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Ion-Exchange Reaction on Cubic Ammonium Molybdate in Acidic and Alkaline Media—Exchange of Structural NH_4^+

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The alkali metal ion exchange reaction on cubic ammonium molybdate (CAM) cation exchanger was studied in acidic as well as alkaline media. The ion-exchange reaction and TPD-Mass thermogram of CAM indicated the presence of structural NH_4^+ as interstitial solid solution. The stuctural NH_4^+ in the H^+ form of CAM (H-CAM) was efficiently exchanged with K^+ as compared with other alkali metal ions in the equilibrated solutions. The exchanger was observed to be stable in acid medium, however structural transformations were observed at high pH. The presence of K^+ and Cs^+ at high pH could act as "Structure Building Ions" for CAM or H-CAM.

The ammonium or alkali metal tungstates have been reported by different authors.[1,2] Such type of materials are of interest because of their conductor properties with high ionic mobility due to existence of atomic sized tunnels within their crystal structure. The ionic mobility of NH_4^+ in ammonium tungstate investigated through NMR study, has been reported by Clark et al.[3] The existence of alkali metal ions (e.g. Rb^+) in tunnel structures of niobium and tantalum oxides have been discussed by Fallon and Gatehouse.[4]

The isopolymolybdates contain zigzag rows of MoO_6 octahedra which share corners in two directions forming MoO_4^{2-} layers.[5,6] The interstices of these layers provide channels for transport of cations (monovalent ions). These cations exist as solid solution in metal oxide structure.[7] The displacement of NH_4^+ or exchange of alkali ions (especially K^+) with NH_4^+ in heteropolyacid salts has been extensively reviewed by Amphlett[8] and Clearfield et al.[9] However less interest has been devoted to the study of mobility or transport of cations (e.g. NH_4^+) in the tunnel structure of molybdenum oxides, particularly through ion-exchange investigations.

The synthesis, characterization, and ion-exchange behavior of CAM along with the chromatographic separations of alkali metal ions have already been reported.[10,11] The present work was carried out to investigate the ion-exchange process of structural NH_4^+ in H-CAM through the maximum exchange capacity for alkali metal ions with respect to the crystal system of H-CAM. Ion-exchange equilibria, thermal analyses and X-ray diffractometry were employed for these investigations.

Experimental

Reagents. All the reagents used were analytical grade chemicals of Wako Pure Chemical Ind., Japan. Rubidium hydroxide and cesium hydroxide solutions were prepared through anion-exchange reaction by eluting the corresponding metal chloride solution through a column of Dowex 2-X8 anion exchanger in OH^- form. The N_2 gas was incorporated to avoid the CO_2 contamination in the resulting solutions.

Preparation of CAM and Conversion to H-CAM and A-CAM The cubic ammonium molybdate (CAM) $[(NH_4)_{0.78}(NH_4)_2]O_{1.39}\cdot 14.16MoO_3\cdot 6.08H_2O$ cation exchanger was prepared by the reaction of hexaammonium heptamolybdate and HNO_3 at 60 ±0.5 °C following the previously reported procedure.[10] CAM was converted to its H^+ form (H-CAM) $[(H)_{0.68}(NH_4)_2]O_{1.34}\cdot 14.16MoO_3\cdot 6.92H_2O$ by conditioning with 0.5 mol dm^{-3} HNO_3, using a column. H-CAM (100—200 mesh) was used throughout this work unless otherwise stated. The H-CAM when conditioned with 0.5 mol dm^{-3} NH_4NO_3 solution was converted to NH_4^+-form (A-CAM) $[(NH_4)_{0.68}(NH_4)_2]O_{1.34}\cdot 14.16MoO_3\cdot 5.26H_2O$.

X-Ray Diffractions. X-ray diffractions were taken with a JEOL JDX-7E and a Rigaku Denki Co. (Japan), model CN-5320 A-1/CN-2155 D-5 X-ray diffractometers. The crystal structures were deduced by using SANDMAN computer programs.[12—14]

Thermal Analyses and TPD-Mass Spectra. A Rigaku Denki Thermoflex, model 8001, was used 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 Temperature Programmed Desorption-Mass (TPD-Mass) spectrometry for investigating the desorption of structural ammonia and water in H-CAM was performed on a Quadrupole Mass Analyser MSQ-300 ULVAC. The sample was heated in an evacuated tube in the heating system provided with the said analyzer, at the same heating rate mentioned above. Each component was determined under an appropriate mass number. An adequate quantity of NH_3-gas was used as a reference for the investigation of ammonia in H-CAM.

Ion Selectivity, Maximum Exchange Capacity, and pH Titration. The distribution coefficients (K_d) were determined batchwise by equilibrating H-CAM (0.1 g) with 10 cm^3 solutions of 10^{-4} mol dm^{-3} alkali metal ions in different concentrations of HNO_3 at 30±0.5 °C with intermittent shaking.

