The Removal of Nitrogen Monoxide by the Dry Iron(II) Complex Immobilized on Chelate Resin. The Preparation and Characterization of the Complex

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A new dry-type adsorbent for nitrogen monoxide was successfully prepared from an iron(II) salt and a chelate resin containing iminodiacetic acid moieties. The capability of adsorbing nitrogen monoxide depended greatly on the method of preparation. The very active adsorbent was prepared by mixing 31.4 mmol of iron(II) sulfate and a commercial chelate resin containing 21.0 mmol of iminodiacetic acid moieties; the mixture was dried after the solid parts had been washed with methanol. The resulting solid adsorbent could adsorb more than 99% of the nitrogen monoxide from 6 dm^3 of nitrogen gas containing 1000 ppm of nitrogen monoxide within 25 min. This high capability for adsorbing nitrogen monoxide was derived from the increase in the surface area (43.1 $m^2 g^{-1}$) of the resin-immobilized iron(II) complex upon washing with methanol. The mechanism for the increase in the surface area is also discussed.

The atmosphere has been fairly well improved by the recent high technologies for protecting the environment. The concentration of nitrogen monoxide (NO), which is a source of pollution such as photochemical smog in the atmosphere has, however, not decreased in the past decade. Therefore, advanced technology for the removal of NO is strongly desired. At the present time, the catalytic reduction of NO into nitrogen by a gaseous reducing agent like ammonia is practically adopted, especially for such statistic sources as heavy oil and coal boilers.[1-3] Other methods under investigation involve the absorption of NO by molten salts, where the catalytic reduction proceeds partially,[4] and the absorption of NO by an aqueous solution of iron(II)–ethylenediaminetetraacetic acid (Fe(II)–EDTA), which can form a complex with NO.[5-8] Since an aqueous solution of Fe(II)–EDTA absorbs NO and desorbs it reversibly, this method has potential for use as an absorbent for recovering NO; i.e., the absorbed NO can be used again as a resource for nitrogen industries. However, this solution involves Fe(II) ions, which are easily oxidized into inactive Fe(III) ions by the contaminated oxygen. A reducing agent is necessary to avoid this deactivation of the complex in this system. Moreover, the recovery of the complex from the solution is difficult because of the homogeneity of the solution.

The immobilization of a metal complex, in general, offers the following advantages:[9] 1) the protection of the active site of the metal complex; 2) an increase in the activity by the polymer effect, and 3) easier handling because of the solidification of the complex by using a polymer support. Some polymer complexes have been investigated in order to apply them to catalysts and to the absorbents of carbon monoxide and ethylene.[10-13] Since, however, few studies have been reported on the application of a polymer complex for the removal of NO, it is significant to investigate an absorbent composed of the polymer complex with the above advantages. We have successfully prepared an aqueous dispersion by mixing an aqueous solution of Fe(II) ions with a chelate resin involving iminodiacetic acid moieties instead of EDTA in order to achieve easier handling and higher stability than the aqueous solution of Fe(II)–EDTA.[14,15] The resulting dispersions can absorb NO effectively, even at a low concentration, and can desorb NO reversibly upon heating at a higher concentration. The chelate resin-immobilized Fe(II) complex (CR–Fe(II)) can easily be recovered from the dispersions by filtration. Moreover, it has a higher durability against oxygen than Fe(II)–EDTA, the usual absorbent of NO, since the central atom of Fe(II) can be protected by polymer matrices.

We have examined the preparation of the dry-type, water-free chelate resin-immobilized Fe(II) complexes in order to develop more active and stable absorbents. Dry-type absorbents have been expected to have the following advantages: 1) contamination with the solvent vapor can be avoided in the recovery of NO; 2) much of the heat loss can be avoided when the adsorbed NO is recovered by heating, and 3) the handling of the adsorbent is easy enough to be applied to the moving sources of NO. To the best of our knowledge, nothing has yet been reported about the dry-type adsorbent of NO except for the active carbon[16] and the active carbon fiber-supported FeOOH.[17] Since the adsorption by these adsorbents is mainly based on a physical interaction between NO molecules and the adsorbents, they are not usually used for the removal of NO at extremely low concentrations. Now, we have successfully prepared a dry-type adsorbent of NO composed of the polymer complex.[18] In the present paper, the preparation and characterization of the

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polymer complex and its capability of adsorbing NO are reported.

Experimental

Materials. A commercial chelate resin (Diaion CR-10; mean diameter of the particles, 0.5 mm) purchased from Mitsubishi Chemical Industry, Ltd., was used in a swollen state, as it was, or in a dry state by drying after washing with a large amount of methanol since the commercial resin is swollen with water. One gram of the swollen resin was determined by pH titration to contain 0.98 mmol of iminodiacetic acid moieties. One gram of the resin dried in vacuo, on the other hand, has 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 adsorbent.

The reagent-grade solvents were used without further purification.

The iron(II) sulfate 7 hydrate and the Fe(II) chloride *n* hydrate (the *n* was determined to be 4.59 by the 1,10-phenanthroline method[19]) were used without further purification.

The gases of NO and nitrogen mixed at designed NO concentration were purchased from Takachiho Shoji, Ltd., and were used without further purification.

Preparation of the Adsorbent. 1) Preparation of the Aqueous Dispersions of the Chelate Resin-Immobilized Iron(II) Complex: The chelate resin containing 21.0 mmol of iminodiacetic acid moieties (21.4 g in a swollen state or 7.53 g in a dry state) and 31.4 mmol of Fe(II) salts were stirred in 50 $\mathrm{cm^3}$ of water under nitrogen for 24 h to immobilize any Fe(II) ions on the resin. We will hereafter call the resulting aqueous mixture the "aqueous dispersion."

