ADSORPTION OF COBALT(II) ION BY TITANIUM-BASED OXIDES IN HIGH TEMPERATURE WATER

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Abstract – Titanium-based adsorbents such as TiO_2 and Fe-Ti-O were prepared by hydrolysis of $Ti(OC_3H_7)_4$ and alkalinizing an equimolar mixed solution of $TiCl_4$ and $FeCl_2$ followed by heat treatment of their hydroxides, respectively. The prepared Fe-Ti-O adsorbent was found to be stable nonstoichiometric ferrous and ferric titanium oxides with pseudobrookite and rutile structures. The Co^{2+} adsorption characteristics of the adsorbent in high temperature water were investigated in the autoclave. Co^{2+} adsorption capacity of the Fe-Ti-O adsorbent was determined to be larger than that of TiO_2 at high temperatures. The enthalpy changes of 34 and 49 $kJ \cdot mol^{-1}$ due to the adsorption of Co^{2+} on the TiO_2 and Fe-Ti-O adsorbents indicate that the adsorption is endothermic in the experimental temperature range (15-280 °C). From this preliminary study, titanium-based oxides are shown to have good potential applicability for reactor water purification as high temperature adsorption media.

Key words: TiO_2, Fe-Ti-O, Adsorbents, Cobalt(II) Ion, Reactor Water Purification

INTRODUCTION

Inorganic oxide adsorbents [Amphlett, 1964] have been reviewed for the removal of soluble corrosion products and are attractive alternatives for water purification systems in pressurized water reactors (PWRs) or boiling water reactors (BWRs) because of the limitations of organic ion-exchange materials in their use, namely decomposition and oxidation at higher operating temperatures. Higher thermal efficiency and simplification of the clean-up system could be realized by using the inorganic adsorbents, made up of stable oxides, which can be operated at reactor water conditions. The inorganic adsorbents also have an advantage for their waste solidification with the direct ceramization of soluble corrosion products on an adsorbent matrix.

In water-cooled nuclear reactors, corrosion products are transported from the structural materials of the primary coolant circuit into the neutron flux in the reactor core, and out again to deposit on out-of-core areas such as the steam generator surface. A major radiation source in water cooled reactors has been identified to be activated corrosion products, mainly ^{60}Co, which is generally considered to be supplied from the primary side of nuclear reactors as Co^{2+} ions. Therefore, replacements of organic resin adsorbents, especially with inorganic compounds such as $Zr_2(PO_4)_3$ [Michael et al., 1961], ZrO_2 [Michael et al., 1961; Tewari and Lee, 1975; Tewari et al., 1973; Tewari and McIntyre, 1975; Ahrland and Carleson, 1971; Balakrishnan and Buckley, 1988], Al_2O_3 [Tewari and Lee, 1975; Tewari and McIntyre, 1975], Fe_3O_4 [Tewari et al., 1973], $NiFe_2O_4$ [Tewari and Lee, 1975; Tewari and McIntyre, 1975], TiO_2 [Kikuchi et al., 1978; Kikuchi et al., 1979; Kawamura et al., 1984], and composite oxides with TiO_2 [Fujita et al., 1980, 1985; Hata et al., 1986]

which can be applied in high temperature water, have been investigated. Among these inorganic adsorbents, TiO_2 has turned out to have the highest selectivity for cobalt ion and is recommended for purification in the high temperature system. There are also several potential advantages in using composite oxides, including particularly TiO_2 based oxides, with respect to enhancement of their adsorption capacity and hydrothermal stability with leaching resistance at high temperature. The Co^{2+} adsorption in high temperature water is known to be mainly controlled by TiO_2 in the composite adsorbent. Thus, some efforts have been made to improve its adsorption capacity and/ or selectivity by employing the method of loading of TiO_2 on substrates or the preparation of various types of composites such as supported TiO_2 on stable porous media and TiO_2 based composite oxides. However, few studies on the influence of the preparation methods on material characterization and adsorption characteristics of TiO_2 and Fe-Ti-O adsorbents have been reported.

The purpose of the present paper is to describe the preparation of TiO_2 and Fe-Ti-O adsorbents, examine their material characterization, and analyze the Co^{2+} adsorption characteristics of the two adsorbents considering the influence of the preparation methods on adsorption capacity at a high temperature.

