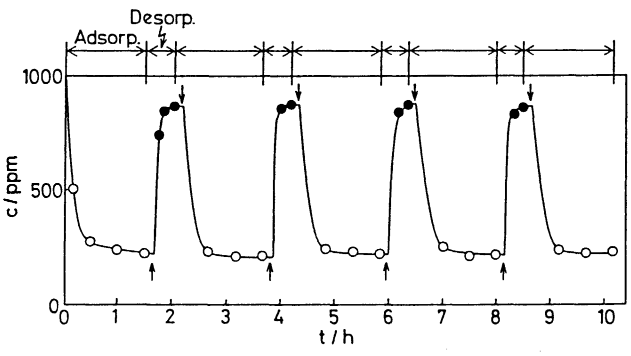

Fig. 9. Changes of the concentration (c) of NO in the gas phase with time (t) during the adsorption (○) of NO at 25 °C by Fe(II)-chelate resin adsorbent and desorption (●) of NO at 80 °C from the adsorbent. To adjust the temperature to a desired value, adsorbent was kept in the thermostat for 10 min without circulating the gas after adsorption (↑) or desorption (↓) of NO.

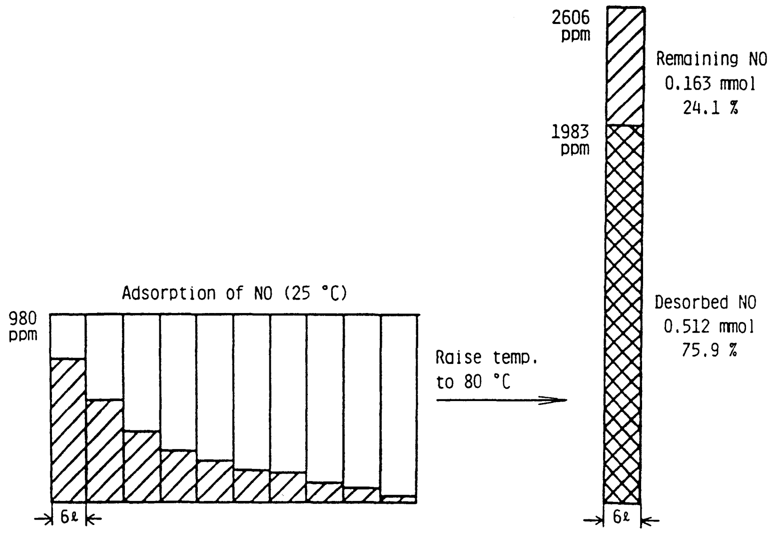

Fig. 10. The schematic presentation of the release of the cumulatively adsorbed NO from the adsorbent. Desorption of NO was carried out by circulating 6 dm^3 of pure nitrogen through the dispersions at the rate of 1.6 $dm^3\ min^{-1}$ till the equilibrium was attained after the dispersion was saturated with 980 ppm of NO by the contact with 6 dm^3 of nitrogen containing 980 ppm of NO for 10 times at 25 °C.

tion than that of the original gas is important. In order to test this possibility, the accumulated adsorption of NO was examined. After the first 6-dm^3 bag of the mixed gas had been circulated at 25 °C through the adsorbent until the equilibrium was reached, the remaining gas in the gas phase of the system was replaced by another 6 dm^3 of the fresh mixed gas, followed by a second circulation through the adsorbent. Ten repetitions of this procedure caused the adsorbent to be equilibrated with 980 ppm of NO. The total amount of NO adsorbed on the dispersions was 0.675 mmol. Then, 6 dm^3 of pure nitrogen was newly introduced into the system and circulated at 80 °C through the aqueous dispersions already saturated with 980 ppm of NO. This treatment released 0.512 mmol of NO, which corresponded to 76% of the total amount of that adsorbed , at the concentration of 1983 ppm. The above results are schematically illustrated in Fig. 10. These facts indicate that the concentrated NO can be obtained from the dilute one; that is, the concentrated recovery of NO is possible by using the present dispersion system.

