Supporting Information

Computational Details:

Since the gas-phase thermochemical reaction energies computed by the RPBE functional was obviously deviant from experimental results according previous report,[1,2] it is essential to make a sensitivity analysis based on experimentally determined gas-phase reaction enthalpy. Inspired by the work of Peterson et al.,[2] a similar analysis was performed and shown in Figure S1. We analyzed the reaction enthalpies of 21 reactions including 11 species (see Table S1), and the results of theoretical calculation present that the systematic error found in all species containing OCO backbone, particularly CO_2, HCOOH, CH_3COOH, and $HCOOCH_3$ are obvious. Among all reactions, 14 reactions are influenced by species containing OCO backbone, while the rest reactions are unaffected. As shown in Figure S1, the mean absolute error of unaffected reactions is 0.07 eV, which is small and can be neglected. However, the mean absolute error of affected reactions is 0.26 eV at 0 eV correction, and the optimal correction to OCO-containing species is 0.33 eV with the mean absolute error of 0.04 eV. Based on the above analysis, we apply the correction of 0.33 eV for CO_2 and HCOOH in current work. The adsorbate solvation effects were considered approximately in the same manner as in the previous study.[2-7] Hydroxyl adsorbates (*OH) and hydroxyl functional groups (*R-OH) were stabilized 0.5 eV and 0.25 eV, respectively, and the stabilization of *CO and *CHO is 0.1 eV. The asterisk (*) indicates a species bound to the surface. The free energy of gas-phase molecules was calculated under the standard state pressure of 101,325 Pa, while the free energy of liquid-phase molecules, such as H_2O, HCOOH, CH_3OH, was computed as ideal gas employing their corresponding vapor fugacity. In this work, a fugacity of 3534 Pa, 19 Pa and 6080 Pa was applied for H_2O, HCOOH and CH_3OH,[6,8] respectively. To obtain the cohesion energy, the energy of the bulk metal needs to be calculated. The hexagonal-close-packed structure of Sc, Ti, Co, Zn, Y, Zr, Tc, Ru, Cd, body-centered-cubic structure of V, Cr, Mn, Fe, Nb, Mo, and faced-centered-cubic structure of Ni, Cu, Rh, Pd, Ag were used. The Monkhorst-Pack grids of k-point sampling for each bulk phases using a grid of spacing $2\pi\times0.025$ $Å^{-1}$ in the Brillouin zone. Other calculational details are consistent with the

calculations in the main text.

