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A New Synthetic Route for Mixed-Valence Compounds: Leaching Treatments of Hydrogen Molybdenum Bronze

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In order to explore the possibilities of a new synthetic route, based on selective extraction of the same atomic species with different valences, for mixed-valence compounds, leaching treatments of H_xMoO_3 with various x values with various kinds of solutions were investigated. Both oxidation-type (pseudooxidation) and reduction-type (pseudoreduction) products could be obtained by these simple treatments without oxidizing or reducing agents. Their formation mechanisms were elucidated from various investigations of solutions as well as solids. Moreover, novel hydrated hydrogen–alkali metal co-insertion compounds of layered molybdenum oxide with larger hydrogen contents were obtained by the treatments. © 2001 Academic Press

Key Words: **synthetic pathway; mixed-valence compounds; molybdenum oxide bronze.**

INTRODUCTION

Syntheses of novel materials and development of novel synthetic routes are very important subjects to solid state chemists. The former seem to be strongly related to the latter. Many researchers have worked on these subjects and numerous synthetic techniques have been proposed. To the best of our knowledge, key words for the recent trends in materials' syntheses are "extreme circumstances" (1–4) "thin film" (5, 6), and "soft chemistry" (7–11). We have thought that the last is the easiest technique for people to use.

Recently we have found that a simple leaching treatment, based on selective extraction due to differing solubilities of the same atomic species with different valences, will provide an interesting synthetic route for mixed-valence compounds (12). In order to explore the possibilities of the route, leaching treatments of hydrogen molybdenum bronze H_xMoO_3 (with various x values) with various kinds of solutions were investigated in detail in the present work. It was found that both pseudooxidation and pseudoreduction products could be obtained by these simple leaching treatments without oxidizing or reducing agents. Phase-changing mechanisms during the treatments were also investigated. Moreover, it was found that novel hydrated molybdenum bronzes (hydrogen–alkali metal co-insertion compounds with larger hydrogen contents) could be obtained by the treatments. The details will be presented.

BACKGROUND

Hydrogen Molybdenum Bronzes (H_xMoO_3)

These are a series of hydrogen insertion compounds of layered MoO_3. They are of great interest for technological applications due to their specific features and properties (13–15). Five distinct phases with different hydrogen contents have been studied: 1) **I**, $0.21 < x < 0.40$ (blue, orthorhombic); 2) **II′**, $0.25 < x < 0.6$ (blue, monoclinic); 3) **II**, $0.85 < x < 1.04$ (blue, monoclinic); 4) **III**, $1.55 < x < 1.72$ (red, monoclinic); and 5) **IV**, $x = 2.0$ (green, monoclinic) (13, 14, 16–23). As for the positions of hydrogen atoms (or protons) in these bronzes there are two different kinds of sites ("intralayer" and "interlayer" sites). The manner in which protons occupy the positions varies depending on the hydrogen content (14, 16, 23).

Hydrated Molybdenum Bronzes $(M\cdot nH_2O)_yH_xMoO_3$

These are hydrated metal–cation intercalation compounds of layered MoO_3 and have been expected to be interesting catalysts with special reaction fields as well as ion conductors. Although several kinds of metal cations can be intercalated into the host (24, 25), hydrated alkali metal bronzes are the most popular ones. In these bronzes a small amount of protons (up to $x =$ ca. 0.15) are usually co-inserted (26–32). The bronzes with greater amounts of protons (up to $x =$ ca. 0.5) have also been synthesized by chemical reduction of H_xMoO_3 (30), or by heavy reduction of MoO_3 (31, 32), with alkali metal dithionite. However, any co-insertion bronze with $x >= 1.0$ has not been obtained so far.

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EXPERIMENTAL

Materials and Leaching Procedures

In the present work three phases (**I**, **II**, and **III**) of hydrogen molybdenum bronzes with various hydrogen contents were used as starting materials. They were prepared, as mentioned previously (19), and were confirmed to be single pure phases by X-ray diffraction (XRD) and compositional analyses. Aqueous HCl (2.5 M), water, and aqueous M_2CO_3, $M = \mathrm{Li}$, Na, K, Rb, Cs (0.18 M for Li_2CO_3, because of its low solubility, and 1.25 M for others), were used as acidic, neutral, and basic treatment media, respectively.

