Formic Acid Decomposition from Pd^{2+} complexes : Plausible Pathways for C-H Activation of Formate

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Hydrogen has long been recognized as a clean and sustainable energy carrier because it only generates water as a byproduct after it is utilized as a fuel in a fuel cell. Although it contains high gravimetric energy density of 142 MJ/kg, its low volumetric energy density (10.7 kJ/L) limits its application. Formic acid (HCOOH, FA) has been regarded as a promising hydrogen storage material with its high volumetric hydrogen storage capacity of 53g-H_2/L.

In this work, we present our study that FA decomposes to generate CO_2 and H_2 in the presence of aqueous Pd^{2+} complex solutions at 333 K. Pd^{2+} complexes were reduced to Pd^0 species during the reaction. Since C-H activation of Pd^{2+}-bound formate is occurred for both Pd^{2+} reduction and H_2/CO_2 gas generation, FA decomposition pathways with several Pd^{2+} species were explored using density functional theory (DFT) calculations. Rotation of formate bound to Pd^{2+}, β-hydride elimination, and subsequent CO_2 and H_2 elimination by formic acid were examined. In addition, pathways for Pd^{2+} reduction to Pd^0 were explored computationally.