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Changes in Surface Appearance of Silver Chloride De-ammoniated after Complexation with Liquid, Gaseous and Aqueous Ammonia[1)]

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Particles of AgCl were soaked in liquid NH_3 or exposed to gaseous NH_3. The ammine complexes thus formed were unstable when exposed to the atmosphere but showed characteristic X-ray patterns and differential scanning calorimetry (DSC) curves. The complex formed by soaking was found to be the triammine complex from the weight decrease after de-ammoniation and the AgCl particles recovered were seen to be porous rods on scanning electron micrographs. On the other hand, the sesquiammine complex was formed by prolonged exposure to gaseous NH_3. The AgCl particles obtained *via* this complex retained the external form of the original particles and were also porous when observed under an electron microscope.

The specific surface areas of the particles obtained *via* the triammine and the sesquiammine complexes were greatly increased and reached 2.9 ± 0.1 and $1.4 \pm 0.1\ m^2/g$, respectively. These particles were disintegrated to some extent by applying mechanical force but the specific surface areas were decreased due to contraction of the pores resulting from the intrinsic plasticity of AgCl.

In addition, AgCl was dissolved in aqueous NH_3 and the NH_3 was subsequently removed by evaporation and by freeze-drying. In the case of evaporation, AgCl was recovered as large polyhedral crystals. Since porous particles of AgCl were absent, it is clear that the crystals were directly formed from the aqueous solution without separation of solid ammine complexes. On the other hand, when the aqueous solution was freeze-dried, the recovered particles of AgCl showed porous structure and the specific surface area was found to be $3.5\ m^2/g$. Therefore, it was considered that an ammine complex—presumably the diammine complex—crystallized out during freezing of the aqueous solution.

Finally, the apparent specific volumes were measured and it was found that the intraparticle void, and in some cases the external shape of the secondary porous particles, exerted a considerable influence on the packing.

Keywords——AgCl ammine complex; surface appearance after de-ammoniation; plastic deformation; scanning electron microscopy; specific surface area measurement; apparent specific volume measurement; differential scanning calorimetry

It was previously confirmed[1,2)] that many organic compounds form molecular adducts with NH_3 and that the size of particles of the compounds could be greatly reduced by eliminating the combined NH_3 from the adducts. In the case of inorganic materials, adduct formation generally occurs in the form of the ammine complex or the ammoniate; however, no attempt was made to examine the micromeritical changes of the particles recovered *via* the complex or the ammoniate.

In the present paper, ammine complexes of AgCl were isolated by treating AgCl with liquid and gaseous NH_3 or were formed in solution by dissolving AgCl in aqueous NH_3. AgCl was recovered by eliminating the added NH_3 from the solid complexes or from the solution. Considerable differences in the surface appearance as well as in the specific surface area were noticed among the original and the recovered AgCl particles.

Experimental

Materials——1. AgCl: Reagent of special grade. Under the electron microscope, it was observed as masses of round pebbles. 2. NH_3: Liquid NH_3 in a steel bomb. The guaranteed purity was over 99.999%. 3. Ammonia water: Special grade reagent containing 25.0 w/v% of NH_3.

Complex Formation and Subsequent Elimination of NH_3—1) Soaking in Liquid NH_3: The apparatus and the procedure were almost the same as described in the previous papers.[1,2] In each run, 5 g of AgCl was used and the volume of liquefied NH_3 was kept at about 30 ml by adjusting the flow from the bomb. Since both AgCl and the ammine complex were slightly soluble in liquid NH_3, the content in the flask was in some cases agitated with a magnetic stirrer to promote complexation.

After soaking had been carried out for several hours, introduction of NH_3 was stopped, and the free and combined NH_3 were eliminated by allowing the mixture to stand in the open air. The residue was determined by X-ray diffractometry to be AgCl itself.

2) Exposure to Gaseous NH_3: A sample flask equipped with an Hg manometer and containing 5 g of AgCl was evacuated, then NH_3 gas was introduced gradually at about 25 °C until the content was partly or completely saturated. When the complexed product was exposed to the open air, only AgCl was recovered.

3) Mixing with Aqueous NH_3: AgCl (1.0 g) was dissolved in 100 ml of 15% ammonia water at room temperature. After filtration, the solution was kept at 70 ± 2 or 37 ± 1 °C. In each case, crystals of AgCl was separated as NH_3 was removed from the solution.

