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Oxidation of $CaSi_2$ layered crystals with $CoCl_2$ solutions

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A layer-structured crystal $CaSi_2$ was found to be oxidized with $CoCl_2$ aqueous solutions. The Co^{2+} ions of the solution were reduced to metal at the edge surface of the crystals, while the interlayer calcium atoms of the crystals were removed as cations into the solution. A large amount of hydrogen was evolved during the reaction, which was attributed to a reduction product of water with a reactive silicon network generated by the deintercalation of calcium from $CaSi_2$. The saturation magnetization of the cobalt metal deposited on the surface increased as the reaction proceeded, approaching that of the bulk metal. The oxidation mechanism of the $CaSi_2$ is discussed on the basis of the chemical analysis data.

1. Introduction

The structure of calcium disilicide $CaSi_2$ [1–3] consists of corrugated trigonal silicon layers with calcium atom layers sandwiched between them (Fig. 1). In an attempt to isolate the layered silicon structure, Yamanaka *et al.* [4] studied the deintercalation of calcium from the interlayer space by an electrochemical oxidation using aprotic solutions. Although a part of the interlayer calcium could be successively deintercalated, the product was very reactive with the electrolytes and, furthermore, owing to the general feature of a layer-structured crystal, the layered fragments were easily depleted from the supporting electrode as the reaction proceeded. It was shown that the further oxidation was very difficult on the anode.

Extensive studies have been made of the modification of the layered silicon structure by chemical oxidations. Kautsky and co-worker [5–7] treated the crystal in a dilute hydrochloric acid solution; the interlayer calcium atoms were removed as Ca^{2+} ions with vigorous evolution by hydrogen. During this process, the reactive silicon layers are simultaneously oxidized to hydrous silica, which is called siloxene. Recently, Yamanaka *et al.* [8] studied the oxidation of siloxene with water, and found an interesting oxygen adsorption phenomenon with the formation of new types of $\equiv Si\cdot$ dangling bonds. Although the siloxene prepared by Kautsky was amorphous to X-rays, Weiss *et al.* [9] performed the reaction under milder conditions by using a concentrated HCl solution and found that the deintercalation of calcium from $CaSi_2$ could be done topochemically; the corrugated silicon layer structure was maintained with each silicon atom bonded to H and OH groups, alternately. Hennge [10–12] studied the oxidation of $CaSi_2$ with halogens and halogen compounds. Because the silicon layers are very reactive to halogen compounds, the resulting solids are a mixture of halogenated layered silicon derivative, such as $(SiCl)_n$ and $(SiBr)_n$, and the corresponding calcium halides. A veriety of layered organic derivatives was prepared by the chemical modification of these halogenated compounds [13].

The reducing power of $CaSi_2$ is so high that it is not necessary to use strong oxidizing agents; common transition metal cations will have sufficient power for the oxidation of $CaSi_2$ structure. In this study, the oxidation of $CaSi_2$ with $CoCl_2$ aqueous solutions was attempted, and the mechanism of the reaction is discussed.

2. Experimental procedure

2.1. Oxidation reactions

The preparation of $CaSi_2$ crystals by a r.f. heating in a water-cooled copper crucible has been described elsewhere [8]. The crystal aggregates, with a size of about 3 mm diameter, were dispersed in $CoCl_2$ solutions with concentrations in the range 5×10^{-4} to 0.2 M at 50 °C under continuous stirring. The hydrogen evolved during the reaction was collected by a gas burette. The evolution of hydrogen ceased after about 2 h. The solid product was separated by filtration using a Teflon filter, and washed with distilled water, followed by drying in dry air.

