Quantum chemical study on the temperature dependence of separation of molecular hydrogen and deuterium using dihydrogen complexes

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Abstract. Hydrogen (H_2) has been called an ideal next-generation energy carrier. There are two ways of adsorption of molecular hydrogen, chemisorption and physisorption, but since chemisorption is strong and physisorption is weak, an intermediate way of adsorption is needed to realize reversible adsorption and desorption at room temperature. In this study, we investigate the feasibility of reversible adsorption/desorption at room temperature for two solid-phase Mn hydrogen molecular complexes, Mn-PCy_3-H_2 (denoted Mn1) and Mn-dppe-H_2 (denoted Mn2), by means of quantum chemical calculations. After performing structural optimization calculations using the hybrid functional M06-2x, the Gibbs energies were calculated at four temperatures (150 K, 225 K, 450 K, and 600 K) to estimate the temperature at which the Gibbs energy of the interaction becomes zero (the temperature at which the dissociation rate and adsorption rate are comparable). The estimated temperatures were about 256 K for Mn1 and 284 K for Mn2. From the experiment, the temperature at which the interaction Gibbs energy becomes zero was determined to be about 241 K for Mn1 and about 340 K for Mn2. In addition, since the adsorption Gibbs energy for deuterium molecules D_2 and H_2 are not the same, we investigated the possibility of separating D_2 and H_2. From the adsorption measurement experiment at 293K, the deuterium/hydrogen separation coefficient of Mn1 was 2.25. The calculation results showed that the deuterium/hydrogen separation coefficient of Mn1 was approximately 2.40 at 298K. Therefore, the obtained values from the single molecule model calculations are in good agreement with the data obtained from the crystal experiments, and quantum chemical calculations are useful in this study.