In another experiment, 0.5 g of AgCl was dissolved in 150 ml of 5% ammonia water. Then, the solution was directly freeze-dried. Both NH_3 and water were eliminated in the vapor state, and the residue was again AgCl.

Measurement of Weight Decrease by Desorption——A flask equipped with a stopcock was used for soaking and for weighing. After free NH_3 had largely evaporated from the soaking mixture, the flask was half-closed,[3] and the weight decrease was measured continuously with a chemical balance. The desorption rate became progressively slower under normal atmospheric conditions, and the pressure in the sample flask was reduced to about 50 mmHg. Weighing was repeated intermittently until the weight of the sample reached a constant value. The surrounding temperature was maintained at 25 ± 1 °C during the course of measurement.

Measurement of Weight Increase by Sorption——Using the same apparatus as that for complexation with gaseous NH_3, the weight increase due to the uptake of NH_3 was measured at intervals. Throughout the measurement, the sample flask was kept at 25 ± 1 °C.

X-Ray Powder Diffractometry——The instrument used was a JEOL JDX-7F X-ray diffraction analyzer (Cu-$K\alpha$ radiation, $\lambda = 1.542$ Å, Ni filter). The scanning speed was 4 °/min; therefore, about 6 min were needed for one run between 2θ values of 25 and 50 °. In the case of the ammine complexes, the sample chamber was cooled with dry ice, if necessary.

Scanning Electron Microscopy——Appearances of the original AgCl and AgCl recovered after complexation and subsequent de-ammoniation were observed with a scanning electron microscope (Hitachi-Akashi model MSM-4).

Measurement of Specific Surface Area——A BET gas adsorption apparatus (model P-850, Shibata Chemical Apparatus Mfg. Co., Ltd.) was used. In most cases, a sample weight of 3—5 g was taken. The adsorbate was N_2 gas.

Differential Scanning Calorimetry (DSC)——A SSC/560S differential scanning calorimeter (Seiko Instruments & Electronics Ltd.) was used. The heating rate adopted was 1 or 5 °C/min.

Measurement of Apparent Specific Volume——An appropriate amount of the sample was taken in a 10 ml graduated tube with a flat bottom. Tapping from a height of 10 cm was repeated 300 times, then the apparent specific volume was measured.

Results and Discussion

Identification of Ammine Complexes

1. Complex Formed by Soaking in Liquid NH_3——The curve in Fig. 1 shows the weight decrease of the sample wetted with a trace of liquid NH_3. From the change in weight between the initial shoulder and the final horizontal section, the molecular ratio of the complex was determined to be 1 : 3 ($AgCl : NH_3 = 1 : 3.06 \pm 0.07$). Also, the presence of the middle plateau indicated that the release of NH_3 occurred by way of the more stable sesquiammine complex ($AgCl : NH_3 = 1 : 1.47 \pm 0.09$).

The same de-ammoniation process was demonstrated by repeated X-ray measurements as shown in Fig. 2. The X-ray patterns of the sample were ultimately simplified to that of AgCl belonging to the cubic system; however, new diffraction peaks (2θ: 28.9, 34.4, 42.0 ° *etc.*)

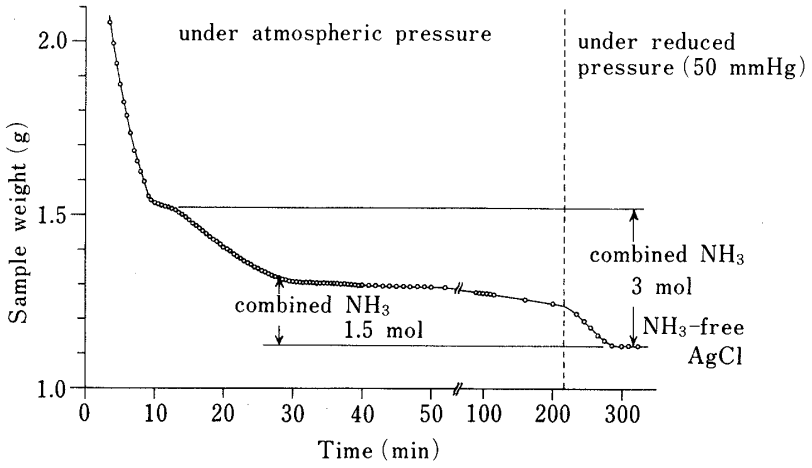

Fig. 1. Weight Decrease Due to Desorption from the Ammine Complex of AgCl Prepared by Soaking AgCl in Liquid NH_3 (25 ± 1 °C)

