  Bull. Chem. Soc. Jpn., 62, 3457—3463 (1989)

Synthetic Inorganic Ion-Exchange Materials. LI. Synthesis, Characterization, and Thermal Decomposition of Cubic Ammonium Molybdate

Abdul Jabbar KHAN, Masamichi TSUJI, and Mitsuo ABE*
Department of Chemistry, Faculty of Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152
(Received April 27, 1989)

A crystalline cubic ammonium molybdate (CAM) was synthesized by the reaction of hexaammonium heptamolybdate and HNO_3 at 60 °C. The X-ray diffraction pattern showed a body-centered cubic structure with crystal lattice of 12.94±0.005 Å. Ammonia free molybdic acid was not obtained even at high acid concentration. CAM contains both exchangeable and structural ammonium ions. On the basis of chemical and thermal analyses and amount of exchangeable H^+, the empirical formula of the H^+ form of CAM referred to $[H_{0.68}(NH_4)_2]O_{1.34}\cdot 14.16MoO_3\cdot 6.92H_2O$. CAM was found to be stable at relatively high acid concentration and temperature, and was suitable for column operations by grading to the desired mesh size.

The oxides and hydrous oxides of molybdenum have been known since 1826.[1] This field got a real interest after Carpenie.[2] Preparation and structure of various molybdenum oxides, hydrates or ammonium molybdates have been studied by different authors. According to Jander et al.[3] the polycondensation of tri, hexa, 12, and 24 molybdates takes place at low pH. A significant number of authors have investigated the polymerization reaction through different analytical means.[2,4-14] A general review for normal ($M_2Mo_3O_{12}$), poly ($M_2Mo_nO_{3n+3}$), and basic ($n<3$) molybdates has been reported by Gleitzer.[15] Ma[16] and Kiss et al.[17] have reported the formation of different Mo(VI) oxide hydrates with ill-defined composition, through the thermal decomposition of ammonium heptamolybdate tetrahydrate. According to Tytko et al.[18] the aqueous chemistry of polymolybdates is very complex. The acid concentration controls the protonation to mono and dibasic species of MoO_4^{2-} present in basic solutions.

Hydrous Mo(VI) oxide or isopolymolybdates have been the subject of research of a significant number of workers. Even though Abe[19] has reported some ion-exchange behavior of $MoO_3\cdot nH_2O$, further investigations were still required to study the optimum conditions or rate of reaction for the synthesis of such compounds. In addition the formation of a product with definite composition by the reaction of hexaammonium heptamolybdate and nitric acid has not been known with certainty. Moreover the definite ion exchange behavior of these materials has not been reported prior to our study.

The present investigations were therefore carried out to describe the systematic synthesis, characterization, thermal decomposition, and some ion-exchange properties of crystalline cubic ammonium molybdate (CAM) as an ion exchanger.

Experimental

Synthesis of CAM. The optimum conditions and reagent specifications for the synthesis of the final product were set up through consideration of starting material and its concentration, $[H^+]/[Mo(VI)]$ mole ratios, aging time and temperature. The apparent rate of reaction for the product formation was determined for a series of samples with different mole ratios. The yields (%) of different products were calculated from the change in molybdenum concentration in the supernatant solutions with respect to the aging time. The Mo concentration was determined by Inductively Coupled Plasma (ICP) spectrometer, model SPS-7000, Seiko Instruments Inc. (Japan). The final synthesis of CAM was carried out as follows.

A 0.2 M (M=mol dm^{-3}) (as Mo-concn) solution of hexaammonium heptamolybdate was added slowly to an equal volume of 0.2 M HNO_3 solution with constant stirring. The mixed solution was kept at 60 °C for three days and then cooled at room temperature. A yellow product was filtered under suction and washed with deionized water till pH>2 and dried in air at room temperature.

H-CAM. CAM (100—200 mesh) was conditioned with 0.5 M HNO_3 in a column till no ammonium ion was detected in effluent, followed by washing with deionized water till pH>2 and was dried in air. The product was again sieved and rewashed to remove the adherent tiny particles. H-CAM thus obtained was finally dried in air and then over silica gel.

A-CAM. The NH_4^+ form of CAM was obtained by successive batch equilibration of H-CAM with 0.1 M NH_4NO_3 solution.

