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Supporting Information for Accurate Adsorption Energies of Carbon-species on Copper Catalysts

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Table S1. Comparison of adsorption energies calculated using PBE-D3/M06 with the force convergence criteria of 0.02 eV/Å and 0.05 eV/Å, respectively.

Adsorbate	Surface	Site	Adsorption energies (eV)	
			0.05 eV/Å	0.02 eV/Å
*CO	Cu(100)	top	-0.59	-0.59
		bridge	-0.58	-0.58
		hollow	-0.20	-0.20
*CO	Cu(110)	top	-0.49	-0.48
		long bridge	0.43	0.40
		short bridge	-0.36	-0.36
		hollow	0.41	0.41
*CO	Cu(111)	top	-0.54	-0.54
		bridge	-0.31	-0.31
		hcp hollow	-0.49	-0.49
		fcc hollow	-0.46	-0.45
H_2O	Cu(111)	phy	-0.37	-0.37
H_2			0.02	0.01
CO_2			-0.16	-0.16
CH_3OH			-0.44	-0.44
HCOOH			-0.48	-0.48

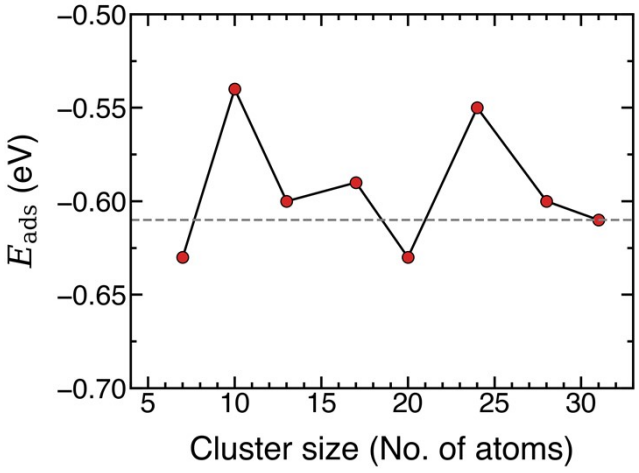

Figure S1. Calculated adsorption energies of CO on Cu clusters of different sizes. The clusters were created based on the Cu(111) surface.

Table S2. Adsorption energies (eV) of 18 additional C-species on copper surfaces, calculated using PBE and PBE-D3/M06, for machine learning model training and testing.

Species	PBE	Molecular mass	PBE-D3/M06
*C_2H_2/Cu(111)	-0.11	26	-0.20
CH_4/Cu(111)	-0.07	16	-0.14
C_3H_8/(Cu100)	-0.04	44	-0.41
*CHCOH/Cu(100)	0.64	42	0.92
*CHOH/Cu(100)	1.13	30	1.60
*CH_3O/Cu(100)	-1.25	31	-1.08
*CCO/Cu(100)	0.67	40	1.00
*H_2COO/Cu(100)	0.38	46	0.70
C_2H_6/(Cu100)	-0.10	30	-0.33
CH_4/(Cu100)	-0.07	16	-0.21
C_2H_6/Cu(111)	-0.10	30	-0.32
*CHCHO/Cu(100)	-0.28	42	0.13
*CHCO/Cu(100)	-0.44	41	-0.29
C_6H_6/(Cu100)	-0.09	78	-0.77
CH_2O/Cu(111)	-0.04	30	-0.17
CH3COCH3/Cu(111)	0.01	58	-0.44
CH3OCH3/Cu(111)	-0.02	46	-0.38
*H2COOH	-0.11	47	-0.38

Table S3. Free-energy corrections (G_{corr}, including zero-point energy and entropy) and solvation corrections (E_{sol}). G_{corr} is computed relative to CO_2, H_2, and H_2O. All values are reported in eV. Data were taken from Refs 1 and 2.

System	G_{corr}	E_{sol}
*COOH/Cu(100)	0.542	-0.47
*CO/Cu(100)	0.115	-0.02
*COOH/Cu(110)	0.542	-0.43*
*CO/Cu(110)	0.115	-0.02
*COOH/Cu(111)	0.542	-0.38
*CO/Cu(111)	0.115	-0.02
	Gas Phase	
H_2(ref)	-0.03	-
CO_2	-0.24	-
CO	-0.44	-
H_2O	0.02	-

The solvation correction for *COOH on the Cu(110) surface was estimated by averaging the values for the Cu(100) and Cu(111) surfaces[2], as no experimental or computational data are available in the literature.

Table S4. Calculated and experimental adsorption energies (eV) of CO on Cu(111). Values in parentheses indicate coverage in monolayers (ML). Experimental data were taken from Ref. 3.

Source	**FHI-aims (slab+cluster)**	**VASP (slab)+ORCA[a] (cluster)**	**Expt.**
This work	-0.54	-0.49	-0.57 (1/6)
Ref. 4	-	-0.47	-0.59 (1/4)

[a] The computational setup from Ref. 4 was used here to validate the difference in adsorption energies arising from the methodology.

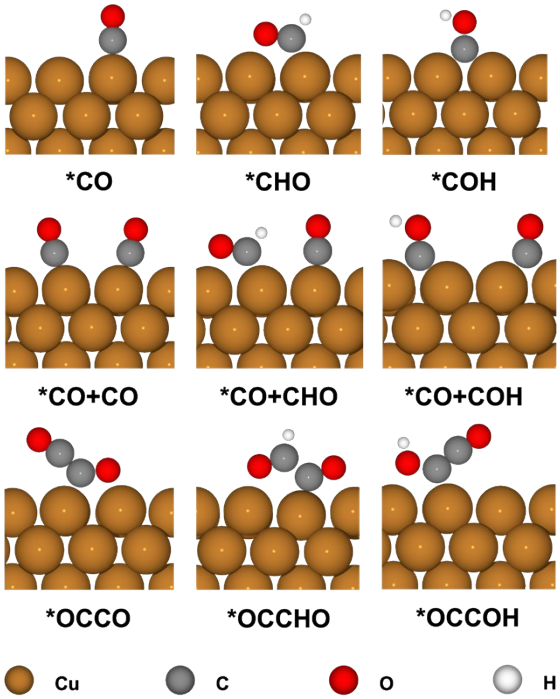

Figure S2. Side views of C-species adsorbed on Cu(100) surfaces. All illustrations are based on structures optimized using PBE-D3.