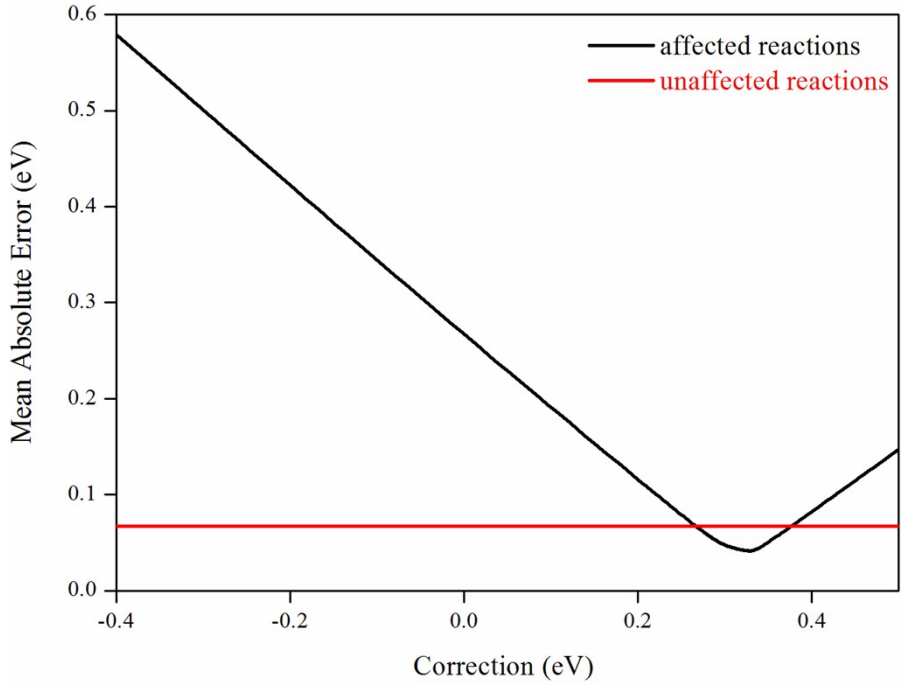

Fig. S1 Selective analysis for reactions with and without species containing OCO backbone. 'affected reactions' stands for the reactions including CO_2, HCOOH, CH_3COOH and $HCOOCH_3$, while 'unaffected reactions' refers to the rest reactions containing none of these species.