2) Preparation of Dry Adsorbent by Washing: The supernatant of the aqueous dispersion prepared as above was removed by decantation. After the solid part of the aqueous dispersion had been washed with 50 $\mathrm{cm^3}$ of another solvent (a washing solvent) 4 times, drying it at 50 °C in vacuo gave a dry-type solid adsorbent.

3) Preparation without Washing: A solid adsorbent was prepared only by evacuating water from the aqueous dispersion at 50 °C in vacuo.

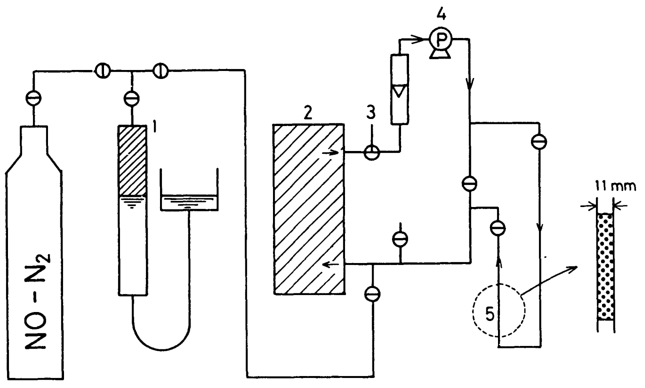

Fig. 1. Schematic diagram of gas adsorption apparatus. 1. Gas burette. 2. Gas holder. 3. Sampling outlet. 4. A gas-circulating pump. 5. An adsorbent column.

Adsorption of NO. The adsorption experiments of NO were carried out by using the closed circulation system illustrated in Fig. 1. After putting an adsorbent in a column of 11 ϕ, 6 $\mathrm{dm^3}$ 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, after which the sample gas was circulated through the column at the rate of 1.6 $\mathrm{dm^3\ min^{-1}}$. Changes in the NO concentration in nitrogen were traced by sampling the mixed gas in a 100 mm-cell and measuring the absorbance at 226.5 nm.

Measurement of the Spectrum of the Adsorbent. The electronic spectra of the solid complexes were measured with a Hitachi model 340 spectrophotometer equipped with an integrated reflection apparatus. The ESR spectra were measured with a JEOL PE-1X ESR spectrometer. The chelate resin–Fe(II)–NO complex for the spectroscopic measurement was prepared by placing the solid adsorbent in contact with pure NO at 1 atm for 24 h.

Measurement of the Specific Surface Area. The BET surface area of the dry-type adsorbent was measured from the amount of adsorbed nitrogen at 77 K with a Micromeritics Instrument Co., Ltd., model 2200A rapid surface-area analyzer. The sample was completely dried by heating the sample at 90 °C for 40 min under a nitrogen stream before the measurement.

Electron Microscopy and X-Ray Microanalysis. Scanning electron microscopy (SEM) and X-ray microanalysis (EPMA) on the resin of the adsorbents were carried out by the use of a Hitachi model X-650 micro-scanning X-ray analyzer, the resolution of the X-ray image of which is around 100 Å. The sample beads were cut with a stainless steel cutter and then coated with gold so that cross-sections of the beads were irradiated by an electron beam. The distributions of Fe and S atoms were evaluated by the intensity of the characteristic X-ray.

Measurement of the Immobilized Iron(II) Ions on the Resin. The concentration of Fe(II) ions in the supernatant of the aqueous dispersion was measured by the 1,10-phenanthroline method.[19] The amount of immobilized Fe(II) ions was calculated from the discrepancy in the amount of initially charged Fe(II) ions and that of Fe(II) ions remaining in the supernatant after the immobilization. The amount of immobilized Fe(II) ions was 16.2 mmol when 7.53 g of the chelate resin containing 21.0 mmol of iminodiacetic acid moieties and 8.72 g of $FeSO_4$ was used.

Results

Preparation of the Adsorbent and Its Capability to Adsorb NO. The supernatant of the adsorbent dispersions prepared from Fe(II) sulfate and the chelate resin had a light green color due to the dissolution of Fe(II) sulfate. The light greenish color of the aqueous solution gradually diminished due to the immobilization of the dissolved Fe(II) ions onto the resin through ion-exchange. In contrast, the chelate resin (solid part) acquired a light green color by the immobilization. The immobilization completed within a few hours. The amount of immobilized Fe(II) ions was found to be 16.2 mmol. The solvent-free adsorbent prepared only by removing the water from the aqueous dispersion in vacuo adsorbed any scarcely NO in spite of the immobilization of the Fe(II) ions on the resin, as is shown by open circles in Fig. 2. In contrast, the adsorbent prepared by drying after the immobilizing resin has been washed 4 times with 50 cm^3 of a "washing solvent" had the capability of adsorbing NO. Especially, the adsorbent prepared by washing with methanol shows so high a capability that almost all the NO in the system was adsorbed within 25 min, as is illustrated by the closed circles in Fig. 2.[20]

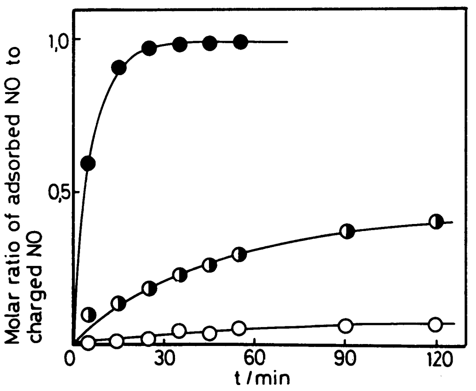

Fig. 2. Adsorption curves for NO by the chelate resin-immobilized adsorbent prepared by drying after washing with methanol (●), water (◑), and without washing (○). These adsorbents were prepared from 21.4 g of chelate resin and 8.72 g (31.4 mmol) of $FeSO_4\cdot 7H_2O$. Adsorption experiment was carried out by circulating 6 dm^3 of nitrogen containing 1000 ppm of NO at room temperature at the rate of 1.6 dm^3 min^{-1}.

