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Supplementary Information

Insights into the crucial role of Zn promoter for methanol dehydrogenation to methyl formate over Cu(111) catalyst

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The differences between DFT and DFT-D3 calculation methods

Table S1 list the adsorption energies of CH_3OH, CH_2O, CH_3OCHO and CO using DFT and DFT-D3 calculations. The results show that both DFT and DFT-D3 calculation have very close values of the adsorption energies for the reaction of methanol dehydrogenation.

Table S1. Adsorption energies(kJ/mol) of CH_3OH, CH_2O, CH_3OCHO and CO on Cu catalysts surface with and without DFT-D3 dispersion correction.

catalysts / molecules	$Cu_3Zn(111)$		Cu(111)	
	Without DFT-D3	With DFT-D3	Without DFT-D3	With DFT-D3
CH_3OH	-53.0	-51.1	-40.4	-42.7
CH_2O	-23.7	-21.3	-43.6	-50.7
CH_3OCHO	-33.0	-41.6	-37.5	-48.4
CO	-82.1	-91.5	-105.4	-119.5