pH-Insensitive Brønsted Acid-Base Site Embedded in a Pentanuclear Scaffold

([1]*Graduate School of Engineering, Osaka University*, [2]*Institute for Molecular Science,* [3]*SOKENDAI,* [4]*JST PRESTO*) ○Misa Tomoda,[1,2,3] Hitoshi Izu,[1,2] Yutaka Saga,[1] Mio Kondo,[1,4] Shigeyuki Masaoka[1]

Keywords: Heterometallic Multinuclear Complex; Acid-Base Response; Hydrogen Evolution Reaction; Changes in Catalytic Activity

Hydrogen ion (H^+) is a cation which consists of a single proton and exhibits the highest positive charge density. The behaviors of H^+ play an essential role as the origin of functions in both biological systems and artificial functional materials. In general, the behaviors of H^+ can be interpreted by the conventional Brønsted-Lowry acid-base theory. According to the theory, the behavior of H^+ is quite sensitive to the concentration of H^+ (*i.e.*, pH), and it is quite difficult to maintain the properties/function of compounds bearing Brønsted acid/base sites throughout a wide range of pH. Here, we successfully developed an unconventional Brønsted acid/base site, which exhibits pH-insensitive nature.

Our study started with the investigation on acid-base responding behaviors of heterometallic pentanuclear complexes, **Ru_2Co_3OH** and **Ru_2Co_3O** (Figure 1). Upon addition of 3 eq. of a strong base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, pK_a = 24.3) to an acetonitrile solution containing **Ru_2Co_3OH**, no UV-vis absorption spectral change was observed, indicating that no deprotonation reaction proceed. Additionally, the protonation reaction of **Ru_2Co_3O** was conducted by using the conjugated acid of DBU, DBU-H^+. In this case, protonation reaction also did not proceed. These unusual acid-base responding behaviors of the complexes indicated that Brønsted acid-base sites at the triangular core are in the unique environment.

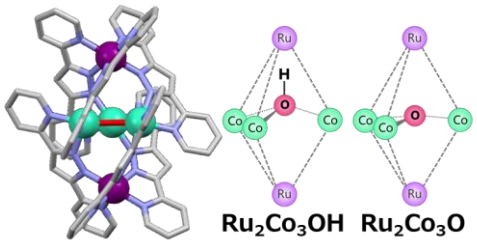

Figure 1. The molecular structures of heterometallic pentanuclear complexes, **Ru_2Co_3OH** (left) and **Ru_2Co_3O** (right).

Subsequently, we investigated redox behaviors of **Ru_2Co_3OH** and **Ru_2Co_3O** (Figure 2), and it was revealed that the confined H^+ largely affects their redox behaviors. We also found that the catalytic activity for hydrogen evolution reaction can be controlled by the presence/absence of H^+ at the sites. Current study offers a new class of compounds, which can maintain the properties/function as a Brønsted acid/base in a wide range of pH.

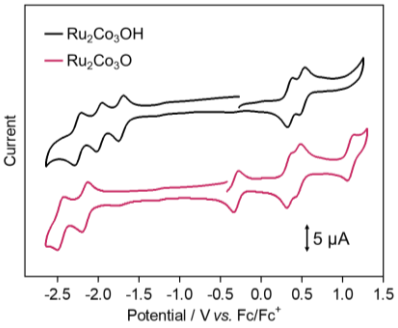

Figure 2. CVs of **Ru_2Co_3OH** and **Ru_2Co_3O**.