Figure 3 reveals the adsorption curves of NO by the adsorbent prepared from Fe(II) chloride instead of sulfate according to the same method as was used with the sulfate. The adsorbent prepared from Fe(II) chloride by washing with methanol also shows as high a capability for the adsorption of NO as that of the adsorbent from the sulfate. The adsorbents obtained from chloride without washing or by washing with water, however, have a higher capability than the corresponding adsorbents prepared from the sulfate illustrated in Fig. 2.

A freeze-dried absorbent was also prepared by freeze-drying after the solid part of the aqueous dispersion had been washed with water. However, it has almost the same capability as the adsorbent dried at 50 °C in vacuo, as is shown in Fig. 4. Table 1 compares the amount of NO adsorbed by the dry-type adsorbent, the original chelate resin itself, the powder of the Fe(II) sulfate, and that of Fe(II) chloride. This table clearly

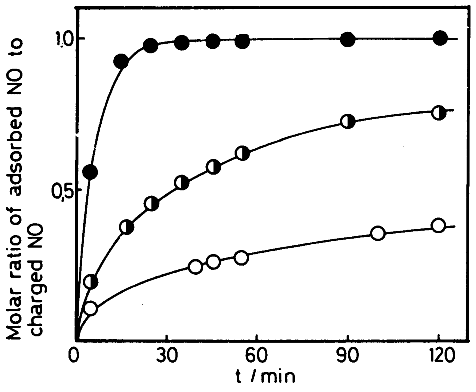

Fig. 3. Adsorption curves for NO by the CR–Fe(II) complex prepared from 31.4 mmol of $FeCl_2$ and 21.4 g of chelate resin by drying after washing with methanol (●), water (◑), and without washing (○). The adsorbent was contacted with 6 dm^3 of nitrogen containing 1000 ppm of NO at room temperature at the rate of 1.6 dm^3 min^{-1}.

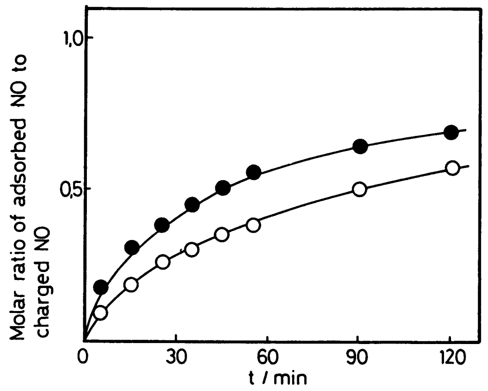

Fig. 4. Effect of the drying temperature on the adsorption of NO. The adsorbents were prepared by drying at 50 °C (○) and by freeze-drying (●) after washing the CR–Fe(II) complex with water. The adsorbent was contacted with 6 dm^3 of nitrogen containing 1000 ppm of NO at room temperature at the rate of 1.6 dm^3 min^{-1}.

Table 1. Adsorption of NO by the Dry-Type CR–Fe(II) Adsorbent and Its Starting Materials

Material	Amount/g	Amount of adsorbed NO[a]/mmol
Chelate resin[b]	7.53	0.0
$FeCl_2\cdot 4.59H_2O$	6.56 (31.4 mmol)	0.0
$FeSO_4\cdot 7H_2O$	8.72 (31.4 mmol)	0.0
CR–Fe(II)[c]	9.02	0.246

a) Adsorption experiments were carried out by placing the material in contact with 6 dm^3 of nitrogen containing 1000 ppm of NO. The initially charged amount of NO was 0.246 mmol. b) The commercial chelate resin dried after having been washed with ethanol. c) A dry-type chelate resin–Fe(II) adsorbent prepared by drying after washing with methanol. See text for details.

Table 2. Effects of Solvents for the Immobilization of Iron(II) Ions on the Adsorbing Capability for NO[a)]

Solvent	Molar ratio of adsorbed NO to charged NO	
	In 15 min	At equilibrium[b)]
Water	0.170	>0.425
Methanol	0.173	>0.536
Ethanol	0.443	0.921
2-Propanol	0.263	>0.794
Acetone	0.139	>0.502
Acetonitrile	0.111	>0.464
Chloroform[c)]	0.023	0.026

a) Adsorbents were prepared from 50 cm^3 of a solvent, 31.4 mmol of $FeCl_2$, and 21.4 g of the chelate resin swollen with water. b) When the equilibrium was not attained within 180 min, the ratio of the adsorbed NO at this time is shown in this column. c) The adsorbent was prepared from chloroform, $FeCl_2$, and dried chelate resin which had previously been washed with ethanol.

indicates that the adsorption of NO does not take place only by means of each starting material, but the adsorbent resulting from mixing the starting materials does.

The preparation of adsorbent dispersions was examined from 21.4 g of water-swollen chelate resin, 31.4 mmol of $FeCl_2$, and 50-cm^3 portions of various organic solvents. The color of the supernatant became light green in each system and then gradually faded through the immobilization of the Fe(II) on the resin, which showed the light green color in contrast. In this system, the supernatant is actually composed of the organic solvent and water derived from the water-swollen resin. The ratio of water to the organic solvent is calculated to be 0.27 (v/v), because 21.4 g of the chelate resin contains 13.4 g of water. The adsorbent was prepared by removing the solvent from the above dispersion in vacuo at 50 °C. The amounts of NO adsorbed by these adsorbents are listed in Table 2; the table shows not very high adsorbing capabilities in this method except for the adsorbent prepared with ethanol.

