NMR Study on Proton Behavior of Hexagonal Hydrogen Molybdenum Bronze obtained by Ion Exchange

Noriyuki SOTANI, Yohei NISHINO, and Kazuo EDA
Department of Chemistry, Faculty of Science, Kobe University, Tsurukabuto, Nada, Kobe 657-8501, Japan

(Manuscript submitted January 31, 2003; accepted March 25, 2003)

Abstract
Hexagonal hydrogen molybdenum bronze was obtained from alkali decamolybdate with tunnel structure by the reduction with nascent hydrogen. A maximum amount of inserted hydrogen was H/Mo=1.5. Hydrogen insertion accompanied the change in the amount of structural water and the removal of alkali ions. NMR spectrum proved the existence of several types of proton. We proposed the various models of proton clusters and the proton distribution of each model. We also discussed the effect of alkali ions in the tunnel-site by the results of the simulation of NMR spectrum.

1 Introduction
The alkali-metal decamolybdate (in abbreviate deca) consists of double chains of edge-sharing MoO₆ octahedra linked by common corners, forming wide (ca. 0.3 nm diameter) tunnels occupied by alkali-metal cations.[1] Presence of such (one-dimensional) tunnels suggests that there should be rich intercalation chemistry and related (low-dimensional) properties to investigate. Hydrogen intercalation of this compound is, therefore, of interest in materials science and applied science.

It has been known that hydrogen intercalation easily occurs on deca and makes hexagonal hydrogen molybdenum bronze under a condition where proton and alkali-metal cation can exchange.[2] In the ideal Mo-O framework of deca 1/6 of Mo sites are randomly vacant and 5 protons are necessarily incorporated to attach to the oxygens surrounding the vacant Mo site, forming two OH₂ and one OH, for the charge valence compensation (Fig.1).

In the present work behaviors of inserted and originally contained protons were investigated by proton-NMR.

2 Experimental
Preparation of intercalation products: 0.05 mole of deca was suspended in HCl aqueous solution (2-3
mol/dm³) at 276-278 K. A desired amount of Zn powder was divided into several portions of 0.5 g and added to the suspended solution in 5 min intervals. To prevent oxidation of the sample, nitrogen gas was bubbled into the solution. After the reaction, the sample was homogenized by stirring at 276-278 K for more than 1 day. Then, samples were collected with a suction filter, washed with distilled water till no Cl⁻ ion was detected, and dried in a desiccator. The contents of hydrogen inserted were determined by redox titration.

**NMR measurement and analysis:** Proton NMR was detected at liquid nitrogen temperature (77 K) using a pulsed NMR spectrometer operating at 11 MHz. Absorption spectra were obtained by Fourier transformation of the solid echo signals measured by using the zero-time-resolution method (90° - 90° pulse system).

Simulated spectra of model structures with various proton arrangements were calculated using a simulation program built previously.[3] The line-shape analysis of NMR spectrum was performed by least-square fitting of a linear combination of some simulated spectra to observed one.

### 3 Results and Discussion

**Hydrogen intercalation and ion exchange:** Figure 2 shows hydrogen uptake (molar ratio H/Mo) and alkali metal contents (molar ratio M/Mo, M=alkali-metal) during the Zn/HCl reduction of the samples (hydrogen intercalation). Hydrogen intercalation \((1/x \text{ MoO}_3 + 1/2 \text{ H}_2 \rightarrow 1/x \text{ H}_x\text{MoO}_3)\) proceeded simultaneously with proton/alkali-metal ion exchange \((\text{M}^+(s) + \text{H}^+(1) \rightarrow \text{H}^+(s) + \text{M}^+(1))\), but the former was strongly dependent on progressive degree of the latter. That is, hydrogen intercalation was promoted under the condition of lower population of tunnel-site cation (highly ion-exchanged condition), while it proceeded very slowly when the population was high (poorly exchanged condition). And the behavior of the ion exchange depended on the kinds of tunnel-site cations: i.e., the cation with a larger ionic radius (Cs⁺) remained until larger amount of Zn addition, indicating they were more resistant to exchange than those with smaller radii. The hydrogen uptake reached to a maximum value of 1.5 H/Mo (molar ratio) after the tunnel-site cations were wholly removed. According to XRD analysis, only minor structural changes were observed as peak shifts and broadening of XRD peaks, caused by the hydrogen intercalation, and it was suggested that the tunnel structure of alkali-metal decamolybdate remained in all the intercalation products.

**Hydrogen in original deca:** Figure 1 shows the arrangements of oxygen atoms surrounding the vacant Mo site. In an ideal deca structure, 5 hydrogen atoms are attached as

![Fig. 2 Compositional Changes during the Zn/HCl reduction of Na deca (a), K deca (b), and Cs deca (c).](image-url)
protons to these oxygen atoms, as mentioned above. But, there are various modifications in hydrogen contents of real deca (see the values of hydrogen content per a vacant Mo site, H/Movan, in Table 1). For example, some (around one tenth, ideal M/Mo=0.2) of tunnel-site cations are also vacant and this lack might provide one more proton attached to the oxygen atoms for the charge valence compensation. Thus, maximum 6 protons gather around the Mo vacancy, forming proton clusters. Therefore, we calculated NMR spectra of up to 6 spin clusters available and performed line-shape analysis of the observed NMR spectra using the calculated spectra.