Hydrogen molybdenum bronze (1 g) was usually treated with the solution (14 ml) at room temperature or 353 K for a desired time. The treatment was carried out in an air-free atmosphere using a hand-made apparatus composed of vacuum and N_2 lines. After the treatment the solid was separated from the solution by filtration, washed well with water, and investigated for its structure and composition. As for the solution, its pH value was measured and molybdenum species in it were investigated by UV–vis and Raman spectroscopy. (Because we had no proper redox titrations, which could be used over a wide pH range, the reducing power of the solution could not be investigated.)

Measurements

The XRD patterns of the samples were measured using a MAC Science X-ray diffractometer with $\mathrm{Cu}K\alpha_1$ radiation (40 kV, 35 mA). The Li, Na, K, Rb, Cs, and Mo contents of the samples were determined with a Hitachi 180-80 atomic absorption spectrometer with the 670.8, 589.0, 766.5, 780.0, 852.1, and 313.3 nm lines, respectively. The oxidation state of Mo or the hydrogen content of the sample was determined by reducing power titration (33). Thermogravimetric and differential thermal analyses (TG–DTA) of the samples were carried out with a Mac Science TG–DTA 2010S system both in air and in N_2 at a heating rate of $10\ \mathrm{K\ min^{-1}}$. UV–Vis and Raman spectra of the solution were recorded with a Perkin Elmer Lambda 40 UV–vis spectrometer with a 0.1-cm quartz cell and a Perkin Elmer system 2000R NIR FT-Raman spectrometer, respectively.

RESULTS AND DISCUSSION

We carried out many experiments and obtained many results, including some confusing ones. For easy understanding of them, we will refer to final products formed by the treatments first and then discuss the phase-changing processes, referring to dissolved species as well as compositional and structural changes of solids during the treatments.

Final Products Obtained by Leaching Treatments

All phase changes driven by the leaching treatments were completed within 3 h. In Table 1 the products obtained by the treatments at 353 K for 3 h are summarized together with pH values of the solutions, oxidation states of Mo (O.S. Mo) in solids, and yields. According to the table, by HCl (acid) treatments, phases **I** ($x = 0.26$ and oxidation state of $\mathrm{Mo}^{5.74+}$) and **II** ($x = 0.89$, $\mathrm{Mo}^{5.11+}$) turn into MoO_3 + phase **I** ($\mathrm{Mo}^{5.97+}$, averaging over the mixture) and phase **I** ($\mathrm{Mo}^{5.70+}$), respectively, although phases **II** ($x = 1.03$, $\mathrm{Mo}^{4.97+}$) and **III** ($x = 1.49$, $\mathrm{Mo}^{4.51+}$) show no changes. On the other hand, by alkaline (basic) treatments, all phases used change to phases with oxidation states lower than their initial ones. The products vary depending on the kinds of starting solids and treatment solutions. For the hot water (neutral) treatments no phase change was observed. Thus, it should be emphasized that the acidic treatment preferentially leads to oxidation-type products, while the alkaline treatment gives reduction-type products. Because we never used oxidizing or reducing agents for the treatments, it might be concluded that the phase changes observed are not due to oxidation or reduction of the materials. However, because it is well known that the redox potential of chemical species, such as molybdenum species, varies depending on the pH, the above results might be related rather to the differing redox potentials with the pH variations. In this case trace amounts of O_2 or solvent (H_2O) etc. might act as oxidant or reductant. Repeating experiments with caution against accidental contamination of oxidants/reductants such as incomplete removal of air from the treatment solution, we attempted to examine whether there were any unanticipated oxidants/reductants in the treatment solutions used. We especially ascertained that the confusing results observed for the HCl treatment (that is, the treatment of phase **III** gives no oxidation product and no increment in O.S. Mo, unlike that of phase **I**) were not due to mistakes in the experiment. From this we could conclude that the phase changes observed for the HCl treatments were not due to any oxidants, because phase **III**, which was most oxidizable of the three phases used (34), was never oxidized by the treatment. We also confirmed that alkaline treatment of MoO_3 with aqueous Na_2CO_3 gave no reduction-type product. This proves the absence of reductants for the alkaline treatments, although the treatments lead to the reduction-type products in most cases. We then notice that the yields become small when some phase change occurs during the treatments (Table 1). It should be especially noted that the solid is completely solved in 14 ml of the solution for the HCl treatment of phase **II** with $x < 1.0$. This indicates a large dissolution of species from solid to solution during the phase change. From the yields and the O.S. Mo changes it is subsequently suggested that formation of the oxidation-type products results from preferential

