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Progress in the Intercalation of Pyridine and Other Organic Bases into Crystalline Bismuth Molybdenum Oxide Hydrate, $BiMo_2O_7OH{\cdot}2H_2O$

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Introduction

The synthesis of a novel bismuth molybdate, $BiMo_2O_7OH{\cdot}2H_2O$,[1] provided a starting material for a potential catalyst of selective oxidation/ammoxidation reactions. The existing family of bismuth molybdates includes three industrially important active phases, known as alpha (α-($Bi_2Mo_3O_{12}$)),[2,3] beta (β-($Bi_2Mo_2O_9$)),[4,5] and gamma (γ-(Bi_2MoO_6)),[6,7] which are all used as catalysts for the partial oxidation of hydrocarbons. They possess several key structural features[8] which are also present in $BiMo_2O_7OH{\cdot}2H_2O$, but the latter is inactive due to its thermal instability at temperatures greater than 200 °C, whereas the active bismuth molybdates are required to operate at temperatures between 300 and 400 °C.

The intercalation of many different organic molecules into layered solids has been the subject of extensive research in recent years, on compounds such as clays and tetravalent metal phosphates.[9] The intercalation of organic guest molecules can be thought of as an intermediate step in the synthesis of a pillared, layered solid. It may be possible to substitute the organic material for a complex metal species of comparable size, for example the aluminum "Keggin" ion ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$). The subsequent calcination would transform the ions into metal oxide "pillars" that strongly bind to the host layers and, hence, create a compound of much higher surface area and greater thermal stability.

The intercalation of pyridine into the title compound has been previously investigated by Murakami et al.[10] and Song et al.,[11] although incorrect formulas ($Bi_2Mo_3O_{12}{\cdot}3.86H_2O$ and $Bi_2Mo_3O_{12}{\cdot}4.75H_2O$) for the starting material were reported in both papers. In the work by Murakami et al.,[10] very little characterization of the intercalate was reported. In the more extensive recent work of Song et al.,[11] the X-ray powder diffraction data were indexed on a monoclinic unit cell and the infrared spectroscopic data indicated that the pyridine is coordinately bonded to the host layers.

At the time of the latter publication, we had independently started our own investigation of the intercalation chemistry of the material correctly formulated as $BiMo_2O_7OH{\cdot}2H_2O$ with the long-term goal of making new selective oxidation catalysts. In this note, we describe our work on some of the same systems reported by Song et al.,[11] but our characterization strongly disputes some of their conclusions regarding the nature of the intercalated species and crystal chemistry of the solids.

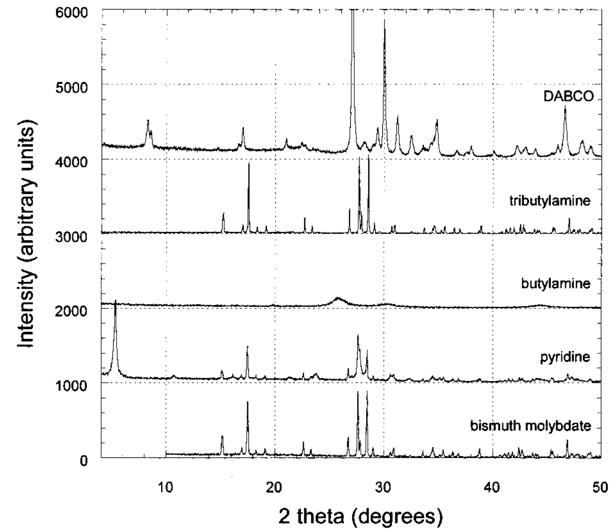

Figure 1. X-ray powder diffraction patterns of $BiMo_2O_7OH{\cdot}2H_2O$ and its products with organic bases.

Experimental Section

The crystalline starting material, $BiMo_2O_7OH{\cdot}2H_2O$, was prepared under mild, hydrothermal conditions as reported by Hriljac et al.[1] Intercalation of pyridine was attained by refluxing a mixture of 10 g of $BiMo_2O_7OH{\cdot}2H_2O$ and 50 mL of pyridine for a period of 4 days. A reaction within a sealed bomb at the increased temperature of 150 °C for 24 h was also attempted. The resulting yellowish-green solid was washed with distilled water and acetone and dried in air for several hours. Anal. Calcd for $BiMo_2O_7OH{\cdot}0.43C_5H_5N{\cdot}1.17H_2O$: C, 4.52; H, 0.79; N, 0.99. Found: C, 4.41; H, 0.77; N, 1.03.

