Supporting information

Nickel single atom catalyst supported on gallium nitride monolayer: First principles investigations on the decisive role of support on the electrocatalytic reduction of CO_2

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Table S1: *Calculated dissolution potential values for Ni SACs supported on different monolayer supports.*

Catalyst	$U^{o}_{diss}\,(eV)$	n	$E_f\,(eV)$	$E_f/n \quad (eV)$	$U_{diss}\,(eV)$
Ni@GaN	-0.23	2	-2.8	-1.4	**1.17**
Ni@MoS_2	-0.23	2	-3.8	-1.9	**1.67**
Ni@Mo_2C	-0.23	2	-5	-2.5	**2.27**
Ni@C_2N	-0.23	2	-4.7	-2.35	**2.12**
Ni@Graphyne	-0.23	2	-5.4	-2.7	**2.47**

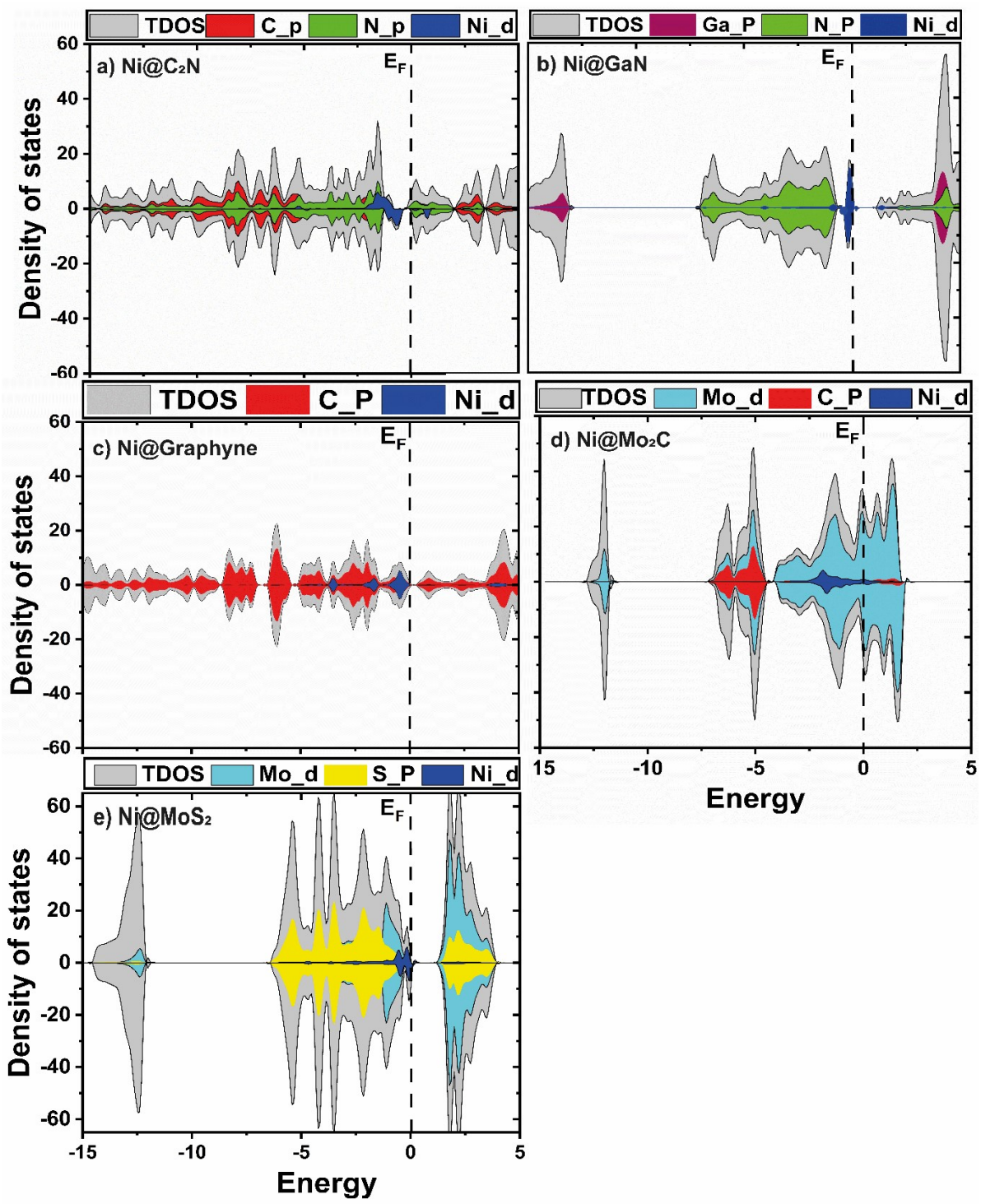

Fig. S1. *Spin polarized orbital projected density of states (oPDOS) of Ni SACs supported on different monolayers. Colour codes for the orbital contributions are given in the plots. Fermi-level is set to zero.*