TABLE 1
Results of the Leaching Treatments of H_xMoO_3 with Various Solutions

Treatments	Solution pH		O. S. Mo[b]		Yields	
(*A*/*B*)[a]	Initial	Final	Initial	Final	(wt%)	Products[c]
			Acid			
I/HCl	– 0.0*	0.1	$Mo^{5.74+}$	$Mo^{5.97+}$	32	MoO_3 + **I**
II/HCl[d]	– 0.0*	0.1	$Mo^{5.11+}$	$Mo^{5.70+}$	4	**I**
II/HCl	– 0.0*	0.2	$Mo^{4.97+}$	$Mo^{4.92+}$	76	**II**
III/HCl	– 0.0*	0.3	$Mo^{4.51+}$	$Mo^{4.51+}$	82	**III**
			Neutral Medium			
I/H_2O	5.7	2.9	$Mo^{5.70+}$	$Mo^{5.70+}$	74	**I**
II/H_2O	5.7	3.3	$Mo^{5.22+}$	$Mo^{5.25+}$	76	**II**
III/H_2O	5.7	4.0	$Mo^{4.51+}$	$Mo^{4.51+}$	76	**III**
			Base			
I/Cs_2CO_3	12.1	9.8	$Mo^{5.74+}$	$Mo^{4.57+}$	8	**III**
I/Li_2CO_3	11.1	5.9	$Mo^{5.71+}$	$Mo^{5.65+}$	34	HyBr
I/Li_2CO_3[e]	11.1	9.5	$Mo^{5.71+}$	$Mo^{4.57+}$	7	HyCIBr
I/Na_2CO_3	11.6	9.1	$Mo^{5.71+}$	$Mo^{4.60+}$	18	HyCIBr
I/K_2CO_3	11.9	9.5	$Mo^{5.71+}$	$Mo^{4.51+}$	18	HyCIBr
I/Rb_2CO_3	11.9	9.6	$Mo^{5.71+}$	$Mo^{4.63+}$	17	HyCIBr
II/Cs_2CO_3	12.1	10.9	$Mo^{5.11+}$	$Mo^{4.40+}$	53	**III**
II/Li_2CO_3	11.1	6.8	$Mo^{5.22+}$	—	33	**III** + **II**
II/Li_2CO_3[e]	11.1	9.8	$Mo^{4.98+}$	$Mo^{4.56+}$	17	**III**
II/Na_2CO_3	11.6	9.7	$Mo^{4.98+}$	$Mo^{4.37+}$	37	**III**
II/K_2CO_3	11.9	10.1	$Mo^{4.98+}$	$Mo^{4.36+}$	48	**III**
II/Rb_2CO_3	11.9	10.1	$Mo^{4.98+}$	$Mo^{4.39+}$	32	**III**
III/Cs_2CO_3	12.1	11.5	$Mo^{4.51+}$	$Mo^{4.33+}$	68	**III**

[a] *A*/*B* means a treatment of solid *A* with solution *B* at 353 K for 3 h. [b] The oxidation state of Mo in solid. [c] See the text. [d] 4.5 ml of the treatment solution was used, because the solid was completely solved in 14 ml of the solution. [e] 0.14 g of the starting solid was treated with 14 ml of the treatment solution (0.18 M). * Negative values around −0.1 were obtained actually.

dissolution (extraction) of Mo species having a lower oxidation state (for example, Mo^{V}), while that of the reduction-type products is due to extraction of Mo^{VI} species. By Raman and UV–vis investigations we also ascertained that the molybdenum species in solution were evidence of not redox reaction but the extraction. (For example, when the oxidation-type products were formed by HCl treatment, the amount of molybdenum species with a lower oxidation state increased in solution. If the products were formed by some oxidation reaction, the amount of molybdenum species with a higher oxidation state should increase, but an increase of the species with a lower oxidation state is expected for the phase change due to the extraction. A detailed discussion on molybdenum species in solution will be given later.) Therefore, it is noted that both oxidation-type (pseudooxidation) and reduction-type (pseudoreduction) products are obtained by selective extraction of specific species from solid to solution through simple leaching treatments without oxidizing or reducing agents. This finding will provide for an effective control of the oxidation state of materials or effective synthetic routes to mixed-valence compounds.