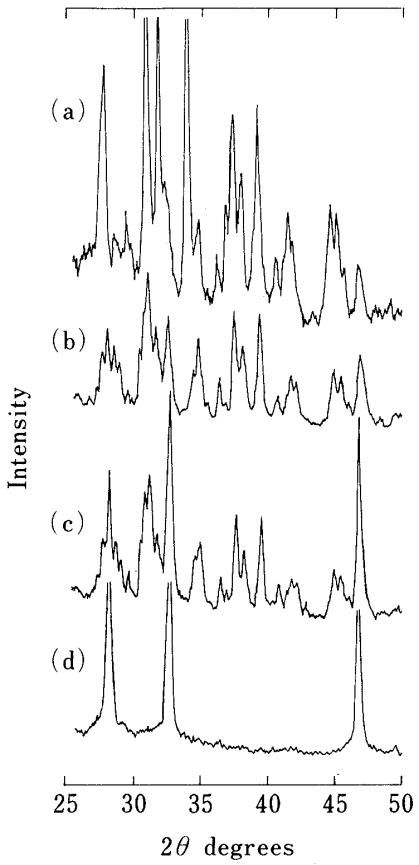

Fig. 2. X-Ray Diffraction Pattern of the Triammine Complex of AgCl and Its Changes during Measurement

(a) Immediately after sampling, (b) after 7 min, (c) after 14 min, (d) after 28 min (pattern of AgCl alone; complete desorption).

appeared in the repeated runs which were similar to those of the sesquiammine complex formed by exposure to NH_3 gas. It was thus confirmed that the triammine complex was formed by soaking with liquid NH_3 and that AgCl was recovered under open conditions *via* the sesquiammine complex.

In contrast, two different DSC curves were obtained under closed conditions with the same triammine complex (Fig. 3). At a slow heating rate, all the peaks appeared below 100 °C, while at a rapid heating rate, the peaks shifted to significantly higher temperatures. Although conclusive assignments were now difficult, each of the first peaks may be ascribed to either the stable or the metastable peritectic liquefaction of the triammine complex. Also, as described

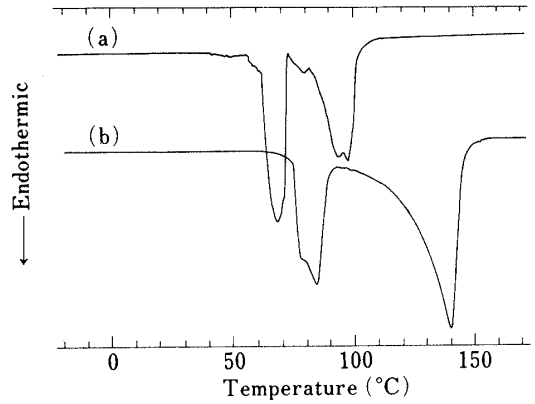

Fig. 3. DSC Curves of the Triammine Complex under Closed Conditions

(a) Heating rate, 1 °C/min; sample weight, 20.5 mg.
(b) Heating rate, 5 °C/min; sample weight, 6.7 mg.

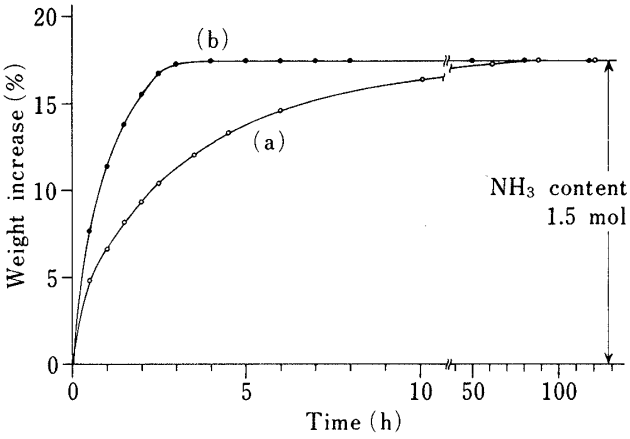

Fig. 4. Weight Increase of AgCl Particles Due to Sorption of Gaseous NH_3 (25 ± 1 °C)

(a) Curve for the original particles (specific surface area, 0.3 m^2/g).
(b) Curve for the once-desorbed particles (specific surface area, 1.4 m^2/g).