The maximum exchange capacity for alkali metal ions on H-CAM was determined by batch experiment using 0.1 mol dm^{-3} MNO_3 ($M=Li^+$, Na^+, K^+, Rb^+, or Cs^+) solution in

10^{-4} mol dm^{-3} HNO_3. H-CAM (0.25 g) was equilibrated at 30±0.5 °C by the successive addition of each 25 cm^3 of the above solution, till no further uptake of respective metal ion. Similarly the topotactic K^+/NH_4^+ exchange was investigated by equilibrating A-CAM with KNO_3 solution.

The pH titration experiments were conducted by equilibrating H-CAM (0.1 g) with 10 cm^3 solution of a constant ionic strength of 0.1, containing different ratios of MNO_3/MOH or NH_4NO_3/NH_3 aq, at 30±0.5 °C with intermittent shaking.

The pH of the supernatant solutions were determined by a Toa Dempa HM-5B pH meter, the metal ion concentrations by an atomic absorption spectrophotometer, NH_4^+ by Nessler's method and the Mo(VI) cocentration by an Inductively Coupled Plasma (ICP) Spectrometer SPS-7000, Seiko Instruments, Japan.

Results and Discussion

Characteristics of CAM. The X-ray diffraction patterns, IR-spectra, and thermal analysis for CAM and H-CAM or A-CAM were observed to be the same as reported.[10] A-CAM was observed to possess two types of NH_4^+, the H^+-exchangeable NH_4^+ (EA-NH_4^+) and structural NH_4^+ (SA-NH_4^+). A reversible NH_4^+/H^+ exchange reaction was also studied on H-CAM.[10] However the present study showed that beside EA-NH_4^+, H-CAM was capable of exchanging SA-NH_4^+ too, with different selectivity for alkali metal ions. Hence A-CAM showed to possess two types of exchange sites i.e. H^+-exchangeable NH_4^+-site (EA-site) and structural NH_4^+-site (SA-site).

Selectivity of Alkali Metal Ions. The log-log plot (Fig. 1) of K_d vs. [HNO_3] was linear with a slope of -1 indicating an ideal ion-exchange reaction for all alkali metal ions except K^+. The selectivity sequence was observed to be $Cs^+>Rb^+>K^+>Na^+>Li^+$, in proportion to the increasing order of ionic radii (Table 1). The slope for K^+ was >-1 showing greater uptake irrespective of increase in HNO_3 concentration. These observations indicated that even though the exchange reaction for alkali metal ions at low metal ion concentration (i.e. 10^{-4} mol dm^{-3}) was preferred at EA-site, K^+ was more selective for SA-site (the release of NH_4^+ to the equilibrated solution by the uptake of K^+ was the experimental evidence for the exchange reaction).

TPD-Mass Spectroscopy. The TPD-Mass analysis (Fig. 2) showed two step loss of ammonia (solid-line peaks) and water (dashed-line peaks). The peaks around 120 °C indicated the loss of adsorbed ammonia and water on H-CAM, whereas the peaks at 200—350 °C corresponded to the presence of structural NH_4^+ and H_2O. Two peaks for structural H_2O were

