

First-principles Theoretical Study of Chemical Reactions in Heterogeneous Catalysts

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In 2019-2020, we carried out theoretical analysis of chemical processes at surfaces and interfaces, formic acid adsorption and decomposition on Cu(111) [1], enhancement of CO₂ hydrogenation by O-C-O bending vibration mode [2], trimer formation of NO Cu(111) [3], and CO oxidation and oxygen reduction reaction at Pt single atom catalyst supported by graphene edges [4]. We also investigated dopant in semiconductors, namely, transition metal doped ZnSnAs₂ [5], and As and B codoping in Si [6]. In this report, we report the enhancement of CO₂ hydrogenation by vibration excitation [2].

Recently, formic acid (HCOOH) has been considered as a potential material for hydrogen storage. Storage of HCOOH is easier and safer compared with other hydrogen storage material because HCOOH is a non flammable liquid at STP. HCOOH can be decomposed on metal surfaces through dehydrogenation process into CO₂ and H₂, or dehydration process into CO and H₂O. Cu catalysts have been reported to selectively decompose HCOOH through dehydrogenation process. The decomposition of HCOOH does not occur on Cu(111) when exposed to the gas phase HCOOH at room temperature. On the Cu(111) surface, HCOOH was reported to form polymeric structures when exposed to the gas phase HCOOH at low temperatures, then the decomposition occurs by heating those polymeric HCOOH.

In the present study, we have investigated

the adsorption and decomposition mechanisms of monomeric HCOOH on Cu(111) by using density functionals that account for the vdW forces and compared with room temperature experimental results.

Our calculations were performed using the STATE (Simulation Tool for Atom TEchnology) code[7]. Here, we compared results obtained using the PBE functional with those using the van der Waals density functionals (vdW-DFs), i.e., optB86b-vdW and rev-vdW-DF2 [8] functionals. We also included the dispersion correction proposed by Grimme with PBE (PBE-D2). The implementation of the self-consistent vdW-DF in the STATE code is described in Ref. [9].

The reaction path for the decomposition (E_{dec}) of the OH-perpendicular configuration on the Cu(111) surface is shown in Fig. 1. The calculated activation energies of decomposition (E_{dec} 's) with ZPE correction are 0.37 eV, 0.31 eV, 0.32 eV, and 0.30 eV for PBE, PBE-D2, rev-vdW-DF2, and optB86b-vdW functionals, respectively, indicating that the E_{dec} are almost independent among the considered functionals in this work. PBE-D2 and vdW-DFs produce lower E_{dec} than E_{des} by (0.16–0.27 eV).

Figure 2 shows the calculated desorption and decomposition rates per surface adsorbate. In this analysis, we used the calculated results by rev-vdW-DF2 energy functional. At low temperatures, the decomposition process

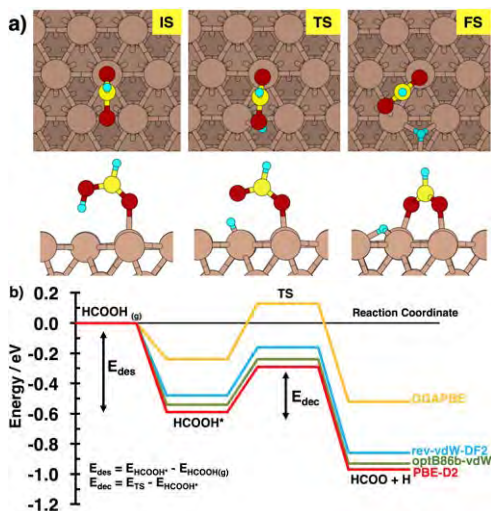


Figure 1: (a) Decomposition process of the OH-perpendicular configuration. IS, TS, and FS represent initial state, transition state, and final state, respectively. (b) Energy profile for the OH-perpendicular configuration decomposition on Cu(111).

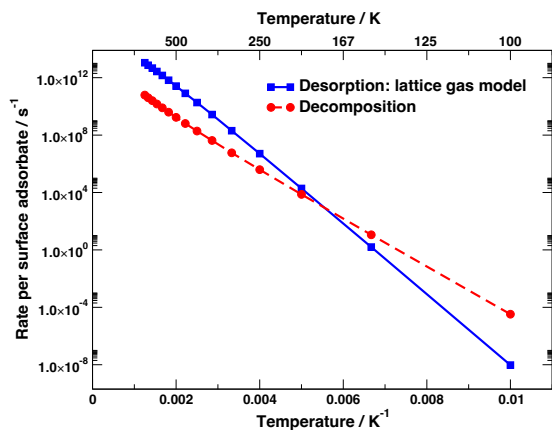


Figure 2: Calculated reaction rates per surface adsorbate for the desorption and decomposition of OH-perpendicular configuration. Red dashed line with circle and blue solid line with square dots line represent the decomposition and desorption rates obtained by using the 2D lattice gas, respectively.

becomes faster than the desorption process, while at higher temperatures, the desorption process becomes dominant due to large pre-exponential factor for the desorption process and the transition temperature between the two processes is ~ 187 K. These results are in very good agreement with the experimental situation that there is no HCOOH decomposition on Cu(111) by exposing the surface to the gas phase HCOOH at room temperature.

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