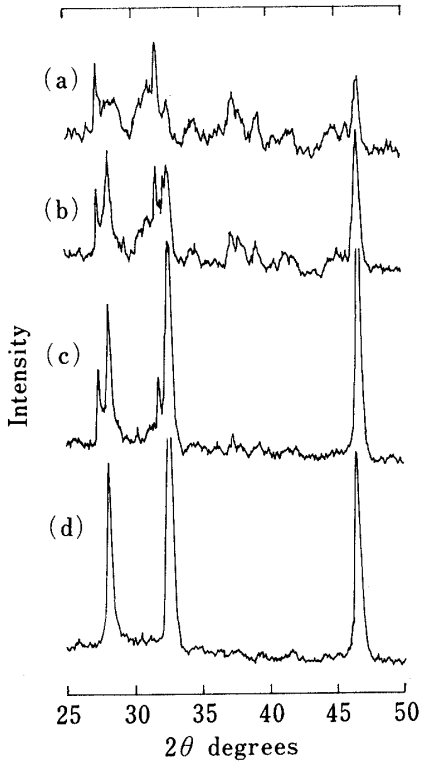

Fig. 5. X-Ray Diffraction Pattern of the Sesquiammine Complex of AgCl Prepared by Exposure to Gaseous NH_3 and Its Changes during Measurement

(a) Immediately after sampling, (b) after 7 min, (c) after 21 min, (d) after 35 min (pattern of AgCl alone; complete desorption).

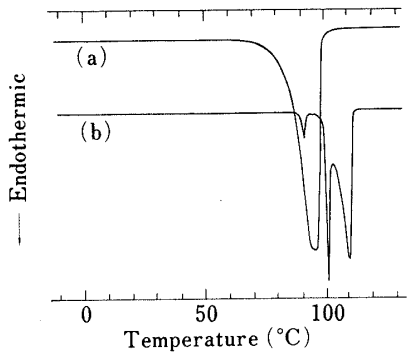

Fig. 6. DSC Curves of the Sesquiammine Complex of AgCl under Closed Conditions

(a) Heating rate, 1 °C/min; sample weight, 13.7 mg.
(b) Heating rate, 1 °C/min; sample weight, 15.9 mg.

later, the second peaks below and beyond 100 °C may be due to melting of the sesqui- and probably the monoammine complex, respectively.

2. Complex Formed by Exposure to Gaseous NH_3——As shown in Fig. 4, the original particles of AgCl absorbed NH_3 gradually until the amount reached just 1.5 mol per mol of AgCl ($AgCl : NH_3 = 1 : 1.48 \pm 0.02$). However, as reported in the literature,[4] once the combined NH_3 was removed, the recovered AgCl particles could be saturated with NH_3 much

more rapidly. In any case, it was certain that the sesquiammine complex was formed by sorption. It was also confirmed from the changes of X-ray patterns in Fig. 5 that the complex was de-ammoniated directly to AgCl in the atmosphere.

On the other hand, as shown in Fig. 6, the sesquiammine complex gave two different DSC curves at the same heating rate. The single endothermic peak in one curve (a) is clearly assignable to melting of the complex itself. Accordingly, the initial small peak in the other curve (b) should be attributable to partial melting of the complex; however, the appearance of the higher two peaks is difficult to explain. The monoammine complex, which is known as the lowest and the most stable one among the complexes between AgCl and NH_3, may be