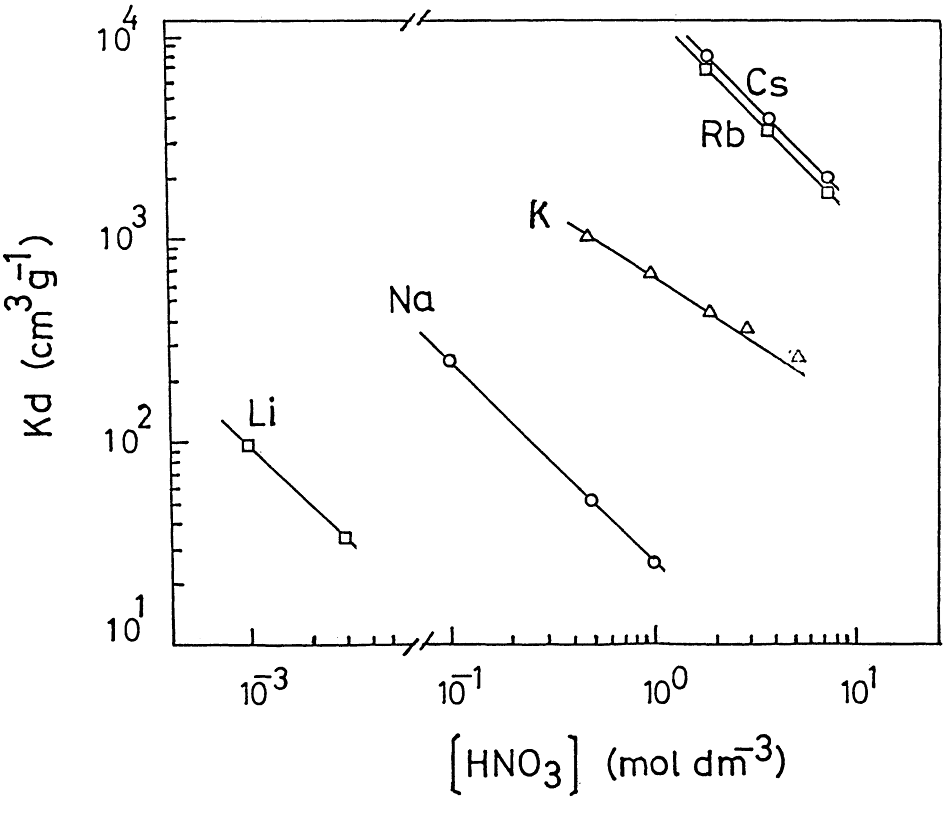

Fig. 1. Distribution coefficients for alkali metal ions on H-CAM as a function of HNO_3 concentration.
H-CAM: 0.10 g, Init. [M^+]: 10^{-4} mol dm^{-3}, Soln. Vol.: 10 cm^3, Temp.: 30 ±0.5 °C.

Table 1. Maximum Ion-Exchange Capacity of Alkali Metal Ions Equilibrated at pH<4 and the Lattice Constant (a) of H-CAM (a=12.94 Å) after Metal Ions Uptake

Ions	r_{eff}[a]	r_{hyd}[c]	Max capacity	Lattice const (a)
	Å	Å	±0.005 mequiv g^{-1}	Å
Li^+	0.59	3.7	0.15	12.939
Na^+	0.99	3.3	0.70	12.965
K^+	1.37	2.5	1.21	12.915
Rb^+	1.52	>2.4	1.05	12.920
Cs^+	1.67	2.4	0.95	12.950
NH_4^+	1.61[b]	2.5	0.31	—
H_3O^+	1.45[c]	2.85	—	—

a) Ref. 18. b) Ref. 19. c) From Stokes radii or Ref. 20.

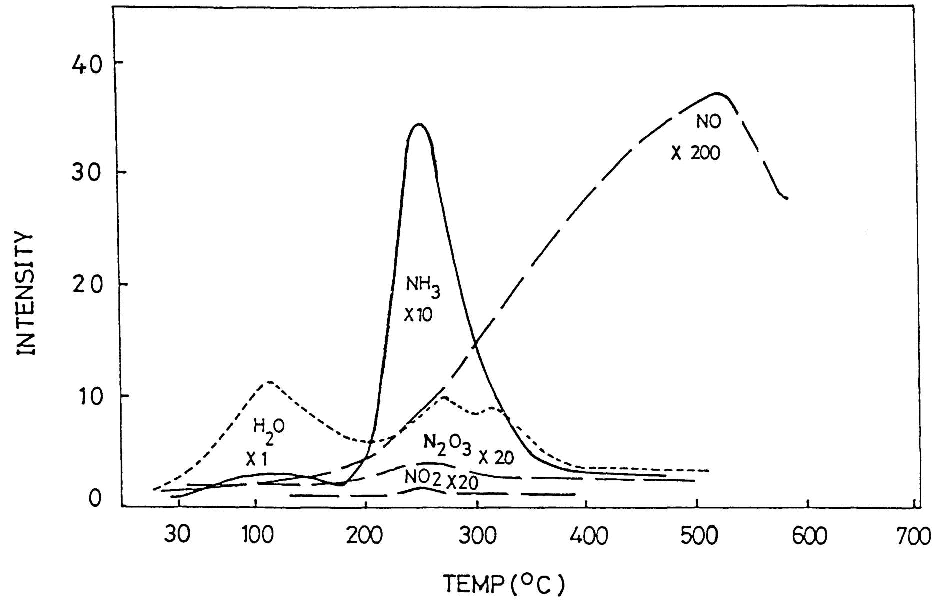

Fig. 2. The TPD-Mass thermogram of H-CAM.
H-CAM: 0.0053 g; Heating: 10 °C min^{-1}; B. K. Press: 4×10^{-7} Torr (1 Torr =133.322 Pa); Init. Intensity: 20×10^{-8} (NH_3 m/z=17), 20×10^{-7} (H_2O m/z=18), 10×10^{-9} (NO m/z=30 and NO_2 m/z=46), 10×10^{-8} (N_2O_3 m/z=76); Heating atm.: vacuum.

observed at temperature >250 °C. The former peak indicated the loss of structural H_2O whereas the latter one stood for the H_2O formed as a result of oxidation of structural NH_4^+ by MoO_3 into NO_x (broken-line peaks). This fact was supported by change in color of the product to black by heating H-CAM upto 600 °C in TPD-Mass experiment. The increase in the NO-peak with the rise of temperature may be attributed to the desorption of the adsorbed nitrogen oxide on molybdenum oxide, in accordance with the observations of Schiavello et al, on WO_3.[15]

The coexistence of structural NH_4^+ and H_2O, made it clear that structural NH_4^+ might stay as an interstitial solid solution in H-CAM lattice. The structural H_2O is probably the water molecules coordinated to Mo(VI) within the layers as noticed by Kerbs,[16] forming the adsorption centers (exchange sites) for NH_4^+ (or K^+ etc.). These observations signified the probability of SA-site being active for K^+ uptake. The presence of intervening NH_4^+ and H_2O molecules have also been reported by Matsumoto et al.[17] in ammonium pentamolybdodisulfate trihydrate.