The attempted intercalation of *n*-butylamine and tri-*n*-butylamine was carried out by refluxing a mixture of 1 g of $BiMo_2O_7OH{\cdot}2H_2O$ and 10 mL of the respective amine for 4 days, or by 1 day of reaction in a sealed bomb at 150 °C. For the intercalation of 1,4-diazabicyclooctane (DABCO), 5 g of the reactant was dissolved in 20 mL of distilled water and refluxed with 1 g of $BiMo_2O_7OH{\cdot}2H_2O$ for 4 days.

X-ray powder diffraction patterns were recorded using a Siemens D5000 diffractometer. Further analysis in the form of infrared spectroscopy using a Perkin-Elmer Paragon 1000 FT-IR spectrometer and high-resolution solid-state MAS NMR spectroscopy using a Chemagnetics CMX Infinity 300 spectrometer was performed on the products. ^{13}C and ^{15}N NMR spectra were recorded at 75.4 and 30.4 MHz, respectively, using a Chemagnetics 7.5 mm magic angle spinning probe with a spinning frequency of 5000 ± 2 Hz. Cross polarization (from ^1H) and high-power TPPM decoupling[12] (with field strength of ca. 62 kHz) were implemented and isotropic chemical shifts are reported relative to tetramethylsilane (^{13}C) and nitromethane (^{15}N). TGA and DTA curves were obtained with a Stanton-Redcroft STA 1500 analyzer by heating the solids to 600 °C at a heating rate of 10 °C/min.

Results and Discussion

The contrast in the diffraction pattern of $BiMo_2O_7OH{\cdot}2H_2O$ and that of the novel pyridine intercalate, formulated by us as

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(1) Hriljac, J. A.; Toradi, C. C. *Inorg. Chem.* **1993**, *32*, 6003.
(2) van den Elzen, A. F.; Rieck, G. D. *Acta Crystallogr.* **1973**, *B29*, 2433.
(3) Theobald, F.; Laarif, A. *Mater. Res. Bull.* **1985**, *20*, 653.
(4) van den Elzen, A. F.; Rieck, G. D. *Mater. Res. Bull.* **1975**, *10*, 1163.
(5) Chen, H.-Y.; Sleight, A. W. *J. Solid State Chem.* **1986**, *63*, 70.
(6) van den Elzen, A. F.; Rieck, G. D. *Acta Crystallogr.* **1973**, *B29*, 2436.
(7) Theobald, F.; Laarif, A.; Hewat, A. W. *Ferroelectrics* **1984**, *56*, 219.
(8) Buttrey, D. J.; Jefferson, D. A.; Thomas, J. M. *Philos. Mag. A* **1986**, *53*, 897.
(9) Ohtsuka, K. *Chem. Mater.* **1997**, *9*, 2039.
(10) Murakami, Y.; Imai, H. *J. Mater. Sci. Lett.* **1990**, *10*, 107.
(11) Song, Y.; Zhao, A. *J. Radioanal. Nucl. Chem.* **1998**, *231*, 17.
(12) Bennett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *J. Chem. Phys.* **1995**, *103*, 6951.

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Table 1. TGA Data for the Reaction Products of $BiMo_2O_7OH{\cdot}2H_2O$ with Pyridine (BiMo·py), *n*-Butylamine (BiMo·ba), and Tri-*n*-butylamine

guest molecule	first mass loss (as % of original mass)	temp range (°C)	second mass loss	temp range	third mass loss	temp range
pyridine	3.5	150−250	5.3	250−350		
n-butylamine	1.8	20−140	2.8	140−370		
tri-*n*-butylamine	15.6	20−320	4.4	320−470	1.8	470−530

Table 2. Infrared Bands of Pyridine Intercalate (BiMo·py) and Pyridine on Acid Solids in the 1400−1700 cm^{-1} Region

pyridine intercalate (BiMo·py)	pyridinium ion	coordinately bonded pyridine
1483	1485−1500[a]	1447−1460[b]
1538	1540[a]	1488−1503[b]
1611	1620[a]	1580[b]
1634	1640[a]	1600−1633[b]

[a,b]Referenced to ref 13.

Table 3. ^{13}C Shifts (ppm) of Pyridine Intercalate (BiMo·py) and Pyridine/Pyridinium Ion in Solution

	ring position		
	2 and 6	3 and 5	4
pyridine	150.4[a]	124.1[a]	136.4[a]
pyridinium ion	142.6[b]	129.1[b]	148.5[b]
BiMo·py	141.9	127.5	148.1

[a,b]Referenced to ref 14.

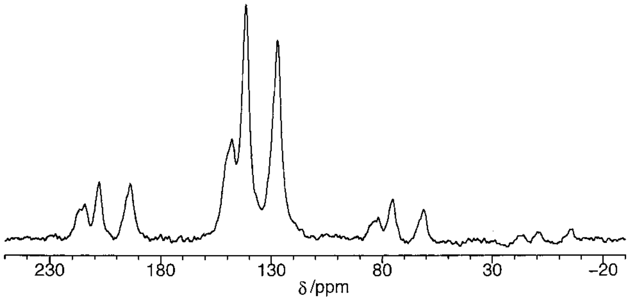

Figure 2. High-resolution ^{13}C NMR spectrum of **BiMo·py**. A total of 9280 transients were acquired with a recycle delay of 5 s.