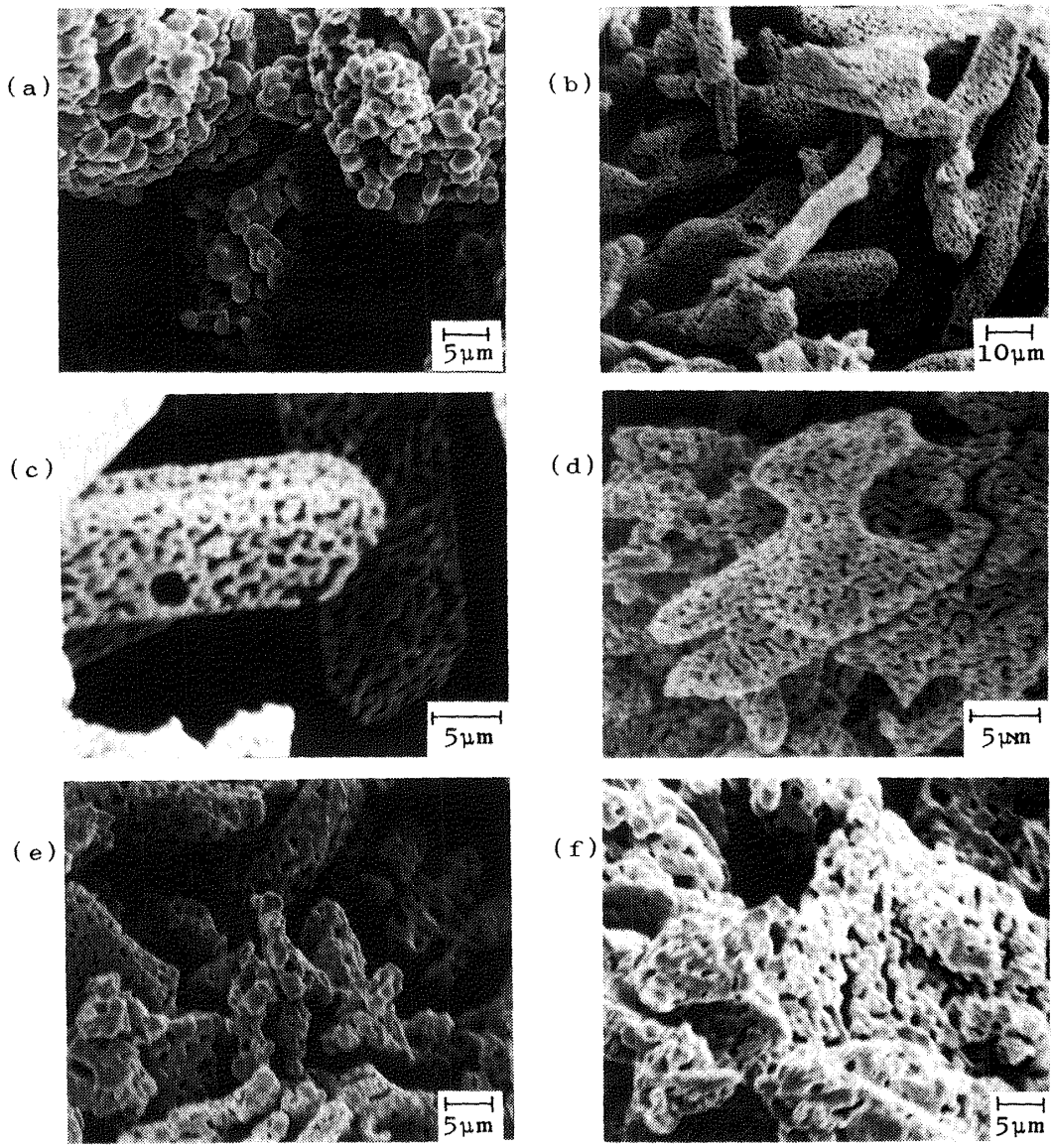

Fig. 7. Scanning Electron Micrographs of the Original Particles of AgCl and of Particles Recovered *via* Soaking in Liquid NH_3

(a) Original particles (commercial product), 2000×.
(b) and (c) Particles recovered *via* soaking, 1000× and 3000×.
(d) Particles recovered *via* soaking under stirring, 3000×.
(e) Particles after trituration with agate mortar and pestle (300 strokes) of the particles recovered *via* soaking, 2000×.
(f) Particles after disintegration with a high-speed mixer (2000 rpm for 20 min) of the particles recovered *via* soaking suspended in water, 2000×.

concerned in the phase reactions producing these heat effects.

Incidentally, the complex formed in the aqueous NH_3 solution could not be separated and identified. However, it is considered that the one will be the ionizable diammine complex, which is well known in analytical chemistry.

Changes in External Appearance and in Specific Surface Area after De-ammoniation

1. Particles of AgCl *via* Soaking in Liquid NH_3——Electron micrographs of the original AgCl and AgCl recovered after soaking are shown in Fig. 7. The particles before soaking consisted of round pebbles with almost smooth surfaces, while those formed by way of soaking were rod-like in external shape but showed a rough structure with many irregular pores. It is likely that these porous rods are "skeleton" particles originated from the crystals of the triammine complex.