In order to avoid the effect of water in the solvent, the adsorbent dispersion was prepared from ethanol (the solvent used for immobilization), the dried chelate resin, and $FeCl_2$, which is soluble in ethanol. The ethanol solution of $FeCl_2$ offered a brownish color, although the aqueous solution was light green. The immobilization of Fe(II) scarcely proceeded, since, though the resin was colored a little brownish, no fading in the color of the supernatant was observed. The removal of the ethanol by the adsorbent dispersions gave the resin-immobilized Fe(II) complex and a large amount of $FeCl_2$ salts which were not immobilized on the resin. The adsorbing capability of the adsorbent prepared by the above method is illustrated with closed circles in Fig. 5; it is not so high as that given by the washing method. The adsorbent prepared by using chloroform as a solvent scarcely adsorbs any NO at all, as is shown by the open circles in the same figure. In this system, the Fe(II) ions could not be immobilized on the resin because $FeCl_2$ does not dissolve in chloroform. These results indicate that chloroform is not an appropriate solvent for the immobilization of Fe(II) on the resin.

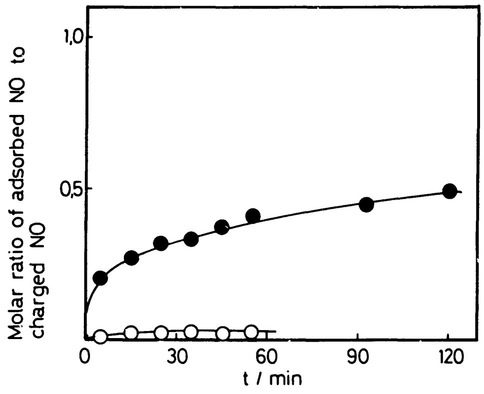

Fig. 5. Effect of the solvent used for immobilization of Fe(II) ions on the adsorbing capability for NO. The adsorbents were prepared from 7.53 g of the dried chelate resin, 31.4 mmol of $FeCl_2$, and ethanol (●) or chloroform (○) for immobilization of Fe(II) ions on the resin. See text for details.

Among the methods examined, the method to prepare the most effective adsorbent has turned out to be the use of water as a solvent for the immobilization, followed by drying under a vacumm after washing the swollen CR–Fe(II) complex with methanol (vide infra).

Adsorbing Capability for NO and Specific Surface Area of the Dry-Type Chelate Resin-Iron(II) Complex Prepared by Washing with a Solvent. We have shown in the previous paragraph that the adsorbent prepared by drying after washing the swollen CR–Fe(II) complex with methanol has the highest adsorbing capability for NO among those examined. Table 3 indicates the effect of the washing solvent on the capability for adsorbing NO. An obvious difference in the adsorption rate of NO is observed in the solvent used for washing the swollen CR–Fe(II), but there is no significant difference in its appearance. The adsorbent prepared by using methanol or ethanol adsorbs NO at the initial rate of 1.54×10^{-2} mmol min^{-1}. The adsorption rate, however, slightly decreases in the case of acetone. A significant decrease in the adsorption rate is observed in the case of water and chloroform, which is immiscible with water. Table 3 also shows the specific surface area (A/m^2 g^{-1}) of each adsorbent, as measured by the BET method, which clearly demonstrates that the adsorption rate is in reasonable linear relationship with the specific surface area.

The above results show the best method of preparation to be as follows: 1) the immobilization of the Fe(II) ion on the resin has to be carried out in water, and 2) the drying of the CR–Fe(II) dispersion