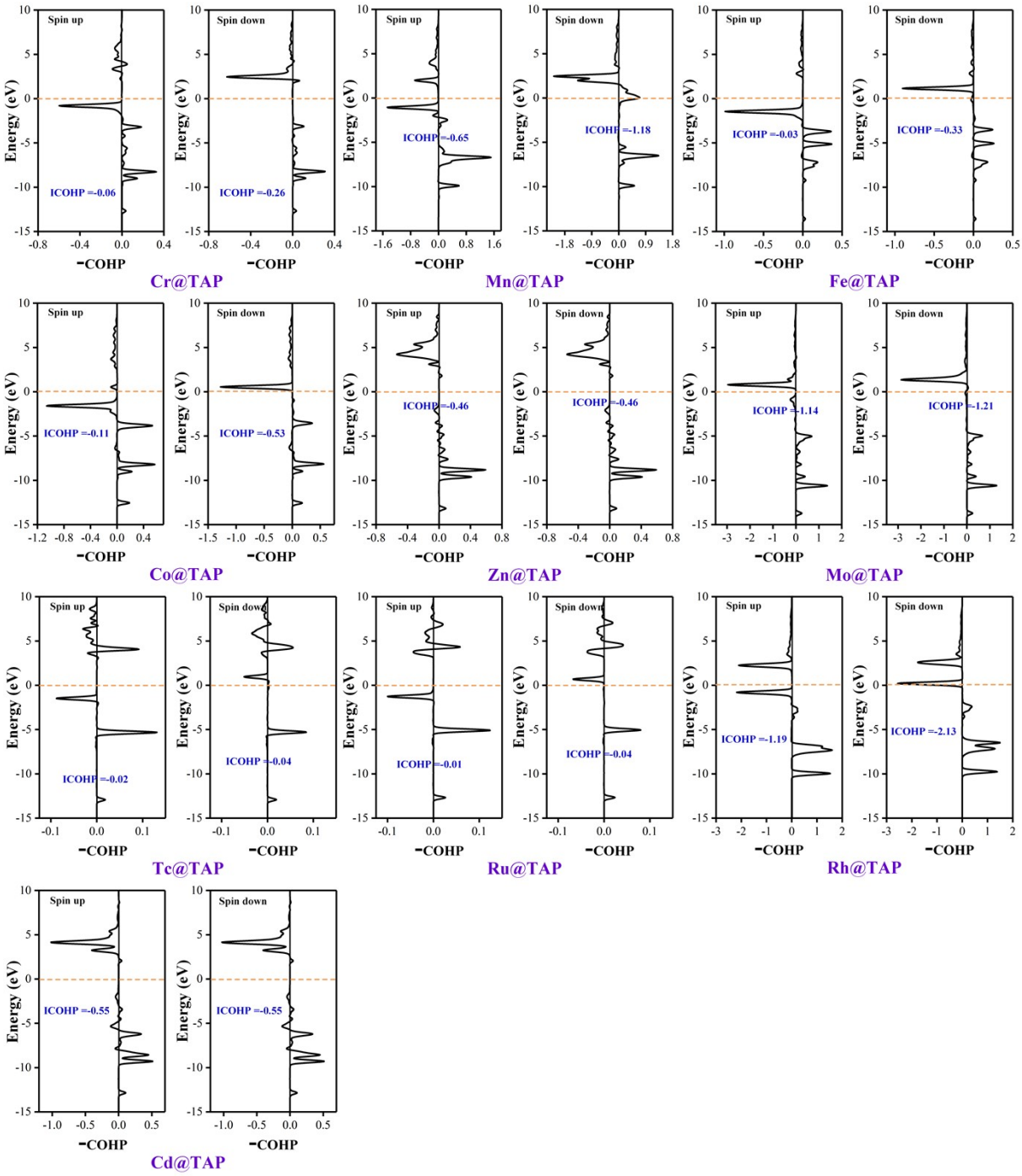

Fig. S2 The projected crystal orbital Hamilton population (pCOHP) between TM atom and atom of product connected to TM atom. The products of TM@TAP (TM = Cr, Zn, Mo, Cd) are HCOOH. The products of Mn@TAP and Rh@TAP is CO. The products of Tc@TAP and Ru@TAP are CH_4. The products of Fe@TAP and Co@TAP are CH_3OH and HCHO, respectively.The dashed line denotes the Fermi level. The bonding and antibonding contributions are displayed on the right and left, respectively.

Table S1 Reactions equations, the experimental reference enthalpies (ΔH_{ref}) from NIST,[9] theoretical uncorrected enthalpies (ΔH_{unc}), corrected enthalpies (ΔH_{cor}) with +0.33 eV for OCO-containing species, together with absolute error before and after correction. All values are in eV. (at 25 °C and 101325 Pa).

Reaction	ΔH_{ref}	ΔH_{unc}	error	ΔH_{cor}	error
$CO_2 + H_2 \rightarrow CO + H_2O$	0.43	0.81	0.38	0.48	0.05
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-1.71	-1.37	0.34	-1.70	0.01
$CO + 3H_2 \rightarrow CH_4 + H_2O$	-2.14	-2.18	-0.04	-2.18	-0.04
$CO_2 + H_2 \rightarrow HCOOH$	0.15	0.21	0.06	0.21	0.06
$CO + H_2O \rightarrow HCOOH$	-0.27	-0.60	-0.33	-0.27	0.00
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	-0.55	-0.22	0.33	-0.55	0.00
$CO + 2H_2 \rightarrow CH_3OH$	-0.98	-1.03	-0.05	-1.03	-0.05
$3H_2 + CO_2 \rightarrow 1/2CH_3CH_2OH + 3/2H_2O$	-0.89	-0.62	0.27	-0.95	-0.06
$2H_2 + CO \rightarrow 1/2CH_3CH_2OH + 1/2H_2O$	-1.32	-1.42	-0.10	-1.42	-0.10
$10/3H_2 + CO_2 \rightarrow 1/3C_3H_8 + 2H_2O$	-1.3	-0.98	0.32	-1.31	-0.01
$7/3H_2 + CO \rightarrow 1/3C_3H_8 + H_2O$	-1.72	-1.79	-0.07	-1.79	-0.07
$7/2H_2 + CO_2 \rightarrow 1/2C_2H_6 + 2H_2O$	-1.37	-1.06	0.31	-1.39	-0.02
$5/2H_2 + CO \rightarrow 1/2C_2H_6 + H_2O$	-1.8	-1.87	-0.07	-1.87	-0.07
$3H_2 + CO_2 \rightarrow 1/2C_2H_4 + 2H_2O$	-0.66	-0.36	0.30	-0.69	-0.03
$2H_2 + CO \rightarrow 1/2C_2H_4 + H_2O$	-1.09	-1.17	-0.08	-1.17	-0.08
$11/4H_2 + CO_2 \rightarrow 1/4CH_2{=}CHCH{=}CH_2 + 2H_2O$	-0.65	-0.33	0.32	-0.66	-0.01
$7/4H_2 + CO \rightarrow 1/4CH_2{=}CHCH{=}CH_2 + H_2O$	-1.08	-1.13	-0.05	-1.13	-0.05
$2H_2 + CO_2 \rightarrow 1/2CH_3COOH + H_2O$	-0.67	-0.47	0.20	-0.64	0.03
$H_2 + CO \rightarrow 1/2CH_3COOH$	-1.10	-1.28	-0.18	-1.11	-0.01
$2H_2 + CO_2 \rightarrow 1/2HCOOCH_3 + H_2O$	-0.17	-0.11	0.06	-0.28	-0.11
$H_2 + CO \rightarrow 1/2HCOOCH_3$	-0.60	-0.92	-0.32	-0.76	-0.16

Table S2 The binding energy (E_b) and cohesive energy (E_c). All values are in eV.

