Supporting Information

Interaction of Magnesium Hydride Clusters with Nb Doped MgO Additive Studied by Density Functional Calculations

K.S. Sandhya, D. Pukazhselvan, Duncan Paul Fagg, Nobuaki Koga
Department of Complex Systems Science, Graduate School of Information Science, Nagoya University, Japan
Nanoengineering Research Group, Centre for Mechanical Technology and Automation (TEMA), Department of Mechanical Engineering, 3810-193 Aveiro, Portugal
Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Honmachi, Kawaguchi 332-0012, Japan

1. Electronic structure of Mg$_3$NbO$_4$ cation: S1
2. Electronic structure of Mg$_3$NbO$_4$–H$_2$:S2
3. Optimized structures of Mg$_3$NbO$_4$–mH$_2$ (m = 1 – 4) for category I and II.: S3
4. Optimized structures of Mg$_4$O$_4$–mH$_2$ (m = 1 – 4): S4
5. Three different isomers of Mg$_3$H$_x$ clusters.: S6
6. Optimized complex structures of Mg$_3$NbO$_4$–Mg$_x$H$_x$ (x = 0, 2, 4, 6, 8, 10) system.: S8

1. Electronic structure of Mg$_3$NbO$_4$ cation

The cationic Mg$_3$NbO$_4$ cluster has a $C_{3v}$ symmetric structure as shown below.

![Diagram of Mg$_3$NbO$_4$ cation]

Its possible electronic configurations in the frontier orbital levels are shown in Fig. S1 accompanied with the corresponding molecular orbitals. 1a$_1$ orbital mainly consists of Nb d orbital, whereas 2a$_1$ orbital extending over the entire cluster is a combination of Mg and Nb atomic orbitals. The degenerate e symmetric orbitals consist of Nb d orbital and Mg hybrid atomic orbitals. If the electronic configuration of the cluster is assumed to be a closed-shell, the most stable 1a$_1$ orbital is doubly occupied. However, the difference in energy between these orbitals is not large enough, the triplet state having two singly occupied orbitals could be more stable. The present calculations showed that the triplet state shown in Fig. S1b bearing two singly occupied orbitals (SOMOs) and degenerated lowest unoccupied orbitals (LUMOs) is the most stable. These SOMOs and LUMOs are expected to play a role in interacting with other molecules. Hereafter, 1a$_1$ and 2a$_1$ orbitals are called SOMO1 and SOMO2, respectively.

When the hydrogen molecule coordinates to a metal atom, its binding mechanism is discussed in terms of donation and back-donation as shown in Fig. S2. Because the occupied bonding $\sigma$ orbital does not have a node, electron donation from it is possible to the vacant metal orbital without a node. Opposite to this, back-donation occurs from the occupied metal orbital.
with a node to the unoccupied $\sigma^*$ orbital. In addition, note that, because the Mg cation has formally no valence electrons, back-donation from the Mg cation is not taken into account.

\[
\begin{align*}
\text{a)} & & \text{b)} & & \text{c)} \\
\text{2a}_1 & & \text{2a}_1 & & \text{2a}_1 \\
\text{1a}_1 & & \text{1a}_1 & & \text{1a}_1
\end{align*}
\]

Fig. S1. Possible electronic configurations of Mg$_3$NbO$_4$ cation in the low-lying electronic states, a) $^1\text{A}_1$, b) $^3\text{A}_1$, and c) $^3\text{E}$, and d) the relevant molecular orbitals.

Fig. S2. (a) Electron donation from and (b) back-donation to the hydrogen molecule.

2. Electronic structure of Mg$_3$NbO$_4$–H$_2$

The above argument and the shape of molecular orbitals shown in Fig. S1 suggest that, when the hydrogen molecule attacks the Mg atoms, the hydrogen molecule would interact with the $2a_1$ and $e$ orbitals of Mg$_3$NbO$_4$ to donate electrons. Because the $1a_1$ orbital has only small lobes on the Mg cations, it does not participate into the interaction. The orbital correlation diagram for this case is
shown in Fig. S3a. The $\sigma$ orbital of the hydrogen molecule interacts with the 2$a_1$ orbital as well as the $e$ orbitals to form the orbital $\phi_1$ representing the electron donation between Mg and the hydrogen molecule. The shapes and energies of the singly occupied orbitals $\phi_2$ and $\phi_3$ are similar to those of the 1$a_1$ orbital and one of the $e$ orbitals of Mg$_3$NbO$_4$. This is because they do not interact with the hydrogen molecule. When the hydrogen molecule attacks the Nb cation, the interactions are different as shown in Fig. S3b. While the $\sigma$ orbital of the hydrogen molecule similarly interacts with the 2$a_1$ orbital, the orbital representing the back-donation from the Nb $d$ orbital to the $\sigma^*$ orbital ($\phi_7$) is occupied by an electron. The singly occupied 1$a_1$ orbital consisting of the $d$ orbital with a proper nodal character realizes the back-donation to the $\sigma^*$ orbital of the hydrogen molecule. Accordingly, the larger binding energy in the attack of the hydrogen molecule to Nb in Mg$_3$NbO$_4$ than that in the attack to Mg can be ascribed to the contribution from the back-donation. This also accounts for the longer H–H bond distance.

Fig. S3. Orbital correlation diagram for the attack of the hydrogen molecule to a) Mg and b) Nb in Mg$_3$NbO$_4$ cation.

3. Optimized structures of Mg$_3$NbO$_4$ – mH$_2$ ($m = 1 – 4$) for category I and II
4. Optimized structures of Mg₄O₄ – mH₂ (m = 1 – 4)
$\text{SCF Energy} = -805.113946470$
5. Three different isomers of Mg₆H₈ clusters

SCF Energy = -805.141436706

SCF Energy = -805.141700805

Mg₃NbO₄-Mg₄
6. Optimized complex structures of $\text{Mg}_3\text{NbO}_4-\text{Mg}_x\text{H}_y$ ($x = 0, 2, 4, 6, 8, 10$) system