EXPERIMENTAL

1. Preparation of Co^{2+} Solution and Adsorbents

All chemicals were of GR grade quality and used without further purification. All Co^{2+} solutions were prepared with deionized water from a NANOpure purification system (Barnstead 18.5 Mohm). The $Co(NO_3)_2 \cdot 6H_2O$ was used for preparing stock solution of which Co^{2+} ion concentration was 5.0×10^{-5} $mol \cdot dm^{-3}$. This concentration is low enough to avoid experimental error due to the bulk precipitation of $Co(OH)_2$ in a high temperature

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aqueous solution [MacDonald et al., 1972].

1-1. TiO₂ Adsorbent

The TiO₂ was prepared by using the sol-gel technique from alkoxide starting material. The particulate Ti(OH)₄ sol solution was prepared by hydrolysis of titanium (IV) tetraisopropoxide (Ti(OC₃H₇)₄) while adding 7 % ammonium hydroxide (NH₄OH) solution with the stirring speed of 1,000 rpm at room temperature for 1 hour. The possible reaction for this hydrolysis is:

$$Ti(OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH \qquad (1)$$
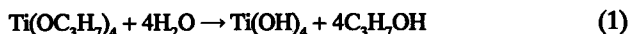
The different pH values (pH=4-11) of the solution at the end of precipitation in the hydrolysis reaction were set to be constant before the solution was aged overnight. The precipitate was filtered off, washed with deionized water, and dried at 100 °C. The dried powder was ground, sieved to 100-120 mesh size, and calcined at 600 °C for 6 hours.

1-2. Composite Oxide (Fe-Ti-O) Adsorbent

Mixed particulate sol solution was prepared by alkalinizing an equimolar mixture of 1 M ferrous (II) chloride (FeCl₂·4H₂O) and 1 M titanium (IV) chloride (TiCl₄) solution while adding 2.5 M sodium hydroxide (NaOH) solution with the stirring speed of 1,000 rpm at room temperature for 1 hour. The pH value at the end of precipitation was controlled 9. The resultant precipitate was aged overnight at the same temperature and pH after the precipitation reaction. And then it was filtered with a glass fiber filter of 1.0 μm, washed thoroughly with deionized water in Soxhlet's extractor until no chloride ions could be detected in the rinsed liquid, and dried at 100 °C. The dried powder was then analyzed and the molar ratio of Fe to Ti was found to be about unity. These powders were crushed and sieved, and a fraction of 100-120 mesh size was pressed into pellets (20-mm diameter, 10-mm height) without binder. The pellets were formed in a cylindrical die at 4 MPa for 0.5 min. A typical firing cycle was ambient to 600 °C at 10 °C·min⁻¹, 600 °C to the desired temperature at 5 °C·min⁻¹, isothermal hold for 2 hours, and then cooled at 20 °C·min⁻¹ to room temperature in a box furnace (Nabertherm HT 16/17). The calcination temperatures used in this experiment were between 700 and 1,400 °C. The heat-treated samples were again crushed and sieved, and a fraction of 100-120 mesh size was used in the following experiments.

2. Batch Experiments

Adsorption experiments were carried out at elevated temperatures in 1 dm³ capacity of stirred autoclave (Parr bench top reactor with magnetic drive), which was made of hastelloy C-276 with temperature controller (Parr model 4843). The temperature in the autoclave was measured by type J thermocouples and maintained with an accuracy of ±2 °C. The operation temperature range of the autoclave in this work was 150-280 °C. The adsorbed amount of Co²⁺ ion on the adsorbents with 100-120 mesh size particles was determined from the concentration change of the Co²⁺ solution after batch adsorption had reached equilibrium. An adsorption equilibrium time took about 5 hours for 0.2 g of the adsorbent in the stirred autoclave system containing 0.5 dm³ cobalt solution. In order to avoid errors due to precipitation of Co(OH)₂ in the bulk solution, $pH_{25°C}$

was kept to be 7. During or after the adsorption experiment, a 5 cm³ portion of the suspended solution was sampled, centrifuged at 3,000 rpm for 10 minutes, and the Co²⁺ concentration of a small portion of the supernatant solution was measured. Small changes in the Co²⁺ concentration of the solution due to adsorption were determined by atomic absorption spectroscopy (Perkin-elmer 5100PC).