Chemical Composition. The chemical composition of H-CAM was determined by the chemical and thermal analyses. A known quantity (0.1 g) of the sample was dissolved in an adequate volume of 0.1 M NaOH solution. The total ammonia was then determined by Nessler's method spectrophotometrically at 400 nm using a double beam spectrophotometer, model UV-150-02, Shimadzu Co. (Japan). The total molybdenum content of H-CAM was determined gravimetrically by lead(II) acetate precipitation following the Japan Industrial Standards method No. K-8905.

Thermal Analysis. The Rigaku Denki Thermoflex, model 8001, was employed for thermogravimetry (TG) and differential thermal analysis (DTA) at a heating rate of 10 °C min^{-1} using α-Al_2O_3 as a reference material. The ammonia evolved during the thermal decomposition of H-CAM in N_2 gas atmosphere and collected in 0.05 M H_2SO_4

was also determined spectrophotometrically by Nessler's method.

X-Ray Diffraction, IR Spectra, and Electron Microscopy. X-Ray diffractions were carried out with JEOL JDX-7E X-ray diffractometer, Rigaku Denki Co. (Japan), model CN-5320 A-1/CN-2155 D-5 and Philips Automated powder diffractometer model PW-1700, using Ni-filtered Cu $K\alpha$ radiations. The crystal structure was deduced by SANDMAN computer programs.[20-22] The IR spectra were measured by KBr disk method on a JASCO IR spectrometer, model DS-701 G. The JEOL scanning microscope, model JSM-T220, was incorporated for the study of crystal morphology and growth.

Reagents. Hexaammonium heptamolybdate tetrahydrate (Wako Pure Chemical Ind., Ltd. Japan) was used without further purifications. All other reagents used were also of analytical grade.

Results and Discussion

Synthesis. No precipitation was observed even at reasonably long keeping of the mixed solutions at room temperature. Fast precipitation at elevated temperatures (>80 °C) resulted in the reduction of the apparent crystal size. In order to decide the optimum conditions for synthesis, the rate of reaction was studied at different mole ratios of $[H^+]/[Mo(VI)]$ at 60 °C. The prereaction specification of the reactants is given in Table 1 along with yields of the samples in percent. The time dependence of yield in Fig. 1 is shown for the samples A—E. The crystal formation was slower with an increase in the $[H^+]/[Mo(VI)]$ mole ratio greater than unity. Yield of the products decreased with the increase in acid concentration (samples C—E or Q—S), whereas at very low acid concentration (sample A) it resulted in a composite product formation which required maximum aging time at 60 °C. Hence the acid concentration affected both the yield and the composition of CAM.

Table 1. The Specification of Reactants and Yield (%) of Products

Sample	Concn in mixed soln		Mole ratio	Yield
	[Mo(VI)]/M	$[H^+]$/M	$[H^+]/[Mo(VI)]$	%
A	0.11	0.055	0.5	46
B	0.11	0.11	1.0	99
C	0.11	0.55	5.0	86
D	0.11	0.88	8.0	51
E	0.11	1.10	10.0	51
N	0.06	0.03	0.5	0
P	0.06	0.06	1.0	98
Q	0.06	0.30	5.0	88
R	0.06	0.48	8.0	76
S	0.06	0.60	10.0	60

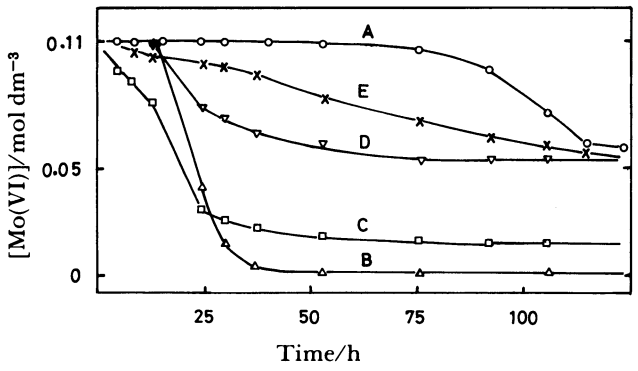

Fig. 1. Change in the concentration of Mo(VI) at different mole ratios of H^+/Mo(VI). Aging temp: 60 ±0.5 °C; initial [Mo(VI)]: 0.11 mol dm^{-3}; mole ratio: 0.5(A), 1.0(B), 5.0(C), 8.0(D), and 10.0(E).

