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Synthesis of Cesium Bismuth Molybdate Hydrate as a New Inorganic Ion Exchanger

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Cesium bismuth molybdate hydrate was synthesized from bismuth molybdate hydrate and cesium nitrate in aqueous solution, and reversively changed to bismuth molybdate hydrate in nitric acid. Cesium ion in cesium bismuth molybdate hydrate was easily exchanged with potassium, rubidium and ammonium ions while bismuth molybdate hydrate had no reaction except with cesium ion.

Bismuth molybdates have been applied to the selective oxidation catalyst. Bismuth molybdates have various compositions and phases. Preparation methods have been proposed by many investigators.[1-5] α-$Bi_2Mo_3O_{12}$ is synthesized by means of heating the precipitate from the acidic solution with bismuth and molybdate ions. The lattice parameter of the precipitate, bismuth molybdate hydrate, was determined and the intercalation of the compound with organic molecules such as pyridine was found in previous papers.[6,7] The purpose of this work is to synthesize a new inorganic exchanger from bismuth molybdate hydrate for the modification of bismuth molybdates.

Bismuth molybdate hydrate was synthesized from the mixture of the nitric acid solutions of bismuth nitrate and sodium molybdate.[6,7] After stirring for 3 days, the white precipitate was washed, filtered and air-dried. The ratio of molybdenum to bismuth was determined by use of inductively coupled plasma atomic emission spectrometer (SPS1500 Seiko Elec. Co.) to be 2.0. Therefore, bismuth molybdate hydrate is represented as $HBi(MoO_4)_2 \cdot nH_2O$ (n=2.80). Bismuth molybdate hydrate (5 g) reacted with the cesium nitrate in aqueous solution (2 M, 100 ml) at 373 K. The concentration of cesium was determined by atomic adsorption method. Cesium bismuth molybdate hydrate (1 g) reacted with various nitrates in aqueous solution (1 M, 100 ml) at 353 K.

Cesium bismuth molybdate hydrate was synthesized from the reaction of bismuth molybdate hydrate and cesium nitrate in aqueous solution at 373 K. The pH in the solution decreased when the reaction proceeded. Then, cesium hydroxide was added to the solution to be kept pH at 7. The Cs to Bi ratio in cesium bismuth molybdate was reached to be 0.98. The Mo to Bi ratio in the solid did not change during the reaction. The X-ray diffraction data were indexed with a monoclinic unit cell. The lattice parameters were determined by using the program RLC3$^{8)}$ to be a=9.710±0.008 Å, b=10.872±0.007 Å, c=8.129±0.006 Å, β=98.62±0.08 °. Cesium bismuth molybdate hydrate reversively changed to bismuth molybdate hydrate in 0.5 M nitric acid at 373 K.

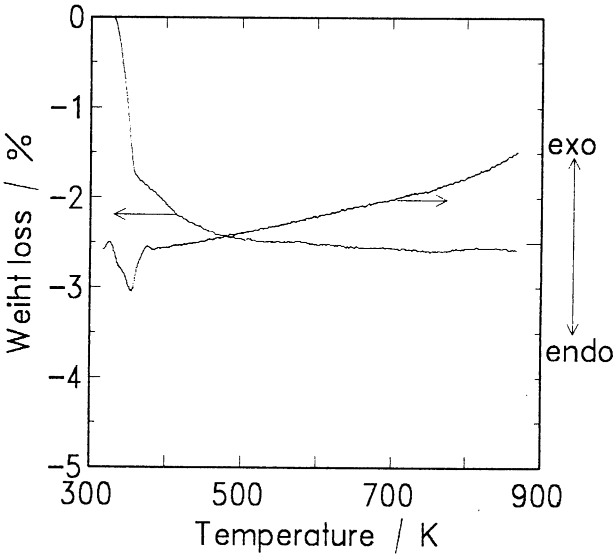

Fig. 1. TG-DTA of cesium bismuth molybdate hydrate.

The weight decrease and the endothermic peak were observed at 352 K in thermal analysis data of cesium bismuth molybdate hydrate as Fig. 1 shows. These are caused by the liberation of the crystal water. The amount of the water decreased is 1.0 molecule per a unit of cesium bismuth molybdate. After the dehydration, cesium bismuth molybdate, $CsBi(MoO_4)_2$,$^{9)}$ was identified by use of X-ray diffraction. No phase change in cesium bismuth molybdate was observed at the temperatures of 523-873 K while bismuth molybdate hydrate transformed to α-$Bi_2Mo_3O_{12}$ and MoO_3 at 617 K.$^{7)}$

Cesium bismuth molybdate is isomorphous with $CsPr(MoO_4)_2$.$^{11)}$ The basic structure consists of cesium, molybdate, bismuth and another molybdate layers which are piled in order onto (010). The directions of a, b, and c axes in cesium bismuth molybdate hydrate, $CsBi(MoO_4)_2 \cdot H_2O$, correspond to those in $CsBi(MoO_4)_2$ as shown in Table 1. In the unit cell of the former, the b axis which is perpendicular to the layers expanded, the length of a axis of the former nearly doubled and that of c axis little changed in comparison with that of the latter.