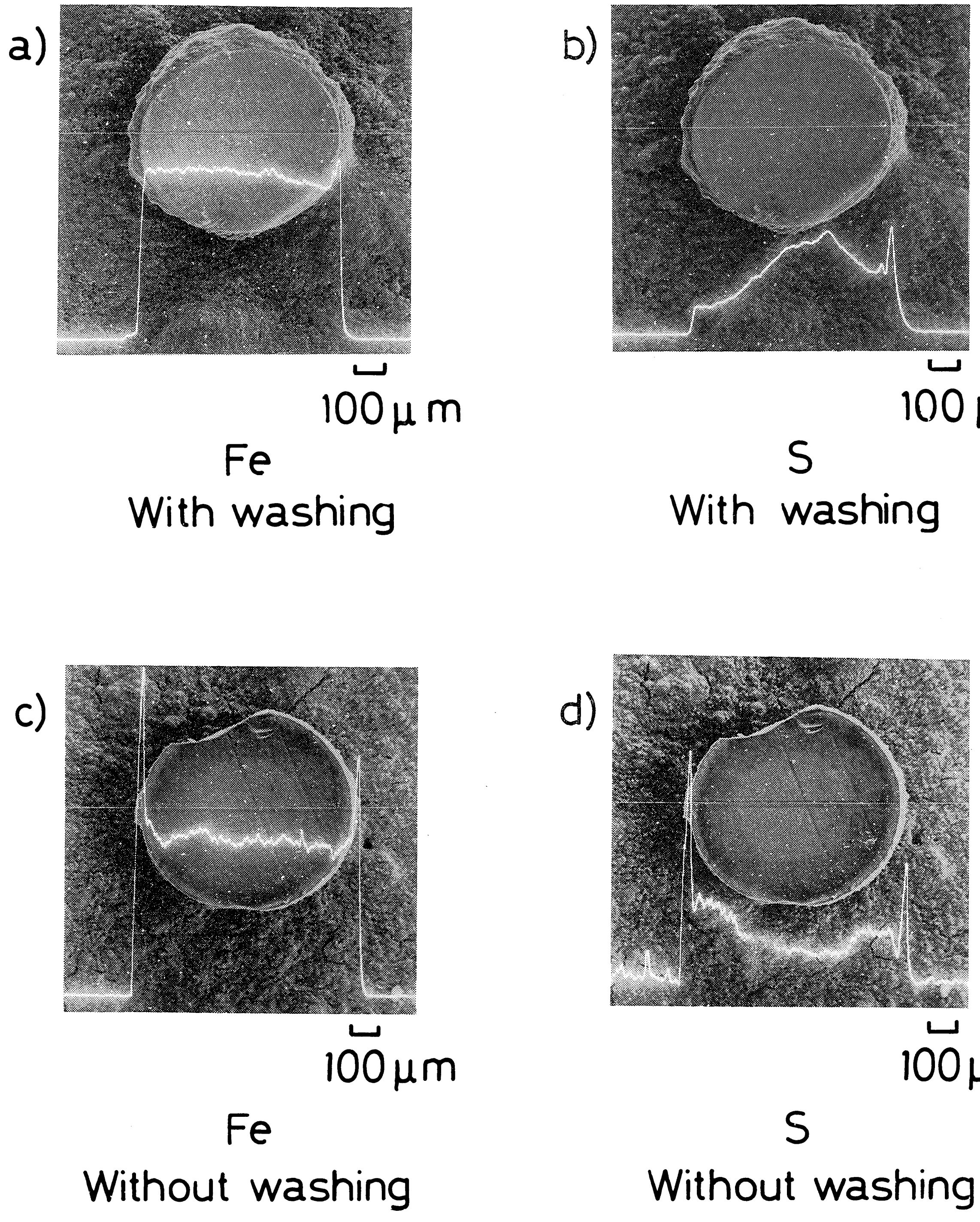

Fig. 6. SEM photographs and EPMA data of the cross-section of the dry adsorbents prepared from $FeSO_4$ and the chelate resin with washing with ethanol (a, b) or without washing (c, d).

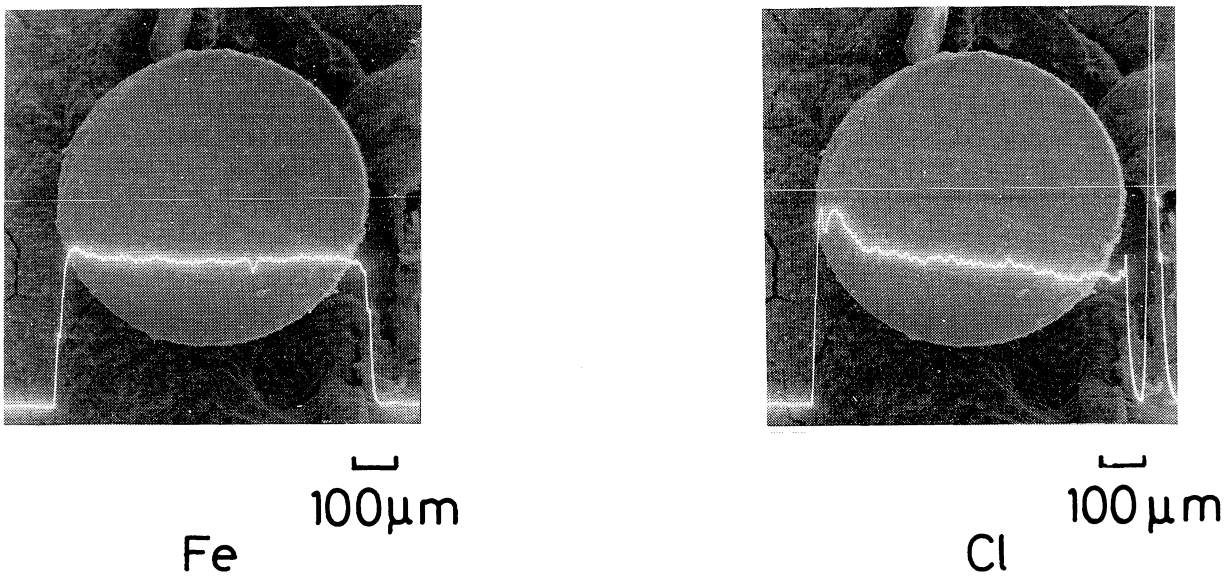

Fig. 7. SEM photograph of the cross section of the adsorbent prepared from $FeCl_2$ and the chelate resin without washing and its EPMA traces for Fe and Cl.

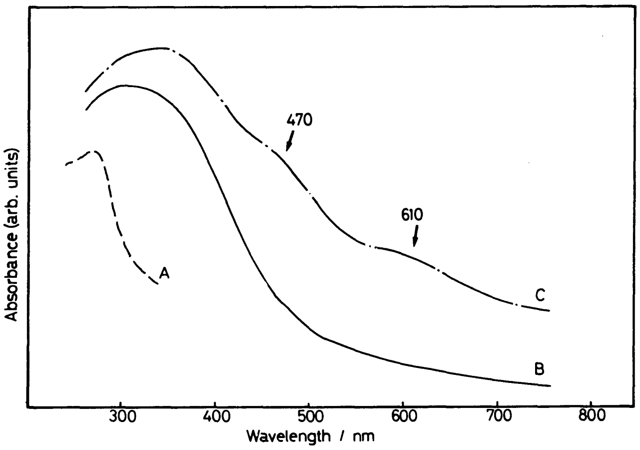

Fig. 8. Electronic spectra of the NO adsorbent and the related materials. A(– – –): chelate resin, B(——): CR–Fe(II), and C(——·——): CR–Fe(II)–NO.

had better to be carried out after washing the resin with an organic solvent miscible with water, especially with methanol. Moreover, the effect of the washing has turned out to be an increase in the surface area of the adsorbent.

