CHEMISTRY LETTERS, pp. 1921-1924, 1985.

ADSORPTION AND DESORPTION OF NITROGEN OXIDE BY IRON(II)-CHELATE RESIN COMPLEXES

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Iron(II) ions (14.7 mmol) immobilized on chelate resin (7.53 g) adsorbed 78% of total nitrogen oxide contained in 6 dm^3 of nitrogen at the concentration of 1000 ppm at 25 °C. The nitrogen oxide was released rapidly by 83% of that adsorbed by raising the temperature from 25 °C to 80 °C. Adsorption and desorption cycles on this adsorbent could be performed repeatedly without deterioration.

The separation of trace nitrogen oxide present in an exhaust gas by absorption is significant from the viewpoint of improvement of the atmosphere. The absorption of nitrogen oxide was previously investigated mainly by using an aqueous solution of ethylenediaminetetraacetato-iron(II) (Fe(II)-EDTA) complex and a reducing agent such as sodium sulfite.[1-6] In this case, absorbed nitrogen oxide turns to mainly imidobissulfate by reaction with sodium sulfite. We have reported that iron(II) ions can be immobilized on chelate resins involving iminodiacetic acid moieties to increase durability and ease of handling by using a solid resin instead of an aqueous solution, and that the resulting mixtures of chelate resin-immobilized Fe(II) complexes in the aqueous solution can adsorb nitrogen oxide.[7] If the nitrogen oxide can be easily released from the adsorbing complexes, the adsorbents can be regenerated and the released nitrogen oxide can be used as a starting material for chemical syntheses. In this regard, we have been interested in the desorption of the nitrogen oxide from the chelate resin-immobilized Fe(II) complexes which had adsorbed nitrogen oxide. In the present letter, we would like to report the release and recovery of nitrogen oxide by raising the temperature of the adsorbent.

The adsorbent was prepared as follows:[7] An aqueous solution of $FeSO_4 \cdot 7H_2O$ (8.72 g) was added to the fine crosslinked polystyrene resin (Mitsubishi Chemical Industries Co. Ltd., Diaion CR-10, 7.53 g, about 10 μm in diameter) involving iminodiacetic acid moieties (21.0 mmol). After stirring the mixtures for 48 h, the total volume of the mixtures was adjusted to 50 cm^3 by adding a small amount of water.

Since the capacity of the adsorbent for adsorption of nitrogen oxide depended on the temperature, the adsorption experiments were carried out at various temperatures by circulating 6 dm^3 of nitrogen containing 1000 ppm nitrogen oxide

Table 1. Adsorption of nitrogen oxide by Fe(II)-chelate resin complexes at various temperatures

Temperature/°C	Amount of adsorbed NO[a]/mmol	Apparent equilibrium constant[b]	
		$K_c\ H^{-1}$/atm^{-1}	K_c/dm^3 mol^{-1}
25.0	0.191 (78%)[c]	60.1	31.1×10^3
39.5	0.134 (58%)	23.2	14.8×10^3
59.8	0.069 (29%)	7.00	5.35×10^3
80.0	0.025 (11%)	2.02	1.67×10^3

a) Initial amount of nitrogen oxide = 0.24 mmol.

b) H = Henry's constant.

c) Molar percent of amount of adsorbed nitrogen oxide to initial amount of nitrogen oxide.

in the same way as reported in the previous paper.[7)] In order to change reaction temperature, the adsorbing vessel was kept in a thermostat at a designed temperature for about 10 min. After that, the gas was circulated bubbling through the adsorbent mixtures with a gas pump at the rate of 1.6 dm^3 min^{-1}. Concentration of nitrogen oxide was followed by sampling the mixed gas in a 100 mm-cell and measuring the absorbance at 226.5 nm. Results are shown in Table 1. The amount of adsorbed nitrogen oxide at equilibrium decreases with raising temperature. The adsorbed nitrogen oxide at 80 °C is about 13% of that at 25 °C. For quantitative comparison of the adsorption capacity, the equilibrium constants were calculated for adsorption of nitrogen oxide, according to the following reaction scheme, where CR is the chelate resin.

$$NO_{gas} \rightleftharpoons NO_{aq} \qquad (1)$$

$$\text{CR-Fe(II)} + NO_{aq} \rightleftharpoons \text{CR-Fe(II)-NO} \qquad (2)$$

Adsorption of nitrogen oxide by resin-immobilized Fe(II) (Eq. 2) is a heterogeneous reaction between the Fe(II) complex immobilized on the resin and nitrogen oxide in water. However, the equilibrium constants were calculated by assuming that the Fe(II) complex was homogeneously dispersed in the water.[8)] The amount of iron(II) immobilized on the resin (7.53 g) was determined to be 14.7 mmol by individual experiments. The concentration of nitrogen oxide in water was calculated by Henry's law due to the equilibrium (Eq. 1). Equilibrium constants for Eq. 2 at various temperatures are also shown in Table 1. The van't Hoff's plot formed a straight line, and the enthalpy change (ΔH) in the reaction of Eq. 2 was -10.9 kcal mol^{-1} (1 cal=4.184 J).