TM@TAP	[1]E_b	[2]E_c
Sc	-9.35	-4.36
Ti	-9.03	-5.60
V	-8.47	-5.61
Cr	-7.38	-4.05
Mn	-6.57	-3.49
Fe	-6.86	-4.75
Co	-7.28	-5.39
Ni	-7.01	-4.91
Cu	-5.40	-3.70
Zn	-4.09	-1.25
Y	-9.18	-4.30
Zr	-9.69	-6.32
Nb	-8.78	-7.10
Mo	-8.80	-7.38
Tc	-10.83	-9.48
Ru	-8.15	-6.77
Rh	-8.30	-6.10
Pd	-6.18	-3.91
Ag	-3.96	-2.74
Cd	-3.38	-0.88

[1]E_b is computed by $E_b = E_{TM@TAP} - E_{TM} - E_{TAP.}$

[2]E_c is calculated by $E_c = E_{TM,\ bulk}/n - E_{TM,}$ where $E_{TM,\ bulk}$ is the energy of metal crystal, n represents the number of metal atoms in its corresponding crystal, and E_{TM} is the energy of single metal atom.

Table S3 Adsorption energy (ΔE_{ads}) of different products for CO_2RR.

TM@TAP	CO	HCOOH	HCHO	CH_3OH	CH_4
Cr	-0.28	-0.49	-0.36	-0.47	-0.15
Mn	-0.36	-0.70	-0.55	-0.69	-0.22
Fe	-1.12	-0.52	-0.45	-0.56	-0.20
Co	-0.77	-0.44	-0.37	-0.49	-0.16
Zn	-0.19	-0.59	-0.46	-0.63	-0.19
Mo	-1.72	-0.39	-1.21	-0.25	-0.13
Tc	-2.16	-0.42	-0.35	-0.44	-0.17
Ru	-2.08	-0.41	-0.37	-0.44	-0.16
Rh	-0.34	-0.36	-0.28	-0.32	-0.10
Cd	-0.17	-0.52	-0.42	-0.55	-0.19

Table S4 Zero-point energy (ZPE, in eV), entropy corrections (TS, in eV) and enthalpy corrections ($\int C_p dT$, in eV) at T = 298.15 K for gaseous molecules. ZPE and S are from NIST.[9]

Species	ZPE	TS	$\int C_p dT$
CO_2	0.31	0.66	0.09
CH_4	1.18	0.58	0.10
H_2O	0.56	0.58	0.10
H_2	0.27	0.40	0.09
CO	0.13	0.61	0.09
HCOOH	0.89	0.77	0.11
HCHO	0.70	0.68	0.10
CH_3OH	1.35	0.74	0.12

Table S5 Zero-point energy (ZPE), entropy corrections (TS) and enthalpy corrections ($\int C_p dT$) at T = 298.15 K for adsorbed species. All values are in eV.

Sc@TAP	ZPE	TS	$\int C_p dT$
*H	0.14	0.03	0.02
*COOH	0.61	0.29	0.12
*OCHO	0.61	0.24	0.11
*OH	0.31	0.17	0.08

Ti@TAP	ZPE	TS	$\int C_p dT$
*H	0.23	0.01	0.01
*COOH	0.62	0.22	0.11
*OCHO	0.59	0.30	0.12
*OH	0.32	0.17	0.07