Ion Exchange Capacity and Thermal Analysis. The maximum ion exchange capacity on H-CAM for all alkali metal ions in HNO_3 medium, ionic radii, and lattice constants of metal ion-exchanged forms of H-CAM i.e. M-CAM (M=Li, Na, K, Rb, or Cs) are given in Table 1. The maximum exchange capacity of H-CAM was observed to be in the order $Li^+<Na^+<Cs^+<Rb^+<K^+$. The equivalents of NH_4^+ released were equal to the equivalents of metal ions uptaken. In the view of experimental maximum

exchange capacity for K^+, the theoretical capacity of H-CAM could be calculated equal to 1.2 mequiv g^{-1}.

The change in the lattice constant of H-CAM after metal ions uptake is shown in Table 1. Almost no change was indicated with the uptake of Li^+. An increase in the lattice constant (a) of H-CAM was observed in Na^+ and Cs^+ exchanged forms ($a_{Na} > a_{Cs} > a_{\text{H-CAM}}$), whereas decrease in lattice constant was indicated by the uptake of K^+ and Rb^+ ($a_K \leqslant a_{Rb} < a_{\text{H-CAM}}$). However no transformation of H-CAM was observed in acid medium. The ion-exchange reaction on H-CAM especially at SA-site

Table 2. Percent Water Contents of H-CAM and Its Metal Ions Exchanged Forms (M-CAM). Data Calculated from Thermogravimetric (TG) Analyses

Samples	H_2O Contents %
H-CAM	5.30
Li-CAM	5.58
Na-CAM	6.45
K-CAM	5.53
Rb-CAM	4.66
Cs-CAM	4.47

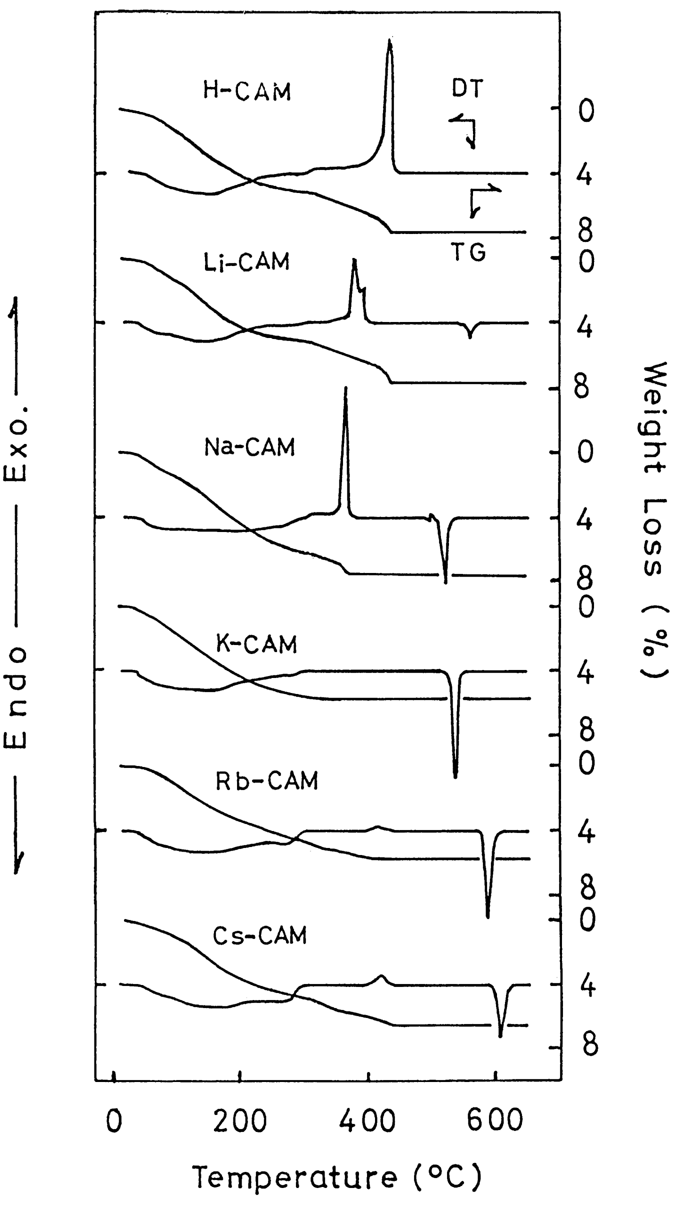

Fig. 3. The differential thermal (DT) and thermogravimetric (TG) curves of H-CAM and alkali metal ion-exchanged forms (M-CAM).
H-CAM or M-CAM: 0.0482 g; Heating: 10 °C min^{-1}; Heating atm.: ordinary.

seemed to be dependent on hydration of M^+ ions. The change in lattice with the uptake of M^+ ions may be attributed to the arrangement or size of hydration sphere (water molecules) around the respective ion in the tetrahedral layers (exchange sites). According to Diamond and Whitney,[21] the arrangement or size of the hydration sphere (water molecules) in the exchanger depends on the kind of metal ions.