The equilibrium concentration of Co²⁺, C (moles·dm⁻³), and the average amount of adsorbed Co²⁺ per unit adsorbent, q_{av} (moles·g⁻¹), are calculated from the initial concentration of Co²⁺, C_o (moles·dm⁻³), and the fraction of the adsorbed Co²⁺,

$$q_{av} = \frac{V(C_o - C)}{W_s} \qquad (2)$$

where V is the volume of the solution (dm³) and W_s is the weight of adsorbent (g). The distribution coefficients, K_d (dm³·g⁻¹), of Co²⁺ were calculated by the following equation.

$$K_d = \frac{C_o - C}{C} \cdot \frac{V}{W_s} \qquad (3)$$

3. Material Characterization

Specific surface areas of the adsorbents were obtained by BET method at 77 °K using a continuous flow method with the Quantachrome autosorb-6 sorption system (model AS-6/Po). The accuracy of the method was judged to be ±2.5 % or better based on the measurements of standard reference material with known surface areas. And the mean apparent density was determined by the liquid pycnometer technique. Thermogravimetric and differential thermal analysis (TG-DTA) with the Netzsch system (STA 409) were used to characterize the thermal processing and crystallization behavior of the prepared adsorbent. The rate of temperature increase for TG-DTA operation was 10 °C·min⁻¹. The X-ray diffraction (XRD) patterns of the prepared adsorbents were measured to identify the crystal structures at room temperature with a Rigaku Denki (Max/3D) X-ray diffractometer, filtered CuK_{α1} radiation (λ=1.5418 Å) and CoK_{α1} radiation (λ=1.7889 Å) being used at a scanning rate of 2 °·min⁻¹.

RESULTS AND DISCUSSION

1. Effect of Adsorption Temperature

The temperature dependence of Co²⁺ adsorption is exhibited in Fig. 1. The increased Co²⁺ adsorption capacity of the two adsorbents with high temperature is attributed to the adsorption of hydrolyzed species of cobalt. Tewari et al. [Tewari and Lee, 1975; Tewari et al., 1973; Tewari and McIntyre, 1975] have reported that the adsorption of Co²⁺ on oxides increases with pH and temperature. The Co²⁺ adsorption at high temperature seems to be due to increased hydrolysis of Co²⁺ accompanied by surface precipitation and formation of an insoluble Co(OH)₂ followed by reaction with the substrate to form an oxide compound with the loss of water. The reaction mechanism is suggested as follows:

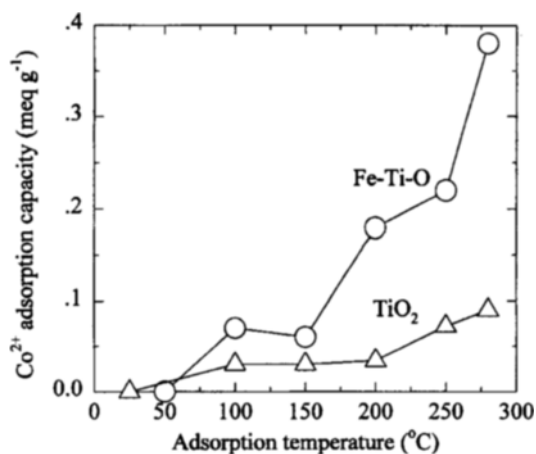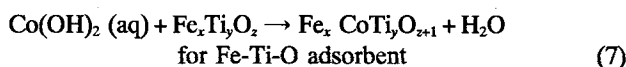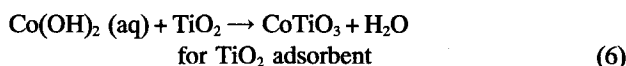surface precipitation with hydrolysis reaction;

$$Co^{2+} + H_2O \longleftrightarrow Co(OH)^+ + H^+ \qquad (4)$$

$$Co^{2+} + 2H_2O \rightarrow Co(OH)_2 \ (aq) + 2H^+ \qquad (5)$$
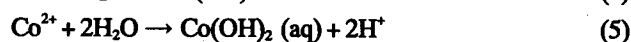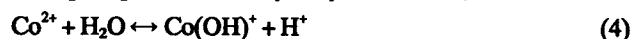
Fig. 1. Variation of Co^{2+} adsorption capacity of adsorbents with adsorption temperature (Initial Co^{2+} concentration: 5.0×10^{-5} mol·dm^{-3}, Adsorption time: 6 hours).