2.2. Analyses

The X-ray powder diffraction (XRD) patterns were recorded by using CuK_α radiation with a nickel filter. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed on the samples compressed and coated with an electrically conductive gold film. Magnetization curves were measured by using a vibrating sample magnetometer (VSM) over a magnetic field of -1.5–1.5 T. The amount of calcium removed from the $CaSi_2$ crystal

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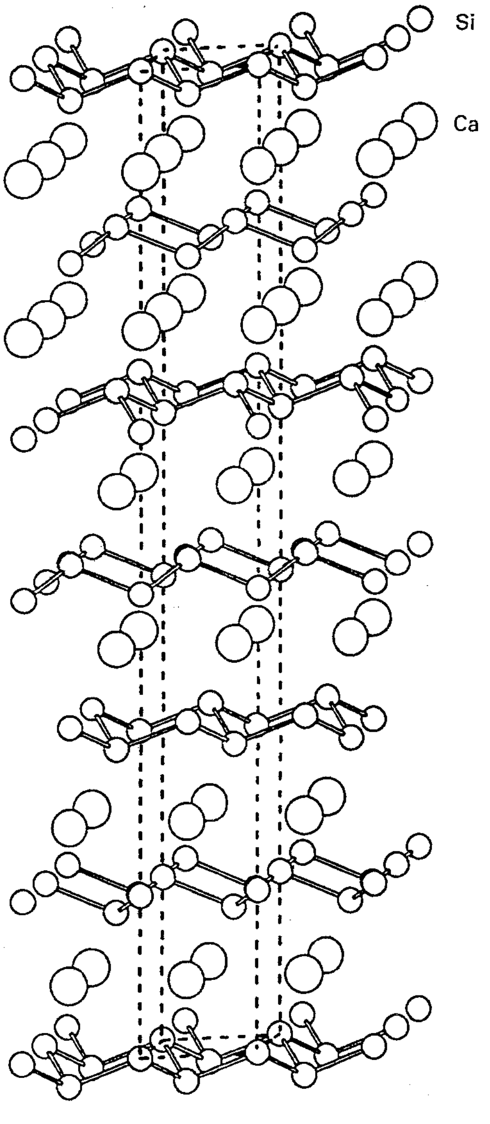

Figure 1 Schematic structural model of the layer-structured $CaSi_2$.

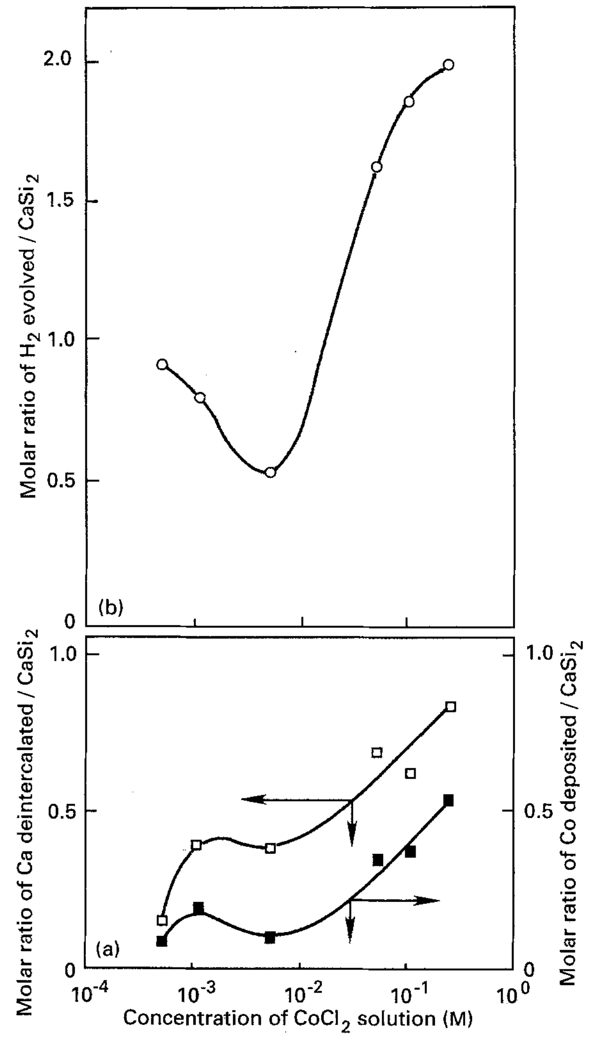

Figure 2 (a) The molar ratio of calcium deintercalated and that of cobalt deposited per mole of $CaSi_2$ as a function the concentration of $CoCl_2$ solution. (b) The number of moles of hydrogen evolved along with the respective reaction.

was determined by atomic absorption analysis of the $CoCl_2$ solution used for the oxidation. The oxidized solid samples were evaporated to dryness, and then a weighed amount was dissolved in a 5% HF solution. The amount of cobalt taken up by the solid was determined on this solution by atomic absorption analysis. The BET surface area of the compounds was determined using a conventional nitrogen gas adsorption apparatus with a computer control.