$BiMo_2O_7OH{\cdot}0.43C_5H_5N{\cdot}1.17H_2O$ (as discussed below and subsequently referred to as **BiMo·py**) shown in Figure 1 indicates a significant change in the structure of the original material. An intense peak at a 2θ angle of 5° and with a d spacing value of 16.46 Å corresponds to an 11.41 Å increase in the interlayer region of $BiMo_2O_7OH{\cdot}2H_2O$ along the direction perpendicular to the host layers and, hence, the successful intercalation of pyridine. The indexing of the **BiMo·py** data was attempted using Bruker's Win-index 3.0.6 program. No suitable unit cell was found, indicating a lack of regularity in the position of the pyridine between the layers. The reaction product of $BiMo_2O_7OH{\cdot}2H_2O$ and *n*-butylamine (**BiMo·ba**) is virtually amorphous, as indicated by the pattern shown in Figure 1. The apparent complete break up of the layered structure may be due to the strong basicity of *n*-butylamine (pK_b 3.23 compared to pK_b 8.75 for pyridine). The attempted reaction of $BiMo_2O_7OH{\cdot}2H_2O$ and tri-*n*-butylamine failed, as determined by X-ray diffraction (Figure 1). The inability of tributylamine to swell the interlayer spaces of the host material is not unexpected, since the size of the molecule is likely to cause steric hindrance and prevent the reaction from proceeding. The reaction product of $BiMo_2O_7OH{\cdot}2H_2O$ and 1,4-diazabicyclooctane (DABCO) is the γ-phase bismuth molybdate (γ-(Bi_2MoO_6)), as confirmed by its diffraction pattern in Figure 1. This particular phase formation is not specific to DABCO and occurs with other bases of similar strength, whose reactions are not reported here.

The formula of **BiMo·py** was determined from both TGA and elemental analysis, carried out on samples from the same batch. The formula calculated from the TGA data (Table 1) is $BiMo_2O_7OH{\cdot}0.36C_5H_5N{\cdot}1.15H_2O$. The first mass loss of 0.60 mg (3.5% of the original mass) corresponds to the loss of water from the structure, occurring at temperatures between 150 and 250 °C. The second mass loss of 0.90 mg (5.3% of the original mass) corresponds to the loss of the pyridinium ions from the interlamellar regions, resulting in the formation of $BiMo_2O_{7.5}$. This compound is unstable and decomposes above 300 °C to form a mixture of α-($Bi_2Mo_3O_{12}$) and MoO_3. The elemental analysis data yielded a formula of $BiMo_2O_7OH{\cdot}0.43C_5H_5N{\cdot}1.17H_2O$, somewhat contradicting the results from the TGA. The most likely reason for the discrepancy is an experimental error in the TGA data, since the end point for the first mass loss and the starting point for the second mass loss are unclear from the analysis curve. On that basis, the **BiMo·py** formula of $BiMo_2O_7OH{\cdot}0.43C_5H_5N{\cdot}1.17H_2O$ is considered to be the most reliable representation of the intercalate.

The infrared data (Table 2) provide strong evidence that a pyridinium ion is formed in **BiMo·py**. Of particular note is the observation of a band at ca. 1540 cm^{-1}, assigned to a $N^+{-}H$ bending motion.[13] This contradicts the findings of Song et al., who conclude that pyridine is coordinately bonded to molybdenum atoms on the host layers. However, the use of MAS NMR reinforces the evidence collected from the infrared analysis. An initial comparison of common characteristic ^{13}C shifts [14] (Table 3) further verifies the presence of the guest molecule between the host layers. The large ^{13}C line width of ca. 200 Hz (Figure 2) is probably indicative of considerable static disorder of the guest molecules within the interlayer spaces. The ^{13}C MAS NMR data alone appear to confirm the presence of pyridinium ions, although there is some ambiguity regarding the assignment of the shifts. If the shift at 141.9 ppm was assigned to the carbon in the 4 position and the shift at 148.1 ppm was assigned to the carbons in the 2 and 6 positions, they would be fairly similar to the characteristic shifts of pyridine. However, the relative peak intensities point to the more intense shift at 141.9 ppm being that of the 2 and 6 carbons rather than the 4 carbon. To clarify beyond doubt which species is present in **BiMo·py**, ^{15}N MAS NMR was performed on the solid. The advantages of using ^{15}N NMR rather than ^{13}C NMR are the larger chemical shift range of ^{15}N and the greater sensitivity of the ^{15}N chemical shift to protonation of the lone pair electrons. The positive identification of pyridinium ion formation is confirmed by the resonance at 181.5 ppm, which compares favorably to the resonance of 187.5 ppm, observed for pyridinium ion formation on clays[15] (Table 4).