adsorption reactions with substrate;

$$Co(OH)_2 \text{ (aq)} + TiO_2 \rightarrow CoTiO_3 + H_2O$$
$$\text{for TiO}_2 \text{ adsorbent} \qquad (6)$$

$$Co(OH)_2 \text{ (aq)} + Fe_xTi_yO_z \rightarrow Fe_x CoTi_yO_{z+1} + H_2O$$
$$\text{for Fe-Ti-O adsorbent} \qquad (7)$$

At a high temperature, the strong adsorption mechanism such as irreversible chemical reaction illustrated by the Eqs. (6) and (7) would be dominative. High temperature conditions seem to increase multiple surface coverage of Co(OH)$_2$ by adsorption. Based on the preparation conditions which show favorable adsorption capacities, Co^{2+} adsorption capacity of the composite Fe-Ti-O was found to be about 4 times larger than that of TiO$_2$ alone at high temperature as shown in Fig. 1. This is probably due to the electrical conductivity of the crystals, which is higher in composite oxide in contrast to TiO$_2$ alone. Accordingly, it seems that the interaction of the relatively large Co^{2+} ions on the surface of the Fe-Ti-O adsorbent is more favorable than the corresponding interaction onto the surface of TiO$_2$.

The temperature dependence of adsorption equilibrium, in general, is related to standard enthalpy change by the following equation (Van't Hoff equation):

$$\ln K_d = -\frac{\Delta H^o}{2.303RT} + C \qquad (8)$$

where, K$_d$=distribution coefficient (cm^3·g^{-1}), which is defined as the ratio of the concentrations of the Co^{2+} in the adsorbent and in the solution,
ΔH^o=standard enthalpy change (kJ·mol^{-1}),
R=gas constant (kJ·K^{-1}·mol^{-1}),
T=temperature (K), and
C=constant.

The distribution coefficients (K$_d$) of Co^{2+} ions, as a function of the temperature for TiO$_2$ and Fe-Ti-O adsorbents, are plotted as shown in Fig. 2. Analysis of the slope gives ΔH^o of about 34 and 49 kJ·mol^{-1}, respectively. The standard enthalpy change of the adsorption reaction of Co^{2+} on prepared adsorbents indicates that the reactions are endothermic and their enthalpy
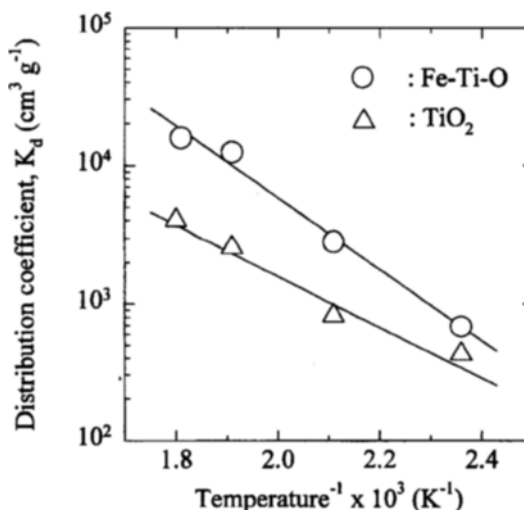
Fig. 2. Distribution coefficient versus temperature (Initial Co^{2+} concentration: 5.0×10^{-5} mol·dm^{-3}, Adsorption time: 6 hours).

change is much higher than that of simple ion-exchange reactions. The ion-exchange reactions are generally known to have smaller values of enthalpy changes than 8.4 kJ·mol^{-1} and the enthalpy changes due to Co^{2+} adsorption on the surface of TiO$_2$ and Fe-Ti-O adsorbents also exceed that of the dissolution of Co(OH)$_2$ (~19 kJ·mol^{-1}). This result can be explained by multilayer adsorption at higher coverages. At high temperatures the adsorbed cobalt might react with the substrate to produce oxide compounds containing cobalt. The larger values of ΔH^o for cation adsorption on the surface of TiO$_2$ are probably connected with the formation of spinel type compounds (CoTiO$_3$), while those of Fe-Ti-O with the formation of nonstoichiometric mixed oxide (Fe$_x$CoTi$_y$O$_{z+1}$).