Next it should be noted that the phases that resulted depended on the kinds of treatment solutions as well as starting solids used, and contained some interesting phases which have never been prepared by usual synthetic routes. (This may provide some hints for future applications.) Figure 1 shows the XRD patterns of the product phases obtained by leaching phase **I** ($x = 0.26$, $Mo^{5.74+}$) with the various alkali metal carbonate (M_2CO_3) solutions at 353 K for 3 h, respectively. According to the figure, these treatments of phase **I**, except for the Cs_2CO_3 treatment, lead to formation of compounds other than a series of H_xMoO_3. Although their XRD patterns are rather broad, they are similar to the ordinary hydrated alkali metal molybdenum bronzes (named HyBr) (24, 25) and can be explained well with the orthorhombic lattice constants (in nm, $a = 0.38$, $b = 1.85$, $c = 0.38$ for Li; $a = 0.38$, $b = 1.93$, $c = 0.37$ for Na; $a = 0.38$, $b = 2.14$, $c = 0.37$ for K; and $a = 0.38$, $b = 1.90$, $c = 0.37$ for Rb, respectively) which are comparable with those of HyBr (24–29, 32, 35). The compositional analysis showed that these compounds contained a 0.25–0.39 (0.25 for Li, 0.30 for Na, 0.39 for K, and 0.28 for Rb) M/Mo (molar ratio) of alkali metal cations, indicating incorporation of alkali metal cations during the leaching treatments.

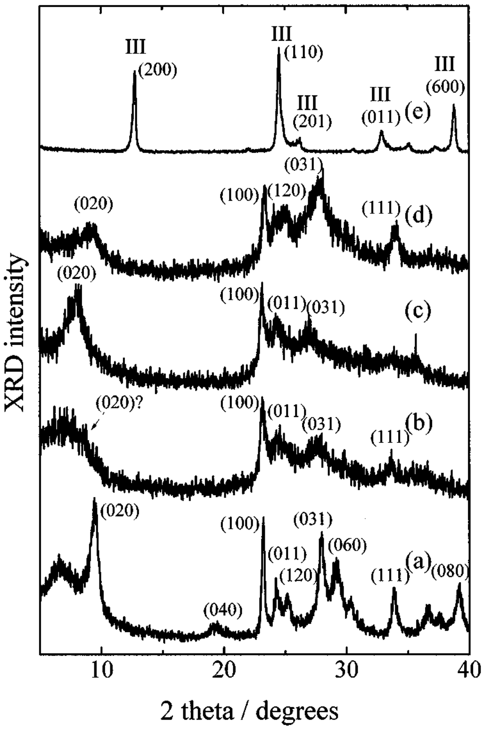

FIG. 1. XRD patterns of the products obtained by treating phase **I** with M_2CO_3 solutions at 353 K for 3 h; M = Li (a), Na (b), K (c), Rb (d), and Cs (e). Symbol III indicates phase **III**.

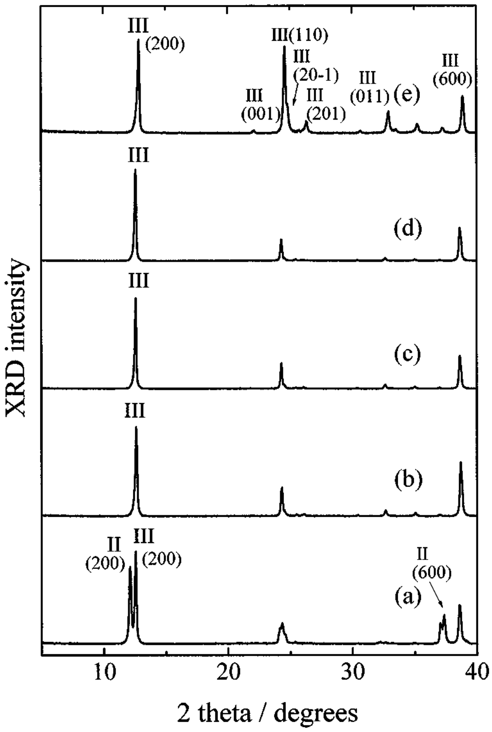

FIG. 2. XRD patterns of the products obtained by treating phase **II** with M_2CO_3 solutions at 353 K for 3 h; M = Li (a), Na (b), K (c), Rb (d), and Cs (e). Symbols II and III indicate phases **II** and **III**, respectively.