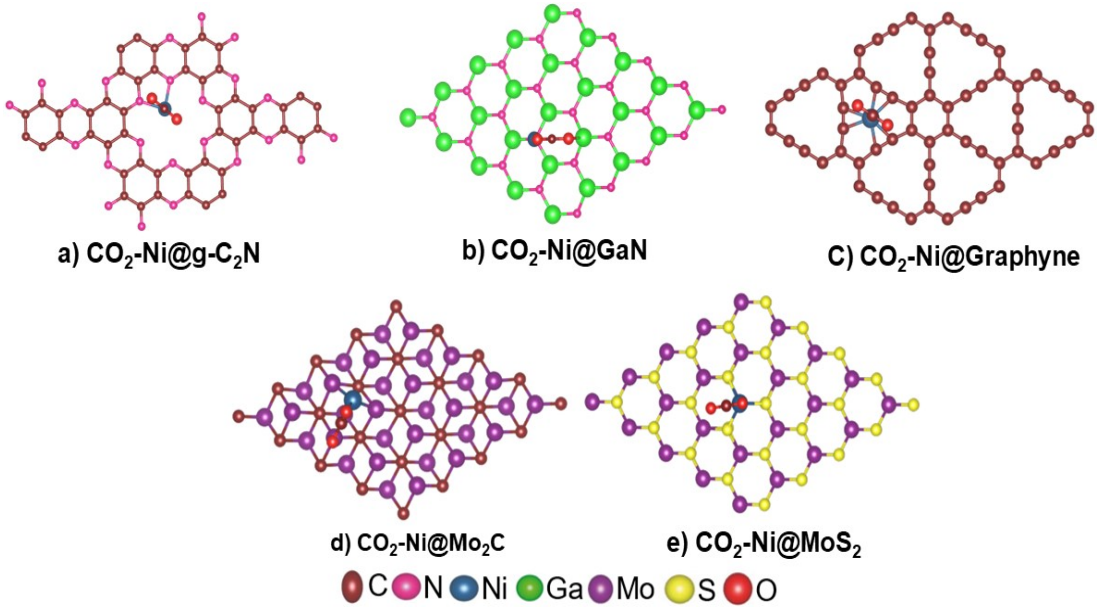

Fig. S2: *Top views of CO_2 adsorbed on (a)Ni@C_2N (b) Ni@GaN (c) Ni@Graphyne (d) Ni@Mo_2C (e) Ni@MoS_2.*

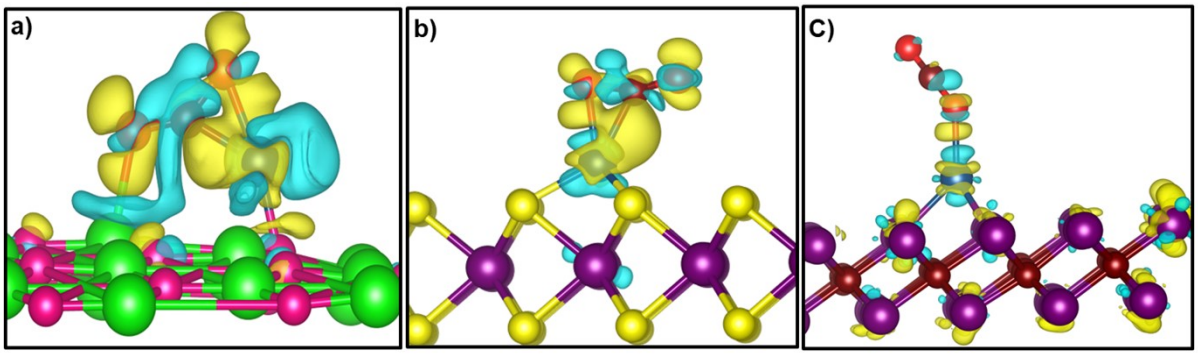

Fig. S3*: Charge density difference plots of CO_2 adsorbed on (a) Ni@GaN (b)Ni@MoS_2 (C)Ni@Mo_2C catalysts. Yellow and cyan represents charge accumulation and depletion, respectively. The isosurface value was set to 0.002 e/bohr^3.*