The maximum yield was observed at the mole ratio of 1.0 upto aging time of 72 h irrespective of the HNO_3 concentration. A similar trend was also observed for those of samples P—S. Sample B, due to maximum yield and reasonable rate of formation, was considered for the bulk preparation and subjected to further investigations. In the case of lower concentration of HNO_3, no product was observed in sample N upto the same aging time as for sample A.

Scanning Electron Microscopy (SEM) and X-Ray Diffraction. The SEM photograph of the crystals (Fig. 2) showed the hexagonal crystal shape of CAM arising from the wall of the beaker like cluster of flowers and the crystals were quite large (100—200 μm) in size. Almost the same X-ray diffraction patterns were observed for all samples (B—E or P—S) studied (Fig. 3), except sample A which showed a mixture of CAM and unknown materials in the JCPDS files. The crystal system of the samples was indexed to the body centered cubic structure of space group I43m (Td^3) with a lattice constant (a_0) of 12.94±0.005 Å (Table 2). The H-CAM and A-CAM also showed the same a_0 value within the experimental error.

Thermal Analyses. The TG and DTA curves of CAM and A-CAM (Fig. 4) indicated a broad endothermic peak around 150—160 °C due to loss of H_2O, a small exothermic peak at around 300 °C due to loss of exchangeable NH_4^+ and a strong exothermic peak at around 430 °C due to loss of structural ammonia and water. The small exothermic peak at around 300 °C vanished in the DTA curve of H-CAM (Fig. 5) due to absence of exchangeable NH_4^+. However, a distinct rise in the DTA curve at around 310 °C ending in a sharp exothermic peak at around 430 °C indicates the existence of structural ammonia with different bonding strength. The fractions of ammonia evolved during thermal decomposition of H-CAM was collected with respect to each rise in heating temperature and analyzed (Fig. 6). The evolution profile was in accordance with the weight loss vs. temperature shown by the TG curve (Fig. 5). However the collected ammonia was 33.1% of the total ammonia (1.54%) in H-CAM. Obviously a considerable amount of NO_x was formed due to the oxidation of NH_3, even though the N_2 gas atmosphere was incorporated. It can be estimated that the evolved ammonia at 310—430 °C is

