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Synthesis of Co-substituted Zeolites in the presence of cobalt complex with EDMA

Masanao Kato^a, Takuji Ikeda^{b,*}, Tetsuya Kodaira^c, Shio Takahashi^d^a Department of Materials Engineering, Nagaoka National College of Technology, 940-8532 Nagaoka, Nigata, Japan^b Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 983-8551, 4-2-1 Nigatake, Sendai, Japan^c Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 305-8565, Central 5, 1-1-1 Higashi, Tsukuba, Japan^d Alps Electric Co. Ltd., 940-8572, 1-3-5 Higashitakami, Nagaoka, Nigata, Japan

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ABSTRACT

In the presence of a monovalent cobalt complex with EDMA, we sought to synthesize zeolite from aluminosilicate gels in hydrothermal conditions. Using these gels, we obtained three kinds of zeolites, i.e., of the **MOR**-, **MFI**-, and **ANA**-type. We characterized in detail the obtained **MOR**- and **ANA**-type zeolite by means of thermal analysis, UV-Vis-IR spectrometry and TOF-SIMS measurement. The results showed that cobalt atoms are located in the **MOR**- and **ANA**-type framework (namely through Co atom substitution), and not in the micropores as a complex. On the other hand, a small number of cobalt atoms are distributed in a micropore of the **MFI**-type zeolite as a cation.

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1. Introduction

Zeolites including metal cations are highly attractive as catalysts and chemical reaction fields. In particular, the substitution of transition metals such as Fe, Ti, Ni, Co, and V atoms into various types of zeolite frameworks is strongly expected to have wide industrial use due to the high catalytic properties and high chemical stability of these zeolites [1]. Zeolites with transition metal atoms located in the pore were prepared by ion exchange in most cases, but their catalytic lives are short because the metal cation can be removed from the pore. Thus, zeolites in which the atoms are sited in the framework have been sought, some of which (in most cases the aluminophosphate framework) have been synthesized [2]. Although such zeolites have been synthesized directly from gels containing the metal cation, metal complexes in some cases have been substituted in synthesizing zeolites [2–9]. For example, **NON**-, **AST**-, and **DOH**-type zeolites which belong to clathrasil were synthesized using the cobalt(III) cation, $[\text{Co}(\text{III})(\eta^5\text{-C}_5\text{H}_5)_2]^+$, as a structure directing agent (SDA) [10]. Freyhardt et al. reported that large-pore high-silica zeolite UTD-1 with 14-membered ring was synthesized using bis-(pentamethylcyclopentadienyl)-cobalt(III) hydroxide, $[(\text{Cp}^*)_2\text{Co}]\text{OH}$, as an SDA molecule [11,12]. Many zeolites with cobalt-substituted aluminophosphates (CoAPO) [13–19] have been well-known so far. However, although a few zeolites with cobalt-substituted

aluminosilicate such as **MFI**-, **ANA**-, and **PHI**-type have been reported [20–22], but mordenite (**MOR**)-type has been scarcely reported.

It is well known that many zeolites have been mainly synthesized by the hydrothermal process using aluminosilicate gel, and that, as the alternate method, synthesis from the gels with template molecules such as tetraalkylammonium cation has been attempted for a long time. It has been expected that the metal complex compounds act as a template in the synthetic process, and some zeolites have been obtained as described above [10–12,23–25].

In this work, we attempted the hydrothermal synthesis of zeolites in the presence of a cobalt complex with EDMA (ethylenediamine-*N*-monoacetic acid, also known as *N*-(2-aminoethyl)-glycine; molecular formula: $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2$). Cobalt (III) cation serve the most useful complex because it is known as one of the most stable complex against the substitution reaction of ligand molecules [10–12,23–25]. EDMA is a monovalent and tridentate ligand, and forms a positive monovalent complex of $[\text{Co}(\text{III})(\text{EDMA})_2]^+$ via air oxidation of Co(II) after complexation. We surmised that a monovalent complex would be more favorable than a trivalent complex such as a complex with ethylenediamine because of higher solubility of its silicate compounds to the aluminosilicate gel than the trivalent complex.