Table S2: *Calculated d-band center values for Ni SACs supported on different monolayer supports.*

Catalyst	**d-band center**
Ni@GaN	-0.45
Ni@MoS_2	-0.99
Ni@Mo_2C	-1.32
Ni@C_2N	-1.25
Ni@Graphyne	-1.00

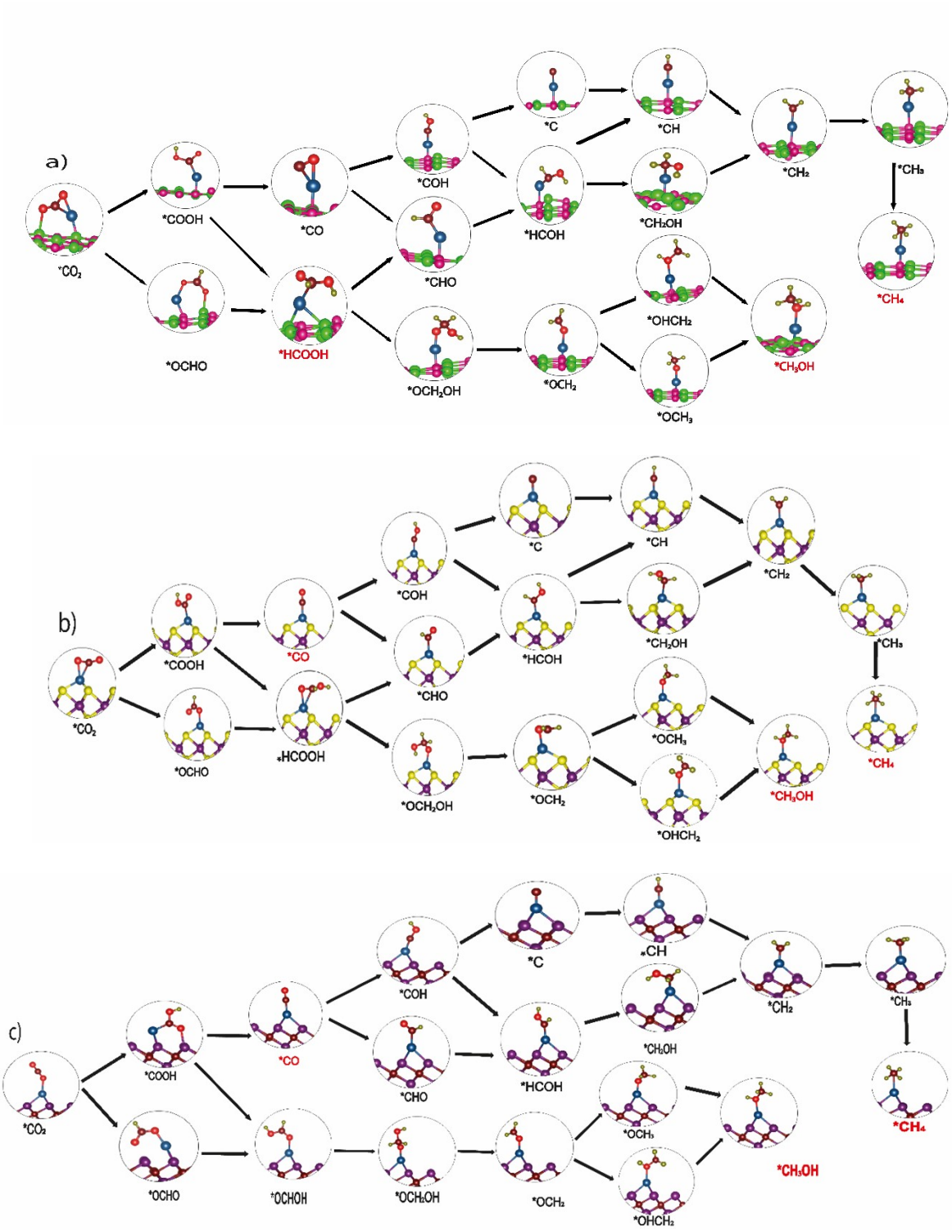

Fig. S4*: Screenshots of optimised geometries of various intermediates involved in the CO_2 conversion to HCOOH, CH_3OH, CH_4 on* ***(a)*** *Ni@GaN* ***(b)*** *Ni@MoS_2* ***(c)*** *Ni@Mo_2C catalysts.*