3. Results

3.1. Reactions

The oxidation reactions were carried out by dispersing $CaSi_2$ crystals into $CoCl_2$ solutions of different concentrations. The number of moles of calcium deintercalated and that of cobalt deposited were determined per mole of $CaSi_2$ used, and the results are shown in Fig. 2, together with the number of moles of hydrogen evolved from the same $CaSi_2$. In the series of the reactions, the same volume of $CoCl_2$ solutions with different concentrations were used. Therefore, the molar ratio of the total $CoCl_2$ to $CaSi_2$ varied in the range of 25–5 and the range 0.5–0.05 for the $CoCl_2$ solutions in higher (0.2–0.05 M) and lower (5–0.5 mM) concentration regions, respectively. In the higher concentration region, about 70%–80% of the calcium in $CaSi_2$ was removed from the interlayer space. It should be noticed that much larger amount of hydrogen gas was evolved along with the removal of the calcium. This will be discussed later in relation with the mechanism of the reaction.

The XRD patterns of the products obtained by the oxidation in different concentrations of $CoCl_2$ solutions were measured. The diffraction peaks of the products are attributed to those of the original $CaSi_2$ crystals, though the intensities decrease with the concentration of the $CoCl_2$ solution used, that is, with the amount of calcium removed from the crystals. Diffraction peaks due to the formation of a new crystalline phase were not observed. This finding suggests that the crystalline $CaSi_2$ is changed into an X-ray amorphous phase by the oxidation; the peaks observed can be assigned to the $CaSi_2$ crystals remaining unreacted. The sample obtained by the oxidation in a 0.2 M $CoCl_2$ solution was annealed under vacuum at temperatures ranging from 100–600 °C. After allowing to stand for 1 h at each heating step, the sample was taken out to measure the XRD pattern. A new series of the diffraction peaks due to cobalt metal appeared in the patterns measured after treatment at temperatures above 500 °C, the intensities of which increase with increasing temperature. This result suggests that the Co^{2+} ions taken up by $CaSi_2$ in the oxidation reaction were in the form of cobalt metal in a finely dispersed phase, which crystallized into cobalt metal by the annealing.

3.2. Magnetic properties

The oxidation reactions were carried out under a continuous stirring using a magnetic stirrer. As the reaction proceeded, the solid sample was cleaved into very thin platelets and adhered to a stirrer piece. Magnetization of the samples prepared by using different concentrations of $CoCl_2$ solutions was measured by a VSM at room temperature. The magnetization curves observed are shown in Fig. 3. All the curves have hysteresis loops characteristic of ferromagnetic material, though the coercive magnetic field and the field for saturation magnetization are much larger than those of the bulk cobalt. The saturation magnetization per mole of cobalt were calculated on the basis of the amount of cobalt taken up by the solid, and are plotted in Fig. 4 as a function of the molar ratio of