Discussion

Complex Formation and Determination of the Equilibrium Constant. The appearance of a new peak at 320 nm upon the immobilization of the Fe(II) ions on the resin suggests the complex formation of Fe(II) with IDA moieties in the resin, as this peak does not exist in the separate spectra of Fe(II) and chelate resin. The new shoulder peaks at 450 nm and 600 nm appearing in the immobilized resin upon the contact with NO correspond to the charge-transfer band caused by the complex formation between NO and Fe(II). The appearance of such a charge-transfer band is observed in the case of an aqueous solution of an Fe(II)SO$_4$ or a monomeric Fe(II)-polyamine-*N*-carboxylic acid complex such as Fe(II)-EDTA.[15] These facts indicate that the adsorption of NO by the present aqueous dispersions proceeds through the complex formation between Fe(II) and NO, as in the case of the homogeneous aqueous solution of Fe(II)-EDTA or Fe(II).[16]

The above adsorbing reaction is considered to start from the dissolution of gaseous NO into water and to proceed according to Eqs. 1 and 2. Assuming the first-order reaction for the NO adsorption, i.e.:

$$\mathrm{NO_{gas}} \rightleftharpoons \mathrm{NO_{aq}} \tag{1}$$

$$n(\mathrm{NO_{aq}}) + \mathrm{CR\text{-}Fe(II)} \overset{K}{\rightleftharpoons} \mathrm{CR\text{-}Fe(II)\text{-}(NO)_n} \tag{2}$$

$$\begin{aligned} K &= [\mathrm{CR\text{-}Fe(II)\text{-}NO}]/([\mathrm{CR\text{-}Fe(II)}]\times[\mathrm{NO_{aq}}]) \\ &= [\mathrm{CR\text{-}Fe(II)\text{-}NO}]\times H/([\mathrm{CR\text{-}Fe(II)}]\times p_{\mathrm{NO}}) \end{aligned} \tag{3}$$

$$\begin{aligned} K &= n_{\mathrm{NO}}\times H/([\mathrm{CR\text{-}Fe(II)}]_0\times p_{\mathrm{NO}}) \\ K\times p_{\mathrm{NO}}/H &= n_{\mathrm{NO}}/[\mathrm{CR\text{-}Fe(II)}]_0 \end{aligned} \tag{4}$$

the 1 : 1 complex formation of NO with the Fe(II) ion (n=1 in Eq. 2), Eq. 3 can be obtained from Eq. 2, where p_{NO} and H are the partial pressure of NO (atm) and Henry's constant respectively. The amount of Fe(II) ions immobilized on the chelate resin, [CR-Fe(II)] in mmol, can have a linear relation with the amount of adsorbed NO n_{NO}; the uncoordinated amount is obtained by substracting the n_{NO} from the amount of the initially immobilized Fe(II) ions, $[\mathrm{CR\text{-}Fe(II)}]_0$. As the CR-Fe(II) exists in a large excess to the adsorbed NO ($[\mathrm{CR\text{-}Fe(II)}]/n_{\mathrm{NO}}=22$ in the present case), however, the amount of unreacted CR-Fe(II), [CR-Fe(II)], can be regarded as the amount of the initially immobilized Fe(II) ions, $[\mathrm{CR\text{-}Fe(II)}]_0$. Thus, Eq. 3 is transformed into Eq. 4. Equation 4 indicates that the partial pressure of NO at equilibrium should be in proportion to the amount of NO adsorbed when the 1 : 1 complex formation proceeds. In fact, the amount of NO adsorbed is in good proportion to the partial pressure of NO, as is shown in Fig. 8, which also indicates that the equilibrium constant, K, of the adsorbing reaction can be calculated according to Eq. 3.