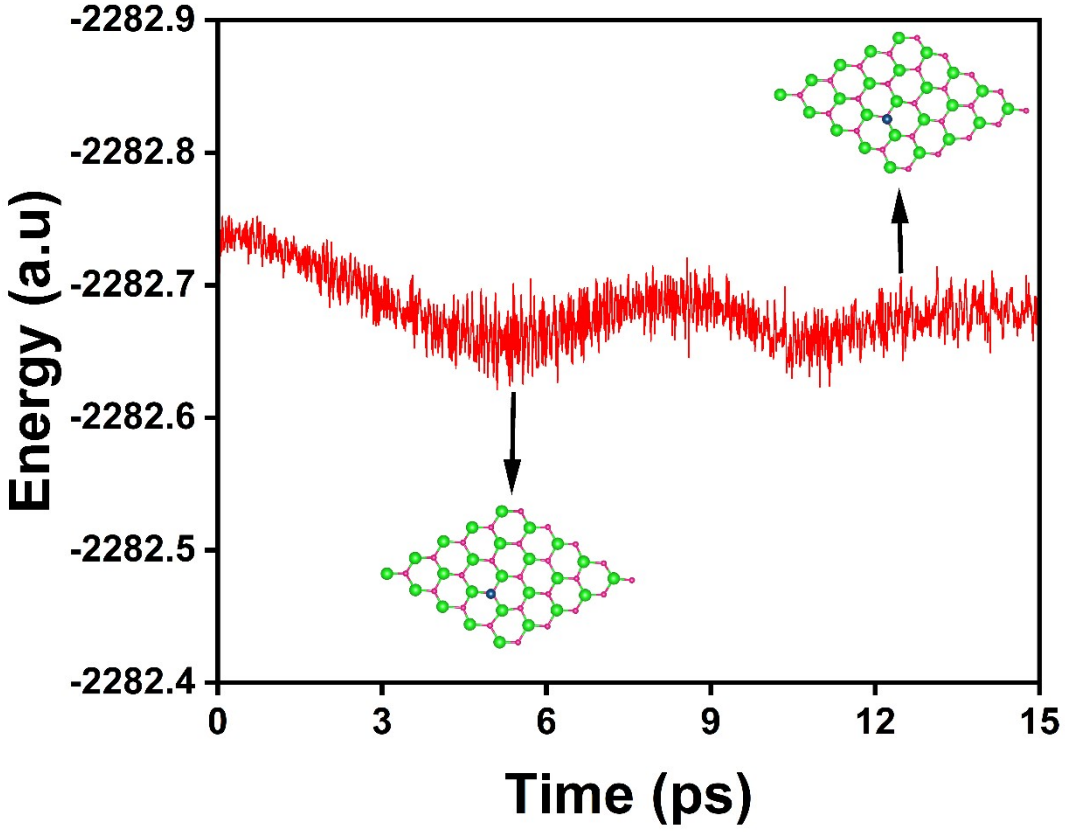

Fig. S5: *Variation of energy versus the AIMD simulation time for Ni@GaN for 15 ps at 600K.The insets are the top views of snapshots of configurations at 5 and 12 ps.*

***Table S3**: Energy, zero-point energy and entropic correction to free energy of the adsorbed species for Ni@GaN, Ni@MoS_2 and Ni@Mo_2C.*

