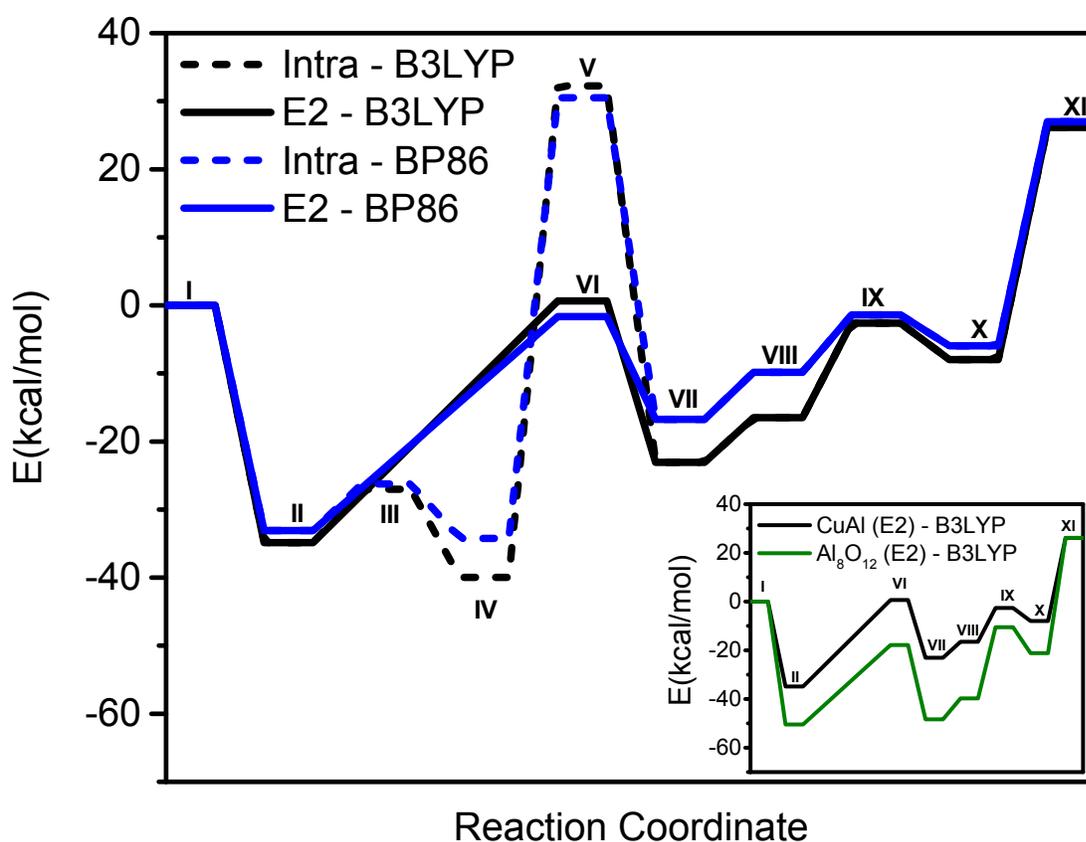


## Supporting Information

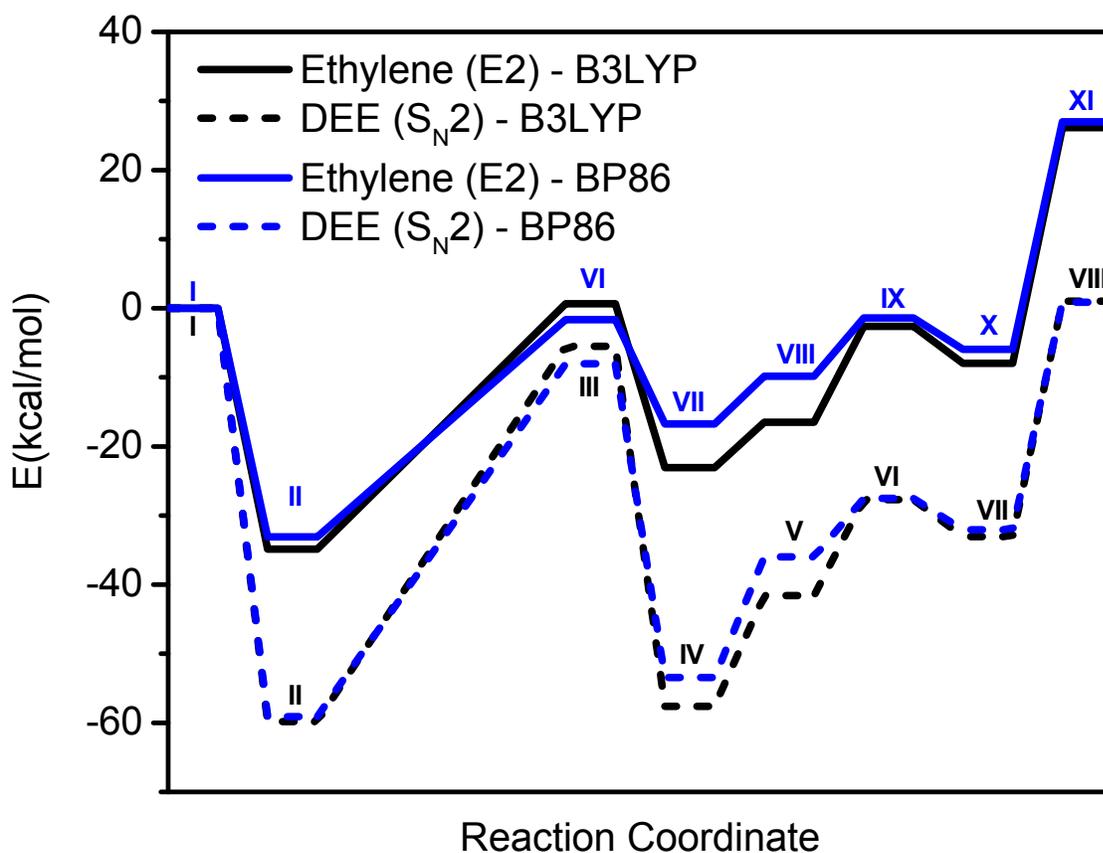
Design of highly selective ethanol dehydration nanocatalysts for ethylene production

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**Figure S1:** Reaction pathways for ethanol dehydration to ethylene on Cu<sub>13</sub>Al<sub>4</sub>O<sub>12</sub> via the sequential (Intra.) and concerted (E2) reaction mechanisms comparing B3LYP and BP86. The roman numerals for each elementary step represent: **I.** Reference state with gas-phase molecular nanocluster and ethanol at infinite separation, **II.** ethanol adsorption, **III.** TS1 in Intra. Mechanism with O-H bond dissociation, **IV.** ethoxide formation, **V.** TS2 in Intra. mechanism of ethylene formation, **VI.** TS for E2 concerted mechanism of ethylene formation, **VII.** physisorbed ethylene and chemisorbed dissociated water on the nanocluster, **VIII.** ethylene desorption, **IX.** TS for water formation, **X.** adsorbed water, and **XI.** final state with water desorption and the regeneration of the catalyst. The inset graph (bottom right) compares the reaction pathway for ethanol dehydration (via E2) on the Cu<sub>13</sub>Al<sub>4</sub>O<sub>12</sub> nanocluster to that of the pure alumina systems, using B3LYP.



**Figure S2:** Reaction pathway energetics for DEE and ethylene formation on  $\text{Cu}_{13}\text{Al}_4\text{O}_{12}$  via the  $\text{S}_{\text{N}}2$  (dashed line) and E2 mechanism (solid line), respectively. The reaction energetics are compared using B3LYP (black colored lines) and BP86 (blue colored lines). The roman numerals (in black) on each step of the DEE mechanism represent: **I.** reference state with the gas phase nanocatalyst and the two ethanol molecules in infinite separation, **II.** both ethanol molecules coadsorbed on the nanocluster (one chemisorbed and the other physisorbed), **III.** DEE formation TS, **IV.** physisorbed DEE and chemisorbed dissociated water on the nanocluster, **V.** DEE desorption, **VI.** water formation TS, **VII.** formation of adsorbed water, and **VIII.** water desorption and regeneration of the nanocluster. The description of the roman numerals (in blue) for ethylene formation are identical to those presented in the caption of Figure S1.