According to the TG–DTA and chemical analysis the hydrogen contents of these samples were $x = 0.10$ for Li and $x = 1.0–1.1$ for the others, while the water contents of the samples were 0.84, 1.23, 0.85, and 0.68 H_2O/Mo (molar ratio) for Li, Na, K, and Rb compounds, respectively. On visual inspection, these compounds were blue in color (as for HyBr) for Li and black for the others. From these results they were identified as Li-HyBr for Li and new hydrated hydrogen–alkali metal co-insertion compounds of layered MoO_3 with higher hydrogen contents ($(M \cdot n H_2O)_{0.25-0.39} H_{1.0-1.1}MoO_3$, named HyCIBr), which have never been prepared (30–32), for others. We have further succeeded in obtaining the HyCIBr type of Li compound by arranging the molar ratio of the starting material (phase **I**) to Li_2CO_3 (Table 1). We also investigated the reason the behavior of phase **I** during the Cs_2CO_3 treatment was different from those during the other alkali metal carbonate treatments. Because it was supposed that the large ionic radius of Cs, which was unfavorable for incorporation into interlayer sites of phase **I**, prevented the formation of HyCIBr-type compound, treatment of Cs-HyBr, which originally had Cs ions in interlayer sites, with a $CsCO_3$ solution was tested. This treatment gave a HyCIBr-type phase and proved that the above difference was directly related to the easiness of incorporation of alkali metal cations concerned. For treatment of phase **II** no alkali metal intercalation-type compounds were obtained (Fig. 2). This seems to indicate that the alkali metal ions cannot be incorporated into the interlayer of phase **II** previously occupied by protons (14, 16).

Finally, we refer to the results for HCl treatment of phase **II**, which are seemingly contradictory to one another. According to the results, upon HCl treatment phase **II** with $x < 1.0$ turns into phase **I**, while the one with $x > 1.0$ does not (Table 1). The former gave no solid phase under the standard conditions of treatment (starting solid 1 g, solution 14 ml), indicating a very high solubility of the starting solid in the solution, but the latter shows lower solubility (Table 1). Regarding these differences with different x values we suppose that they result from thermodynamics. If Mo^V species are preferentially extracted from solids by HCl treatments, as mentioned above, Mo^{VI} species are condensed in solids for phase **II** with $x < 1.0$ (over $Mo^{5.0+}$), while Mo^{IV} species are condensed in solids for phase **II** with $x > 1.0$ (under $Mo^{5.0+}$). We believe that the enthalpy gain resulting from dissolution of Mo^V species cannot overcome the disadvantage in enthalpy caused by the condensation of Mo^{IV} species in solids for the latter case, although no thermodynamic data to substantiate this suggestion have been obtained yet.

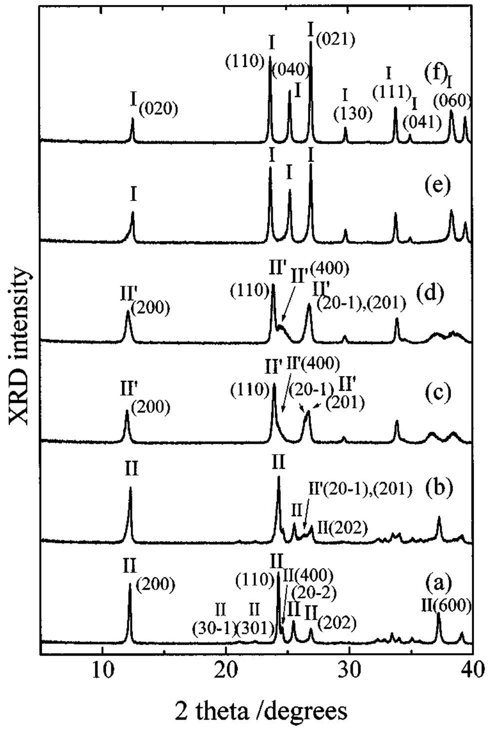

FIG. 3. Changes in the XRD pattern of the solid phase during the HCl treatment of phase **II** at 353 K; treatment time = 0 (a), 5 min (b), 30 min (c), 1 h (d), 2 h (e), and 3 h (f). Symbols II, II′, and I indicate phases **II**, **II′**, and **I**, respectively.

