Low Temperature Synthesis of Dispersed Fine Particle of Cobalt Aluminate—A New Application of Zeolite

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Synopsis. $CoAl_2O_4$, with the spinel structure in a dispersed form, was synthesized at 400 °C by using zeolite A as a starting material. A specific surface area of the products was measured by adsorption of $(CH_3)_2CHCH_3$ gas at −110 °C and the mean size of the product particles was estimated to be about 14 nm.

Zeolites have been used as catalysts, adsorbent or ion exchangers owing to their porous structure. In these applications, the zeolitic structure is, of course, preserved. In the present work, zeolite A was used as a source of aluminium for the synthesis of cobalt aluminate. The methods of synthesis and characterization of the product are described in the following.

Experimental

The starting material, Na-A zeolite, was treated several times with 0.1 mol dm^{-3} $CaCl_2$ solution, and $Ca_{5.7}Na_{0.2}H_{0.3}(AlO_2)_{11.9}(SlO_2)_{12.1}$ was obtained. This zeolite (abbreviated as Ca_6-A) was further ion-exchanged, at 80±1 °C for 3 days, with solutions of $CoCl_2$ or mixed solutions of $CoCl_2$ and $CaCl_2$ of 0.1 (or 0.01) mol dm^{-3}. The pH value of the solution was not strictly controlled during the ion exchange, and the values before and after the ion exchange were in a range of 6.5—5.5 at room temperature, irrespective of the concentration of the solution (0.1 or 0.01 mol dm^{-3}). The composition Co_xCa_{6-x}-A was calculated from the composition of the solution and the material balance. The composition of the solution was determined by spectrophotometry. All chemical reagents used were S.P. grade, and the adsorbate gases used, oxygen and $(CH_3)_2CHCH_3$, had nominal purities better than 99.99 and 99.9%, respectively.

The amount of gas adsorbed was measured by the volumetric method in a clean vacuum system. A vacuum of 10^{-5} Pa was easily attained. Prior to adsorption experiments, the adsorbents were dehydrated at room temperature for 5 h and carefully baked out by raising the temperature stepwise. The samples were finally kept at 400 °C for 6 h in a vacuum of 10^{-5} Pa.

Results and Discussion

$Co_{5.5}Ca_{0.5}$-A zeolite (prepared in 0.1 mol dm^{-3} solution) was heated under various conditions (specified as (a), (b), ⋯) and rehydrated at 20 °C. Its color changed as follows (P denotes pink and B blue),

$Co_{5.5}Ca_{0.5}$-A (P)
→(a) 20 °C in vac.(B)→20 °C rehy.(P)
→(b) 20 °C in vac.(B)→400 °C in vac.(B)→20 °C rehy.(B)
→(c) 400 °C in vac.(B)→20 °C rehy.(B)
→(d) 400 °C in Ar(B)→20 °C rehy.(B)
→(e) 1000 °C in Ar(deep B)→20 °C rehy.(deep B)
→(f) 1000 °C in air(deep B)→20 °C rehy.(deep B)
→(g) 400 °C in air(gray-brown)→20 °C rehy.(gray-brown).

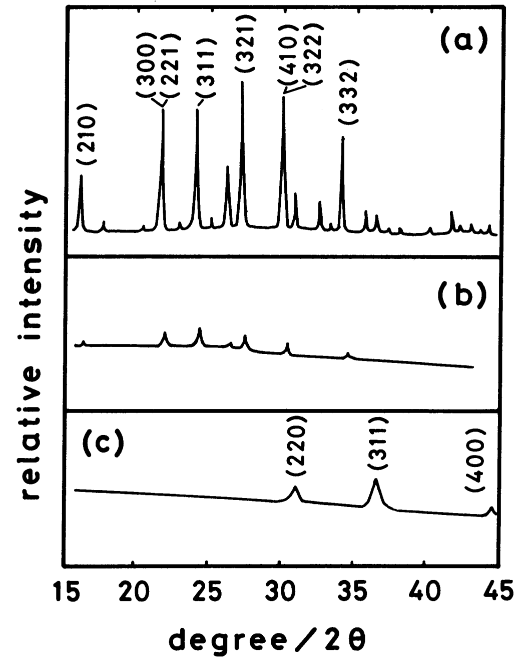

Fig. 1. X-Ray diffraction patterns of Co_xCa_{6-x}-A zeolites heat-treated. Copper radiation (*Kα*, λ=0.154 nm) was used. The patterns in (a) and (c) are characteristic to zeolite A and $CoAl_2O_4$, respectively. The pattern in (b) is characteristic to zeolite A but each peak is much weaker than that in (a). Representative indices of planes are shown in parenthesis. (a) x=0, heated at 400 °C in vacuum (b) x=4.1, heated at 400 °C in vacuum (c) x=5.5, heated at 1000 °C in air.

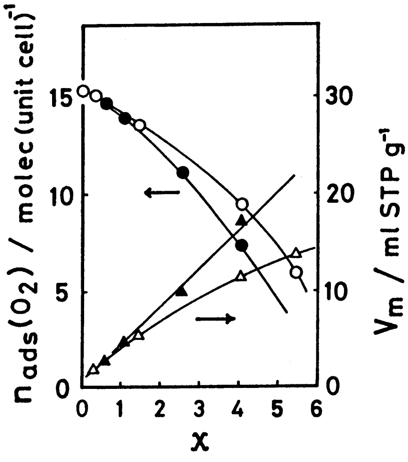

Fig. 2. Adsorptive capacities of Co_xCa_{6-x}-A zeolite heat-treated at 400 °C in vacuum. $n_{ads}(O_2)$; amount of O_2 adsorbed at −196 °C and 2000 Pa, v_m; monolayer capacity of $(CH_3)_2CHCH_3$ at −110 °C. ○△; zeolite prepared in 0.1 mol dm^{-3} solution, ●▲; zeolite prepared in 0.01 mol dm^{-3} solution.