Table 2 indicates the percent water contents of H-CAM and M-CAM samples. The water contents were observed to decrease in Rb and Cs forms (Cs-CAM<Rb-CAM<H-CAM) whereas increased in Li, Na, and K forms (Na-CAM>Li-CAM>K-CAM>H-CAM). The alteration (or arrangement) in the water contents brings alteration in the hydration sphere causing free energy (or entropy) changes which results in lattice change of the exchanger. The changes in water contents of M-CAM samples (Table 2) may correspond to the changes in water molecules of hydration sphere (at exchange site) brought about by the uptake of alkali metal ions on H-CAM. Greater free energy change caused by greater disturbance of hydration sphere resulted in greater change of lattice constants (e.g. a_{Na} and a_{Cs}).

The TG/DTA curves of H-CAM and M-CAM are shown in Fig. 3. The rise in DTA curve of H-CAM at >300 °C ending in a sharp exothermic peak at >430 °C indicated the existence of structural ammonia and

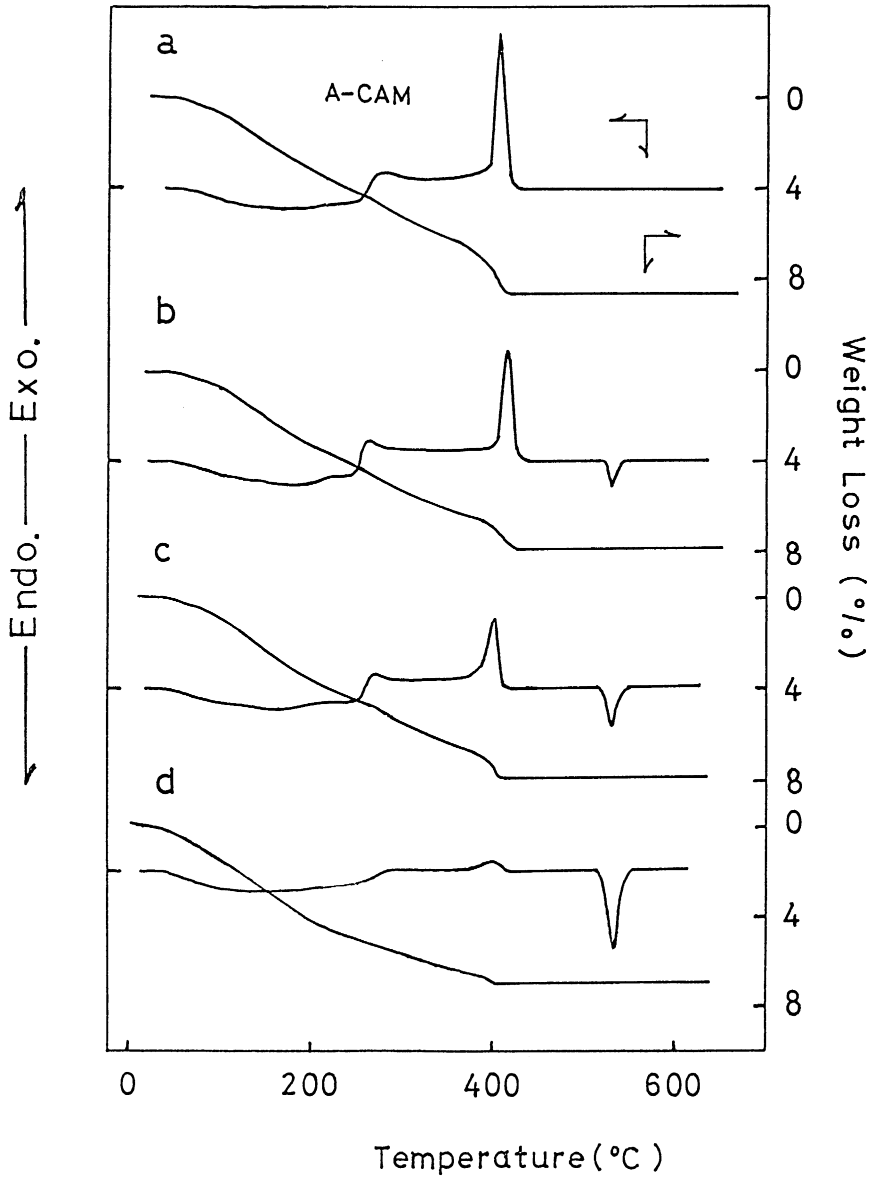

Fig. 4. The differential thermal (DT) and thermogravimetric (TG) curves of A-CAM (a) and K^+-exchanged forms (b—d) at different loadings. A-CAM: 0.0482 g K^+ mequiv g^{-1}: 0.2224 (b), 0.370 (c), 0.9760 (d); Heating: 10 °C min^{-1}; Heating atm.: ordinary.

