CHEMISTRY LETTERS, pp. 655-658, 1985.

CHELATE RESIN-IMMOBILIZED IRON(II) COMPLEXES AS NEW NITROGEN OXIDE ADSORBENTS

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Iron(II) ions were immobilized on the chelate resin by treating crosslinked polystyrene beads involving iminodiacetic acid moieties with iron(II) sulfate in water. The resin-immobilized Fe(II) complexes, especially those prepared with fine beads, can adsorb nitrogen oxide rapidly in water from nitrogen atmosphere containing 1000 ppm nitrogen oxide.

The methods to remove nitrogen oxide, a pollutant, from exhausted air have considerably established by using redox catalysts.[1,2] Among these methods a wet process for NO removal with an aqueous solution of the ethylenediaminetetraacetato-Fe(II) (Fe(II)-EDTA) complexes is noteworthy from the viewpoint of the high capacity for adsorption of NO and spontaneous removal of NO and SO_2 in aqueous solutions.[3-6] In general, immobilization of metal complexes on polymer resins has advantages in easy handling, high durability and so on.[7,8] In the present paper we would like to report first the immobilization of Fe(II) ions on the resin involving iminodiacetic acid (IDA) moieties as ligands instead of EDTA and then the adsorption of NO by the resin-immobilized complexes.

Resin-immobilized Fe(II) complexes were prepared as follows : Desired amount of $FeSO_4 \cdot 7H_2O$ was dissolved in 15 cm^3 of distilled water, and the resulting solution was added to 21.4 g of the commercial chelate resin (Mitsubishi Chemical Industries Co. Ltd., Diaion CR-10, mean diameter of the beads is 0.5 mm) in the sodium form corresponding to 21.0 mmol of IDA moieties. The mixing was performed with a magnetic stirrer or a mechanical shaker. After mixing for 48 h, total volume of the mixtures was adjusted to 50 cm^3 by adding a small amount of water.

This mixture was used as an adsorbent. All these operations were carried out under nitrogen.

The adsorption experiments were carried out by using a closed circulation system: 6 dm^3 of nitrogen containing 1000 ppm NO was introduced into this apparatus at room temperature, and circulated inside the apparatus bubbling through the adsorbent mixtures with a gas pump at the rate of 1.6 $dm^3 \cdot min^{-1}$. Changes of NO concentration in nitrogen were followed by sampling the mixed gas in a 100 mm-cell and measuring the absorbance at 226.5 nm.[9)]

Adsorption of NO by the chelate resin-immobilized Fe(II) complex is illustrated with close circles in Fig. 1, where the molar ratio of Fe(II)/IDA equals to 0.86. Fig. 1 also shows adsorption curves by an aqueous solution of $FeSO_4$ and by that of the Fe(II)-EDTA complex for comparison. Although the Fe(II)-EDTA solution can absorb NO rapidly even at low concentration of Fe(II), the adsorption curve has a maximum at 25 min and then decreases with time probably because of oxidation of Fe(II) ion with trace oxygen contaminated in the system by the leak at the gas pump. The adsorbent mixtures were prepared by adding the chelate resin to the $FeSO_4$ solution as mentioned before, and were composed of the supernatant and the solid parts corresponding to the resin-immobilized Fe(II) complexes. While the aqueous solution of $FeSO_4$ alone scarcely absorbed NO, the adsorbent mixtures adsorbed at a little slower rate than the Fe(II)-EDTA solution. Furthermore, the supernatant of the adsorbent mixtures did not absorb NO but the solid parts did.

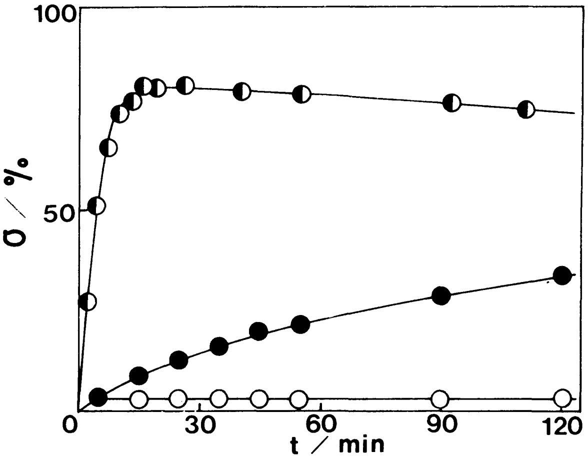

Fig. 1. Adsorption of NO (σ) at 25 °C by Fe(II)-EDTA solution (◐, 0.01 $mol \cdot dm^{-3}$), Fe(II)-SO_4 solution (○, 0.36 $mol \cdot dm^{-3}$) and resin-immobilized adsorbents prepared by mixing 18 mmol of Fe(II)SO_4 and 21.4 g of the chelate resin in water by using a shaker (●). Initial NO concentration = 1000 ppm

The color of the chelate resin beads turned from white to light green by immobilization of Fe(II) ions and the reflection spectrum had a maximum around 340 nm. With adsorption of NO, the color varied to dark green, and new shoulder peaks appeared at 450 and 600 nm, corresponding to the peaks around 430 and 630 nm found in the aqueous solution of Fe(II)-EDTA complex coordinated with an NO molecule.[10)] This consistency of the absorption bands strongly supports the coordination of NO to the immobilized Fe(II) complex.