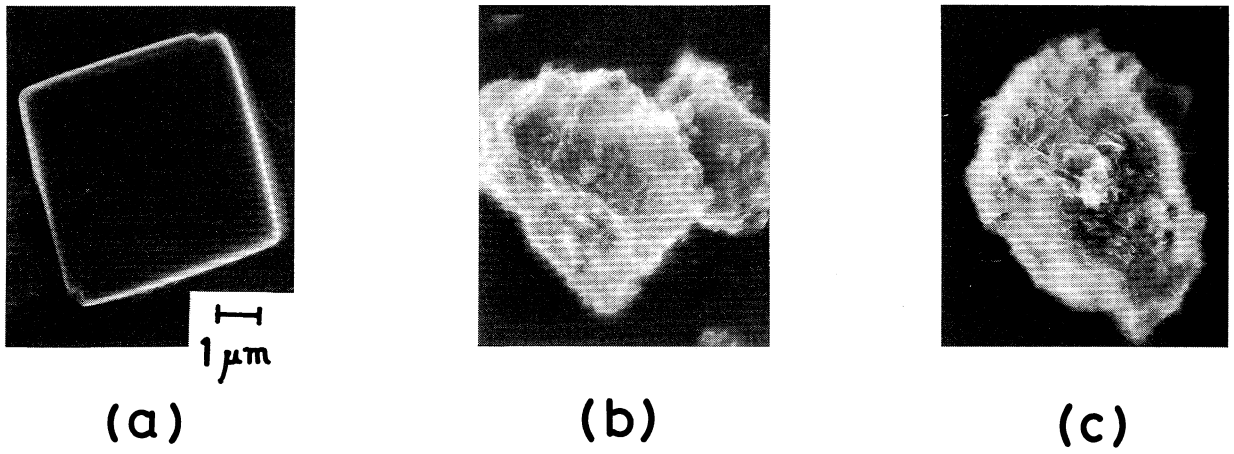

Fig. 3. Electron micrographs of Co_xCa_{6-x}-A zeolite, ion-exchanged with 0.1 mol dm^{-3} solution and then heat-treated at 400 °C in vacuum. (a) $x=0$, (b) $x=4.1$, (c) $x=5.5$.

With samples of $x<5.5$, the same changes were observed, though the color became thin with decreasing x-values. In $Co_{5.5}Ca_{0.5}$-A, heat treatments at 400 °C or higher always caused irreversible changes. All substances produced in treatments (b)—(g) were dipped in water, but did not return to the original color, pink. X-Ray diffractions of heat-treated zeolites were measured, and representative patterns are shown in Fig. 1. All peaks in the diffraction pattern of $Co_{4.1}Ca_{1.9}$-A, in Fig. 1(b), are assigned to zeolite A.[1] The same is the case with zeolites containing less Co than this. The peaks became weak with increasing x and vanished at $x=5.5$. The products in the treatments (e) and (f) contained $CoAl_2O_4$ as judged from their X-ray diffraction patterns[2] (Fig. 1(c)). The products in the treatment (g) gave no X-ray diffraction peaks but gave electron diffraction spots, which could not be assigned to any crystal. Products obtained in the treatments (b)—(d) contained $CoAl_2O_4$ as judged from electron diffraction patterns. The fraction of zeolite decomposed was estimated from the decrease in the adsorption capacity of O_2 which can penetrate into the zeolite cavity.[3,4] The amount of O_2 adsorbed was measured at −196 °C, and is given in Fig. 2. Representative scanning electron micrographs are shown in Fig. 3. In Fig. 3(c), the products are fine flakes. It was observed with the scanning electron microscope that the surface of Co_xCa_{6-x}-A became increasingly rough with the increasing x-value. Their surface became much rougher on heating. From the above results, it is concluded that the fraction of Co_xCa_{6-x}-A decomposed, by heating at 400 °C in vacuum or Ar atmosphere, increases with increasing x and becomes 0.7—0.8[†] at $x=5.5$, and the degradation products contain $CoAl_2O_4$.

The outer-surface area (BET area) of the degradation products was measured by the adsorption of $(CH_3)_2CHCH_3$ at −110 °C, which cannot penetrate into the zeolite cage.[4,5] Monolayer capacities of the products are shown in Fig. 2. The surface area of $CoAl_2O_4$ powder can not be deduced with confidence from this BET area. Now, let us roughly estimate the mean particle size of the products by assuming that the products contain $CoAl_2O_4$, SiO_2, Al_2O_3, and Ca_2SiO_4, all components have a cubic form of the same size, and the cross sectional area of $(CH_3)_2CHCH_3$ molecule at −110 °C is 0.29 nm^2. The edge of the products obtained from $Co_{5.5}Ca_{0.5}$-A was about 14 nm. The size, however, depended upon the ion-exchange condition, as shown in Fig. 2.

$CoAl_2O_4$ with the spinel structure is usually synthesized from CoO and Al_2O_3 at temperatures higher than 1000 °C.[6] In the present work, $CoAl_2O_4$ was obtained at such a low temperature as 400 °C by using (Co,Ca)-A zeolite as a precursor. The precursor method has frequently been used in the synthesis of some spinel compounds.[7–9] The use of zeolite material as a precursor is a new development and further investigations may open a new way of techniques for the synthesis.

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[†] Oxygen gas adsorbs into the zeolite cage, and onto the outer surface of the zeolite and degradation products. In three kinds of adsorptions, the amount of O_2 adsorbed onto the zeolite outer surface is negligible at all x-values. Hence, the fraction of zeolite decomposed is obtained by correcting for the amount adsorbed on the degradation products.