Analysis of the Adsorbent with Electron Microscopy and X-Ray Microanalysis. The distribution of the immobilized Fe(II) salts on the resin beads was analyzed by means of SEM and EPMA. Figure 6 shows SEM photographs of the dry-type adsorbent prepared by drying after washing with ethanol and by drying without washing. The waveline refers to the distributions of Fe and S atoms along the corresponding white straight lines on the cross-sections of the beads. The height of the waveline refers to the density of each atom. For both adsorbents, Fe atoms are homogeneously distributed inside the resin. For the adsorbent without washing, however, the density of Fe atoms is higher on the outer surface than inside the bead, while, for the adsorbent with washing, it is uniformly distributed not only inside the beads, but also on the surface. A low distribution of S atoms is observed both inside and on the surface of the bead. For the adsorbent without washing, however, many S atoms are located near the surface of the bead. These analyses indicate that the $FeSO_4$ is attached to the outer surface of the bead without washing. For the adsorbent prepared from $FeCl_2$, a homogeneous distribution of Fe atoms inside and on the outer surface was observed, as is depicted in Fig. 7.

The above facts clearly indicate that the residual powder of $FeSO_4$, which is not immobilized on the resin, is attached to the outer surface of the resin beads and that it suppresses the diffusion of NO molecules into the inside of the resin, resulting in a low capability for adsorbing NO. On the contrary, the adsorbent with $FeCl_2$ without washing has a sufficient adsorbing capability for NO. This fact also coincides with the results of the EPMA, which show the delocalized distribution of Fe atoms.

Spectra of the Adsorbent. The water-swollen chelate resin before the immobilization of Fe(II) ions is white and has its maximum peak in its electronic spectrum at 280 nm due to the benzene chromophore of the matrices, as is shown by the broken line in Fig. 8. The color of the resin changes from white to light green upon the immobilization of the Fe(II) ions; also, a new peak appears around 300 nm. The exposure of the CR–Fe(II) complex to pure NO rapidly change its color from light green to brown, and new shoulder peaks appear in its electronic spectrum at 470 and

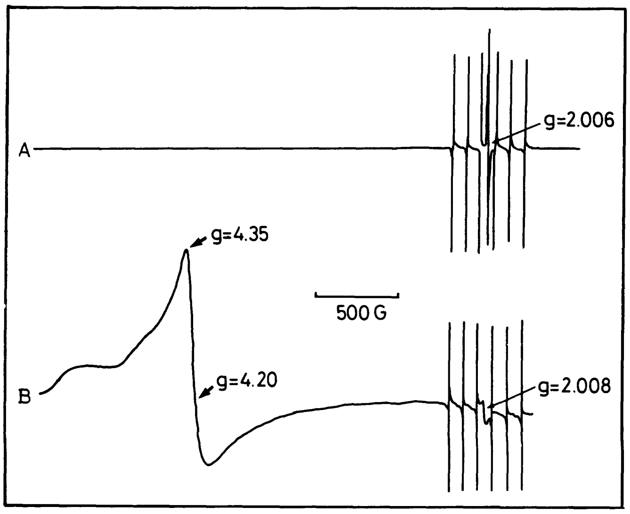

Fig. 9. ESR spectra of chelate resin (A) and CR-Fe(II) complex before the exposure with NO gas (B). Six signals in the same magnitude are derived from a Mn^{2+} marker.

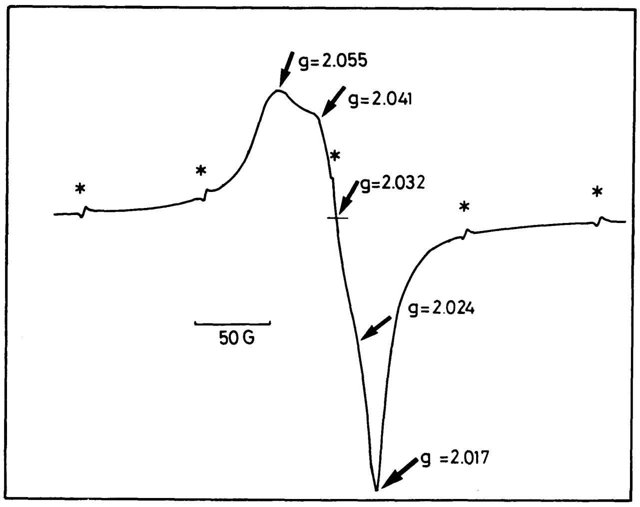

Fig. 10. ESR spectrum of CR-Fe(II)-NO complex at central magnetic field. Five weak signals with asterisks are derived from a Mn^{2+} marker.

610 nm. A similar change has been observed in the case of the absorption of NO by an aqueous solution of the Fe(II)-EDTA complex.⁶⁾

In the ESR spectrum, the dried commercial resin before the immobilization of Fe(II) ions has a sharp signal at g=2.006 assigned to the organic radical, while no signals are observed at low magnetic fileds, as is illustrated in A of Fig. 9. The six sharp signals in Fig. 9 are derived from a manganese marker (S=5/2). By the immobilization of the Fe(II) ions on the resin, the sharp signal at g=2.006 disappears and broad new signals, probably due to the contaminated Fe(III), appear at g=4.20,²¹⁾ as is shown in B of Fig. 9. A new, unsymmetrical, strong, broad signal with unresolved shoulders appears upon the exposure to NO as is shown in Fig. 10. The g values at the maximum and minimum of the signal were 2.055 and 2.017 respectively. In this case, the signal at g=4.20 does not change, as is shown in Fig. 11.