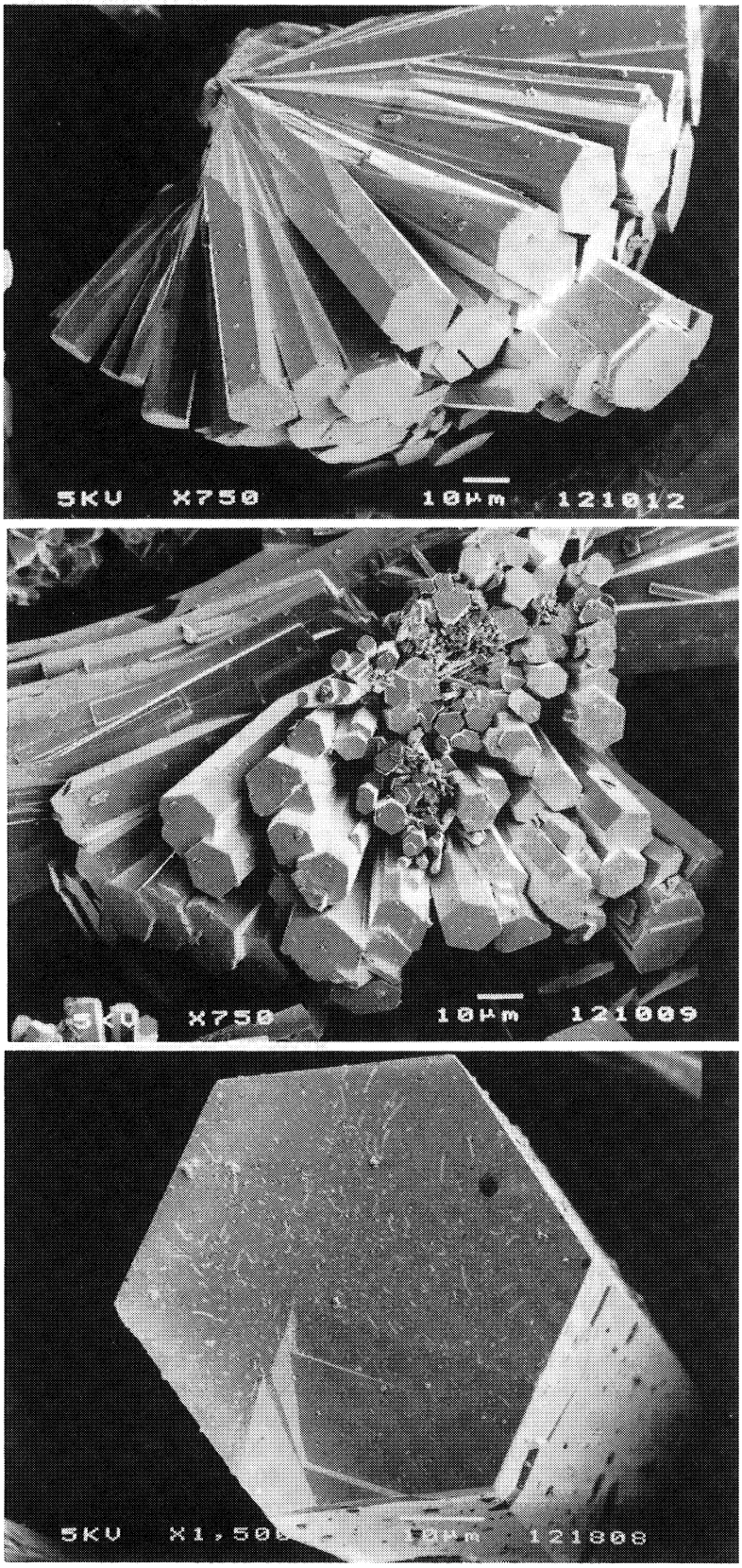

Fig. 2. SEM photograph indicating crystal growth of CAM.

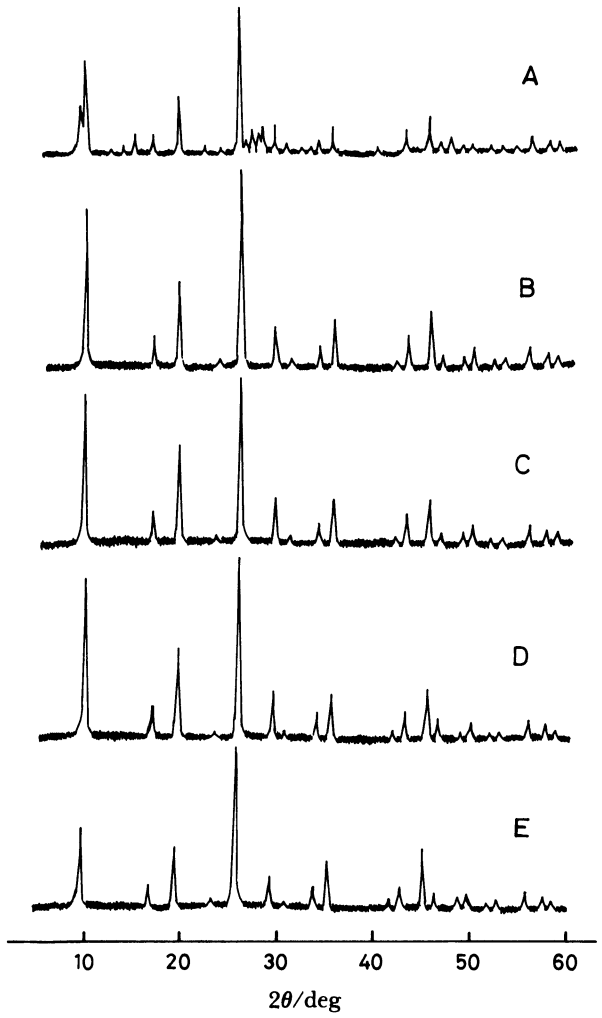

Fig. 3. The X-ray diffraction patterns of the samples A—E, synthesized at different H^+/Mo(VI) mole ratios; X-ray: Cu $K\alpha$.

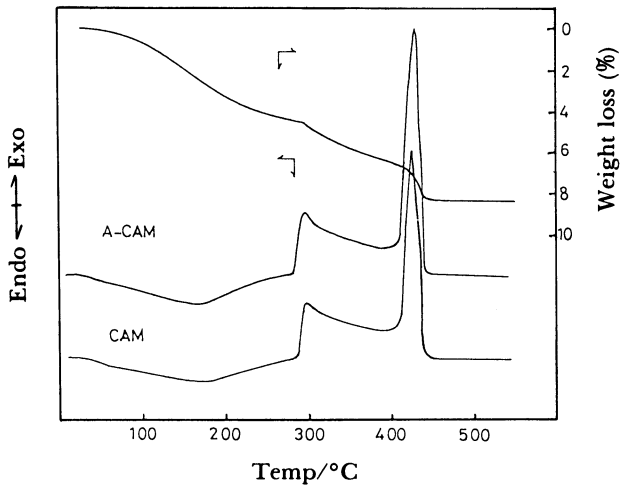

Fig. 4. The TG and DTA curves of CAM and A-CAM. Sample Wt: 0.1010 g; heating rate 10 °C min^{-1}; heating atmosphere: air.