No reaction of bismuth molybdate hydrate with lithium, sodium, potassium, rubidium, and ammonium nitrates occurred in aqueous solutions

Table 1. Lattice Parameters of Various Bismuth Molybdate Hydrate

	a /Å	b /Å	c /Å	β /deg.	
$HBiMo_2O_8 \cdot nH_2O$	6.334	11.593	5.777	113.17	Ref. 6
$NaBiMo_2O_8$	5.28	11.60	5.28	90.00	Ref. 9
$KBiMo_2O_8$	5.41	12.02	5.41	90.00	Ref. 10
$KBiMo_2O_8 \cdot H_2O$	9.58	10.04	8.25	98.2	this work
$RbBiMo_2O_8$	11.63	12.09	5.28	92.5	Ref. 9
$RbBiMo_2O_8 \cdot H_2O$	9.81	10.40	8.27	99.9	this work
$CsBiMo_2O_8$	5.143	9.447	8.209	90.00	Ref. 9
$CsBiMo_2O_8 \cdot H_2O$	9.710	10.872	8.129	98.62	this work
$NH_4BiMo_2O_8$	5.12	9.22	8.10	90.00	this work
$NH_4BiMo_2O_8 \cdot H_2O$	9.51	10.50	8.14	95.7	this work

at 373 K. When the solution was basic, α-Bi_2O_3 was provided. In the presence of chloride ion in the solution, the formation of bismuth oxychloride was observed. The addition of sodium molybdate (1 mol%) to sodium or potassium nitrate solution caused the formation of the corresponding bismuth molybdate salt from bismuth molybdate hydrate. X-ray diffraction data of $NaBi(MoO_4)_2$ and $KBi(MoO_4)_2$ agreed with the previous data.[9,10] The Mo to Bi ratio in both sodium and potassium bismuth molybdates was kept at 2.0 during the reaction though sodium molybdate was added to the solution. In the presence of molybdate ion, proton in the lattice was more easily replaced by sodium and potassium ion than without molybdate ion.

On the other hand, cesium bismuth molybdate hydrate easily reacted with potassium, rubidium and ammonium nitrates in aqueous solutions with the formation of the corresponding bismuth molybdate hydrate salts without any additive. The structure of each product was topotactic with that of cesium bismuth molybdate hydrate as shown in Table. 1. Therefore, cesium bismuth molybdate hydrate is an inorganic ion exchanger for potassium, rubidium and ammonium ions. The contents of water were calculated to be 0.87, 1.00, and 0.96 per molecular unit by use of TG measurement for potassium, rubidium, and ammonium versions, respectively. Therefore, these products were represented as $ABi(MoO_4)_2 \cdot H_2O$ (A=K, Rb, and NH_3). The stability of hydrate depended on the cation size. For the reaction with potassium or ammonium ion, hydrate was formed but gradually change to nonhydrate in air at room temperature. The dehydration of monohydrates at room temperature may result in the contents of water less than 1.00 for potassium and ammonium versions. Rubidium bismuth molybdate hydrate was more stable than potassium version. Water in the hydrate was removed at 347 K. Cesium bismuth molybdate hydrate was the most stable among these hydrate salts. Though cesium bismuth molybdate hydrate was reacted with sodium nitrate in aqueous solution, only nonhydrate, $NaBi(MoO_4)_2$,[9] was obtained. Sodium bismuth molybdate hydrate may be much less stable than potassium version because sodium ion is smaller than potassium ion. No reaction occurred between cesium bismuth molybdate hydrate and lithium nitrate in aqueous solution.

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References

1) K. Aykan, *J. Catal.*, **12**, 281 (1968).
2) Ph. A. Batist, A. H. W. M. Der Kinderen, Y. Leeuwenburgh, F. A. M. G. Metz, and G. C. A. Schuit, *J. Catal.*, **12**, 45 (1968).
3) Ph. A. Batist, J. F. H. Bouwens, and G. C. A. Schuit, *J. Catal.*, **25**, 1 (1972).
4) F. Trifiro, H. Hoser, and R. D. Scarle, *J. Catal.*, **25**, 12 (1972).
5) B. Grzybowska, J. Haber, and J. Komork, *J. Catal.*, **25**, 25 (1972).
6) Y. Murakami, N. Ishizawa, and H. Imai, *Powder Diffraction*, **5**, 227 (1990).
7) Y. Murakami and H. Imai, *J. Mat. Sci. Lett.*, **10**, 107 (1990).
8) T. Sakurai, "Universal Program for Crystallographic Computation," Cryst. Soc. Jpn. (1967).
9) P. V. Klevtsov, V. A. Vinokurov, and R. F. Klevtsova, *Kristallogr.*, **18**, 1192 (1973) [*Sov. Phys. Crystallogr.*, **18**, 749 (1974)].
10) Yu. A. Belikodnyi and V. K. Trunov, *Kristallogr.*, **19**, 763 (1974) [*Sov. Phys. Crystallogr.*, **19**, 474 (1975)].
11) R. F. Klevtsova, V. A. Vinokurov, and P. V. Kievtsov, *Kristallogr.*, **17**, 284 (1972) [*Sov. Phys. Crystallogr.*, **17**, 240 (1972)].

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