Such a change in appearance should reflect an increase in surface area. As expected, the specific surface area of the recovered AgCl increased according to the time of soaking and ultimately attained a maximum value of $2.9 \pm 0.1\ m^2/g$ (Table I).

When the mixture was agitated during soaking with a magnetic stirrer, it was found, as shown in Fig. 7 (d), that the rods disintegrated into irregular particles. However, the porous structure was unchanged. In addition, it was confirmed that stirring of the soaking mixture caused the specific surface area to increase more rapidly to the maximum value, due probably to easier penetration of the liquid NH_3. It is also clear that the irregularity of the particles formed by stirring is ascribable to plastic deformation of the triammine complex itself.

In contrast, when the rods of the recovered AgCl were triturated with a mortar and pestle or when an aqueous suspension of the rods was vigorously agitated with a high-speed mixer, the specific surface area of the product was decreased (Table I). This seems surprising, but is consistent with the change in appearance under the electron microscope. Although the

TABLE I. Specific Surface Areas and Apparent Specific Volumes of the Original AgCl Particles and the AgCl Particles Recovered after Complexation

Source	Period of soaking or sorption	Specific surface area (m^2/g)	Calculated mean diameter[a] (μm)	Apparent specific volume (cm^3/g)
Original AgCl	—	0.3	3.6	0.7
AgCl recovered after				
1) Soaking	1.5 h	1.4 ± 0.2	0.8	1.0—1.2
	5 h	2.9 ± 0.1	0.4	1.3—1.4
2) Soaking under stirring	30 min	3.0	0.4	1.4
3) Soaking and subsequent mechanical disintegration				
a) Trituration with mortar and pestle	300 strokes	0.5	2.2	0.8
b) Agitation of the aqueous suspension with a high-speed mixer	20 min	1.3	0.8	0.6
AgCl recovered after				
1) Single gas sorption	3 h	0.5	2.2	0.8
	24 h	0.9	1.2	1.0
	60 h	1.3	0.8	1.0
	120 h	1.4 ± 0.1	0.8	1.0
2) Repetition of sorption and desorption two, three and four times	Each 24 h	1.4 ± 0.1	0.8	1.7—1.8
AgCl recovered after freeze-drying	—	3.5	0.3	2.7

a) $d = 6/(\rho \cdot S)$; d, mean diameter; ρ, density (5.56); S, specific surface area.

skeleton particles (rods) were somewhat size-reduced, the porous structure was considerably contracted as shown in Fig. 7 (e) and (f). Such a phenomenon can be explained in terms of the inherent plasticity of AgCl.

2. Particles of AgCl *via* Exposure to Gaseous NH_3——Electron micrographs of the product after de-ammoniation are shown in Fig. 8. It is evident that the longer the time of exposure, the more expanded were the secondary particles of AgCl. In each case, the external shape was similar to that of the original particles. The porous surface structure was still observed, but it seemed that the primary particles were bridged more loosely as compared with those obtained *via* soaking. In fact, they were divided into independent fine particles by mild stirring in water (Fig. 8 (c)).

As shown in Table I, the specific surface area was increased very gradually by single exposure and subsequent de-ammoniation, but a maximum was finally reached after about 120 h. On the other hand, the same maximum was more rapidly attained by repeating the cycle even if the first exposure time was insufficient for full complexation. This can be explained in terms of easier penetration of NH_3 gas to the unreacted part of the original AgCl. It is interesting that the maximum value *via* exposure was found to be $1.4 \pm 0.1\ m^2/g$, and was about one-half of the corresponding value *via* soaking. This difference may be related to the difference in the number of NH_3 molecules combined.

3. Particles of AgCl *via* Mixing with Aqueous NH_3——In the compositions of the solutions used in the present experiments, the added AgCl was dissolved completely in the form of the diammine complex.[5] As shown in Fig. 9 (a), when the dissolved NH_3 was eliminated by evaporation, it was found that large polyhedral crystals of AgCl separated out.