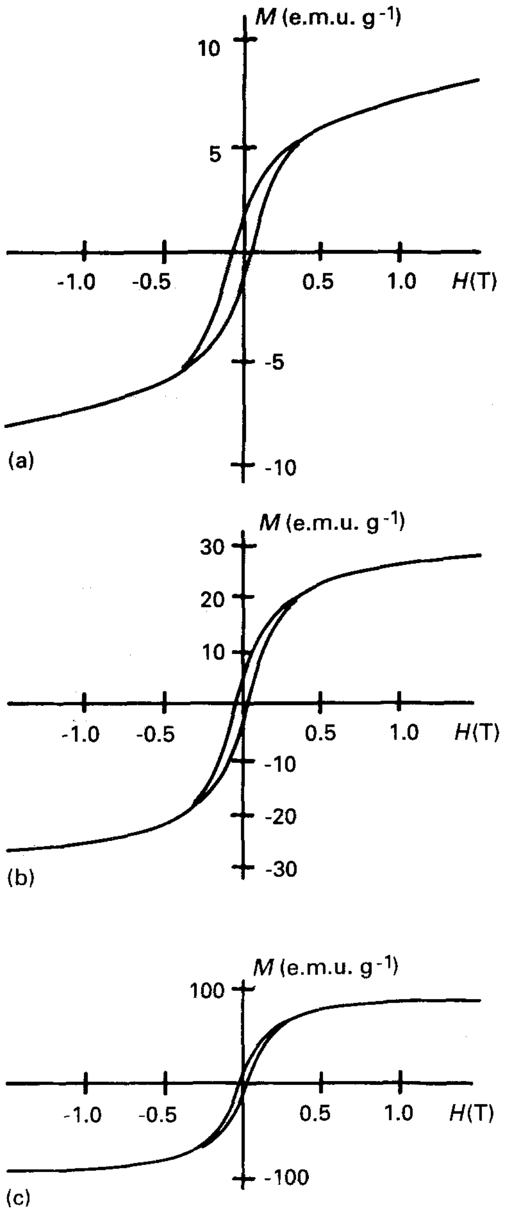

Figure 3 The magnetization curves of the $CaSi_2$ treated in three different concentrations of $CoCl_2$ solutions: (a) 0.005 M, (b) 0.05 M, (c) 0.1 M.

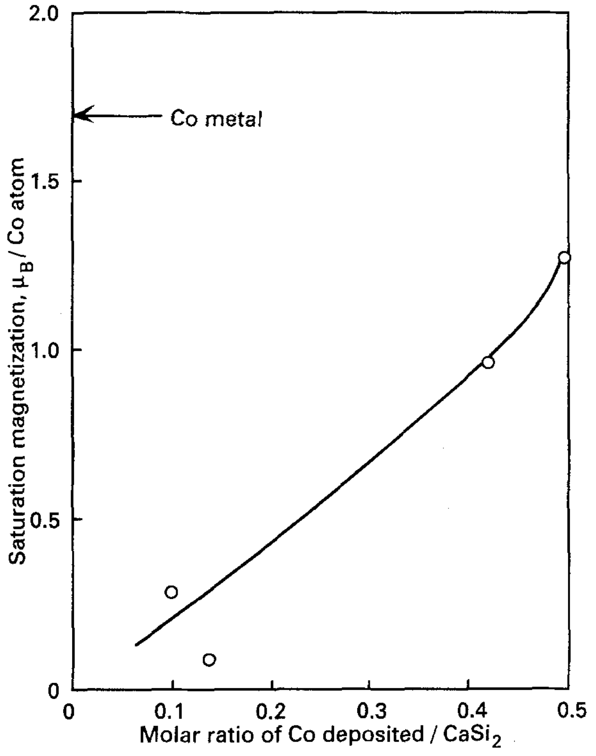

Figure 4 Saturation magnetization of the samples having different degrees of cobalt deposition on the surface.

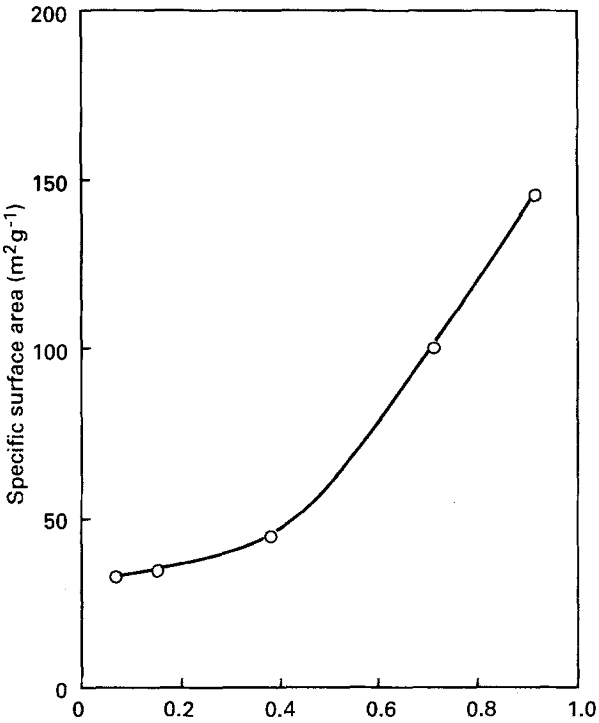

Figure 5 Specific surface area of the $CaSi_2$ samples after different degrees of deintercalation of calcium.