Table 2. The X-Ray Diffraction Data of H-CAM (a_0=12.94±0.005 Å)

d_{obs} / Å	I/I_0 / %	d_{cal} / Å	hkl
9.1573	78.29	9.1500	110
5.2851	14.16	5.2827	211
4.5785	29.09	4.5750	220
3.4542	0.36	3.4584	321 (K_β)
3.4586	100.00	3.4584	321
3.0475	8.24	3.0500	411,330
2.8922	0.96	2.8934	420
2.6412	8.91	2.6413	422
2.5374	14.90	2.5378	510,431
2.2894	0.27	2.2875	440
2.1566	1.73	2.1566	600,442
2.0992	14.41	2.0991	611,532
1.9971	16.38	1.9967	541
1.9500	5.12	1.9508	622
1.8652	1.81	1.8677	444
1.8308	4.05	1.8300	710,543
1.7609	1.60	1.7609	721,633,552
1.7292	2.53	1.7292	642
1.6420	5.69	1.6433	732,651
1.5926	8.20	1.5928	455
1.5688	4.21	1.5692	802
1.5243	0.24	1.5250	660
1.5043	3.18	1.5042	743
1.4656	0.74	1.4652	752
1.4117	0.58	1.4118	842
1.3954	4.08	1.3954	921,556
1.3637	3.63	1.3640	903

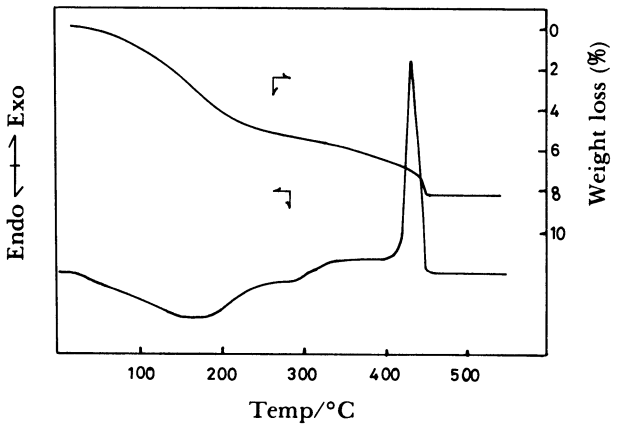

Fig. 5. The TG and DTA curves of H-CAM. Sample Wt: 0.1010 g; heating atmosphere: air; heating rate: 10 °C min^{-1}.

98.7% of the total ammonia, if the evolved ammonia at around 100 °C did not oxidized to NO_x. The powder X-ray diffraction patterns of H-CAM heated upto 300 °C (Fig. 7) showed no change in crystal structure. A little change was indicated upto 400 °C and a mixed X-ray diffraction of H-CAM and orthorhombic MoO_3 was observed. The observed lattice constant was found to be 12.976±0.005 Å. A complete crystal transformation to orthorhombic MoO_3[23] was observed at 660 °C. The little change in structure upto

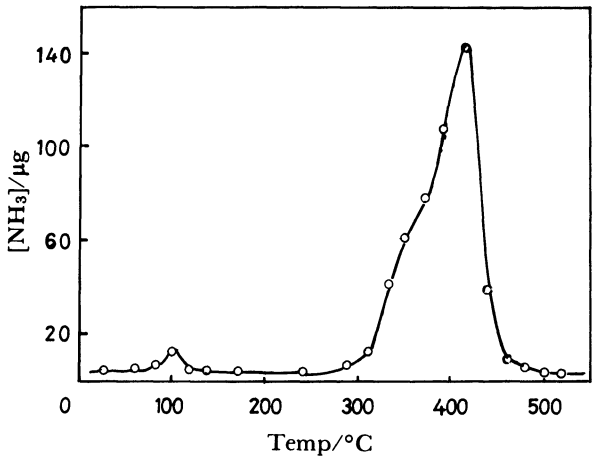

Fig. 6. The ammonia evolved during the thermal decomposition of H-CAM vs. heating temperature. H-CAM: 0.1031 g; heating rate: 10 °C min^{-1}; heating atmosphere: N_2 gas.