The slow adsorption of NO by the resin-immobilized complex was supposed to be due to the small surface area of the resin beads. Therefore, the fine adsorbents were prepared in the same way as mentioned above by using the fine resin beads (about 10 μm in diameter) prepared by grinding the commercial beads with agate mortar and pestle. Adsorption of NO with the ground beads is illustrated in Fig. 2 as well as the case with the original beads. With the ground beads the adsorption of NO occurs rapidly and reaches equilibrium after 25 min. Moreover, the oxidation of the adsorbent by contaminated oxygen does not occur[11)] as it

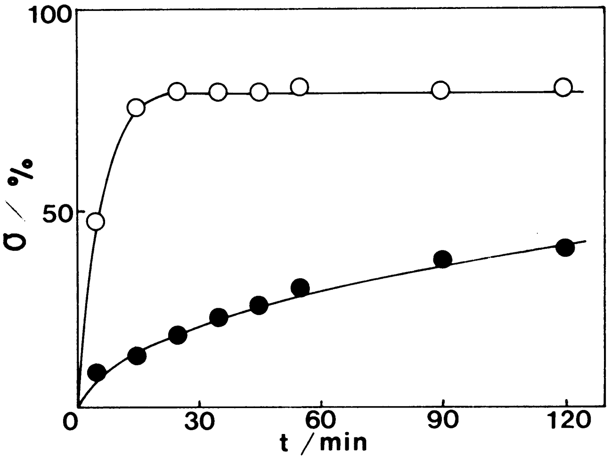

Fig. 2. Adsorption of NO (σ) at 25 °C by resin-immobilized Fe(II) adsorbents prepared from commercial beads (●) and from fine beads ground with agate mortar and pestle (○). Initial NO concentration = 964 ppm. Amount of the resin = 21.4 g. Charged Fe(II) = 31.4 mmol

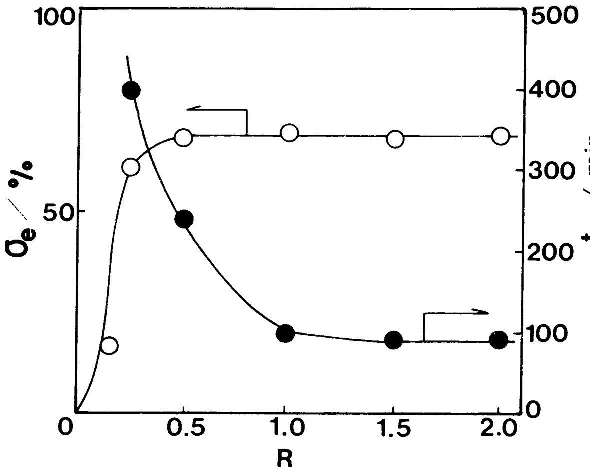

Fig. 3. Amount of adsorbed NO at equilibrium (σ_e,○) and time required to reach equilibrium (t_e,●) against molar ratio (R) of Fe(II) to IDA. Adsorptions were carried out at 30 °C from 1000 ppm NO in N_2 with fine beads. Amount of the resin = 21.4 g (containing 21.0 mmol of IDA moieties).

did with the aqueous solution of the Fe(II)-EDTA complex.

Dependence of charged Fe(II) on the amount of adsorbed NO at equilibrium was examined with the fine adsorbents as shown in Fig. 3.[12] The amount of adsorbed NO increases with increasing amount of charged Fe(II) and reaches saturation at the point that the amount of Fe(II) is half as much as the molar amount of IDA moieties in the resin beads. The adsorption rate, however, gets to saturation at the molar ratio of one. Thus, it became clear that the optimum molar ratio of charged Fe(II) to IDA was one.

The present work was partially supported by the Grant-in-Aid for Scientific Research from the Ministry Education, Science, and Culture.

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[12] To avoid the influence of the particle size, the commercial beads were ground in large scale and all the adsorbents used in Fig. 3 were prepared from the same lot of fine beads.

(Received February 8, 1985)