

Rapid Co-ordination of Nitrogen Monoxide to Iron(II) in a Mixed Valence Iron Complex immobilized on a Chelate Resin in the Dry State

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Rapid co-ordination of nitrogen monoxide with iron(II) has been observed for a chelate resin-immobilized iron(II) and iron(III) complex, compared with the corresponding chelate resin-immobilized iron(II) complex, due to the increase in surface area caused by the introduction of iron(III) into the resin.

We have successfully prepared an iron complex with high nitrogen monoxide (NO) co-ordination capability by the simultaneous immobilization of both iron(II) and iron(III) ions on a chelate resin (CR) containing iminodiacetic acid moieties. Many methods for improvement of the atmospheric environment by removal of nitrogen oxide have been investigated.¹⁻¹⁰ A high NO adsorption capability can be achieved for a chelate resin-immobilized iron(II) complex by increasing the surface area of the resin as we have previously reported.^{11,12} In this system, the adsorption of NO by the CR-Fe^{II} complex proceeds through the co-ordination of NO, as evidenced by the appearance of two charge transfer bands in the electronic spectrum at 470 and 610 nm, characteristic of the Fe^{II}-NO complex.¹² Recently, a successful increase in surface area of the chelate resin has been obtained by the immobilization of iron(III) ions to suppress resin shrinkage. This suppression is probably caused by electrostatic repulsion between the immobilized Fe^{III} ions.¹³ A rise in NO adsorption capability was therefore expected on simultaneous immobilization of both iron(II) and (III) ions on the chelate resin.

The chelate resin-immobilized Fe^{II}/Fe^{III} complex (we call it 'chelate resin-mixed valence iron complex') was prepared as follows. An aqueous solution of 21.0 mmol of FeSO₄ and 5.25

mmol of Fe₂(SO₄)₃ was added to 21.4 g of a commercial chelate resin containing 21.0 mmol of bonded iminodiacetic acid moieties. The resulting mixture was shaken to immobilize both Fe^{II} and Fe^{III} on the resin. The amounts of immobilized Fe^{II} and Fe^{III} were 3.56 and 10.2 mmol, respectively. The solid part was separated by decantation, washed with methanol, and dried *in vacuo* to give the dry complex. All these operations were performed under oxygen-free conditions in order to avoid the oxidation of Fe^{II}. The adsorption experiment was carried out in a closed circulation system introducing 6 dm³ of nitrogen containing 1000 p.p.m. of NO according to our previous paper.^{11,12}

The chelate resin-mixed valence iron complex co-ordinates NO so rapidly that almost all (more than 99%) of the NO in the system was adsorbed within 35 min, as shown in Figure 1. The adsorbed NO could be released by heating, indicating that the adsorption is reversible. The adsorption of NO probably proceeds *via* direct co-ordination of the NO molecule on the vacant site of an Fe^{II} ion, Fe^{II} with six co-ordination sites being considered to be immobilized on the chelate resin through 1 : 1 complex formation with the tridentate iminodiacetate ligands. On the contrary, rapid adsorption was not achieved by an adsorbent composed of the chelate resin and 5.0 mmol of Fe^{II}

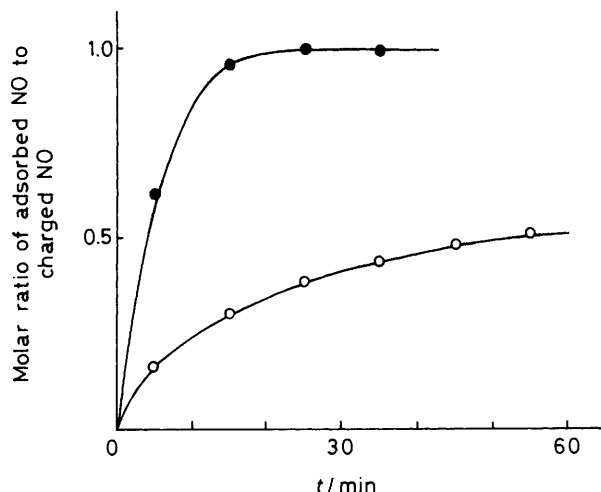


Figure 1. Adsorption of NO by the chelate resin-mixed valence iron complex (●) composed of 10.2 mmol of Fe^{III} and 3.56 mmol of Fe^{II}, specific surface area 128.0 m² g⁻¹; and the chelate resin-immobilized Fe^{II} complex (○) containing 5.0 mmol of Fe^{II}, specific surface area 5.3 m² g⁻¹.