This work was initially planned for the investigation of the role of templating effect of cobalt complex. It is suggested from the resulted synthesized region of obtained three kinds of zeolites such as **MFI**-, **MOR**- and **ANA**-type zeolites that the role of template

* Corresponding author. Tel.: +81 22 237 3016; fax: +81 22 237 5217.

E-mail address: takuji-ikeda@aist.go.jp (T. Ikeda).

molecules of cobalt complex was very weak. But the thermal, optical, TOF-SIMS (Time-of-flight secondary ion mass Spectrometry) analyses and the Rietveld refinement of powder XRD (X-ray diffractogram) of obtained **MOR**- and **ANA**-type zeolites suggest the framework substitution of cobalt cations. In this paper we show the synthesis and analysis of these zeolites.

2. Experimental

2.1. Materials and synthesis

The cobalt-EDMA complex was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Junsei Chemicals Inc. Guaranteed reagent) and EDMA (Toronto Research Chemicals, 98%). To a 20 cm³ aqueous solution of pH 9.18 buffered by phosphate, 0.3 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.5 g of EDMA were added. The resulting dark red solution was then heated on a mantle heater to evaporate the aqueous solvent until a dark red precipitate was obtained. The precipitate was filtered and washed with sufficient ethanol. After drying, the precipitate was used for zeolite synthesis. The composition of the cobalt-EDMA complex determined by the continuous variation method was $\text{Co}(\text{EDMA})_2^+$.

Aluminum hydroxide ($\text{Al}(\text{OH})_3$; Junsei Chemicals Inc. Guaranteed reagent) was dissolved in a calculated amount of sodium hydroxide solution (Nakarai Tesque Inc. Guaranteed reagent) by heating at 343 K for one day. Next, silica powder (Nipsil, $\text{SiO}_2 = 88\%$, $\text{H}_2\text{O} = 12\%$, Nippon Silica Ind.) and a cobalt complex $\text{Co}(\text{EDMA})_2\text{Cl}$ were added to the solutions and stirred for homogenization. The chemical composition of the starting mixture was as follows: $a\text{NaOH}$, $b\text{Co}(\text{EDMA})_2$, $\text{Al}(\text{OH})_3$, $c\text{SiO}_2$, and $d\text{H}_2\text{O}$, where $a/c = 0.1\text{--}1.0$, $c = 5\text{--}35$, $b = 0.05\text{--}0.5$, and $d/c = 30$.

The starting gel was charged into a 20 mL stainless autoclave and heated at 438 K under autogenous pressure. The autoclave was rotated at 30 rpm during hydrothermal synthesis. After heating for 144 h, the obtained product was filtered and washed with sufficient distilled water until the pH of the filtrate was less than 9. Finally, powder samples were prepared by drying at 373 K. Calcined samples were prepared by heating temperature up to 773 K with a rate of temperature increase of 0.7 K/min in airflow.

Additionally, Co ion-exchanged **MOR**-type zeolite was prepared for comparing the electronic state of the Co with optical spectroscopy and mass fragments with TOF-SIMS. Na-form **MOR** powder (Tosoh) of 3 g was soaked into an aqueous solution of 50 ml including 30 mM of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. After stirring for 1 h at room temperature, the solution was warmed up at 323 K for 20 h. Then, ion-exchanged powder was separated from the solution by filtration, and washed with distilled water. This procedure was repeated totally three times, and finally dried at 313 K overnight.

2.2. Physicochemical analysis

Powder X-ray diffraction (powder XRD) data were collected at room temperature on a Bruker D8-Advance Vario-1 diffractometer using modified Debye-Scherrer geometry. The incident X-ray beam was monochromatized by a Ge (1 1 1) primary curved monochromator to give $\lambda = \text{CuK}\alpha^1$. A high-speed 1D position-sensitive detector (BrukerAXS, VANTEC-1) was used with 2θ coverage of 10°. Powder samples were packed into borosilicate glass capillary tubes with an inner diameter of 0.5 mm. Lattice constants were determined using the Le Bail analysis.