water.[10] The DTA curves showed the presence of almost same ammonia contents of H-CAM in Li-CAM and Na-CAM indicating almost no exchange of structural ammonia (SA-NH_4^+) for Li^+ and Na^+ might be due to their selectivity preference for H^+-site or EA-site. In case of K^+ no exothermic peak due to structural ammonia was observed i.e. K^+ had replaced all the SA-NH_4^+ in H-CAM. This preference of K^+/NH_4^+ exchange was consistent with the selectivity of K^+ for SA-site in H-CAM. All of the NH_4^+ in H-CAM was not exchanged with Rb^+ and Cs^+ because of steric effect for their larger ionic radii. The very small exothermic peaks in DTA of Rb and Cs-CAM indicated the presence of unexchanged or remaining ammonia in H-CAM. The TG curves of the respective M-CAM were in accordance with the changes in DTA curves. The endothermic peaks in DTA curves at 500—620 °C indicated the fusion of M-CAM samples in the presence of alkali metal ions. No change in the TG curves was indicated at temperature >500 °C.

Exchange Sites and Metal Ion Uptake. The experimental results from K_d, maximum exchange capacity of alkali ions, and thermal analysis of M-CAM were in consistency for the exchange reaction at EA and SA-sites. Li^+ and Na^+ exchange reaction was favored at EA-site and K^+, Rb^+, and Cs^+ at SA-site in H-CAM. However to investigate the exchange reaction of K^+-Cs^+ at EA-site, the topotactic uptake of K^+ versus the apparent change in ammonia at EA/SA-sites was studied on A-CAM with different loadings of K^+. Figure 4a indicates the TG/DTA of A-CAM. The exothermic peaks at around 270 and 400 °C correspond to the loss of NH_4^+ at EA and SA-sites, respectively. Figure 4b,c indicated that the decrease in SA-NH_4^+ was proportional to the loading of K^+ at SA-site. However near the completion of K^+ uptake (maximum capacity), the exchange at both EA and SA-sites was favored (Fig. 4d). These results also provided an evidence for the discrepancy from slope −1 of K_d values for K^+. The cubic structure of both H-CAM and A-CAM was strictly retained after exchange of metal ions.

pH Titrations. The pH titration of H-CAM for alkali metal ions indicated apparently a monobasic acid, showing a large difference in blank and sample titration curves (Fig. 5). However dissolution of H-CAM occurred at pH >4.0 with a sharp increase in pH in NH_4NO_3/NH_3 aq medium. The equilibrium uptake of Li^+, Na^+, and NH_4^+ was observed to increase with increase in pH upto pH>4.0, whereas K^+, Rb^+, and Cs^+ showed a maximum uptake around