Cobalt adsorbed from solutions on the surface of TiO$_2$ powders has been detected by X-ray photoelectron spectroscopy (XPS). The absolute binding energies of the adsorbed photoelectron lines have been compared to the binding energies for a number of cobalt compounds in order to identify the cobalt species adsorbed on the surface. The mean escape depth for the cobalt 2p electron is 0.6 to 1.0 nm [Tewari and McIntyre, 1975]. The XPS data for cobalt(II) compounds are summarized in Table 1. The Co(2p 3/2) line position observed for cobalt adsorbed at 250 °C on the outer surface of TiO$_2$ is about 781 eV. The observation of these satellites in the adsorbed cobalt spectra confirms that the major adsorbed species are Co(II), as shown in Fig. 3. These observations match those for Co(OH)$_2$, which also has a binding energy of 780.7±0.2 eV among the values of cobalt species as given in Table 1 and a prominent shake-up satellite in this range.

Table 1. XPS binding energies for some cobalt oxides [Tewari and McIntyre, 1975]

	Co(2p 3/2) eV	Co(3p) eV	Co(3s) eV
CoO	779.7±0.15	60.0±0.1	101.9±0.2
Co(OH)$_2$	780.7±0.2	61.1±0.2	102.9±0.2
Co$_2$O$_3$	779.6±0.2	61.4±0.2	103.0±0.2
CoOOH	779.7±0.2	61.2±0.2	103.0±0.2
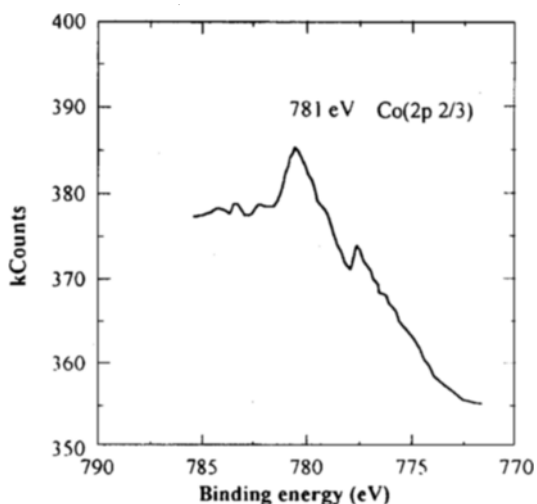
Fig. 3. XPS spectra of surface cobalt in Co(OH)₂ adsorbed on TiO₂ at 250 °C by Al-Kα X-rays.
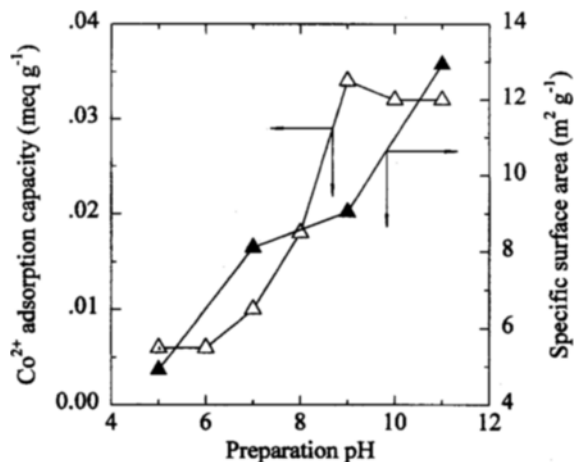

Fig. 4. Effect of preparation pH on specific surface area and adsorption capacity of TiO₂ (Initial Co²⁺ concentration: 5.0×10^{-5} mol·dm⁻³, Adsorption time: 6 hours, Calcination temperature: 600 °C, Adsorption temperature: 200 °C for 6 hours).

2. Effect of Preparation pH on Adsorption Capacity of TiO₂

The effects of the preparation pH of TiO₂ adsorbent on the specific surface area and Co²⁺ adsorption capacity are shown in Fig. 4. The specific surface area of the TiO₂ adsorbent increases and the mean pore radius decreases with an increase in the preparation pH at 25 °C. The TiO₂ adsorbent shows its maximum adsorption capacity when it was prepared at pH 9. It is known that the micro pores (less than 20 Å) do not make contributions to the adsorption of the cobalt complex. The considerable specific surface area with a relatively large fraction of micro pores in adsorbents is not effective for Co²⁺ adsorption as shown in Fig. 4, and it seems to be likely that the pores in the range of mesopore would be needed to allow the hydrated Co²⁺ ions to diffuse into the pores coated with Co(OH)₂ precipitated layers.