Table 2 shows the equilibrium constant at each temperature obtained according to Eq. 3. The equilibrium constant decreases with the increase in the temperature because of the fall in the amount of NO adsorbed. The van't Hoff plots form a straight line, as is shown in Fig. 11, and the equilibrium constants K_c can be expressed as follows by using the temperature T as a parameter:

$$K_c = 3.32\times10^{-4}\times\exp(45.6\times10^3/RT) \tag{5}$$

where $R=8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
The enthalpy (ΔH) and entropy (ΔS) changes were obtained as $-45.6\ \mathrm{kJ\,mol^{-1}}$ and $-68.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$ respectively. The enthalpy change in the absorbing reaction of NO with an aqueous solution of Fe(II)-EDTA was reported to be $-66.1\ \mathrm{kJ\,mol^{-1}}$[8] ($-15.8\ \mathrm{kcal\,mol^{-1}}$), which is lower by $20.5\ \mathrm{kJ\,mol^{-1}}$

Table 2. Adsorption of NO by the Chelate Resin-Immobilized Fe(II) Complex at Various Temperatures

Temp/°C	Adsorbed NO[a]/mmol	Apparent equilibrium constant	
		$K_c\,H^{-1}$/atm^{-1}	K_c/dm^3 mol^{-1}
25.0	0.191(0.78)[b]	60.1	31.1 ×10^3
39.5	0.134(0.58)	23.2	14.8 ×10^3
59.8	0.069(0.29)	7.00	5.35×10^3
80.0	0.025(0.11)	2.02	1.67×10^3

a) Initial amount of NO=0.246 mmol. b) Molar ratio of adsorbed NO to charged NO.

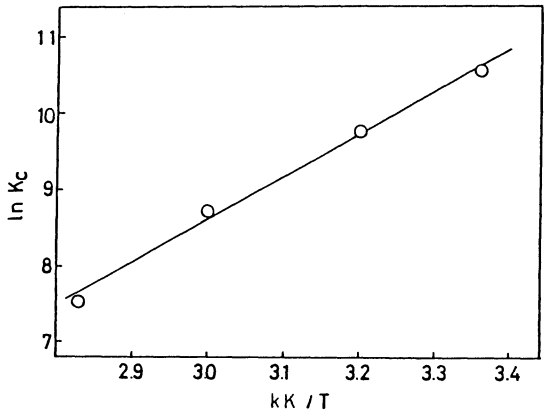

Fig. 11. The van't Hoff's plots for the adsorption of NO. The equilibrium constant at different temperature was calculated from the amount of adsorbed NO and partial pressure of NO at equilibrium according to the eq. 4. Adsorption experiment was carried out by circulating 6 dm^3 of nitrogen containing 980 ppm of NO at the rate of 1.6 $dm^3\ min^{-1}$.

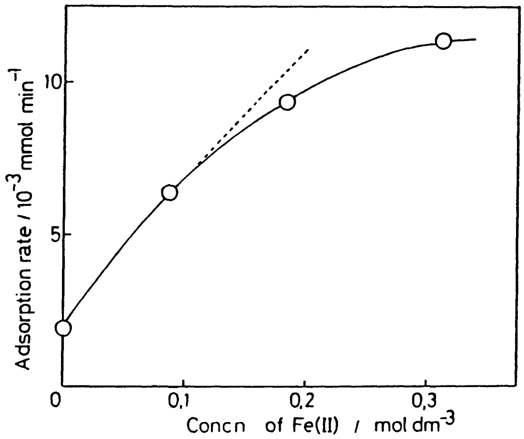

Fig. 12. Dependence of adsorption rate of NO on the concentration of $FeSO_4$ in the supernatant. In this system, amount of Fe(II) ion immobilized was kept constant (saturated) with 14.7 mmol. Adsorption experiment was carried out by circulating 6 dm^3 of nitrogen containing 1000 ppm of NO.

than that of CR-Fe(II). The strong NO-adsorbing capability of Fe(II)-EDTA is considered to be derived from the strong back-donation from Fe(II) to the NO molecule due to the increase in the electron density of the iron atom. In the case of the CR-Fe(II) complex, however, the coordination of NO to the Fe(II) ion is relatively weak due to the electron-releasing effect of the benzyl group compared with the case of the EDTA ligand.