Crystal morphology was observed by field-emission scanning electron microscopy (FE-SEM) on a HITACH S-4800 operating at 2 kV. Energy dispersive X-ray spectroscopy (EDX) installed in a JEOL JSM-6360SA FE-SEM was used for chemical analysis. All samples were coated with an ion liquid (IL) of 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF, Tokyo Chemical Industry Co.,

Inc.) beforehand. The dilution of IL to about 10% concentration by methanol is effective for coating thin layer of IL on the sample. Coating of insulating sample such as silicate with IL is very useful for providing electronic conductivity to the samples [26]. Thermogravimetric analysis was carried out on a Bruker TG-DTA 2000SA using a Pt pan. The measurement temperature rose from 303 K to 1073 K at a heating ramp of 10 K/min. Nitrogen gas adsorption was measured at 77 K for N_2 using a Quantachrome Autosorb-1-MP. Before the measurements, the powder samples (ca. 20 mg) were heated at 673 K for 6 h under vacuum. Carbon and hydrogen contents of **MOR** and **ANA** zeolites were determined by using the CE Instruments EA1110 elemental analyzer.

^1H - ^{29}Si dipolar decoupled (DD) MAS spectra were recorded on a Bruker AVANCE 400WB at 79.5 MHz for ^{29}Si , 104.3 MHz for ^{27}Al , and 400.3 MHz for ^1H . The ^{29}Si and ^{27}Al NMR spectra were obtained with rotor spinning rates of 5 kHz and 12 kHz, respectively, using a Bruker 4 mm VT-MAS-probe. ^{29}Si DDMAS NMR spectra were accumulated with a pulse length of 3.50 μs ($\pi/2$) and a recycle delay of 20 s; ^{27}Al MAS NMR spectra were accumulated using a single pulse sequence with a recycle delay of 4 s. Chemical shifts of ^1H , ^{29}Si and ^{27}Al NMR spectra were corrected using tetramethylsilane (for ^1H and ^{29}Si nuclei) and an aqueous solution of 1 M AlCl_3 (for ^{27}Al nuclei).

Diffuse reflection spectra of obtained samples and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ powdered crystal were corrected using an IR-vis-UV spectrometer (Cary 5000, Varian) at room temperature. Spectra were measured from 280 to 2500 nm. The diffuse reflection spectra were transformed to absorption spectra using the Kubelka-Munk function, $A(\lambda) \propto (1 - r(\lambda))^2 / 2r(\lambda)$, where λ is the wavelength, and $r(\lambda)$ and $A(\lambda)$, which are functions of λ , are the diffuse reflectance and the absorption coefficient, respectively. The relation between the absorption coefficient and the diffuse reflectance is described elsewhere [27]. Furthermore, the transmission spectrum of a cobalt-EDMA aqueous solution, which was converted into an absorption spectrum, was also measured for comparison.

Additionally, TOF-SIMS spectra were collected on an ION-TOF TOF-SIMS V spectrometer. Pressed zeolite powder, without any pre-treatments, was used for the measurements. Clusters of three bismuth atoms (Bi_3), used as the primary ions, were bombarded at the zeolite samples. The accelerating voltage was 25 keV and the ion current was 0.2 pA. The analysis area was $100 \times 100 \mu\text{m}^2$. The primary ions were bombarded at random to prevent charge-up. The bunched mode was used, in which the pulsed primary ion beams were shortened by the buncher to achieve a high mass resolution. Positive and negative ions were measured, and the appearance of main peaks that was negative ions was confirmed.

3. Results and discussion

3.1. Zeolite synthesis

As shown in Fig. 1, three types of zeolites (i.e., **MOR**, **MFI** and **ANA**) were obtained at a region where $\text{Si}/\text{Al} > 5$. At the range where $0.2 < \text{Na}/\text{Si} < 0.4$, **MFI**-type zeolite was synthesized (sample Nos. 1–3 in Table 1). The SEM image and powder XRD pattern of sample No. 3 are shown in Figs. 2a and 3a, respectively. The obtained **MFI**-type crystal had good crystallinity with a sharp habit, and its crystal size was 1 μm wide and 3 μm long. The crystal shape of **MFI**-type zeolite displayed the typical prismatic morphology which is already known [28]. However, a small amount of **MOR**-type zeolite phase was identified as a byproduct in the powder XRD pattern of sample No. 3 (Fig. 3a). The color of the zeolite was slightly pink, suggesting that the cobalt-EDMA complex was decomposed and that the cobalt ion exists in the pore of the **MFI**-type structure.

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