V@TAP	ZPE	TS	$\int C_p dT$
*H	0.16	0.02	0.01
*COOH	0.62	0.25	0.11
*OCHO	0.60	0.25	0.11
*OH	0.34	0.10	0.06

Cr@TAP	ZPE	TS	$\int C_p dT$
*H	0.17	0.02	0.01
*COOH	0.61	0.25	0.11
*OCHO	0.60	0.26	0.11
*CO	0.16	0.24	0.10

*HCOOH	0.91	0.34	0.13
*OH	0.33	0.15	0.07

Mn@TAP	ZPE	TS	$\int C_p dT$
*H	0.15	0.03	0.02
*COOH	0.62	0.23	0.11
*OCHO	0.59	0.27	0.12
*CO	0.16	0.26	0.09
*HCOOH	0.92	0.27	0.12
*COH	0.47	0.15	0.08
*CHO	0.45	0.19	0.09
*OH	0.31	0.16	0.07

Fe@TAP	ZPE	TS	$\int C_p dT$
*H	0.20	0.01	0.01
*COOH	0.63	0.21	0.10
*OCHO	0.61	0.23	0.10
*CO	0.22	0.14	0.06
*COH	0.47	0.12	0.07
*CHO	0.47	0.17	0.08
*CHOH	0.82	0.14	0.07
*CH	0.31	0.09	0.05
*CH_2OH	1.11	0.18	0.09
*CH_2	0.64	0.10	0.05

*CH_3OH	1.41	0.29	0.13
*OH	0.32	0.15	0.07

Co@TAP	ZPE	TS	$\int C_p dT$
*H	0.20	0.01	0.01
*COOH	0.64	0.20	0.10
*OCHO	0.58	0.25	0.11
*CO	0.19	0.20	0.08
*COH	0.47	0.16	0.08
*CHO	0.48	0.17	0.08
*CHOH	0.80	0.14	0.07
*OCH_2	0.76	0.23	0.11
*OH	0.34	0.11	0.06

Ni@TAP	ZPE	TS	$\int C_p dT$
*H	0.15	0.02	0.01
*COOH	0.62	0.22	0.11
*OCHO	0.60	0.25	0.11

Cu@TAP	ZPE	TS	$\int C_p dT$
*H	0.13	0.03	0.02
*COOH	0.60	0.27	0.12
*OCHO	0.56	0.30	0.12

Zn@TAP	ZPE	TS	$\int C_p dT$

*H	0.16	0.02	0.02
*COOH	0.60	0.27	0.12
*OCHO	0.60	0.27	0.11
*HCOOH	0.92	0.31	0.13
*OH	0.32	0.16	0.07

Y@TAP	ZPE	TS	$\int C_p dT$
*H	0.13	0.03	0.02
*COOH	0.60	0.29	0.12
*OCHO	0.60	0.29	0.12
*OH	0.32	0.15	0.07

Zr@TAP	ZPE	TS	$\int C_p dT$
*H	0.16	0.02	0.02
*COOH	0.61	0.26	0.11
*OCHO	0.61	0.24	0.11
*OH	0.31	0.18	0.08

Nb@TAP	ZPE	TS	$\int C_p dT$
*H	0.17	0.02	0.01
*COOH	0.62	0.23	0.11
*OCHO	0.62	0.21	0.10
*OH	0.33	0.13	0.06

Mo@TAP	ZPE	TS	$\int C_p dT$
*H	0.17	0.02	0.02
*COOH	0.61	0.28	0.12
*OCHO	0.60	0.26	0.11
*CO	0.21	0.15	0.07
*HCOOH	0.93	0.27	0.12
*COH	0.48	0.18	0.09
*CHO	0.45	0.21	0.09
*OH	0.33	0.15	0.07

Tc@TAP	ZPE	TS	$\int C_p dT$
*H	0.20	0.01	0.01
*COOH	0.62	0.22	0.11
*OCHO	0.63	0.18	0.10
*CO	0.22	0.14	0.06
*COH	0.49	0.19	0.09
*CHO	0.46	0.19	0.08
*CHOH	0.81	0.15	0.08
*OCH_2	0.74	0.29	0.12
*CH	0.36	0.07	0.04
*CH_2OH	1.10	0.21	0.10
*CH_2	0.63	0.10	0.06
*CH_3OH	1.40	0.33	0.14

