Supplementary Information

Catalytic Oxidation of CO by N_2O on the Neutral Y_2MO_5 (M = Y, Al) Clusters: A Density Functional Theory Study

Hong-Ling Fang[a], Lei Xu[a], Jia Li[a], Bin Wang[a], Yong-Fan Zhang[a,b,c]*, Xin Huang[a,b]*

[a]*College of Chemistry, Fuzhou University, Fuzhou, Fujian 350116, PR China*

[b]*Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen, Fujian 361005, PR China*

[c]*State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, 350002, PR China*

*Corresponding author. Tel.: +86 591 22866139; fax: +86 591 22866156.
E-mail address: xhuang@fzu.edu.cn (X. Huang); zhangyf@fzu.edu.cn (Y. F. Zhang)

Fig. S1 Isomeric structures and their relative energies 0.40 eV above the ground state for Y_3O_x (x = 4–5).

Fig. S2 Isomeric structures and their relative energies 0.40 eV above the ground state for Y_2AlO_x (x = 4–5).

Figs. S3–S4 Calculated energy profile for the reaction of Y_3O_5 cluster with CO_2. The reactants, intermediates, transition states and produces of the reaction are denoted as R, IM*m*, TS*n* and P, respectively. The energies (given in eV) are relative to the entrance channel. Some key bond lengths are given in angstroms.

Figs. S5–S7 Calculated energy profile for the reaction of Y_2AlO_5 with CO. The reactants, intermediates, transition states and produces of the reaction are denoted as R, IM*m*, TS*n* and P, respectively. The energies (given in eV) are relative to the entrance channel. Some key bond lengths are given in angstroms.

Fig. S8 Spin distribution for the structures of Y_3O_5 reacting with CO.

Fig. S9 Spin distribution for the structures of Y_2AlO_5 reacting with CO.

Fig. S10 DFT calculated molecular electrostatic potential maps (MEPs) for CO, CO_2 and Y_2MO_x (M = Y, Al; x = 4–5) clusters. Natural charge distributions for these clusters are given in e.

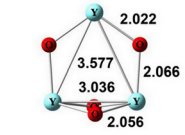
Figs. S11–S12 Calculated the reaction of Y_2AlO_4 with N_2O. The reactants, intermediates, transition states and produces of the reaction are denoted as R, IM*m*, TS*n* and P, respectively. The energies (given in eV) are relative to the entrance channel. Some key bond lengths are given in angstroms.

Table S1 Relative energies of the low-lying states of the Y_2AlO_x (x = 4–5) clusters at the BP86 level (within 0.20 eV), and comparisons with those from the CCSD(T) single-point calculations at the BP86 geometries.

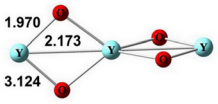
Table S2 Cartesian coordinates for all the optimized structures within 0.40 eV for Y_3O_x and Y_2AlO_x (x = 4–5) at the BP86/Y/Stuttgart+2*f*1*g*/O/Al/aug-cc-pvTZ level of theory.

Table S3 Cartesian coordinates for all the optimized structures shown in the energy profiles of Figs. 5–6, 8–9 at the BP86/Y/Stuttgart+2*f*1*g*/O/Al/C/N/aug-cc-pvTZ level of theory.

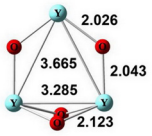
Fig. S1



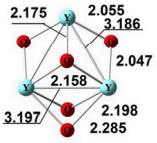
(a) Y_3O_4 C_{2v} ($^2A_1$ 0.52 eV)



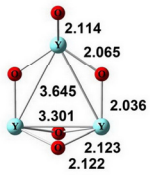
(b) Y_3O_4 D_{2d} ($^2A_1$ 1.52 eV)



(c) Y_3O_4 C_{2v} ($^4B_1$ 3.47 eV)

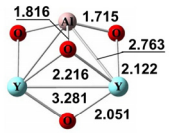


(d) Y_3O_5 C_s ($^2A'$ 1.38 eV)



(e) Y_3O_5 C_s ($^4A''$ 3.41 eV)

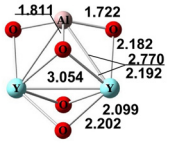
Fig. S2



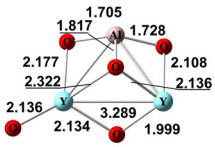
(a) Y_3AlO_4 C_s ($^2A''$ 0.67 eV)