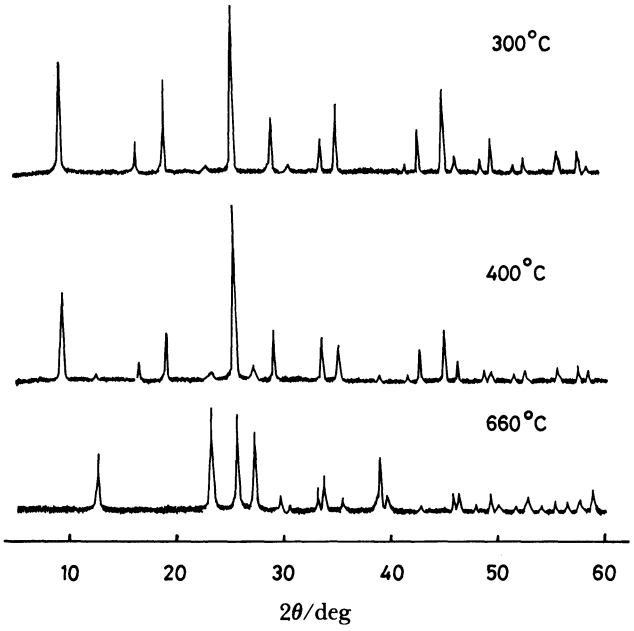

Fig. 7. The X-ray diffraction patterns of the heated samples.

400 °C also supports the evolution of a fraction of structural ammonia and water.

IR Spectroscopy. The IR spectrum of H-CAM (Fig. 8) shows a broad absorption band at 3400 cm^{-1} indicating the ν HOH stretching vibration for water. The absorption at 1600 cm^{-1} is the deformation vibration δ HOH.[24] The absorption bands around 3120 and 1400 cm^{-1} indicate the presence of NH_4^+ [25] as ν_3 and ν_4 stretching vibrations respectively.[28] Since no difference in the IR spectra of CAM and H-CAM was observed in this absorption region, the bands cannot be differentiated as for exchangeable and structural ammonia. The

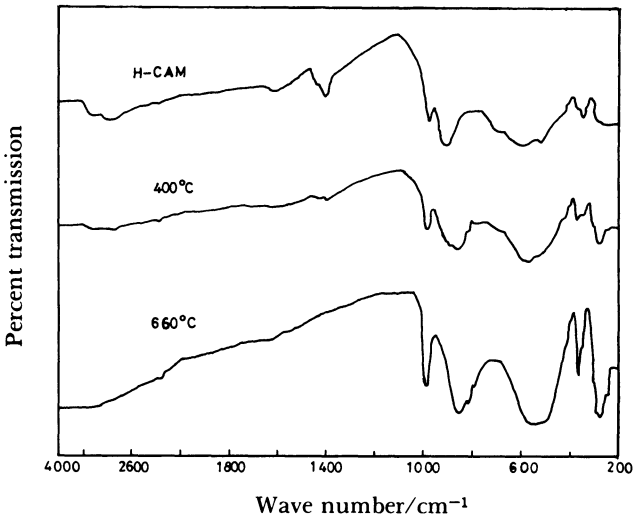

Fig. 8. The IR spectra of H-CAM and heated sample.

Table 3. The Exchange Capacity of H-CAM for NH_4^+

	NH_4^+ uptaken (mequiv g^{-1})	H^+ released (mequiv g^{-1})
1st. Equilibration	0.25_2	0.25_7
2nd. Equilibration	0.03_5	0.05_7
sum	0.28_7	0.31_4

shoulders at 2900 and 1430 cm^{-1} can be assigned to the deformation mode of vibration of NH_4^+. The absorption at 2900 cm^{-1} indicates the combination band of ν_2 and ν_4.[26] The absorption peaks at 3120 and 1400 cm^{-1} diminished at 400 °C and vanished in the IR spectra of heated samples after the exothermic peak at 430 °C. These results supported the scheme of thermal decomposition mentioned above. The strong absorption between 900—1000 cm^{-1} shows the Mo-O stretching vibrations.[27] The weak absorption at 800—900 cm^{-1} in H-CAM can be explained as O-Mo-O stretching vibrations containing ν(O-O) peroxo O_2 vibrations. These absorption bands split into three when oxygen quantity is greater,[28] which can be observed in the IR-spectra of the samples heated at 400 and 660 °C, where H-CAM change to MoO_3 at 660 °C. According to Nakamura et al.[29] the absorption between 500—600 cm^{-1} are due to the M-O-M stretching vibrations. These are the resultant of $\nu(O_2)$ and $\nu_{a,s}$(Mo) complexed together. The absorptions between 200—400 cm^{-1} in H-CAM indicate the Mo-Mo stretching vibrations[30] which become stronger in the heated samples.