The orientation and spatial arrangement of organic molecules present in the interlamellar spaces of layered compounds can be deduced reasonably accurately from X-ray diffraction data. Despite the difficulty in accurately predicting the expansion

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(13) Parry, E. P. *J. Catal.* **1963**, *2*, 371.
(14) Slothers, J. B. *Carbon-13 NMR Spectroscopy;* Academic Press: New York, 1972.
(15) Ukrainczyk, L.; Smith, K. A. *Environ. Sci. Technol.* **1996**, *30*, 3167.

Table 4. ^{15}N Shifts (ppm) of Pyridine Intercalate (BiMo·py) and Pyridine/Pyridinium Ion on Clays

species	chem shift (ppm)	species	chem shift (ppm)
coordinately bonded pyridine	112.7[a]	pyridinium ion	187.5[c]
hydrogen-bonded pyridine	78.8[b]	**BiMo·py**	181.5

[a−c]Referenced to ref 15.

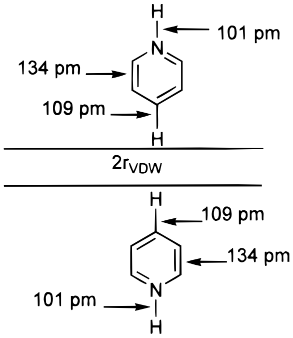

Figure 3. Estimated overall increase in *d* spacing of 12 Å (1200 pm) for the intercalation of two pyridinium ions positioned as shown.

perpendicular to the host layers, arising from the fact that the determination is mainly by nonbonding hydrogen repulsions, the expected increase can be considered as consistent with the increase in van der Waals dimensions. An interlayer space increase of 11.41 Å seen for the intercalation of pyridine into $BiMo_2O_7OH{\cdot}2H_2O$ was compared to the size of the pyridinium ion, calculated using the standard bond lengths for C═C, C−H, and N−H and the van der Waals radius for the H−H repulsion. The overall length of the pyridinium ion is ca. 4.8 Å, and the van der Waals repulsion is ca. 1.3 Å. When these values are compared to the interlayer expansion of 11.41 Å, it is apparent that there is more than one ion lying along the direction perpendicular to the layers. An arrangement of one ion lying directly above another in the same direction (Figure 3) results in an estimated overall increase of ca. 12 Å, a value slightly greater than the observed value of 11.41 Å. This marginally smaller value suggests that the pyridinium ions are arranged in a slightly offset position (Figure 4), similar to the model for the orientation of pyridine intercalated into MoO_3 proposed by Johnson et al.[16] The large peak widths in the ^{13}C and ^{15}N NMR spectra of **BiMo·py** suggest there is considerable disorder of the guest species and, hence, significant perturbation of this arrangement.

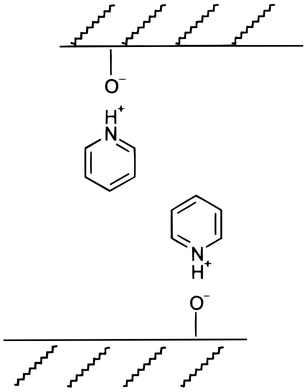

Figure 4. Probable position of the pyridinium ions within the interlamellar region of **BiMo·py**.

Song et al.[11] also reported the intercalation of 2,5-dimethylpyridine and 4-benzylpyridine. The presence of methyl or phenyl groups on the pyridine ring would undoubtedly create larger interlayer spaces, as is reported. These bulky molecules may also have an effect on how the pyridine species bond to the layers since they are likely to prevent the electron pair on the nitrogen from getting too close to the host layers and stripping off the protons to form pyridinium ions, which happens with the smaller pyridine molecule. The attempted intercalation of several substituted pyridines is the subject of ongoing research by the authors of this paper.

Conclusion

We have definitively shown that pyridine intercalation into the material correctly formulated as $BiMo_2O_7OH{\cdot}2H_2O$ occurs with deprotonation of the layers and formation of pyridinium cations. X-ray diffraction data are consistent with a model where the interlamellar region is occupied by two pyridinium ions oriented in a slightly offset position with respect to each other and with the 2-fold axes aligned perpendicular to the layers. Future work will investigate the possibility of replacing the pyridinium ions with inorganic cations, leading eventually to the synthesis of pillared bismuth molybdate catalysts.

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(16) Johnson, J. W.; Jacobson, A. J.; Rich, S. M.; Brody, J. F. *Rev. Chim. Miner.* **1982**, *19*, 420.