Figure 3 and Table 1 show the results. All the observed spectra could be fitted well with a linear combination of the spectra simulated for 2-6 proton clusters. According to the table, larger amount of 2 spin (Pake doublet) species existed in the Na deca. This supported the presence of further hydration water directly attached to tunnel-site cation, which was only observed for Na and Li deca's. Cs deca exhibited much less than 5 protons per a Mo vacancy. This makes us imagine formation of proton species with low cluster numbers. Nevertheless, it showed high distribution of higher cluster numbers (6 or 4 spin species). This might prove the evidence of proton transfer between neighboring Mo vacancy areas.

![Fig 3 Best fitted simulated proton NMR spectra (proton signal) for Na deca (i), K deca (ii), and Cs deca (iii).](image)

Table 1. Proton cluster species of Na, K and Cs deca's.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hydrogen content</th>
<th>6 spin</th>
<th>5 spin</th>
<th>4 spin</th>
<th>3 spin</th>
<th>2 spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na18Mo10O30.95 * 5.90H2O</td>
<td>1.18 (5.90)</td>
<td>0.10</td>
<td>0.03</td>
<td>0.54</td>
<td>0.18</td>
<td>0.35</td>
</tr>
<tr>
<td>K18Mo10O30.95 * 4.28H2O</td>
<td>0.86 (4.28)</td>
<td>0.04</td>
<td>0.01</td>
<td>0.45</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td>Cs18Mo10O30.9 * 3.13H2O</td>
<td>0.63 (3.13)</td>
<td>0.04</td>
<td>0</td>
<td>0.20</td>
<td>0.17</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Moovan means the number of vacant Mo sites.

**Hydrogen in the intercalation compound of deca:** Figure 4 and Table 2 show the results of NMR line-shape analysis for hydrogen intercalation products. As for the products with higher hydrogen contents such as H15.0Mo10O30.0*4.40H2O the line shape analysis was difficult because of strong broadening in spectra caused by the high density of proton. According to Table 2, the water content of the product increased as the ion exchange

(111)
proceeded, until whole exchange. This increase is attributable to incorporation of additional crystal water, which is trapped in the vacant tunnel-sites.

Remarkable changes in proton distribution with hydrogen intercalation were drastic increase in 6 spin species and appearance of Gaussian and 3' spin species. The increase of 6 spin species should be attributed to proton addition to Mo vacancy area, resulting from the lack of tunnel-site cation. On the other hand, the Gaussian species is an isolated proton and 3' spin species is a proton cluster, which adopts a proton separation different from that of 3 spin species. These features are different from those of protons situated around the Mo vacancy and they are attributed to protons inserted by hydrogen intercalation, which are situated on the sites along the double chain of edge-sharing MoO$_6$ octahedra.

![Graph](image)

Fig. 4 Best fitted simulated proton NMR spectra (proton signal) for $\text{H}_2\text{K}_{0.7}\text{Mo}_{10}\text{O}_{30.35} \cdot 6.00\text{H}_2\text{O}$ (i), $\text{H}_3\text{K}_{0.03}\text{Mo}_{10}\text{O}_{30.15} \cdot 6.20\text{H}_2\text{O}$ (ii), and $\text{H}_6\text{Mo}_{10}\text{O}_{30.0} \cdot 6.60\text{H}_2\text{O}$ (iii).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hydrogen content</th>
<th>6spin</th>
<th>5spin</th>
<th>4spin</th>
<th>3spin</th>
<th>3spin'</th>
<th>2spin</th>
<th>Gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}<em>{1.96}\text{Mo}</em>{10}\text{O}_{30.35} \cdot 4.28\text{H}_2\text{O}$</td>
<td>0.86</td>
<td>0.04</td>
<td>0.01</td>
<td>0.45</td>
<td>0.13</td>
<td>0</td>
<td>0.23</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}<em>4\text{K}</em>{0.7}\text{Mo}<em>{10}\text{O}</em>{30.35} \cdot 6.00\text{H}_2\text{O}$</td>
<td>1.62</td>
<td>0.98</td>
<td>0.18</td>
<td>0</td>
<td>0.05</td>
<td>0.30</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>$\text{H}<em>5\text{K}</em>{0.03}\text{Mo}<em>{10}\text{O}</em>{30.15} \cdot 6.20\text{H}_2\text{O}$</td>
<td>1.83</td>
<td>0.88</td>
<td>0.33</td>
<td>0</td>
<td>0.02</td>
<td>0.36</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>$\text{H}<em>6\text{Mo}</em>{10}\text{O}_{30.0} \cdot 6.60\text{H}_2\text{O}$</td>
<td>2.00</td>
<td>0.73</td>
<td>0</td>
<td>0.43</td>
<td>0</td>
<td>0.07</td>
<td>0.48</td>
<td>0.30</td>
</tr>
<tr>
<td>$\text{H}<em>{1.3}\text{Mo}</em>{10}\text{O}_{30.0} \cdot 4.40\text{H}_2\text{O}$</td>
<td>2.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$H_t$: total hydrogen, $H_{ins}$: hydrogen inserted.

References