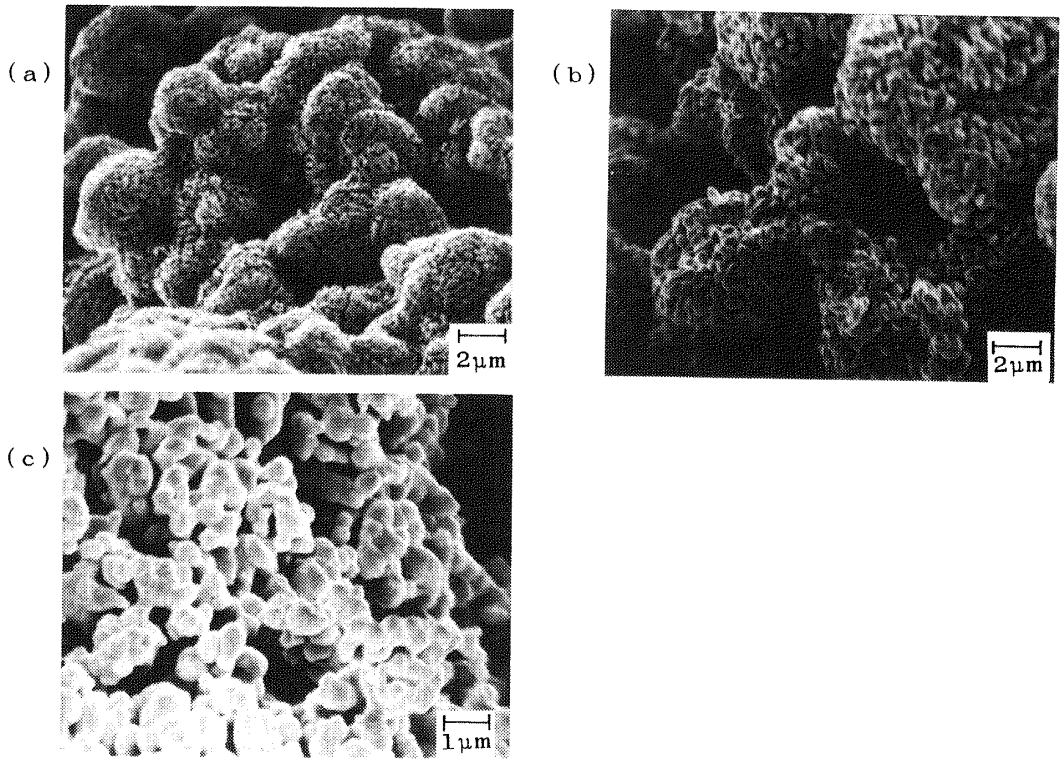

Fig. 8. Scanning Electron Micrographs of AgCl Particles Recovered *via* Exposure to Gaseous NH_3

(a) Particles recovered after exposure for 3 h, 5000×.
(b) Particles recovered after exposure for 120 h, 5000×.
(c) Particles after mild stirring of the particles recovered after 120 h exposure suspended in water, 10000×.

