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A NEW DRY-TYPE ADSORBENT OF CHELATE RESIN-IRON(II) COMPLEXES. PREPARATION AND ADSORPTION OF NITROGEN OXIDE

Naoki TOSHIMA, Hiroyuki ASANUMA, and Hidefumi HIRAI*
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

A new dry-type adsorbent was prepared by washing the chelate resin beads holding iron(II) with a hydrophilic organic solvent, followed by vacuum drying. It adsorbed more than 99% of nitrogen oxide from 6 dm^3 of nitrogen gas containing 980 ppm nitrogen oxide in 25 min. The nitrogen oxide adsorbed on the adsorbent was able to be desorbed by raising temperature up to 100 °C under vacuum.

A lot of methods for removing nitrogen oxide, pollutant in the air, have been studied by using redox catalysts (dry systems)[1-3] or chemical absorbents (wet systems).[4-6] We have reported that an aqueous mixture of iron(II) ions immobilized on the crosslinked polystyrene resin involving iminodiacetic acid moieties works as a wet-type adsorbent in water and adsorbs trace nitrogen oxide in a mixed gas.[7,8] The solid materials prepared by only evacuation of the solvent from the above mixture scarcely adsorbed nitrogen oxide. Now, we have found that the above mixture, if it is treated by some organic solvents before evacuation, can work as a new dry-type adsorbent. This adsorbent has higher activity for adsorption of nitrogen oxide and more stable against air than the corresponding wet-type adsorbent mixture. In the present letter we would like to report the preparation of the dry-type adsorbent and its adsorption capacity of nitrogen oxide.

The dry-type adsorbent was prepared under nitrogen as follows: An aqueous solution of 8.72 g of $FeSO_4 \cdot 7H_2O$ (31.4 mmol) in 50 cm^3 of distilled water was added to 21.4 g of white chelate resin beads swollen with water (Mitsubishi Chemical Industry Co. Ltd., CR-10, containing 21.0 mmol of iminodiacetic acid moieties. Mean diameter is 0.5 mm. Grain size range is 1190-297 μ.) The mixture was shaken by a mechanical shaker for 1 day to immobilize iron(II) ions on the resin beads. After removing the aqueous part which contained 14.6 mmol of iron(II) ions, the solid part was washed with 50 cm^3 of ethanol for 4 times. Amount of iron(II) ions in the filtrate decreased with repeated washing and only trace amount of iron(II) was detected in the 4th filtrate. Amount of immobilized iron(II) was calculated to be 16.2 mmol by deduction of total amount of iron(II) in the filtrate from the charged one. Then the solid part was dried under vacuum at 50 °C. The greenish beads, which had a maximum peak at 320 nm in the electronic spectrum, were obtained as a dry-type adsorbent.

Adsorption experiments were carried out as follows: After putting 9.04 g of the adsorbent into a column in a closed circulation system, 6 dm^3 of nitrogen containing 980 ppm of nitrogen oxide was circulated at the rate of 1.6 dm^3 min^{-1} to contact with the adsorbent. Changes of NO concentration were followed by sampling the circulated gas in a 100 mm-cell and measuring the absorbance at 226.5 nm.

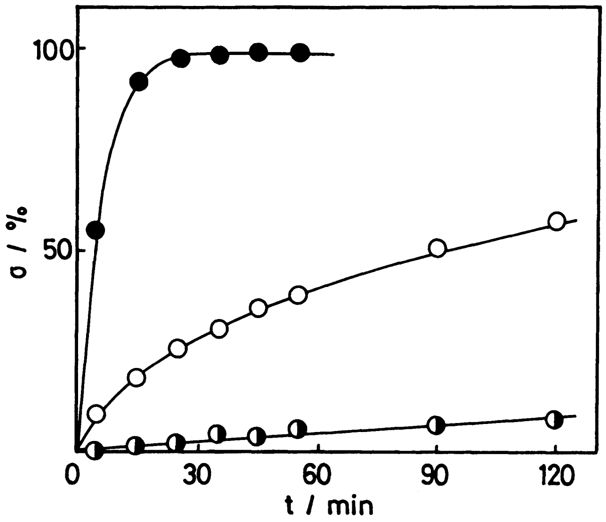

Fig. 1. Adsorption curves for NO at room temperature by a chelate resin-based adsorbent prepared by drying after washing with ethanol (●), water (○), and without washing (◑). Sigma indicates the molar percent of adsorbed NO to charged NO.