(b) Y_3AlO_4 C_s ($^2A'$ 0.75 eV)

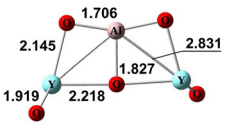
(c) Y_3AlO_4 D_{2d} ($^2A_1$ 1.15 eV)



(d) Y_3AlO_5 C_s ($^2A'$ 0.65 eV)

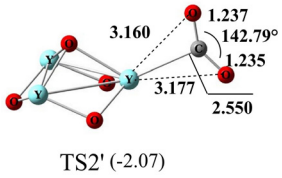


(e) Y_3AlO_5 C_1 (^2A 0.68 eV)



(f) Y_3AlO_5 C_2 (^2B 2.08 eV)

Fig. S3



TS2' (-2.07)

Fig. S4

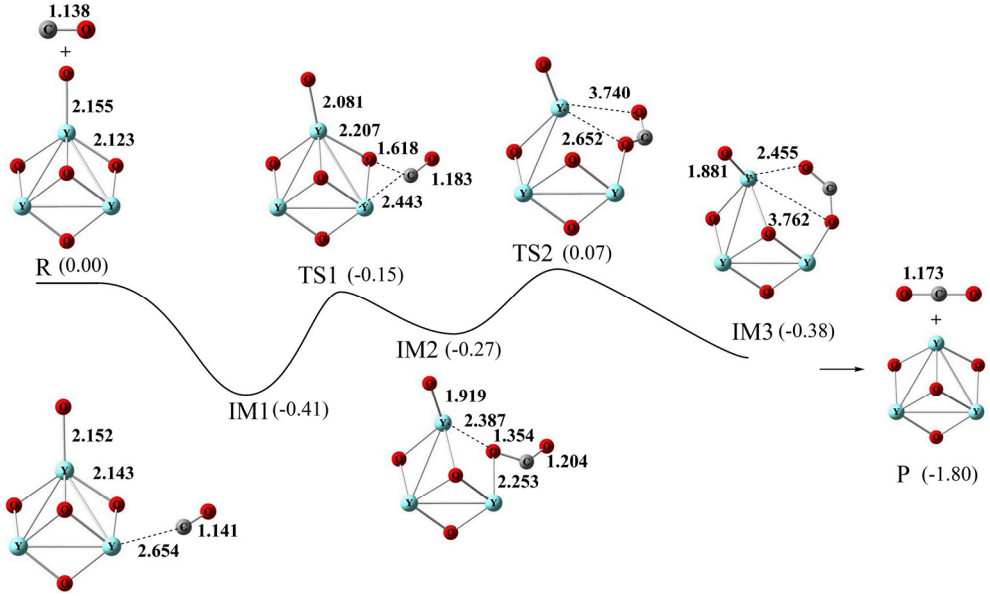


Fig. S5

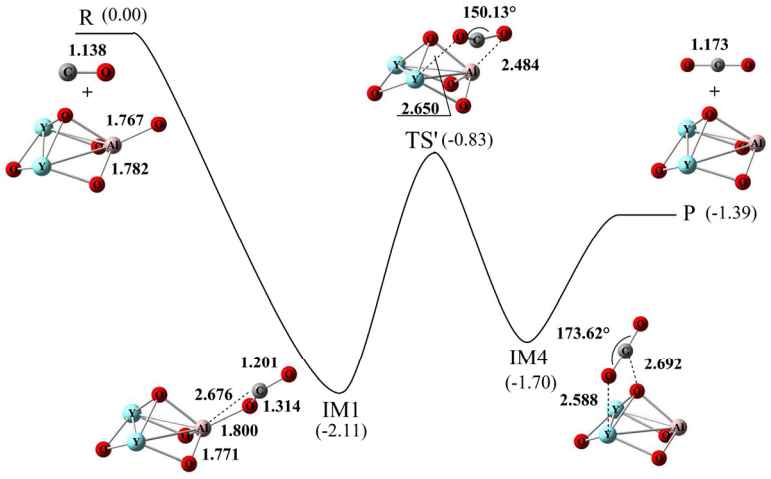


Fig. S6

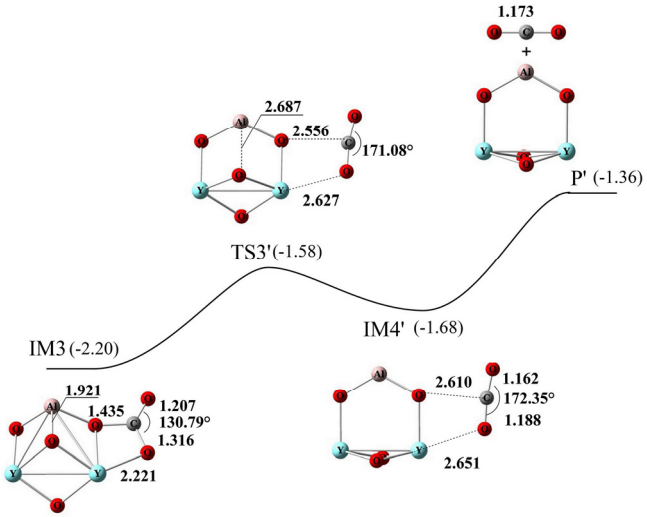