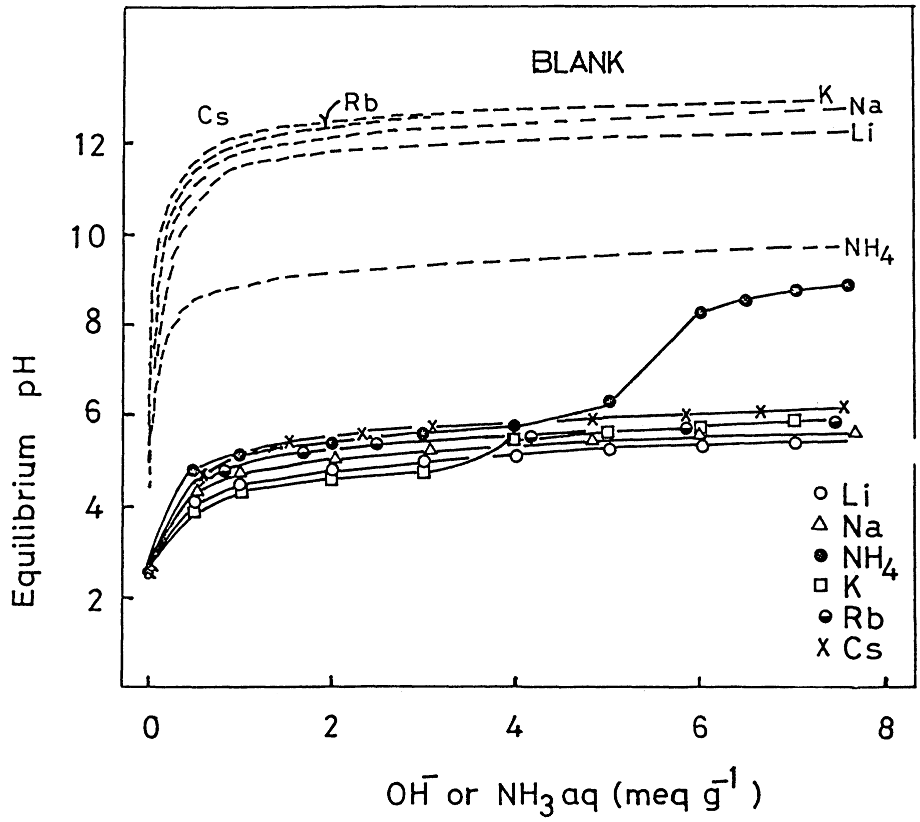

Fig. 5. pH titration curves of H-CAM.
H-CAM: 0.10 g; Soln vol.: 10.0 cm^3; Concn: 0.10 mol dm^{-3} (MCl+MOH) or (NH_4NO_3+NH_3 aq); Temp: 30±0.5 °C.

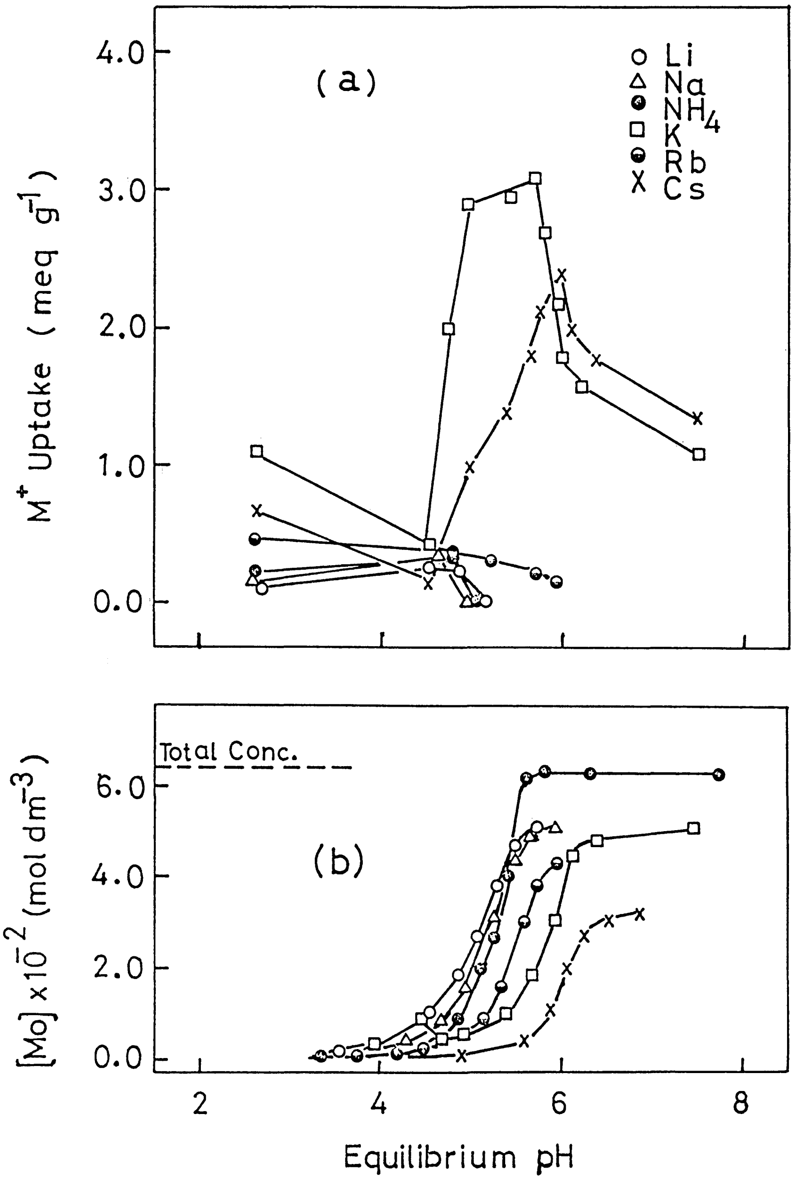

Fig. 6. Uptake of monovalent ions vs. equilibrium pH (a) and [Mo] in the supernatant solutions (b), after pH determination. H-CAM: 0.10 g; Soln vol: 10.0 cm^3; Concn: 0.10 mol dm^{-3} (MCl+MOH) or (NH_4NO_3+NH_3 aq); Temp: 30±0.5 °C.

