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Electronic Supplementary Information

Computational Study of the Carbonyl-ene Reaction between Formaldehyde and Propylene Encapsulated in Coordinatively Unsaturated Metal–Organic Frameworks $M_3(btc)_2$ (M = Fe, Co, Ni, Cu and Zn)

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Table S1

Optimized geometric parameters and partial charges of the isolated $M_3(btc)_2$ clusters and the formaldehyde adsorption complex. For the latter, stabilization energies $E^{(2)}$ are also given (Distances in Å, partial charges in *e* and stabilization energy $E^{(2)}$ in kcal/mol).

$M_3(btc)_2$	**$Fe_3(btc)_2$**	**$Co_3(btc)_2$**	**$Ni_3(btc)_2$**	**$Cu_3(btc)_2$**	**$Zn_3(btc)_2$**
Isolated cluster					
Interatomic distances					
M-M	2.45	2.49	2.33	2.47	2.64
<M-O>	2.00	1.95	1.95	1.96	1.99
Partial charges					
M	1.08	0.80	0.95	0.97	1.27
M (sum)	2.17	1.94	1.92	1.95	2.55
Of	-0.49	-	-	-	-
C	0.24	-	-	-	-
CH_2O	0.00	-	-	-	-
Adsorption complex					
Interatomic distances					
M-M	2.74	2.56	2.39	2.50	2.72
Of-M	2.02	2.11	2.11	2.27	2.09
C-Of	1.23	1.22	1.22	1.21	1.22
Partial charges					
M	1.02	1.00	0.85	0.89	1.17
Of	-0.54	-0.51	-0.48	-0.50	-0.54
C	0.19	0.28	0.28	0.27	0.30
CH_2O	-0.01	0.12	0.14	0.09	0.12
Stabilization energy $E^{(2)}$	18.6	9.0	14.2	8.5	26.9