Fig. 5 shows the X-ray powder diffraction patterns of the TiO₂ adsorbent prepared at pH value of (a) 10, (b) 7 and (c) 4, and calcined at 600 °C for 6 hours. The peaks for anatase
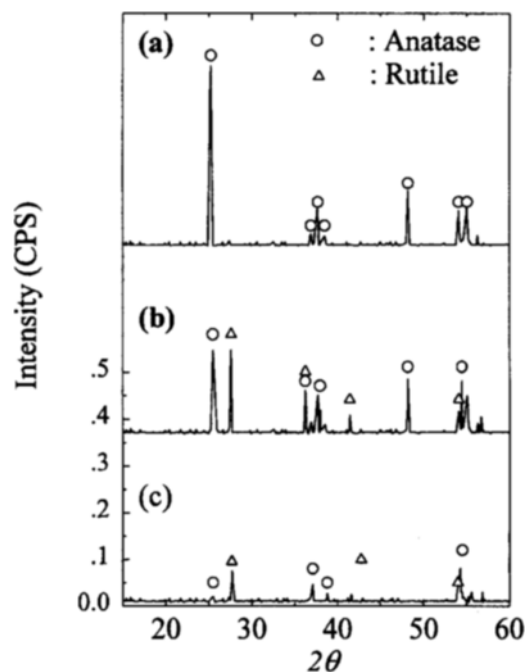

Fig. 5. X-ray diffraction patterns of TiO₂ adsorbents prepared at (a) pH 10, (b) pH 7 and (c) pH 4 followed by heat treatment at 600 °C for 6 hours.

became more dominant and intense with increasing pH. Only anatase peaks appear at pH 10, both anatase and rutile peaks are observed at pH 7, and rutile with a trace of anatase peaks exist at pH 4.

The apparent densities of the TiO₂ adsorbents prepared at pH range of 4-10 were about 3.4-3.9 g·cm⁻³. Although this was not confirmed by IR investigations that were expected to show polymerized cluster variations, gels prepared at high pH with high water contents dried to low bulk density and were predicted to have skeletal structures approaching the dense anhydrous oxide [Hench and Ulrich, 1984].

3. Effect of Heat Treatment of Fe-Ti-O on Adsorption Capacity

Fig. 6 shows the effect of heat treatment temperature on the adsorption capacity of Fe-Ti-O. At about 1,200-1,350 °C heat treatment temperature, superior values were obtained in spite of lower specific surface area in comparison with TiO₂.

In Fig. 7, patterns (a) and (b) illustrate the X-ray diffraction data of Fe-Ti-O powders heat-treated at 1,000 and 1,350 °C, respectively. And pattern (c) in Fig. 7, which is for Fe-Ti-O without heat-treatment, is shown in comparison with heat-treated Fe-Ti-O. Neither the anatase phase of TiO₂ nor spinel-like structure of magnetite phase (FeO-Fe₂O₃) is detected in heat-treated Fe-Ti-O, whereas these phases appeared in Fe-Ti-O without heat treatment. The X-ray patterns of Fe-Ti-O adsorbents calcined at 1,000° and 1,350 °C for 2 hours showed that phases corresponding to pseudobrookite and rutile structures were present, despite the fact that different conditions of heat treatment were used. This result indicates that there is no significant change in the phase composition of the resultant adsorbents due to temperature changes in heat treatments except the intensity of pseudobrookite structure at room temperature. The adsorbents prepared here have a stable phase at room tempera-
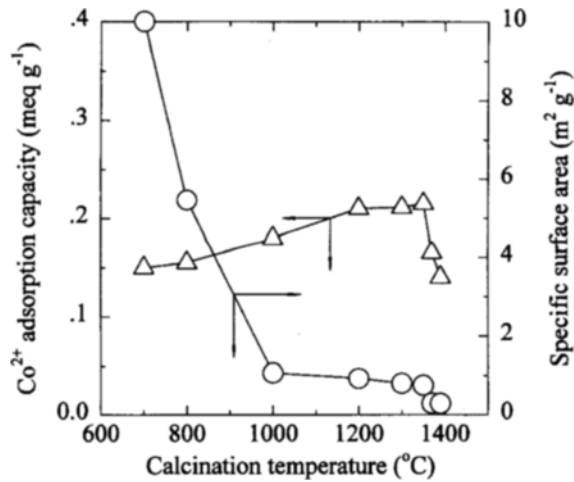
Fig. 6. Effect of calcination temperature on Co^{2+} adsorption capacity of Fe-Ti-O adsorbents (Initial Co^{2+} concentration : 5.0×10^{-5} $mol \cdot dm^{-3}$, Adsorption time : 6 hours, Adsorption temp. : 250 °C).

