

Supporting Information

Newly designed manganese and cobalt complexes with pendant amines for the hydrogenation of CO₂ to methanol: a DFT study

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Evaluation of density functionals

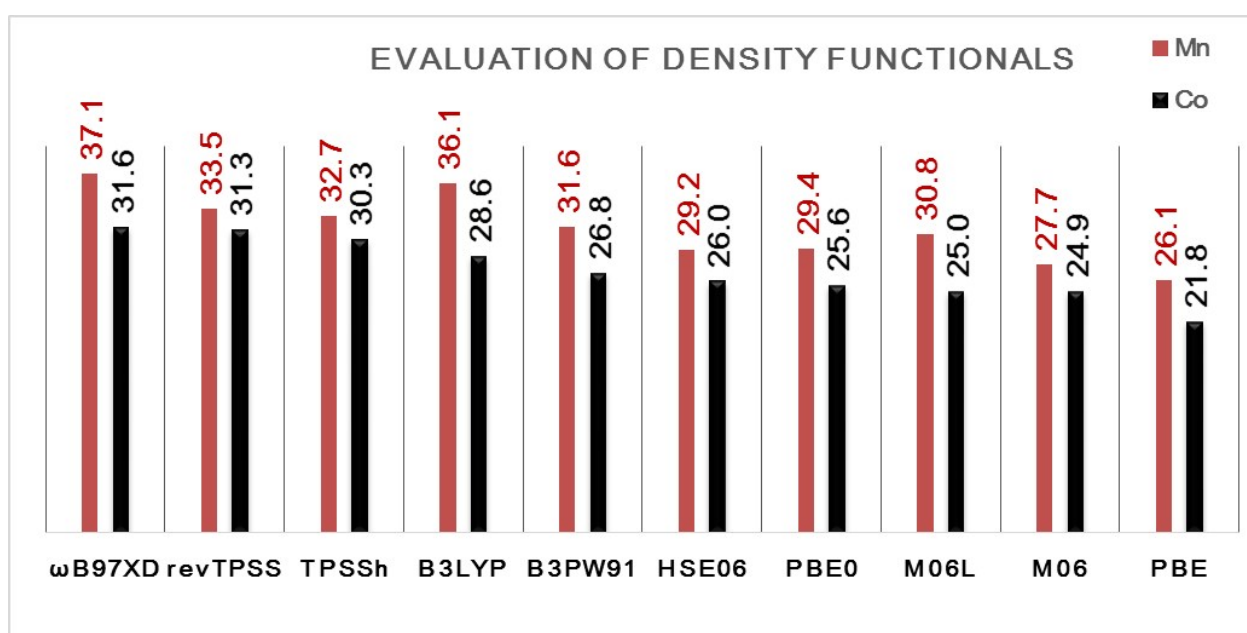


Figure S1. Relative electronic energies of different density functionals for the rate-determining states of the reactions catalyzed by **1**_{Mn-COOH} (**4'**_{Mn} → **TS**_{3,7-Mn}, red) and **1**_{Co-COOH} (**4'**_{Co} → **7**_{Co}, black).

To examine the effect of different density functionals on the calculated energy barriers in this transition metal system, we selected nine other well-known or recently developed density functionals,¹ including pure density functionals M06L,^{2, 3} PBE,⁴ revTPSS,⁵ and hybrid density functionals PBE0, TPSSh,⁵ B3LYP,^{6, 7} B3PW91,⁸ HSE06,^{9, 10} and ωB97XD,^{11, 12} to calculate the relative electronic energies of the rate-determining states (**4'**_{Mn} → **TS**_{3,7-Mn} and **4'**_{Co} → **7**_{Co}) using the same basis set at M06 optimized structures.

As shown in Figure S1, the difference of relative electronic energies of these 10 density functionals is less than 11 kcal/mol, which indicates a moderate dependence of density functionals of these manganese and cobalt systems. The M06 results are very close to the B3PW91, HSE06, PBE0, and M06L results. Therefore, M06 is a suitable functional for the study of these cobalt and manganese systems.

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