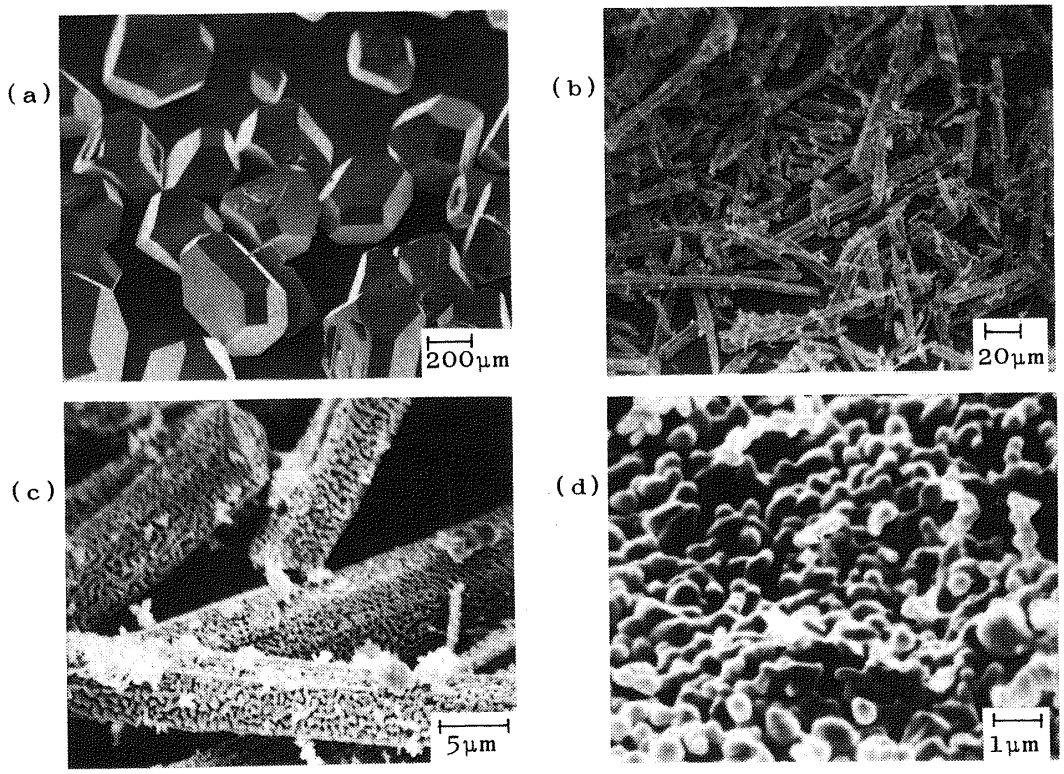

Fig. 9. Scanning Electron Micrographs of AgCl Particles Recovered *via* Mixing with Aqueous NH_3

(a) Crystals after evaporation of aqueous NH_3 solution, 50×.
(b), (c) and (d) Particles recovered after freeze-drying, 400×, 3000×, 10000×.

Since in this case, porous AgCl particles were absent, the crystals must have been directly formed from the solution.

On the other hand, when the aqueous solution was freeze-dried, the product was found to consist of elongated porous rods with some fines attached to them (Fig. 9(b)—(d)). Accordingly, it is evident that the diammine complex, though it was not identified, separated as a solid phase during freezing. As shown in Table I, the specific surface area was determined to be $3.5\,m^2/g$ which is significantly larger than those obtained by the former two processes. This suggests that size reduction due to formation of the eutectic mixture[6] is involved at least in part during the freeze-drying.

Apparent Specific Volumes of the Recovered Particles of AgCl

In order to determine the effects of size, external shape and interparticle void on the packing of the porous material, the apparent specific volumes of the AgCl particles recovered by way of the three ammine complexes as well as that of the original particles were measured under defined conditions. As shown in the last column of Table I, the values differed considerably and it was found that the void or the porosity of the recovered secondary particles was affected as follows.

(1) When stirring of the soaking mixture was applied, the particles after deammoniation became irregular in shape and at the same time, their size was somewhat reduced. However, the apparent specific volume was almost the same as that of the rods obtained simply by soaking. Since the intraparticle void would not be change by stirring, the

effects of the size and shape of the secondary particles should be negligible in such cases.

(2) When the porous rods obtained *via* soaking were triturated or disintegrated in suspension, the products were appreciably size-reduced but the apparent specific volumes were significantly decreased. Thus, the decrease of intraparticle void due to plastic deformation outweighs the increase due to size-reduction.[7)]

(3) The external forms of the original AgCl particles and of particles obtained *via* single exposure were similar; accordingly, the difference between their apparent specific volumes should also have resulted from differences in the void volumes of the particles themselves.

(4) The apparent specific volume after repeated gas exposure was much increased as compared with the volume after a single exposure. Since the specific surface area was the same in both cases, such an increase can be explained in terms of expansion of the void space during repeated de-ammoniation.

(5) The apparent specific volume of particles obtained *via* freeze-drying was found to be much larger than those of particles obtained *via* soaking and gas exposure. Since the rods recovered after freeze-drying were especially elongated, packing would be difficult in particular.

References and Notes

1) This paper forms Part XXII of the series entitled "Studies on Methods of Particle Size Reduction of Medicinal Compounds." The preceding paper, Part XXI: S. Abd-Elfattah, K. Okamoto, K. Chihara, K. Shirotani, Y. Tsuda, E. Suzuki, and K. Sekiguchi, *Chem. Pharm. Bull.*, **31**, 3649 (1983).
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4) H. Hemmi, *J. Chem. Soc. Jpn.*, **53**, 841 (1932).
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6) E. Suzuki, K. Shirotani, Y. Tsuda, and K. Sekiguchi, *Chem. Pharm. Bull.*, **27**, 1214 (1979).
7) It is generally known in powder science (micromeritics) that the apparent specific volume of nonporous particles increases with decrease of their size, if fines are absent.