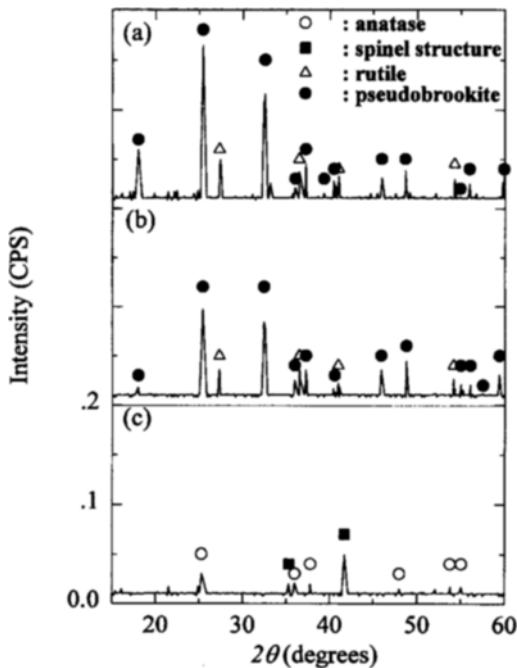
Fig. 7. X-ray powder diffraction patterns of Fe-Ti-O adsorbents heat-treated at (a) 1,350 °C, (b) 1,000 °C and (c) their composite hydroxide before heat treatment.

ture and their synthesis requires slow cooling from the calcination temperature. Mixtures of $FeO \cdot Fe_2O_3$, and TiO_2 (molar ratio Fe : Ti=1 : 1) that are allowed to cool down to room temperature over a period of hours yield a mixture of pseudobrookite and small portion of rutile phases as its major constituent. This is typical of nonstoichiometric iron titanium oxide and suggests that the starting ferrous oxide is partly oxidized during the process of precipitation and calcination in air. These results show that pseudobrookite type structure is good for Co^{2+} adsorption and is more stabilized at high temperature than other structures. However, the heat treatment of the mixed oxide at below about 1,200 °C led to an unstable structure and to decreased adsorp-

tion capacity because of the growth of a decomposition product (rutile) at the lower temperature. The electrical conductivity of the pseudobrookite type structure might enhance Co^{2+} adsorption due to the increase of the possibility of valence oscillation between Fe^{2+} and Fe^{3+} sites [Cotton and Wilkinson, 1988] in contrast to the ilmenite structure of ferrous titanium oxide ($Fe^{II}Ti^{IV}O_3$).
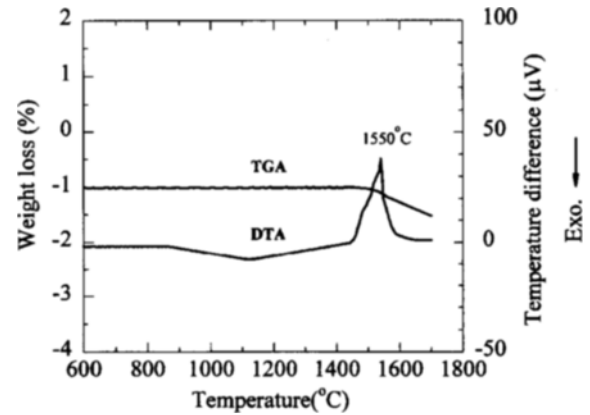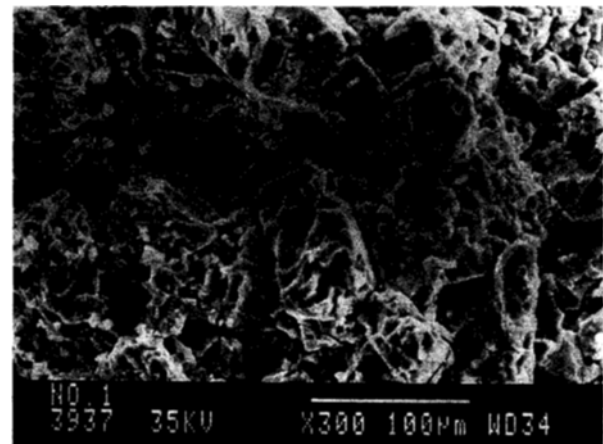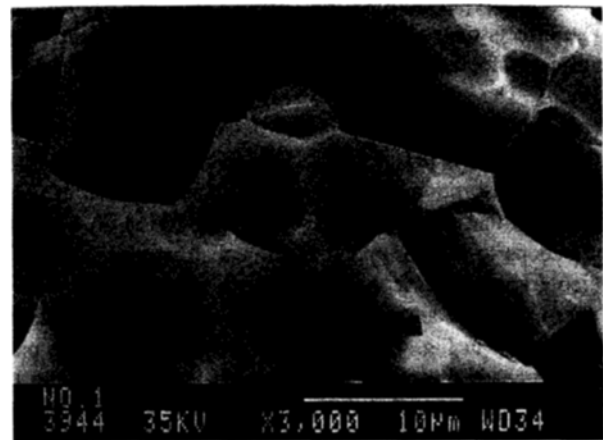