cobalt deposited to $CaSi_2$. The saturation magnetization increases with increasing amount of cobalt deposited, approaching the value of cobalt metal [14] as shown in the figure. These results suggest that in the early stages of the reaction, the particle sizes of the cobalt deposited on the surface were so small that they were in the range of those having superparamagnetic character. Even for the samples having large amounts of cobalt deposited on the surface, large coercive magnetic fields were observed in the hysteresis loops in Fig. 3. This suggests that the primary particle size of the deposited cobalt metal is pretty small. These findings are in good agreement with the fact that the presence of crystalline phase of cobalt metal was hardly detected by the XRD measurement of the samples before annealing. The metal particles are poorly crystalline, and should be smaller than 10 nm in size.

3.3. Surface area

The surface areas were measured on the samples obtained, using different concentrations of $CoCl_2$ solutions. The results are shown in Fig. 5. The $CaSi_2$ layered crystals were disintegrated into a number of thin platelets as the deintercalation of calcium proceeded. The large specific surface area of the oxidized sample and its increase with oxidation indicate that the platelets formed are very thin. The reaction appears to occur by a topochemical mechanism.

3.4. SEM and EDX studies

Fig. 6 shows a scanning electron micrograph of a $CaSi_2$ crystal oxidized in a 0.2 M $CoCl_2$ solution. It is clearly shown that the crystals are cleaved into a number of thin platelets with an apparent thickness less than 0.2 μm. The BET nitrogen adsorption analysis suggests that the real thickness of the platelet is much thinner than the apparent thickness. The location of the cobalt metal deposited was analysed by a line and a plane scanning using an EDX spectrometer. The line profile and the dot map image of CoK_α are shown in Fig. 7. As seen from the photographs, the cobalt is deposited mainly on the edge surface of the crystals (amorphous) rather than on the plane surface. It is also clear that the subsequent deposition of the metal occurs on the metal first deposited as a projection.

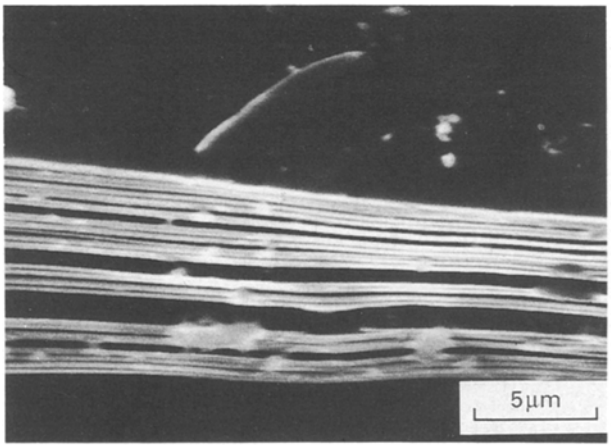

Figure 6 Scanning electron micrograph of the $CaSi_2$ sample after the treatment with a 0.2 M $CoCl_2$ solution.