Adsorption Rate. The increase in the rate of NO adsorption with small particles of the chelate resin suggests that the rate-determining step is the diffusion of the NO dissolved in the water into the resin inside. The adsorbing reaction is considered to occur by means of the following two steps: 1) the dissolution of NO into the supernatant of the dispersions, and 2) the adsorption of the NO dissolved by the CR-Fe(II) complex in the resin. The dissolution of the NO into the supernatant, the first step of the adsorption, is rapid and can always be brought to saturation by vigorous bubbling. The adsorption of the NO dissolved by the CR-Fe(II) complexes, the second step, occurs first on the surface of the resin, and then the NO adsorbed diffuses from the surface to the inside of the resin. This NO diffusion from the surface to the inside of the resin proceeds along with the diffusion of the aqueous solution in the resin. Therefore, the diffusion will be rather slow because of the low mobility of the solution in the resin. Thus, the adsorption of NO will proceed smoothly when large parts of the CR-Fe(II) complex exist near the surface of the resin. The fact that the CR-Fe(II) complex prepared from the ground resin adsorbs NO more rapidly than that prepared from the original resin can be explained by the 50-fold increase in the surface area of the resin by grinding the particles to from 0.5 mm to 10 μm in diameter.

The adsorption rate also increases with the increase in the charged amount of Fe(II) ions as is shown in Fig. 7. The increase in the rate is thought to be attributable to the increase in the amount of the CR-Fe(II) complex in the resin when the ratio (*R*) of the charged Fe(II) ions to the IDA moieties lies below 0.7. When *R* is over 0.7, the adsorption rate still increases, even though the immobilization of the Fe(II) ions is saturated in this region. This fact strongly suggests that the Fe(II) ions in the supernatant are closely connected with the adsorption rate of NO. Figure 12 shows the effect of the concentration of Fe(II) ions in the supernatant on the NO-adsorption rate. In this experiment, the amount of the CR-Fe(II) complexes was kept at saturation. In this case, no diffusion of the Fe(II) ions into the supernatant from the resin was observed because of the strong chelating interaction of the Fe(II) with the IDA moieties. Therefore, these experiments were performed under the same conditions except for the concentration of Fe(II) ions in the supernatant. Moreover, the amount of NO adsorbed at equilibrium was kept constant in each run. Even under these conditions, the adsorption rate depended greatly on the concentration of Fe(II) in the supernatant. The increase in the concentration of Fe(II) in the supernatant brought about the increase in the adsorption rate. On the contrary, the rate was extremely diminished by the exchange of the supernatant with distilled water. It is proposed from these facts that the Fe(II) ions in the supernatant work as accelerators, not as active species, of NO adsorption.

The concentration of NO in the supernatant is calculated to be 1.93×10^{-6} mol dm^{-3} by means of Henry's law when the supernatant is displaced by distilled water and is equilibrated with 1000 ppm of NO in the gas phase at 25 °C. In contrast, if the concentration of Fe(II) ions in the supernatant is 0.2 mol dm^{-3}, the concentration of Fe(II)-NO in the supernatant is calculated to be 1.27×10^{-4} mol dm^{-3} under the same conditions from the equilibrium constant of Eq. 6 (K_1=0.634 atm^{-1}).[16] Thus, when the supernatant contains Fe(II) ions, the concentration of NO in the supernatant 66 times higher than that in the case of the supernatant of pure water. Therefore, the Fe(II) ions work as carriers of NO molecules:

$$\mathrm{NO_{aq}+Fe(II)} \xrightleftharpoons{K_1} \mathrm{Fe(II)\text{-}NO} \qquad (6)$$

$$K_1=[\mathrm{Fe(II)\text{-}NO}]/([\mathrm{NO}]_{\mathrm{aq}}\times[\mathrm{Fe(II)}]) \qquad (7)$$

$$\mathrm{Fe(II)\text{-}NO+CR\text{-}Fe(II)} \xrightleftharpoons{K_2} \mathrm{CR\text{-}Fe(II)\text{-}NO+Fe(II)} \qquad (8)$$