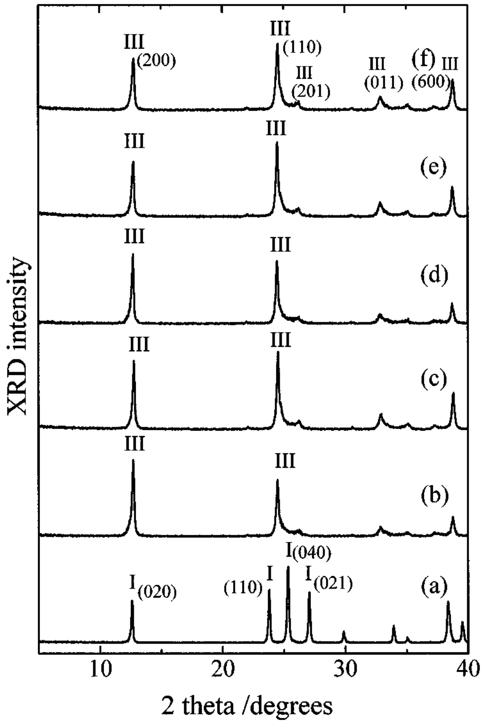

FIG. 4. Changes in the XRD pattern of the solid phase during the Cs_2CO_3 treatment of phase **I** at 353 K; treatment time = 0 (a), 5 min (b), 30 min (c), 1 h (d), 2 h (e), and 3 h (f). Symbols I and III indicate phases **I** and **III**, respectively.

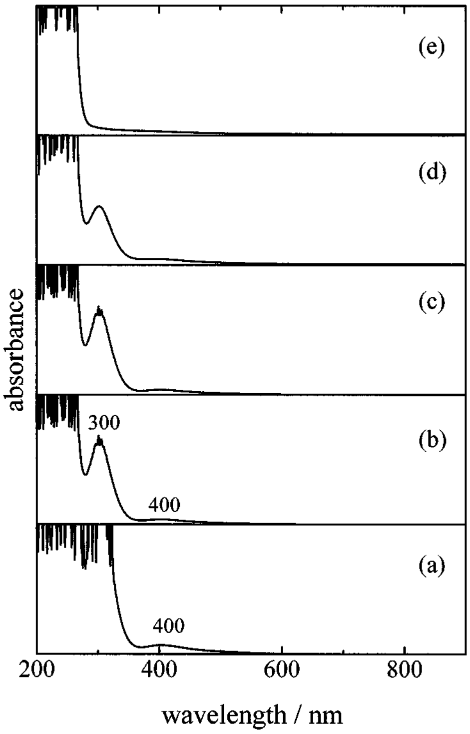

FIG. 5. Changes in the UV–vis spectrum of the solution during the Cs_2CO_3 treatment of phase **I** at 353 K; treatment time = 0 (a), 5 min (b), 30 min (c), 1 h (d), and 2 h (e).

Phase Changes and Molybdenum Species Extracted

With regard to HCl treatments the phase changes proceeded gradually even at 353 K and no phase change was observed at room temperature. Figure 3 shows the progression of structural changes of the product during HCl treatment of phase **II** with a hydrogen content of $x = 0.89$ ($Mo^{5.11+}$) at 353 K. According to the literature data (13, 14, 16–21, 23) the XRD changes observed are attributed to the phase changes from **II** to **II′** to **I**. The x values of the resulting solids were 0.75 ($Mo^{5.25+}$), 0.39 ($Mo^{5.61+}$), 0.37 ($Mo^{5.63+}$), 0.31 ($Mo^{5.69+}$), and 0.30 ($Mo^{5.70+}$) for 5-min, 30-min, 1-h, 2-h, and 3-h treatments, respectively. The solution after the treatment was deep dark red for every case and exhibited absorption peaks at 295 and 380 nm in its UV–vis spectrum, which were attributed to a dimeric (lower valent) oxo-Mo^V species $[Mo_2^VO_4(H_2O)_6]^{2+}$ (36, 37). These bands increased in intensity with the progress of the phase change, indicating an increase in the concentration of the species. A similar increment of $[Mo_2^VO_4(H_2O)_6]^{2+}$ species was observed for HCl treatment of phase **I**. For the treatments of phases **II** with $x = 1.03$ ($Mo^{4.97+}$) and **III** only a minor amount of the Mo^V species was observed in the treatment solution, supporting the absence of phase changes due to extraction.