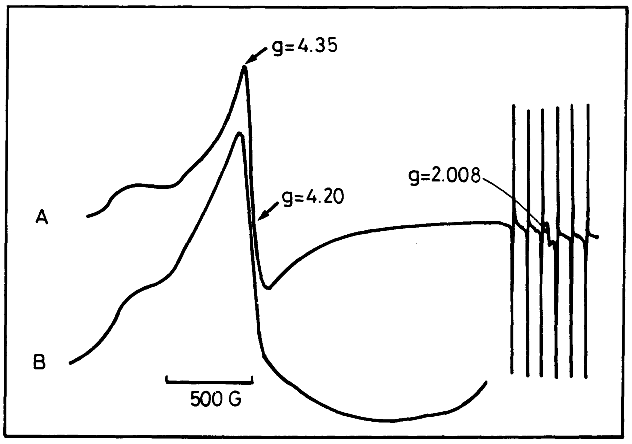

Fig. 11. ESR spectra of CR-Fe(II) (A) and CR-Fe(II)-NO (B) at low magnetic field. Six signals at central magnetic field are derived from a Mn^{2+} marker. The spectrum B in the central magnetic field region is shown in Fig. 10 and omitted in this Figure.

Discussion

Coordination of Nitrogen Monoxide. The appearance of a new band in the electronic spectrum by the immobilization of Fe(II) ions indicates the coordination of Fe(II) ions to the IDA moieties in the chelate resin. Upon the adsorption of NO new shoulder peaks appear at 470 nm and 610 nm; this is similar to the change in the spectrum observed with an aqueous solution of Fe(II)-EDTA or Fe(II) salts.⁶⁾ This change is reported to be due to the coordination of an NO molecule on the Fe(II) ion.⁶⁾ Thus, the adsorption of NO by the present dry-type adsorbent proceeds by the coordination of an NO molecule with the Fe(II) ion in the resin complex.

The ESR signals around g=2.03 appearing upon the contact of the adsorbent with an NO gas are commonly observed in the case of Fe(II)-NO complexes derived from an NO molecule with a free electron.²²⁾ This fact also strongly supports the idea that the adsorption of NO by the present adsorbent proceeds by means of the coordination of NO on the Fe(II) ion. Moreover, the appearance of the signal at around g=2.03, not in the lower magnetic field, indicates the formation of a low-spin (S=1/2) Fe(II)-NO complex.²²⁾ In general, there are two types of Fe(II)-NO complexes. One is a low-spin state (S=1/2), and the other, a high-spin state (S=3/2). When a ligand field is strong enough, a low-spin complex is known to be formed. In the present system, since the IDA moieties in the chelate resin work as strong ligands, the low-spin complexes of Fe(II)-NO are thought to be produced.

Preparation of a Dry-Type Adsorbent with a High Capability for Adsorbing NO upon Washing. From the results of EPMA, the Fe atoms in the adsorbent prepared with washing seem to be distributed homogeneously both inside and on the surface of the resin beads. On the contrary, in the case of the adsorbent prepared without washing, more Fe atoms are distributed on the surface than on the inside of the resin. A similar result is also observed in the distribution of S atoms. These results indicate that the Fe(II) ions which cannot be immobilized on the resin are attached on the surface of the resin beads as $FeSO_4$. This $FeSO_4$ attached on the surface suppresses the diffusion of NO molecules into the resin inside.

The capability for adsorbing NO, especially the adsorption rate of the adsorbent prepared by washing, coincides well with the specific surface area, as is shown in the right column in Table 3. Figure 12 shows the plots of the adsorption rate of NO against the specific surface area. The adsorption rate linearly increases with an increase in the surface area until 24 $m^2 g^{-1}$. This fact clearly demonstrates that the increase in the surface area contributes directly to the increase in the adsorption rate. Over a surface area of 24 $m^2 g^{-1}$, the adsorption rate is so fast that the adsorption apparatus used in this experiment cannot follow the increase in the adsorption rate while keeping a constant rate at 1.54×10^{-2} mmol min^{-1}.

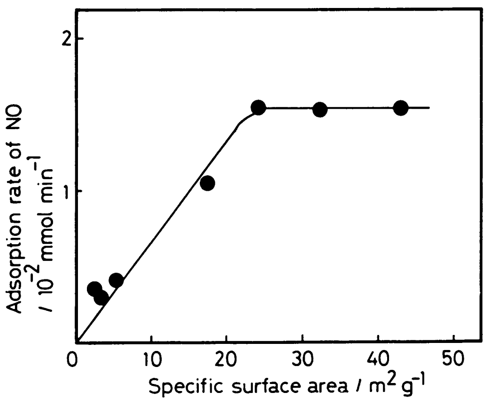

Fig. 12. Correlation of the specific surface area with the adsorption rate of NO by various CR-Fe(II) adsorbents.

The increase in the specific surface area upon washing with an organic solvent can be explained as follows. The chelate resin swells well in water and exists in a rubber state. When the solvent (water) in the resin in the rubber state is exchanged with an organic solvent miscible with water, many microgels will be generated through a phenomenon similar to the "reprecipitation" of the polymer by the addition of a poor solvent to the polymer solution, since the freeze-dried adsorbent from water has a low porosity. The resin is transformed from the rubber state into a glassy state during the exchange of the solvent because of the poor swelling in the organic solvent.[23,24] In this glassy state, the shrinkage of the resin during the drying of the resin is suppressed by the low mobility of the polymer. Consequently, the surface area increases due to the remaining of the pores produced by drying the resin after the exchange of the solvent. On the contrary, the resin swollen in water shrinks during the evacuation of the solvent in the resin, for the polymer chains have a high mobility in the rubber state. In

Table 3. Effects of the Washing Solvents on the Adsorption Rate of NO and the Specific Surface Area of the Adsorbent

Solvent	Adsorption rate[a)]/ 10^{-2} mmol min^{-1}	Ratio of adsorbed NO[b)]	Specific surface area[c)]/$m^2 g^{-1}$
Chloroform	0.36	0.789	2.3
Water	0.30	>0.425	3.2
Acetone	1.04	0.933	17.1
Ethanol[d)]	1.54	0.997	31.1
Methanol[d)]	1.54	0.997	43.1

a) The adsorption rates were evaluated from the amount of NO adsorbed in 15 min. b) Molar ratio of adsorbed NO to charged NO at equilibrium. c) Measured by a BET method. d) No difference in the adsorption of NO between the two adsorbents could be observed because the adsorption occurred too fast.