Ion-Exchange Capacity for NH_4^+. The NH_4^+/H^+ ion-exchange reaction on H-CAM was carried out by batch experiment using 0.1 M NH_4NO_3 solution. A 1.0 g of exchanger was equilibrated by two successive addition with each 10 cm^3 of the above solution (Table 3). The amount of liberated H^+ from H-CAM was

equivalent to NH_4^+ uptake in the first equilibration. However slightly higher $[H^+]$ was observed in the supernatant solution than the amount of NH_4^+ uptaken by H-CAM due to the hydrolysis in the 2nd equilibration. The ion-exchange capacity for NH_4^+ was found to be 0.31 mequiv g^{-1} of H-CAM.

The acidification of hexaammonium heptamolybdate (aqueous solution) did not result into ammonia free molybdic acid even with 7.5 M HNO_3 or HCl solutions. The positive test for ammonia contents in commercially available so-called molybdic acids proves the authenticity of our observations, though the quantity of ammonia varies from product to product depending on the maker. As a matter of fact even a small content of NH_4^+ cannot be ignored from the ion exchange point of study and the empirical composition of the material. Therefore the products reported by different authors[11,25,31-34] as $MoO_3 \cdot H_2O$ or H_2MoO_4 prepared from aqueous solutions of ammonium heptamolybdate seem to be misleading.

The chemical formulae of H-CAM and A-CAM deduced from the chemical and thermal analysis and ion-exchange capacity, can be represented as $[H_{0.68}(NH_4)_2]O_{1.34} \cdot 14.16MoO_3 \cdot 6.92H_2O$ and $[(NH_4)_{0.68}(NH_4)_2]O_{1.34} \cdot 14.16MoO_3 \cdot 5.26H_2O$ respectively. The empirical formula of the CAM is $[(NH_4)_{0.78}(NH_4)_2]O_{1.39} \cdot 14.16MoO_3 \cdot 6.08H_2O$. The presence of 0.10% higher exchangeable NH_4^+ in CAM than that of A-CAM was due to the greater ammonia concentration in the mother liquor (supernatant solution). The amount of ammonia (1.54%) in H-CAM is independent of the preparation method and cannot be removed by washing even with 1 M HNO_3 solution. The results indicated that the amount of water in H-CAM varies slightly. However, the amount of ammonia evolved upto 100 °C (Fig. 6) was only 0.0226% of total ammonia and the weight loss at around 310 to 450 °C was due to evolution of structural ammonia and water. Kiss et al.[17] have reported the possible presence of $[Mo_{14}O_{43}]^{2-}$ polyanions by heating the ammonium heptamolybdate hydrate at 260 °C called as New Phase-1 $(NH_4)_2O \cdot 14MoO_3 \cdot 3.3H_2O$. They assumed the composition of the precipitate obtained from aqueous solutions to be the same as new phase-1. However for lack of information about the exchangeable NH_4^+ and NO_x formation during thermal decomposition, the calculated composition of their reported material seems to be deceptive.

The thermal decomposition reaction of H-CAM can be written as follows,

$$[H_{0.68}(NH_4)_2]O_{1.34} \cdot 14.16MoO_3 \cdot 6.92H_2O \quad (\text{H-CAM})$$
$$\xrightarrow{100-300\,^\circ C} [H_{0.68}(NH_4)_2]O_{1.34} \cdot 14.16MoO_3 + 6.92H_2O(\uparrow)$$
$$\xrightarrow{300-450\,^\circ C} 14.16MoO_3 + 2NH_3(\uparrow) + 1.34H_2O(\uparrow).$$

Conclusion

Crystalline cubic ammonium molybdate (CAM) can be prepared by the reaction of HNO_3 and hexaammonium heptamolybdate under controlled temperature conditions and reagents specifications. The chemical and thermal analyses and the amount of exchangeable H^+ indicated the composition of H-CAM as $[H_{0.68}(NH_4)_2]O_{1.34} \cdot 14.16MoO_3 \cdot 6.92H_2O$. The CAM is suitable for grading to a desired mesh size to be used for column chromatography. A reversible exchange NH_4^+/H^+ reaction would find a new application field as an ion exchanger and a catalyst.