1.173
2.687
2.556
171.08°
2.627
P' (-1.36)
TS3'(-1.58)
IM4' (-1.68)
IM3 (-2.20)
1.921
1.435
1.207
130.79°
1.316
2.221
2.610
1.162
172.35°
1.188
2.651

Fig. S7

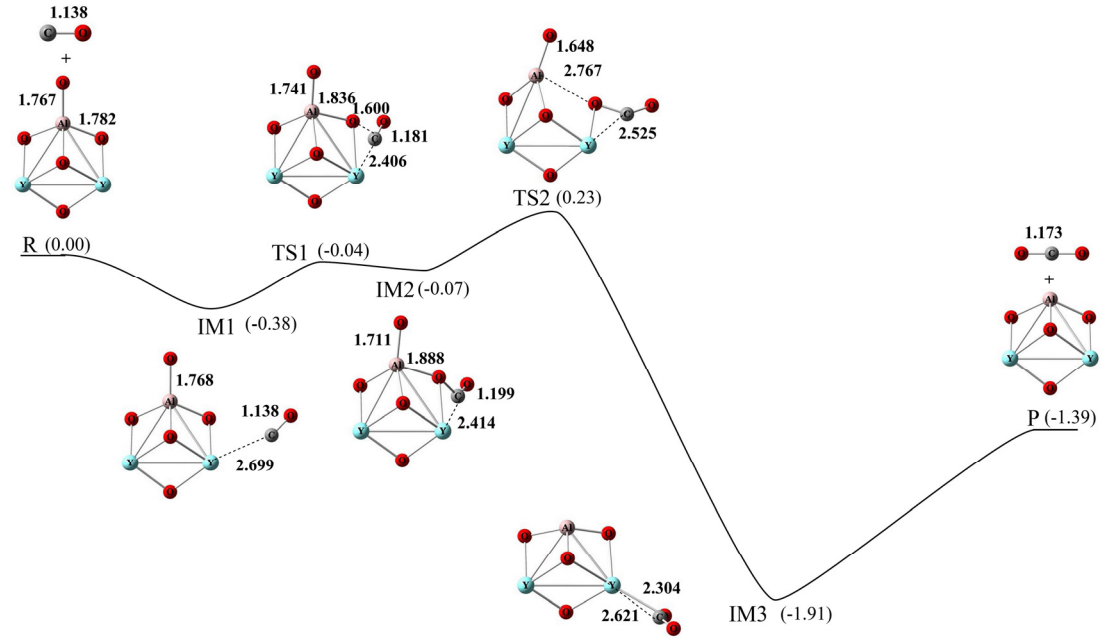

1.138
1.767
1.782
R (0.00)
1.741
1.836
1.600
1.181
2.406
TS1 (-0.04)
1.648
2.767
2.525
TS2 (0.23)
IM2 (-0.07)
IM1 (-0.38)
1.711
1.888
1.199
2.414
1.768
1.138
2.699
1.173
P (-1.39)
2.304
2.621
IM3 (-1.91)