Fig. 8. TG-DTA curve of Fe-Ti-O adsorbent prepared by heat treatment at 1,350 °C.

(X 300)

(X 3,000)

Fig. 9. Scanning electron micrographs of a partially sintered Fe-Ti-O (gel prepared by heat-treating at 1,350 °C).

The result of TG-DTA for the prepared Fe-Ti-O adsorbent which was heat-treated at 1,350 °C is shown in Fig. 8. The profiles of DTA indicate that a large amount of melting phase was starting to be formed at 1,500 °C which seems to have a single endothermic reaction within a relatively narrow temperature range and then a small weight loss due to evaporation was observed at about 1,550 °C. These results suggest that the prepared composite oxide was formed as a kind of single phase compound even though its constituents have no congruent melting. The pseudobrookite region corresponding to the equivalent molar ratio of Ti to Fe in the ternary phase diagram of FeO-Fe$_2$O$_3$-TiO$_2$ system with liquidus temperature line suggests that Fe-Ti-O adsorbent is nonstoichiometric ferrous and ferric titanium oxide (FeO : Fe$_2$O$_3$: TiO$_2 \approx 0.4 : 0.1 : 0.5$). Scanning electron micrographs of a partially sintered Fe-Ti-O are shown in Fig. 9.

After completion of each experiment of the Co^{2+} adsorption, neither ferrous/ferric nor titanium ions could be detected in the solution. This result indicates that the adsorbents of Fe-Ti-O have sufficient hydrothermal stability to serve as a high temperature adsorbent.

CONCLUSIONS

The inorganic adsorbents of TiO$_2$ and Fe-Ti-O were prepared under various experimental conditions and tested for Co^{2+} adsorption at high temperature. TiO$_2$ prepared from its hydroxide sol at the aging condition of pH 9 and the Fe-Ti-O heat-treated at 1,350 °C were shown to have the most favorable adsorption capacities. When these adsorbents were applied in the solution containing Co^{2+} of 5×10^{-5} mol·dm^{-3} at 280 °C in batch adsorption experiments, the Fe-Ti-O type composite oxide was found to have larger adsorption capacity of Co^{2+} with about 0.38 meq·g^{-1} while TiO$_2$ alone had only about 0.09 meq·g^{-1} capacity. The enthalpy changes connected with the adsorption of Co^{2+} on the prepared adsorbents indicate endothermic adsorption and suggest that the Co^{2+} adsorption mechanism was accompanied by a certain irreversible chemical reaction. The specific surface area of adsorbents was not a dominant factor for Co^{2+} adsorption on oxides at high temperature, especially in Fe-Ti-O. The prepared Fe-Ti-O adsorbent was a stable nonstoichiometric ferrous ferric titanium oxide with pseudobrookite and rutile structures. Titanium-based types of composite oxides like Fe-Ti-O seem to be powerful high temperature adsorbents and could be recommended for the removal of ionic contaminants in the primary cooling water of nuclear power plants.

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