Ni@GaN					
Step	**E (eV)**	**E_{ZPE} (eV)**	**S (eVK^{-1})**	**TS (eV)**	**G(eV)**
*CO_2	-316.857233	0.328690	0.000547	0.1630881	-316.691631
*COOH	-319.425272	0.000554	0.605944	0.1651751	-318.984503
*OCHO	-320.313724	0.000437	0.581102	0.13029155	-319.862914
*COOH	-319.321004	0.000609	0.59714	0.18157335	-318.905438
*CHOOH	-323.877534	0.000636	0.918475	0.1896234	-323.148683
*CO	-308.470316	0.000401	0.165283	0.11955815	-308.424591
*OCH_2OH	-327.152373	0.000851	1.227978	0.25372565	-326.17812
*CHO	-311.896459	0.000446	0.447363	0.1329749	-311.582071
*COH	-310.867704	0.000235	0.454007	0.07006525	-310.483762
*OCH_2	-316.136323	0.000453	0.77019	0.13506195	-315.501195
*CHOH	-315.001092	0.000412	0.78224	0.1228378	-314.34169
*C	-297.317501	0.000177	0.051787	0.05277255	-297.318487
*OCH_3	-320.144185	0.000837	1.073842	0.24955155	-319.319895
*$OHCH_2$	-318.35843	0.000875	1.038613	0.26088125	-317.580698
*CH	-303.009759	0.000318	0.327085	0.0948117	-302.777486
*$OHCH_3$	-323.917145	0.000644	1.419246	0.1920086	-322.689908
*CH_2	-308.17012	0.000425	0.614902	0.12671375	-307.681932
*CH_3	-312.901003	0.000571	0.910362	0.17024365	-312.160885
*CH_4	-317.31996	0.00061	1.212199	0.1818715	-316.289632

Ni@MoS_2					
Step	**E(eV)**	**E_{ZPE} (eV)**	**S (eVK^{-1})**	**TS (eV)**	**G(eV)**
*CO_2	-587.563637	0.302154	0.000618	0.18425670	-587.445740
*COOH	-590.645482	0.603614	0.000599	0.17859185	-590.22046
*OCHO	-590.841339	0.589185	0.000653	0.19469195	-590.446846
*CO	-580.970742	0.205472	0.000519	0.15473985	-580.92001
*OCHOH	-594.89086	0.920173	0.000851	0.25372565	-594.224412
*COH	-581.907684	0.446143	0.000458	0.1365527	-581.598093
*CHO	-583.261108	0.434148	0.000507	0.15116205	-582.978122
*OCH_2OH	-597.856888	1.202081	0.000723	0.21556245	-596.870369
*CHOH	-586.765332	0.786436	0.000255	0.07602825	-586.054924
*OCH_2	-587.601273	0.77883	0.000607	0.18097705	-587.00342
*C	-568.827204	0.061959	0.000302	0.0900413	-568.855286
*OCH_3	-590.976745	1.050178	0.000527	0.15712505	-590.083692
*CH_2OH	-590.710841	1.074021	0.000416	0.1240304	-589.760851
*CH	-580.970877	0.203502	0.00031	0.0924265	-580.859801
*CH_3OH	-595.531155	1.405878	0.000562	0.1675603	-594.292837
*CH_2	-579.170696	0.612425	0.00041	0.1222415	-578.680513
*CH_3	-584.136236	0.91042	0.0004	0.11926	-583.345076
*CH_4	-588.787671	1.208436	0.000538	0.1604047	-587.73964

Ni@Mo_2C					
Step	**E(eV)**	**E_{ZPE} (eV)**	**S (eVK^{-1})**	**TS (eV)**	**G(eV)**
*CO_2	-498.588954	0.309628	0.000395	0.11776925	-498.397095
*COOH	-502.97137	0.609714	0.000639	0.19051785	-502.552174
*OCHO	-503.724573	0.627761	0.000636	0.1896234	-503.286435
*COOH	-503.623063	0.526705	0.000724	0.2158606	-503.312218
*CO	-491.787177	0.193857	0.000542	0.1615973	-491.754917
*OCHOH	-505.933667	0.927132	0.000912	0.2719128	-505.278448
*OCH_2OH	-509.458255	1.204563	0.00079	0.2355385	-508.48923
*CHO	-494.564812	0.445339	0.000656	0.1955864	-494.31506
*COH	-493.459351	0.447735	0.000493	0.14698795	-493.158604
*OCH_2	-498.431457	0.761415	0.000692	0.2063198	-497.876362
*CHOH	-497.843831	0.773156	0.00049	0.1460935	-497.216769
*C	-480.93785	0.067148	0.000287	0.08556905	-480.956271
*CH_2OH	-502.280252	1.067916	0.000413	0.12313595	-501.335472
*CH	-485.709716	0.308306	0.000428	0.1276082	-485.529018
*OCH_3	-502.68526	1.065528	0.000665	0.19826975	-501.818002
*CH_3OH	-506.486166	1.398621	0.000583	0.17382145	-505.261366
*CH_2	-490.655899	0.596963	0.000458	0.1365527	-490.195488
*CH_3	-495.70907	0.899217	0.000271	0.08079865	-494.890652
*CH_4	-499.737946	1.198221	0.000615	0.18336225	-498.723088