On the other hand, for alkaline treatments the phase changes proceeded rapidly and were completed within 5 min even at room temperature. Figure 4 shows the progression of structural changes of the product during the

TABLE 2
Raman Band Frequencies of Solutions after the Treatments

Treatments	Band frequencies^a/cm^{-1}			
	Acid			
MoO_3/HCl 3 h	955, 924			373(w)
I($x = 0.27$)/HCl 5 min	978, 955, 918		737	353
I($x = 0.27$)/HCl 3 h	977, 955, 920		739	353
II($x = 0.95$)/HCl 3 h	980		738	353, 318(w)
II($x = 1.03$)/HCl 3 h		No peak		
III($x = 1.45$)/HCl 3 h		No peak		
	Base			
MoO_3/Cs_2CO_3 3 h	1065, 1014		895(s), 841	316(s)
I($x = 0.27$)/Cs_2CO_3 5 min	1065, 1014	944(w)	895(s), 839	316(s)
I($x = 0.27$)/Cs_2CO_3 3 h	1064, 1011		895(s), 839	316(s)
I(x = 0.26)/K_2CO_3 3 h	1066, 1014		896(s), 839	316(s)
II($x = 1.03$)/Cs_2CO_3 3 h	1065, 1012		895(s), 838	315(s)
III($x = 1.45$)/Cs_2CO_3 3 h	1065(s)		895	313

^{a} s, strong; w, weak.

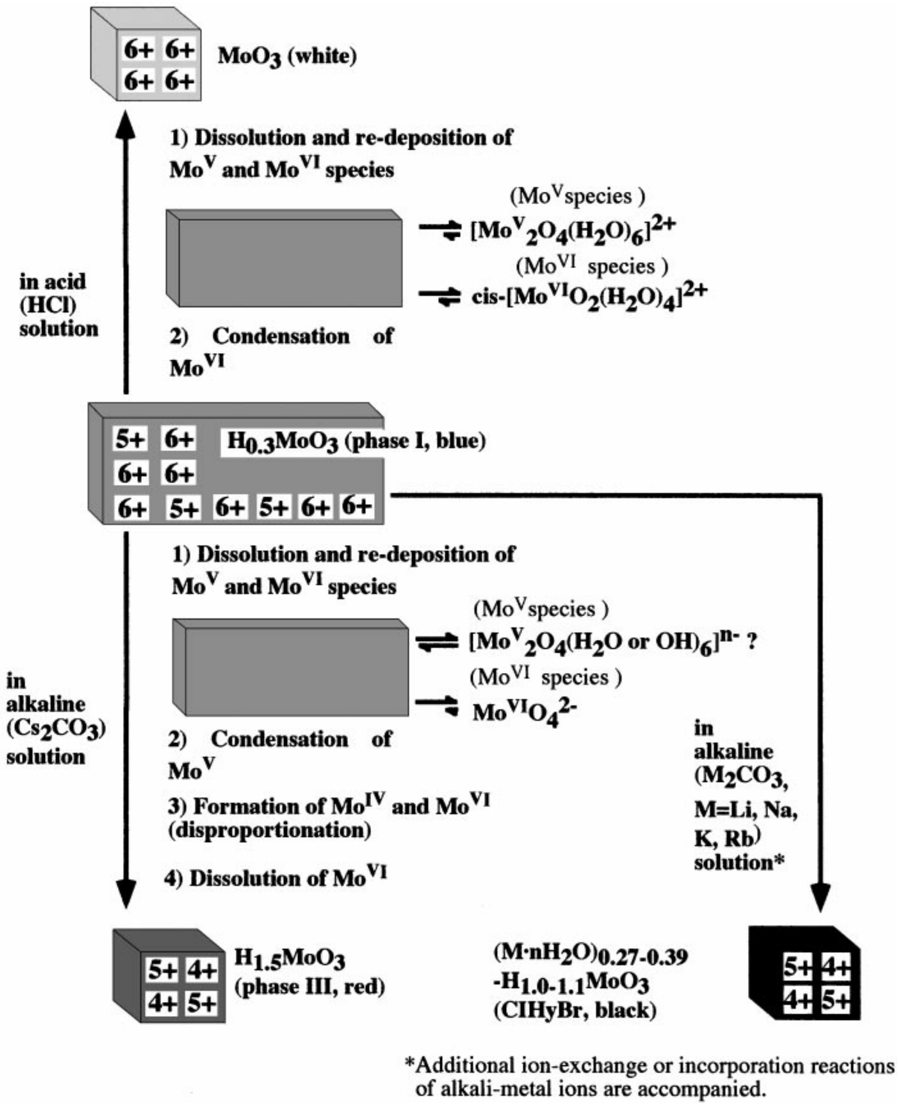

FIG. 6. Schematic model of the phase change mechanisms for the leaching treatments of phase **I**.