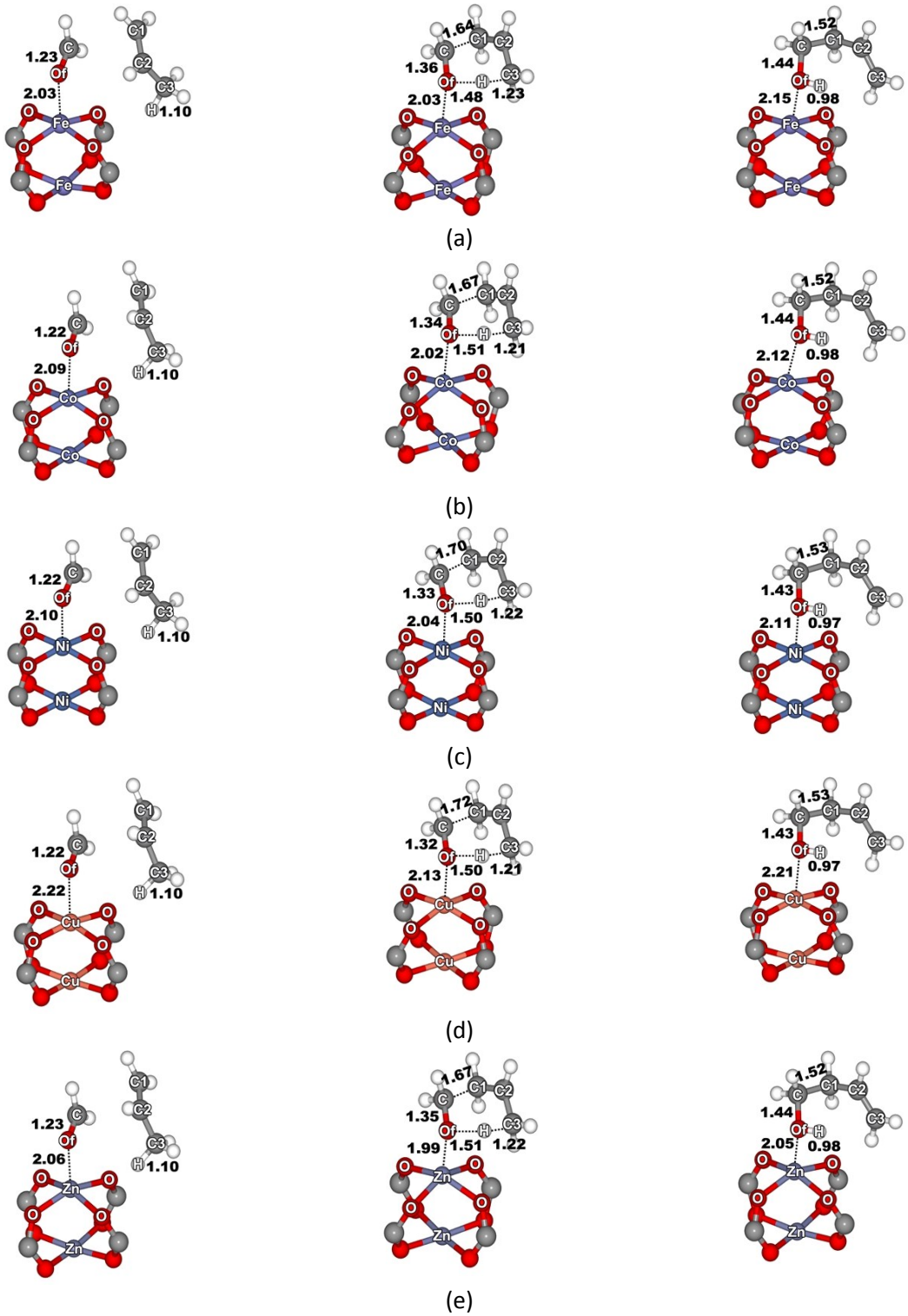


Figure S1. Optimized structures of the species occurring in the carbonyl-ene reaction between formaldehyde and propylene on $Fe_3(btc)_2$ (a), $Co_3(btc)_2$ (b), $Ni_3(btc)_2$ (c), $Cu_3(btc)_2$ (d) and $Zn_3(btc)_2$ (e).

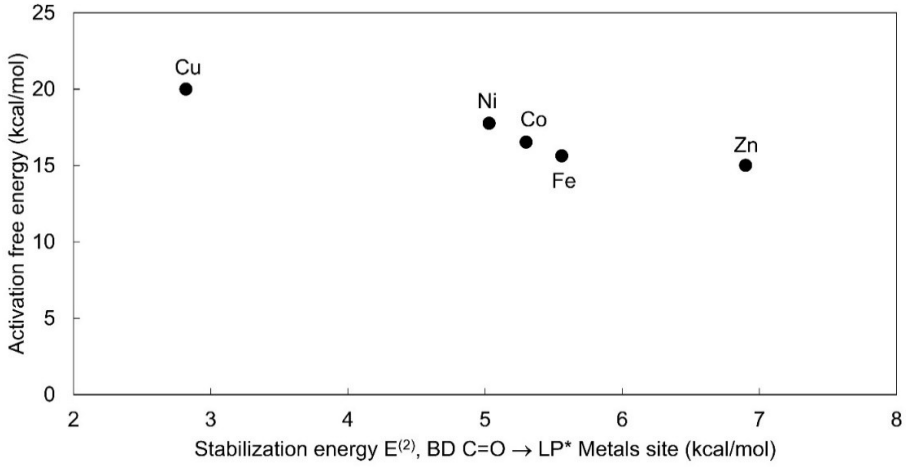
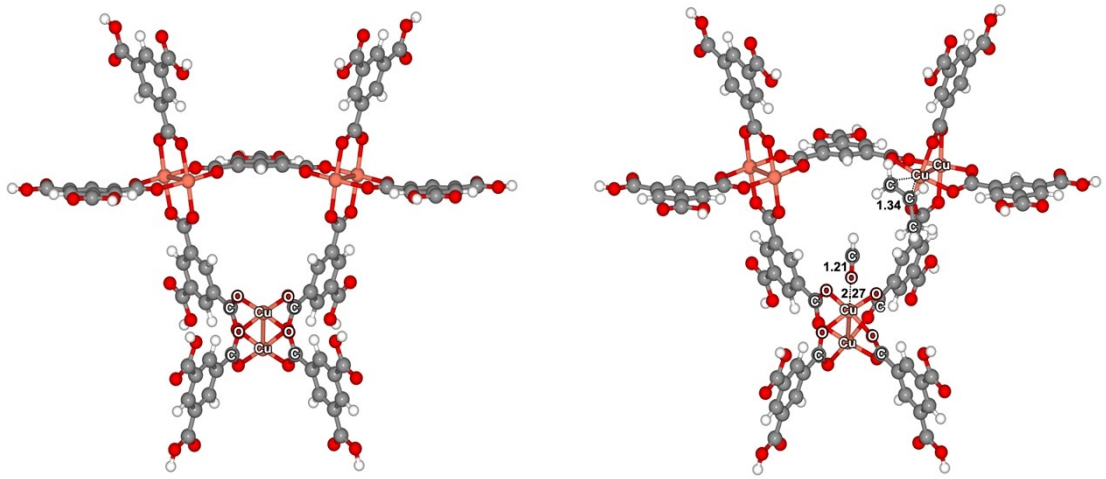


Fig. S2. Stabilization energy $E^{(2)}$ plottet against the activation free energy.



(a) **(b)**

Fig. S3. Extended cluster model of $Cu_3(btc)_2$ (a) and its interactions with formaldehyde on one of the metal centers and propylene on the other metal center (b).

Table S2.
Relative free energies with respect to the reactants for the carbonyl-ene reaction between formaldehyde and propylene on the $Cu_3(btc)_2$ cluster model and on the extended $Cu_3(btc)_2$ cluster.

Reaction Coordinates	Relative free energies (kcal/mol)	
	$Cu_3(btc)_2$	Extended $Cu_3(btc)_2$ clusters
Ads	-1.2	-1.9
co-Ads	1.9	-0.5
TS	21.8 (Ea=20.0)	19.9 (Ea=20.4)
Prod	-7.2	-9.3