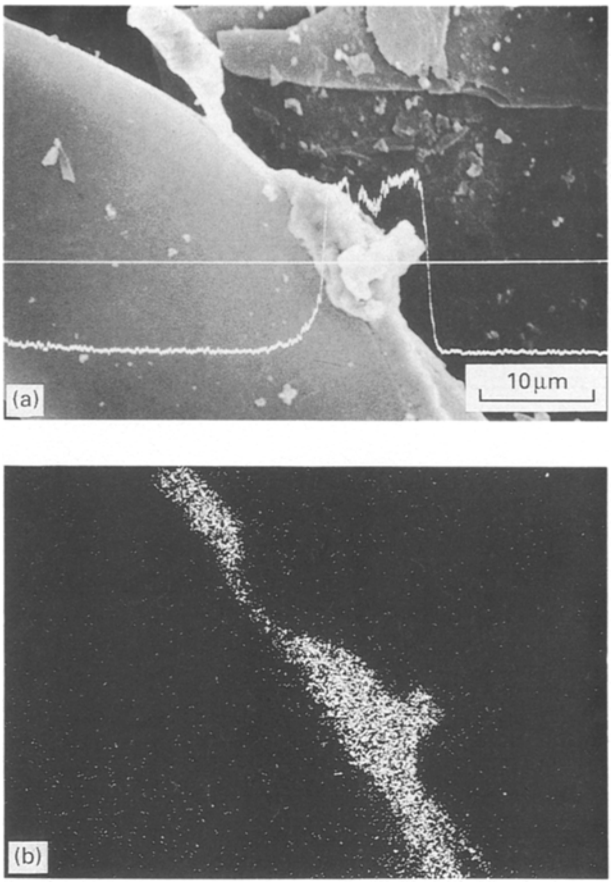

Figure 7 (a) A line profile and (b) a dot map image of CoK_α of the sample shown in Fig. 6.

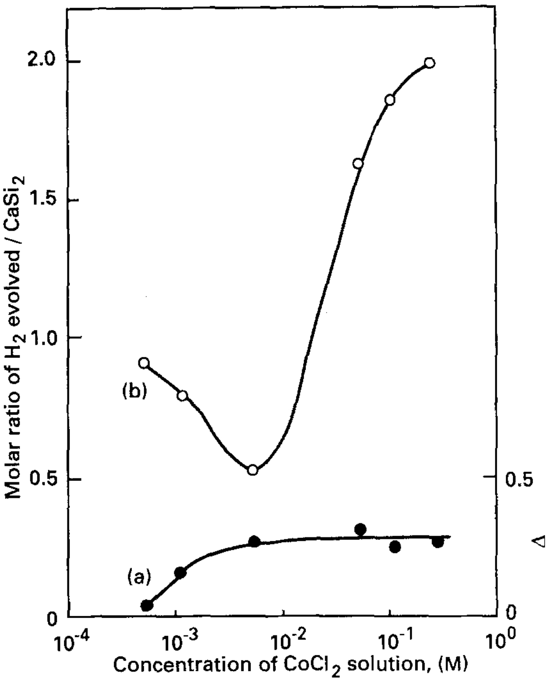

Figure 8 Difference curve. The difference, Δ, (a) (Δ = [the number of moles of calcium deintercalated] − [the number of moles of cobalt deposited] per mole $CaSi_2$), is compared with the number of moles of hydrogen evolved (b).