treatment of phase **I** with $x = 0.26$ ($Mo^{5.74+}$) with Cs_2CO_3 solution at 353 K. According to the XRD results, the phase change from **I** to **III** is completed within 5 min. The chemical analysis, however, showed that O.S. Mo values of the solids were $Mo^{4.72+}$ ($x = 1.28$), $Mo^{4.70+}$, $Mo^{4.66+}$, $Mo^{4.62+}$, and $Mo^{4.58+}$ for 5 min, 30 min, 1 h, 2 h, and 3 h, respectively. This result indicates that the oxidation state gradually decreases even after 5 min or completion of the phase change. The solution color gradually changed from brown (5 min) to greenish brown (3 h). Figure 5 shows UV–vis spectra of the solution during the treatment. In the figure the absorption bands are observed at 300 and 400 nm, and they decrease in intensity with increasing treatment time. These bands are supposed to be due to a derivative of $[Mo^V_2O_4(H_2O)_6]^{2+}$, resulting from, e.g., partial deprotonation of OH_2 or something (37, 38). The above decrease in oxidation state of the solid is followed by the decrease of this species, and is related to the condensation (or redeposition) of the lower-valence molybdenum species from solution to solid. For treatments of phase **I** with other alkali metal carbonate solutions, which led to formation of a different type of compounds (HyCIBr's), the same molybdenum species were also observed in solution, independent of the kind of phases that resulted.

Table 2 shows the results of Raman investigation on the treatment solutions. Because Raman spectroscopy is not so sensitive, only the species with rather high concentrations are observed. However, the investigation is informative, especially for Mo^{VI} species, which are silent to UV–vis spectroscopy. According to the results a dioxo-monomeric cation, *cis*-$[Mo^{VI}O_2(H_2O)_4]^{2+}$ (955, 920, 373 cm^{-1}) (39), and a dimeric cation, $[Mo_2^{V}O_4(H_2O)_6]^{2+}$ (980, 738, 353, 318 cm^{-1}), are identified for the acidic treatments, while a monomeric anion, $Mo^{VI}O_4^{2-}$ (895, 840, 315 cm^{-1}), is recognized for the alkaline treatment. With regard to the weak band observed at 944 cm^{-1} for the treatment of **I**/Cs_2CO_3 (5 min), we suppose that it is related to the Mo^{V} derivative mentioned above. The bands at ca. 1065 and ca. 1015 cm^{-1} are attributed to the C–O stretching vibrations of CO_3^{2-} and HCO_3^{-}, respectively. From this investigation it is noted that the main extracted species is $Mo^{VI}O_4^{2-}$ (with a higher oxidation state) for the alkaline treatments, although only the Mo^{V} species, which was present as a minor species, was discussed above from the UV–vis investigation.

Phase-Changing Mechanisms

From the above results, the mechanisms of the phase changes due to the leaching treatments were elucidated. Except for the differences in the products, there are not very large differences in the mechanisms for all systems investigated. As an example, the phase change processes for phase **I** are illustrated in Fig. 6. The phase changes basically result from dissolution and redeposition of the molybdenum species. Mo^{V} species are preferred in acidic solution, while Mo^{VI} species are preferred in alkaline solution. When Mo^{V} species are highly condensed in a solid, a disproportionation reaction of Mo^{V}–Mo^{V} to Mo^{VI}–Mo^{IV} seems to occur. The lowering in O.S. Mo below $Mo^{5.0+}$ is achieved by additional dissolution of the Mo^{VI} fragment, formed by the disproportionation. The product depends on its stability and structure, the presence of additional reactions, and so on. Formation of phase **IV**, having a higher hydrogen content than phase **III**, for example, was not observed in the present work. We suppose its formation is not allowed thermodynamically (34). An additional ion-exchange reaction (or incorporation reaction of alkali metal ions) can lead to the formation of hydrogen–alkali metal co-insertion-type compounds (the treatments of phase **I** with alkali metal carbonate solutions).

CONCLUSION

The leaching treatments of H_xMoO_3 with various x values with various kinds of solutions were investigated. It could be demonstrated that such leaching treatments could provide interesting and effective synthesis routes of mixed-valence compounds, which could control the oxidation state of materials without using any oxidizing or reducing agents. Moreover, it should be noted that such approaches have the possibility to lead to novel materials. In the present work rather simple systems were dealt with. We suppose that further developments of this synthetic pathway will be achieved by using suitable chelating agents, surfactants, nonaqueous solvents, starting materials, and so on.

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