Nitrogen oxide could be released by bubbling pure nitrogen at 25 °C through the adsorbent which adsorbed nitrogen oxide. The temperature dependence of the adsorbed amount of nitrogen oxide at equilibrium also suggested the release of nitrogen oxide by warming. On the basis of this fact, the following cyclic experiments were carried out. After the adsorbent mixtures were equilibrated with the mixed nitrogen oxide gas at 25 °C by circulating the gas for 90 min at the rate of 1.6 dm^3 min^{-1}, the circulation was stopped and the system was left as it

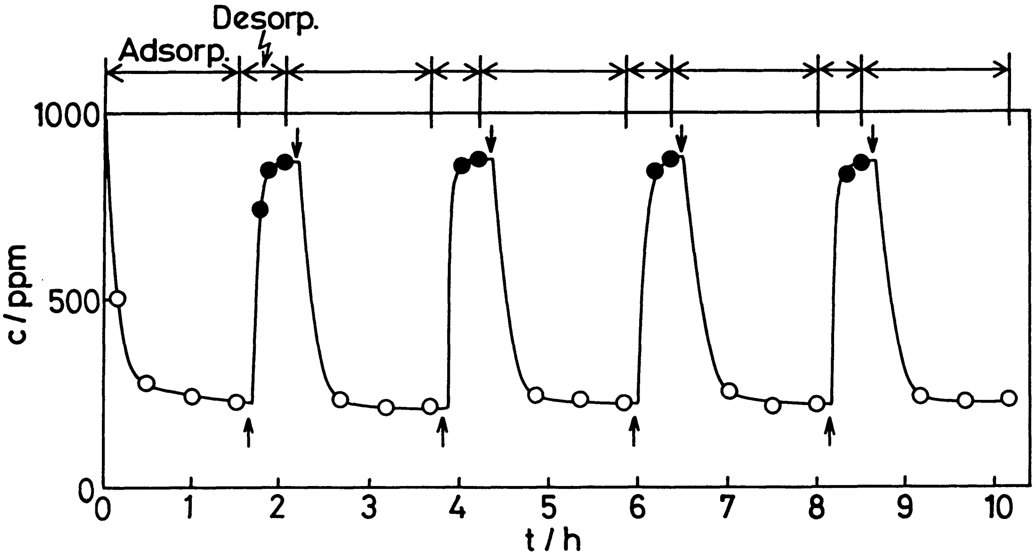

Fig.1. Changes of the concentration (c) of nitrogen oxide in the gas phase with time (t) during the adsorption (○) of nitrogen oxide at 25 °C by Fe(II)-chelate resin adsorbent and desorption (●) of nitrogen oxide at 80 °C from the adsorbent. To adjust the temperature to a desired value, adsorbent was kept in the thermostat for 10 minutes without circulating the gas after adsorption (↑) or desorption (↓) of nitrogen oxide.

was. And the temperature of the adsorbent mixtures was raised up to 80 °C, below which the resin was known to be stable enough. After that the gas was circulated again. At the first circulation, nitrogen oxide was smoothly adsorbed, and the concentration of nitrogen oxide in the gas phase decreased to 220 ppm after 90 min. That is, 78% of nitrogen oxide in the system was adsorbed by the adsorbent mixtures at 25 °C. When the second circulation of the gas started after elevating the temperature to 80 °C, nitrogen oxide was smoothly released and the concentration recovered to 876 ppm. In other words, 85% of nitrogen oxide adsorbed was released and 12% of nitrogen oxide charged remained in the adsorbent at 80 °C. This value of 12% corresponds to the amount of nitrogen oxide adsorbed at equilibrium at 80 °C as shown in Table 1. This cyclic experiment indicates that adsorbed nitrogen oxide can be easily released by treatment with heat and the amount of nitrogen oxide released can be estimated from a difference between the amounts of nitrogen oxide equilibrated at the temperatures of adsorption and desorption, respectively. After release of nitrogen oxide, the circulation was stopped, the temperature was lowered to 25 °C, and then the second adsorption-desorption cycle was recommenced by circulating the gas again. At the second time the same amount of nitrogen oxide as that at the first was adsorbed at 25 °C and desorbed at 80 °C. Figure 1 shows the results of these cycles. The adsorption-desorption cycle was repeated for five times without deactivation. This result indicates that the adsorption of nitrogen oxide by the chelate resin-immobilized Fe(II) complexes is reversible without degradation of the complexes or side reactions of nitrogen oxide such as reduction of nitrogen oxide to dinitrogen oxide. This stability of the complexes in the reversible adsorption of nitrogen oxide is probably due to the protecting effect of the resin.

From the viewpoint of the recovery of nitrogen oxide as a starting material, the release of nitrogen oxide at the concentration higher than that of the original sample gas was examined. After circulating 6 dm^3 of the nitrogen gas containing 980 ppm nitrogen oxide through the adsorbent to reach equilibrium at 25 °C, the remained gas in the gas phase of the system was evacuated, and then another 6 dm^3 of the sample gas was introduced and circulated through the adsorbent. Ten repeat operations saturated the adsorbent with 980 ppm nitrogen oxide. Total amount of nitrogen oxide adsorbed on the adsorbent was 0.675 mmol. Then 6 dm^3 of pure nitrogen was newly introduced into the system and circulated at 80 °C through the adsorbent mixtures already saturated with 980 ppm nitrogen oxide. By this treatment, 0.572 mmol of nitrogen oxide, which is corresponding to 76% of total amount of the adsorbed, was released at the concentration of 1983 ppm. This fact indicates that, by using the present adsorbent, concentrated nitrogen oxide can be obtained from the dilute one as a raw material, that is, concentrated recovery of nitrogen oxide is possible.

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

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(Received September 14, 1985)