Table 4. Effects of the Washing Solvents on the Specific Surface Area of the Chelate Resin-Immobilized Fe(II) Complex

Solvent	Solubility parameter $\delta^{a)}/10^3$ $(J m^3)^{1/2}$	Specific surface area[b)]/$m^2 g^{-1}$
Chloroform	19.0	2.3
Water	47.9	3.2
Acetone	20.3	17.1
2-Propanol	23.5	31.7
Ethanol	26.0	31.1
Methanol	29.7	43.1

a) Quoted from Ref. 25. b) Measured by a BET method.

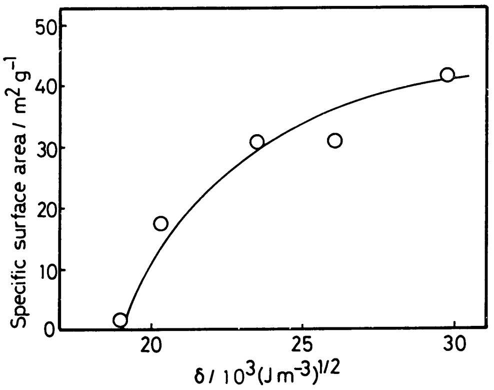

Fig. 13. Relationship between the specific surface area and the solubility parameter (δ) of the solvent used for washing the water-swollen CR–Fe(II) complex.

fact, the adsorbent prepared by washing with the organic solvent is lower in apparent density than that prepared by washing with water.

The surface area increases with the increase in the solubility parameter δ[25] in the order of: acetone, ethanol, and methanol, as is shown in Table 4. The date are plotted in Fig. 13. This parameter δ corresponds to the square root of the cohesive energy density ($(E/V)^{1/2}$).[25] If the solubility parameters δ of two solvents are close to each other, it indicates that their mutual miscibility is high.[25] The adsorbent prepared by chloroform, whose δ is apart from that of water, has a small surface area. On the contrary, the maximum porosity is obtained by the use of methanol, whose δ is close to that of water. These facts indicate that mutual miscibility with water contributes to the surface area (porosity) of the adsorbent. Probably, the solvent with a δ close to that of water, like methanol, will be able to penetrate into the inner portions of the resin and be exchanged with water to make pores through "reprecipitation."

The dry-type resin-immobilized Fe(II) complexes prepared from $FeSO_4$ without washing cannot adsorb NO, while those from $FeCl_2$ can adsorb NO even without washing. From the results of EPMA, $FeCl_2$ seemed not so much attached on the outer surface of the resin as was observed in the case of $FeSO_4$. This phenomenon is probably connected with the crystallinity of the Fe(II) salts. For $FeSO_4$, an excess amount of the salt can form crystals easily and can cause it to attach itself on the surface, resulting in a suppression of the adsorption of NO. On the contrary, since the excess amount of $FeCl_2$ is not attached on the surface, the adsorption of NO takes place.

Concerning the adsorbent prepared by using a hydrophilic organic solvent and a water-swollen resin without the washing treatment, though the immobilization of Fe(II) ions took place, its adsorbing capability for NO was as low as that when using water without washing, except when ethanol was used as the hydrophilic solvent. In these systems, since the solvents used has boiling points lower than that of water, the organic solvent was first removed from the water-mixed solvent by evaporation. Consequently, these adsorbents prepared from the water-mixed solvent were the same as that dried directly from water without an organic solvent. In the case of ethanol, however, the evaporation of an azeotropic mixture of ethanol and water actually proceeded resulting in an adsorbent different from that prepared from only water.

In the case of the adsorbent prepared by using ethanol and the dried chelate resin, the immobilization of Fe(II) ions does not proceed even for $FeCl_2$, which is soluble in ethanol. Since the immobilization of Fe(II) ions occurs by means an ion-exchange with sodium ions in water, the ion-exchange does not proceed smoothly in ethanol, which is not a good electrolyte.

Conclusion

1) The dry-type adsorbent was prepared from 21.4 g of chelate resin (containing 21.0 mmol of iminodiacetic acid moieties) and 31.4 mmol of $FeSO_4$ by drying after the water-swollen CR–Fe(II) complex had been washed with methanol. The resulting adsorbent adsorbed almost all the NO from 6 dm^3 of nitrogen containing 1000 ppm of NO within 25 min.

2) The high adsorbing capability for NO obtained by washing with an organic solvent is derived from the increase in the specific surface area. The surface area greatly depends on the kind of washing solvent used. The maximum porosity (43.1 m^2 g^{-1}) was obtained by using methanol, whose solubility parameter δ was close to that of water. On the contrary, no increase in the surface area was observed with chloroform, whose δ is far from that of water. Thus, it is clarified that the mutual miscibility with water greatly contributes to the increase in the surface area.

3) The adsorbent after the contact with an NO gas exhibits the two shoulder peaks at 470 nm and 610 nm in the electronic spectra. A similar appearance of the peaks is observed with an aqueous solution of a Fe(II)–NO complex. Thus, the adsorption of NO by the present dry adsorbent proceeds through the coordination of NO on Fe(II). Moreover, the CR–Fe(II) complex after the adsorption of NO has signals centered at $g=2.03$ in the ESR spectrum, which is characteristic of the low spin Fe(II)–NO complex. This fact also supports the idea that the adsorption proceeds through the coordination of the NO on the Fe(II) ion in the resin.

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