Table S5. Calculated adsorption free energies (eV) of various C-species (i.e., *CO, *CHO, *COH, *CO+*CO, *CO+*CHO, *CO+*COH, *OCCO, *OCCHO, and *OCCOH) on Cu(100) surfaces using PBE, PBE-D3 and PBE-D3/M06 methods. Deviations (eV) from reference RPA values are also included. The referenced PBE and RPA values were taken from Ref.5

Species	PBE	PBE[5,[a]]	PBE-D3	RPBE	PBE-D3/M06	RPA[5]
*CO	-0.29	-0.26	-0.50	-0.04	-0.02	-0.002
*CHO	0.51	0.50	0.30	0.99	0.85	0.799
*COH	0.66	0.65	0.42	1.22	1.16	1.081
*CO+CO	-0.57	-0.49	-0.98	-0.01	-0.11	0.021
*CO+CHO	0.22	0.26	-0.17	1.02	0.76	0.824
*CO+COH	0.44	0.42	0.27	1.40	1.38	1.348
*OCCO	0.61	0.58	0.88	1.48	1.51	1.399
*OCCHO	0.42	0.39	0.31	1.36	1.03	1.094
*OCCOH	0.58	0.54	0.93	1.39	1.58	1.559
MAE	0.62	0.61	0.74	0.13	0.06	
RMSE	0.66	0.66	0.77	0.17	0.07	

[a] Values from Ref.5 were obtained with VASP and agree closely with our FHI-aims results.

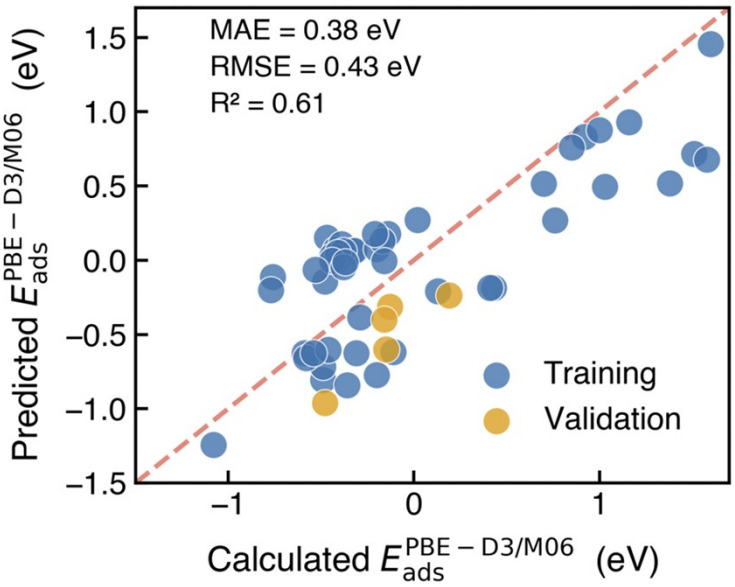

Figure S3. Performance of Linear Regression model in predicting PBE-D3/M06 adsorption energies. Blue and orange circles refer to training and validation data, respectively.

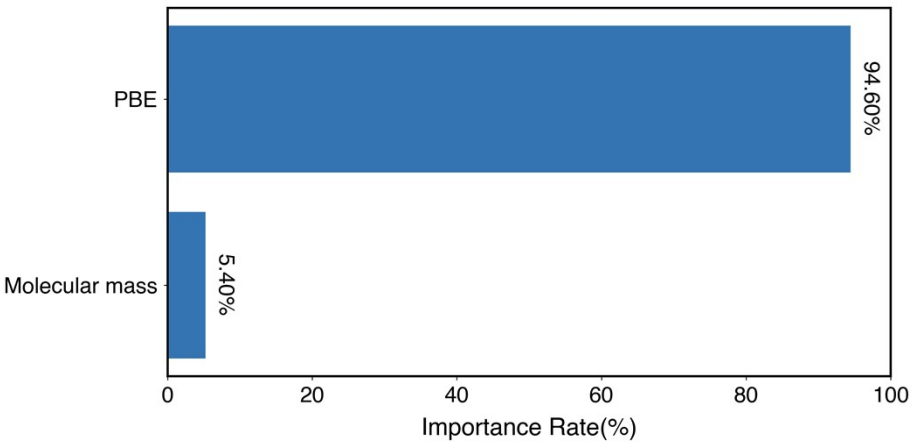

Figure S4. Feature importance ranking of the trained model for predicting PBE-D3/M06 adsorption energies, with PBE values identified as the most influential factor. This is consistent with the fact that the hybrid PBE-D3/M06 method is based on PBE calculations, supplemented with an empirical dispersion correction.

Table S6. Computation times (seconds) for M06 static calculations and PBE-D3 structure relaxations of representative surface adsorption systems, using an AMD 7763 CPU (128 cores).

Systems	Time	
	PBE-D3	M06
*CO/Cu(100)	2939.64	194.73
*CO+*CHO/Cu(100)	12240.81	3305.19
*OCCO/Cu(100)	4568.42	1520.05
*OCCOH/Cu(100)	5591.97	2932.91
C_6H_6/Cu(111)	1376.84	594.03

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