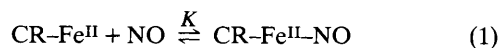
Table 1. Amount of effective Fe^{II} ion in resin complexes, calculated from Langmuir plots.

Complex	Immobilized ion		Surface area /m ² g ⁻¹	Effective Fe ^{II} /mmol	Adsorption efficiency R ^a
	Fe ^{III} /mmol	Fe ^{II} /mmol			
CR-Fe ^{II}	0	16.2	43.1	2.27	0.14
CR-Fe ^{II} , Fe ^{III}	10.2	3.56	128.0	0.93	0.26

^a The adsorption efficiency *R* was determined as the ratio of effective Fe^{II} calculated from the slopes of Figure 2 to the amount of immobilized Fe^{II}.

ions. The specific surface areas of the chelate resin-mixed valence iron complex and the Fe^{II} complex were 128.0 and 5.3 m² g⁻¹, respectively. This fact indicates clearly that the rapid co-ordination achieved in the case of the chelate resin-mixed valence iron complex is attributable to the high surface area caused by the Fe^{III} ions simultaneously introduced into the resin, since Fe^{III} ions have no affinity for NO.¹⁰

The increase in surface area should follow the increase in the amount of iron(II) ions present, these being responsible for the co-ordination of NO. The effective amount of iron(II) ions was therefore calculated, assuming a Langmuir equation for the co-ordinative adsorption (equation 1). The equilibrium constant *K* may be expressed as equation 2 from equation 1. This may be translated to equation 3, where *p* is the partial pressure of NO (atm) and [CR-Fe^{II}-NO] is the amount of NO adsorbed at equilibrium (mmol). [CR-Fe^{II}]₀ is the effective amount of Fe^{II}. Using equation 3, [CR-Fe^{II}]₀ and *K* can be calculated from the slope and the intercept of the ordinate, respectively.



$$K = \frac{[\text{CR-Fe}^{\text{II}}\text{-NO}]}{([\text{CR-Fe}^{\text{II}}]_0 - [\text{CR-Fe}^{\text{II}}\text{-NO}])p} \quad (2)$$

$$1/K = [\text{CR-Fe}^{\text{II}}]_0 (p/[\text{CR-Fe}^{\text{II}}\text{-NO}]) - p \quad (3)$$

Figure 2 illustrates the resulting linear plots of *p* and

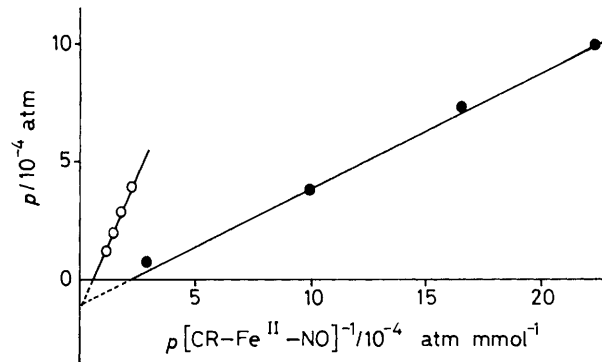


Figure 2. Langmuir plots for the chelate resin-mixed valence iron complex (●) composed of 10.2 mmol of Fe^{III} and 3.56 mmol of Fe^{II}, and the chelate resin-immobilized Fe^{II} complex (○) containing 16.2 mmol of Fe^{II}.

p/[CR-Fe^{II}-NO] for the chelate resin-mixed valence iron complex (●) and the Fe^{II} complex (○) indicating the 1:1 co-ordination of NO, with almost the same dissociation constant (1.0 × 10⁻⁴ atm) for each complex. This fact suggests that the active species of the chelate resin-mixed valence iron complex is the Fe^{II} ion. The effective amount of Fe^{II} calculated from the slope of the plots for the chelate resin-mixed valence iron complex and the Fe^{II} complex are 0.93 and 2.27 mmol, respectively, as listed in Table 1. The efficiency *R* of the Fe^{II} ions can be estimated from the ratio of the effective amount of Fe^{II} to the amount of immobilized Fe^{II}. For the chelate resin-mixed valence iron complex *R* is larger than that for the Fe^{II} complex due to the increase in surface area. Thus, it can be concluded that the co-ordination capability of the chelate resin-immobilized Fe^{II} complexes can be increased by simultaneously introducing Fe^{III} ions into the resin. The rest of the Fe^{II} ions, which have no relation to NO co-ordination, probably exist inside the microspheres, the fundamental components of the resin, into which the NO molecule cannot enter. Further increases in surface area should raise the adsorption efficiency *R*.

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