The adsorbent prepared as above rapidly adsorbed nitrogen oxide. More than 99% of nitrogen oxide in the circulated gas was adsorbed in 25 min. Data are shown by closed circles in Fig. 1. The solid adsorbent, prepared by only removing water under vacuum at 50 °C from the aqueous adsorbent mixture without washing, scarcely adsorbs nitrogen oxide as shown by half-closed circles. The adsorbent, prepared by drying under vacuum after washing with water for 4 times, has some adsorption capacity as illustrated with open circles, which is not so much as that in the case of washing with ethanol.

Now, some adsorbents were prepared by using various washing solvents. Table

Table 1. Effect of the solvent for washing the resin-immobilized iron(II) complexes on the adsorption of nitrogen oxide[a)]

Solvent	Amount of adsorbed NO/%	
	after 15 min	at equilibrium
methanol	94.2	99.3
ethanol	91.7	99.8
2-propanol	90.6	98.7
acetonitrile	66.5	94.7
acetone	63.6	93.6
chloroform	22.0	78.9
hexane	16.2	66.7

a) The adsorbents were prepared from 31.4 mmol of $FeSO_4$ and 21.4 g of the chelate resin beads containing 21.0 mmol of iminodiacetic acid moieties. Adsorption experiments were carried out at room temperature for 6 dm^3 of nitrogen containing 980 ppm nitrogen oxide.

1 shows the amount of adsorbed nitrogen oxide in the present circulation system with these adsorbents. Each adsorbent prepared by using the organic solvent miscible with water like methanol, ethanol, 2-propanol, acetone, and acetonitrile got high adsorption activity, while high activity was not observed when the organic solvents with low affinity for water, such as chloroform and hexane, were used. It became clear that by washing the resin beads with an organic solvent miscible with water, the adsorbent got high activity for adsorption of nitrogen oxide. This activity is thought to be due to high surface area of the adsorbent, which is shown experimentally and will be published elsewhere.

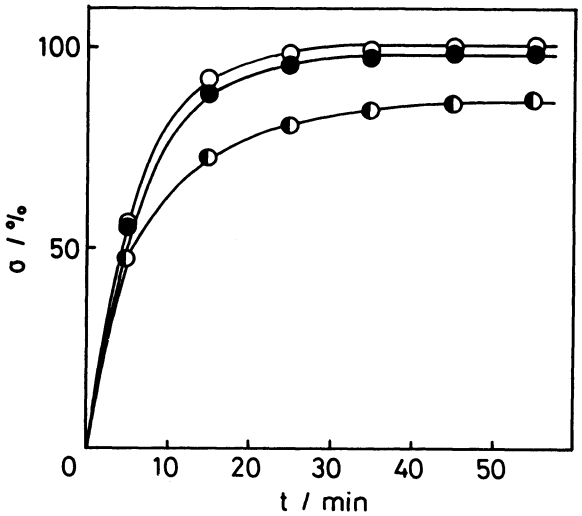

Fig. 2. First adsorption of nitrogen oxide (○) by the dry-type adsorbent prepared by drying after washing with ethanol, second adsorption (◐) without desorption of nitrogen oxide after the first run, and third adsorption (●) after desorption of nitrogen oxide by raising temperature to 100 °C under vacuum (3 mmHg) for 6.5 h.

The dry adsorbent prepared by washing with the organic solvent was stable under air and the adsorption activity scarcely decreased after contact with air for 90 min. This stability against oxygen is due to the absence of water in the system since oxidation of iron(II) ions by oxygen are promoted by the presence of water.[9)]

Figure 2 illustrates the repeated adsorption. The open circles show the first adsorption of nitrogen oxide by the dry-type adsorbent. The curve is the same as that indicated by close circles in Fig. 1. After the first adsorption, the remained gas in the system was removed and another 6 dm^3 of the sample gas was newly introduced into the system. Then the second adsorption experiment was carried out. The data are shown by the half-closed circles in Fig. 2. In this case the adsorbed amount of nitrogen oxide decreases to 87% compared with that of the first adsorption. Now, the NO adsorbed adsorbent was kept at 100 °C under 3 mmHg for 6.5 h for release of nitrogen oxide. After this desorption treatment the 3rd adsorption experiment was carried out under the same conditions as the 1st and 2nd adsorptions. The data are indicated by the closed circles. By this treatment adsorptionactivity recovered almost to the virgin one. This fact indicates that the adsorption of nitrogen oxide by the present adsorbent is reversible and the adsorbent can be regenerated by raising temperature under vacuum.

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