*CH_3	0.96	0.13	0.07
*OH	0.96	0.13	0.07

Ru@TAP	ZPE	TS	$\int C_p dT$
*H	0.21	0.01	0.01
*COOH	0.63	0.22	0.10
*OCHO	0.61	0.25	0.11
*CO	0.22	0.13	0.06
*COH	0.48	0.13	0.07
*CHO	0.48	0.17	0.08
*CHOH	0.82	0.14	0.07
*OCH_2	0.79	0.16	0.08
*CH	0.30	0.11	0.05
*CH_2OH	1.11	0.20	0.09
*CH_2	0.64	0.09	0.05
*CH_3OH	1.40	0.31	0.13
*CH_3	0.96	0.14	0.07
*OH	0.35	0.11	0.06

Rh@TAP	ZPE	TS	$\int C_p dT$
*H	0.21	0.01	0.01
*COOH	0.64	0.20	0.10
*OCHO	0.59	0.24	0.11
*CO	0.18	0.19	0.08

*OH	0.34	0.13	0.06

Pd@TAP	ZPE	TS	$\int C_p dT$
*H	0.12	0.02	0.02
*COOH	0.63	0.22	0.11
*OCHO	0.53	0.35	0.13

Ag@TAP	ZPE	TS	$\int C_p dT$
*H	0.11	0.05	0.03
*COOH	0.59	0.32	0.13
*OCHO	0.54	0.35	0.13

Cd@TAP	ZPE	TS	$\int C_p dT$
*H	0.14	0.04	0.02
*COOH	0.59	0.31	0.13
*OCHO	0.59	0.30	0.12
*HCOOH	0.92	0.29	0.13
*OH	0.31	0.18	0.08

Table S6 The products, ΔG_{max}, adsorption energy (ΔE_{ads}) of some intermediates, and magnetic moment of ten catalysts.

TM@TAP	Products	ΔG_{max} (eV)	ΔE_{ads}(*CO) (eV)	ΔE_{ads}(*OH) (eV)	ΔE_{ads}(*OCHO) (eV)	ΔE_{ads}(*COOH) (eV)	ΔE_{ads}(*CHO) (eV)	Magnetic moment (μ_B)
Cr	HCOOH	0.33	-0.28	0.16	-0.07	0.33	-0.34	3.77
Mn	CO	0.73	-0.36	0.23	-0.20	0.54	-0.34	4.59
Fe	CH_3OH	0.51	-1.12	0.43	0.29	0.03	-0.87	1.41
Co	HCHO	0.36	-0.77	0.85	0.39	-0.02	-0.94	0.40
Zn	HCOOH	0.57	-0.19	0.87	0.18	1.08	0.50	0.00
Mo	HCOOH	0.50	-1.72	-0.50	-0.67	-0.32	-0.99	3.52
Tc	CH_4	1.04	-2.16	-0.12	0.45	-0.30	-1.35	2.47
Ru	CH_4	0.65	-2.08	0.10	-0.27	-0.82	-1.68	1.18
Rh	CO	0.28	-0.34	1.19	0.67	-0.25	-1.12	0.00
Cd	HCOOH	0.71	-0.17	1.20	0.35	1.29	0.67	0.00

$\Delta E_{ads}(*CO) = E(*CO) - E(*) - E(CO)$;

$\Delta E_{ads}(*OH) = E(*OH) - E(*) - (E(H_2O) - 1/2\times E(H_2))$;

$\Delta E_{ads}(*OCHO) = E(*OCHO) - E(*) - (E(CO_2) + 1/2\times E(H_2))$;

$\Delta E_{ads}(*COOH) = E(*COOH) - E(*) - (E(CO_2) + 1/2\times E(H_2))$;

$\Delta E_{ads}(*CHO) = E(*CHO) - E(*) - (E(CO) + 1/2\times E(H_2))$;

where E(*) stands for the energy of catalyst.

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