References

1) J. J. Berzelius, *Pogg.*, **6**, 381 (1826).
2) G. Carpenie, *Bull. Soc. Chim. Fr.*, **1947**, 484.
3) G. Jander, K. Jahn, and W. Henkeshoven, *Z. Anorg. Allg. Chem.*, **194**, 383 (1930).
4) H. Braekken, *Z. Kristallogr.*, **78**, 484 (1931).
5) G. Anderson and A. Magneli, *Acta Chem. Scand.*, **4**, 793 (1950).
6) A. Magneli, *Acta Chem. Scand.*, **2**, 501, 861 (1948).
7) P. Cannon, *J. Inorg. Nucl. Chem.*, **9**, 252 (1959); **11**, 124 (1959).
8) J. B. Goehring and S. Y. Tyree, Abstract 7th International Conference on Coord. Chem., Stockholms, p. 172 (1962).
9) Y. Doucet and S. Bugnon, *J. Chim. Phys.*, **54**, 155 (1957).
10) J. Bye, *Ann. Chim.*, **20**, 463 (1945).
11) I. Lindquvist, *Acta Chem. Scand.*, **4**, 650 (1950); **5**, 568 (1951); **10**, 1362 (1956).
12) M. K. Cooper and J. E. Salmon, *J. Chem. Soc.*, **1962**, 2009.
13) J. Avestone, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **5**, 735 (1964).
14) T. Ozeki, H. Kihara, and S. Hikime, *Anal. Chem.*, **59**, 945 (1987).
15) C. Gleitzer, *J. Less-Common Met.*, **51**, 215 (1977).
16) E. Ma, *Bull. Chem. Soc. Jpn.*, **37**, 171, 648 (1964).
17) A. B. Kiss, P. Gado, I. Asztalos, and A. J. Hegedus, *Acta Chim. Acad. Sci. Hung.*, **66**, 235 (1970).
18) K. H. Tytko and O. Glemser, *Adv. Inorg. Chem. Radiochem.*, **19**, 239 (1976).
19) M. Abe, "Inorganic Ion Exchange Materials," ed. by A. Clearfield, CRC Press, Boca Raton, FL., (1982), p. 190.
20) T. Ito, "X-Ray Studies on Polymorphism," Maruzen Publishing Co., Tokyo (1950).
21) J. W. Visser, *J. Appl. Crystallogr.*, **2**, 89 (1969).
22) W. N. Schreiner, C. Surdukowski, and R. Jenkins, *J. Appl. Crystallogr.*, **15**, 513, 524 (1982).
23) Nat. Bur. Stand. (U.S.) Monogr., **20**, 118 (1984).
24) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).
25) N. Sotani, *Bull. Chem. Soc. Jpn.*, **48**, 6, 1820 (1975).
26) R. C. Plumb and D. F. Hornig, *J. Chem. Phys.*, **23**, 947 (1955); W. Vedder and D. F. Hornig, *ibid.*, **35**, 1560 (1961).
27) A. B. P. Lever, G. A. Ozin, and H. B. Gray, *Inorg. Chem.*, **19**, 1823 (1980).

28) K. Nakamoto, "Infrared and Raman Spect. Inorg. Compd.," 3rd ed., John Wiley & Sons, (1978), pp. 297—298.
29) A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *J. Am. Chem. Soc.*, **93**, 23, 6052 (1971).
30) V. R. Mattes, *Z. Anorg. Allg. Chem.*, **B357**, 30 (1968).
31) Gmelins Handbuch Anorg. Chem., Syst. No. 53, 119 (1935).
32) A. Rosenheim, *Z. Anorg. Chem.*, **50**, 320 (1950).
33) F. A. Cotton and G. Wilkinson, "Adv. Inorg. Chem.," 4th ed., Interscience, N. Y. (1980), p. 850, and references therein.
34) "Dickenson Comprehensive Inorg. Chem.," ed by J. C. Bailer, H. J. Emelens, S. R. Nyholm, and A. F. Trotman, (1973), Vol. 3, p. 735.