$$\mathrm{NO_{aq}+CR\text{-}Fe(II)} \rightleftharpoons \mathrm{CR\text{-}Fe(II)\text{-}NO} \qquad (9)$$

$$\mathrm{d[CR\text{-}Fe(II)\text{-}NO]/d}t=k_1[\mathrm{Fe(II)\text{-}NO}]\times[\mathrm{CR\text{-}Fe(II)}] + k_2[\mathrm{NO}]_{\mathrm{aq}}\times[\mathrm{CR\text{-}Fe(II)}] \qquad (10)$$

$$\mathrm{d[CR\text{-}Fe(II)\text{-}NO]/d}t=k_1K_1[\mathrm{NO}]_{\mathrm{aq}}\times[\mathrm{Fe(II)}] \times[\mathrm{CR\text{-}Fe(II)}]+k_2[\mathrm{NO}]_{\mathrm{aq}}\times[\mathrm{CR\text{-}Fe(II)}] \qquad (11)$$

These considerations suggest the following adsorption mechanism and equations. First, the dissolved NO reacts not only directly with CR-Fe(II) complexes, but also with Fe(II) ions in the solution, thus forming Fe(II)-NO complexes. The Fe(II)-NO complexes can transfer the NO molecules to the CR-Fe(II) complexes according to Eq. 8. The above reaction of Eq. 6 is rapidly equilibrated by the vigorous bubbling of NO, and the equilibrium constant K_1 is expressed as Eq. 7. The aqueous solution of NO resulting from Eq. 1 reacts directly with the CR-Fe(II) complexes to form CR-Fe(II)-NO complexes according to Eq. 9 as well as through the Fe(II)-NO complexes according to Eqs. 6 and 8. Under these conditions, the initial adsorption rate is expressed as Eq. 10 from Eqs. 8 and 9 by neglecting the diffusion of NO into the resin. Consequently, Eq. 11 is obtained by substituting [Fe(II)-NO] by using Eq. 7. This equation theoretically predicts that the adsorption rate will increase with the concentration of Fe(II) ions in the supernatant. In fact, the adsorption rate first increases linearly with the increase in the concentration of Fe(II). When the concentration of Fe(II) is zero, the adsorption proceeds according to Eqs. 1 and 9. At a high concentration of Fe(II) ions, the plots deviated from the line, probably due to the limitation of transferring the NO molecule of the Fe(II)-NO complex to CR-Fe(II).

The equilibrium constant K_2 of Eq. 8 is expressed as Eq. 12. The product of K_1 and K_2 corresponds to an equilibrium constant of the total reaction K, which should coincide with the K of Eq. 3. This means that the quantity of adsorbed NO is determined from the quantity of CR-Fe(II) and the concentration of NO, and that the concentration of Fe(II) ions does not affect the quantity of NO adsorbed at equilibrium:

$$K_2=[\mathrm{CR\text{-}Fe(II)\text{-}NO}]\times[\mathrm{Fe(II)}]/ ([\mathrm{Fe(II)\text{-}NO}]\times[\mathrm{CR\text{-}Fe(II)}]) \qquad (12)$$

$$K_1\times K_2=K$$

Desorption of NO. The adsorbed NO is easily desorbed by heating the dispersions or by bubbling in pure nitrogen. The latter is an operation equivalent to the lowering of the partial pressure of NO. The NO adsorbed at 25 °C can be released by elevating the temperature to 80 °C, leaving 12% of NO in the dispersions; this amount corresponds to the amount of NO adsorbed at 80 °C. This means that the quantity of NO released can be estimated from the difference between the quantities of NO equilibrated at the temperatures of adsorption and desorption. Moreover, no deterioration was observed after five repetitions; this clearly indicates that the adsorbing reaction of NO by the present dispersions proceeds reversibly according to Eq. 2 and that no side reaction, such as the reduction of NO by the Fe(II) ions into N_2O, occurs under these conditions. The reversible adsorption can clearly be understood by the desorption experiment using bubbling pure nitrogen. The amount of desorbed NO coincides again with the amount of NO (0.040 mmol) predicted from the equilibrium constant.

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