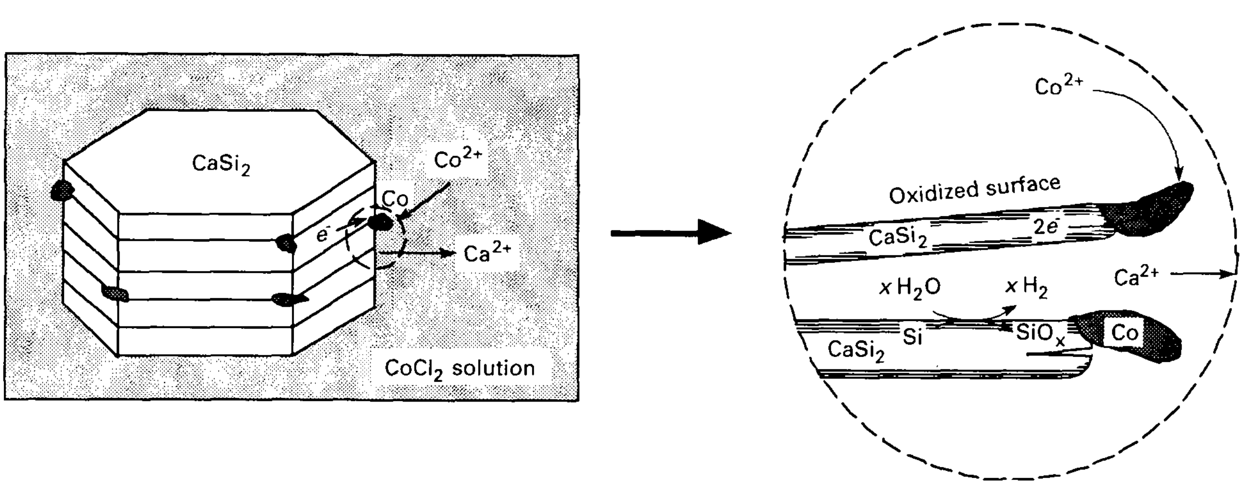

Figure 9 Schematic illustration of the oxidation reaction of $CaSi_2$.

4. Discussion

It is apparent that the oxidation of $CaSi_2$ is initiated by the oxidation of the interlayer calcium atoms with $CoCl_2$ accompanied by the simultaneous deposition of cobalt metal on the surface. As shown in Fig. 2, the ratio of the number of moles of calcium deintercalated to the number of moles of $CaSi_2$ is larger than that of cobalt deposited on the $CaSi_2$. The excess amount of calcium deintercalated is compared in Fig. 8 with the amount of hydrogen evolved as a function of the concentration of the $CoCl_2$ solution. If only the excess amount of calcium is responsible for the formation of hydrogen by the reduction of water, the total amount of hydrogen evolved should be comparable with the excess amount of calcium, which is much smaller than the amount observed. It is apparent that the most of the hydrogen evolved is due to the oxidation of the silicon network with water. As shown by the scanning electron micrograph, and the finding that the BET surface area increases as the reaction proceeds, the $CaSi_2$ layered crystals are cleaved into very thin platelets, exposing the fresh interlayer surface (Si_n) to the $CoCl_2$ solution. Such a surface must be very reactive, and easily oxidized with water, forming hydrogen gas. If a 0.2 M $CoCl_2$ solution is used, almost all calcium atoms are removed with evolution of 2 mol hydrogen per mol $CaSi_2$. The overall equation for the reaction can be written as

$$CaSi_2 + Co^{2+} + xH_2O \rightarrow [Co]^0(SiO_{x/2})_2 + Ca^{2+} + xH_2\uparrow \qquad (1)$$

It is interesting to note that the evolution of hydrogen has a minimum against the concentration of the $CoCl_2$ solution used. This can be interpreted in terms of the presence of two competing reactions. The $CoCl_2$ aqueous solutions are acidic, of the order of pH 3–4. In the lower concentration $CoCl_2$ solution, $CaSi_2$ would be attacked by H^+ ions as in the reaction with a low-concentration HCl solution. In the higher concentration $CoCl_2$ solutions, the reduction by Co^{2+} ions would be more predominant. Therefore, in the $CoCl_2$ solutions with low concentrations, the hydrogen evolution mainly arises from the reduction of H^+ ions with $CaSi_2$, while in the higher concentrations, $CaSi_2$ is first oxidized with the Co^{2+}, which is followed by the cleavage of the crystals into thin platelets. Most of the hydrogen emanates from the oxidation of the silicon network.

The EDX analysis of cobalt indicates that the reduction of Co^{2+} occurs at the edge of the crystal. This can be explained by a schematic model of the reaction shown in Fig. 9. The oxidation of calcium occurs at the edge in the first step, where the interlayer calcium atoms are oxidized and removed from the layer as Ca^{2+} with a simultaneous deposition of cobalt on the edge. The surface plane of the $CaSi_2$ crystals must be oxidized and covered with an electrically insulating oxide layer. The subsequent deposition of cobalt is made on the cobalt metal at the edge, where the transfer of electrons between Ca and Co^{2+} would occur easily. Hydrogen would be evolved from the freshly formed interlayer surface.

From a different point of view, this oxidation reaction can be characterized as a new process for the preparation of finely dispersed cobalt metal on a silica substrate. Because the resulting solids have a surface area as high as 150 $m^2 g^{-1}$, interesting applications to catalysts and reactive adsorbents are expected. This process is not confined to cobalt salts as an oxidant, but a variety of transition metal salts are also applicable, which are now under investigation.

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