pH 3 and decreased with increase in pH (Fig. 6a). The increase in the K^+ and Cs^+ uptake curves at pH>4.5 did not correspond to the uptake of these ions by H-CAM through ion-exchange reaction. Figure 6b indicates the dissolved amount of H-CAM {as [Mo(VI)]} in supernatant solutions at higher pH. The K^+ uptake (Fig. 6a) and [Mo(VI)] in the supernatant solutions (Fig. 6b) showed irregular curves with a break point around pH>4.5. The decrease in the K^+ uptake was due to the dissolution of H-CAM at high pH, however further increase in the uptake curve and an inflexion in the [Mo(VI)] curve at pH>4.5 indicated the complexation of K^+ with the dissolved H-CAM. The X-ray diffractions of the precipitates formed indicated the phase transformation of H-CAM to orthorhombic crystal system (with a totally different composition from H-CAM or K-CAM) at pH around 6.0 (Fig. 7). Almost similar observations were noticed for Cs^+ with a complete structural change to a triclinic form at pH around 6.17. The increase in amount (mequiv g^{-1}) of K^+ and Cs^+ (Fig. 6a) at pH>4.5 indicated the amount of these ions complexed with dissolved H-CAM (i.e. Mo(VI)) at higher pH. In the case of Li^+, Na^+, and Rb^+, no structural transformation or recomplexation was observed, though a slight change in the crystal lattice of H-CAM occurred after the uptake of metal ions, with no much difference in case of Rb^+ due to its

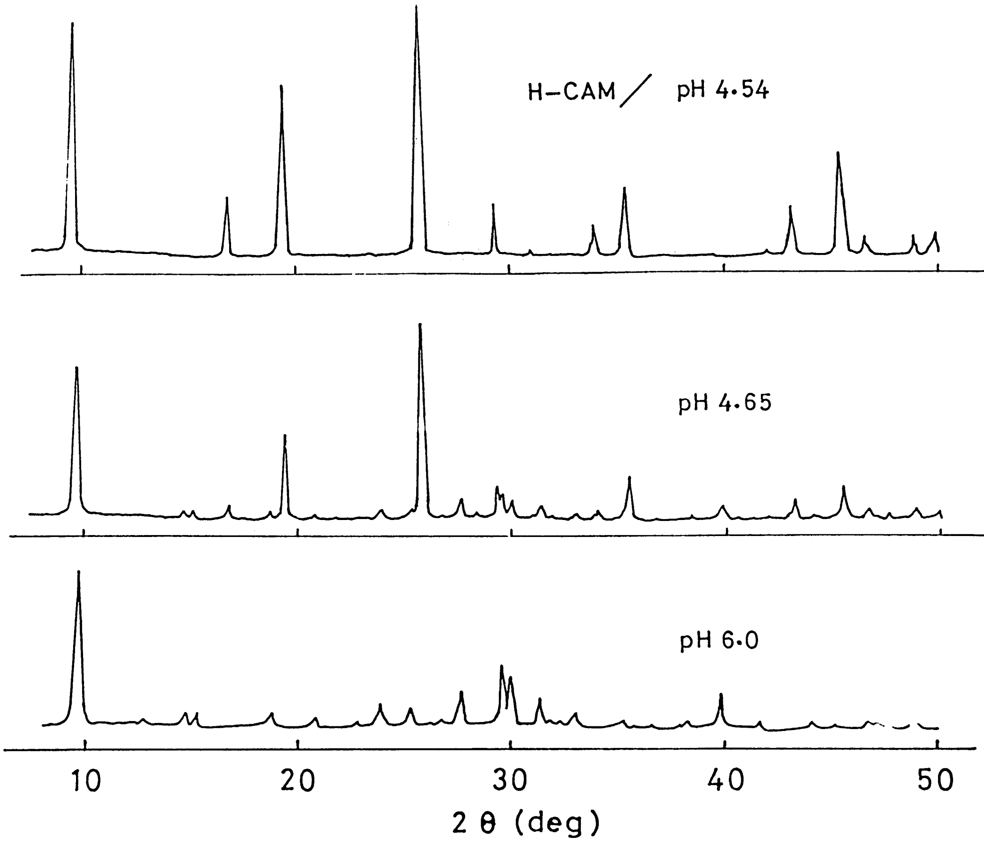

Fig. 7. X-Ray diffraction patterns indicating the pH dependent transformation of H-CAM to orthorhombic K-molybdenum oxide hydrate (KMO) formed (at pH 6.0) during the pH-titration of H-CAM.

nearly similar ionic radius as of NH_4^+.[18,19]

Conclusion

The cubic ammonium molybdate (CAM) cation exchanger possesses two different exchange sites, EA and SA-sites. Both sites were active for exchange of alkali metal ions with different selectivities. The order of selectivity at SA-site and maximum exchange capacity on H-CAM or A-CAM was $K^+ > Rb^+ > Cs^+$. The exchange of these ions for the structural NH_4^+ indicated that the NH_4^+ at SA-sites were mobile (i.e. not fixed up or trapped in the structure), however not accessible for the hydrated H^+ or H_3O^+ to be exchanged with. No change in cubic structure of CAM even with the loss of NH_4^+ indicated that the NH_4^+ seems to be existing in the atomic sized tunnels or layers within the crystal structure and is easy to exchange with ions of greater ionic radii without any alteration in the crystal structure. At high pH, the transformation of CAM or H-CAM to orthorhombic and triclinic-forms of molybdenum oxide in the presence of K^+ and Cs^+ respectively, lead to new concept—"The stucture building of metal oxides by metal ions," for preparation of new inorganic ion-exchange materials.

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