Fig. S8

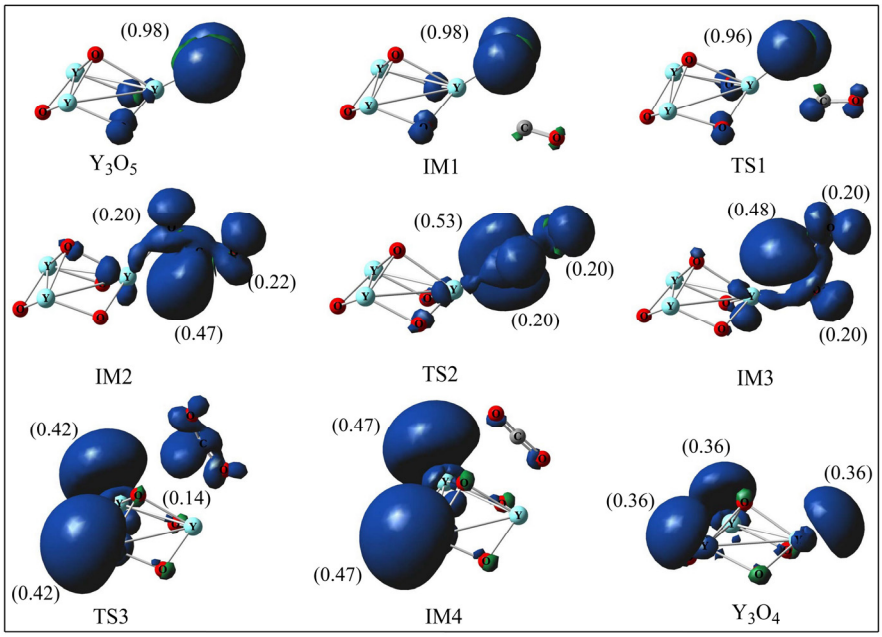

(0.98)
Y_3O_5
(0.98)
IM1
(0.96)
TS1
(0.20)
(0.22)
(0.47)
IM2
(0.53)
(0.20)
(0.20)
TS2
(0.20)
(0.48)
(0.20)
IM3
(0.42)
(0.14)
(0.42)
TS3
(0.47)
(0.47)
IM4
(0.36)
(0.36)
(0.36)
Y_3O_4

Fig. S9

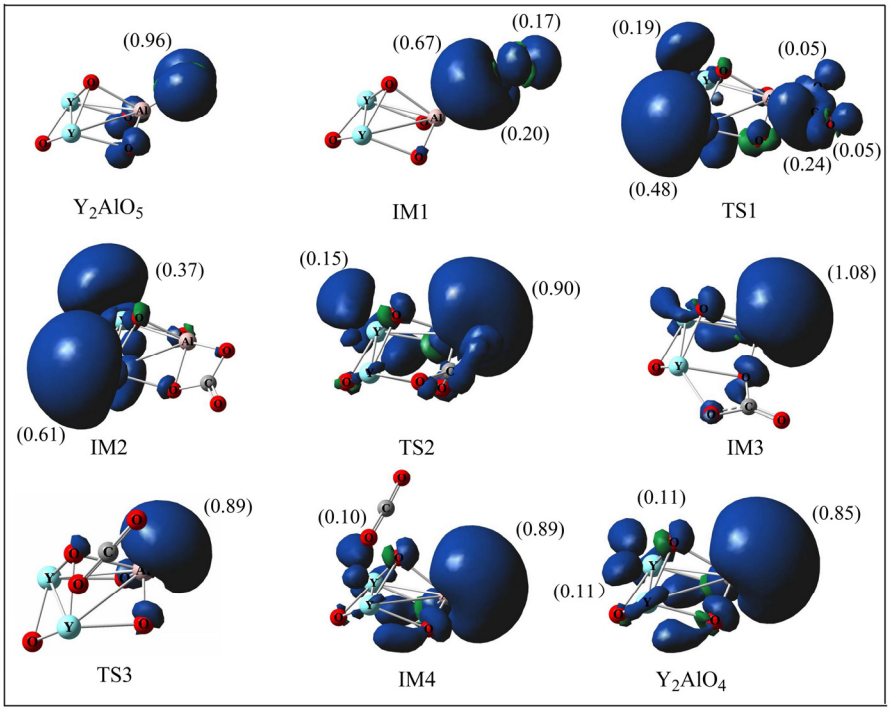

(0.96)
Y_2AlO_5
(0.67)
(0.17)
(0.20)
IM1
(0.19)
(0.05)
(0.05)
(0.24)
(0.48)
TS1
(0.37)
(0.61)
IM2
(0.15)
(0.90)
TS2
(1.08)
IM3
(0.89)
TS3
(0.10)
(0.89)
IM4
(0.11)
(0.85)
(0.11)
Y_2AlO_4

Fig. S10

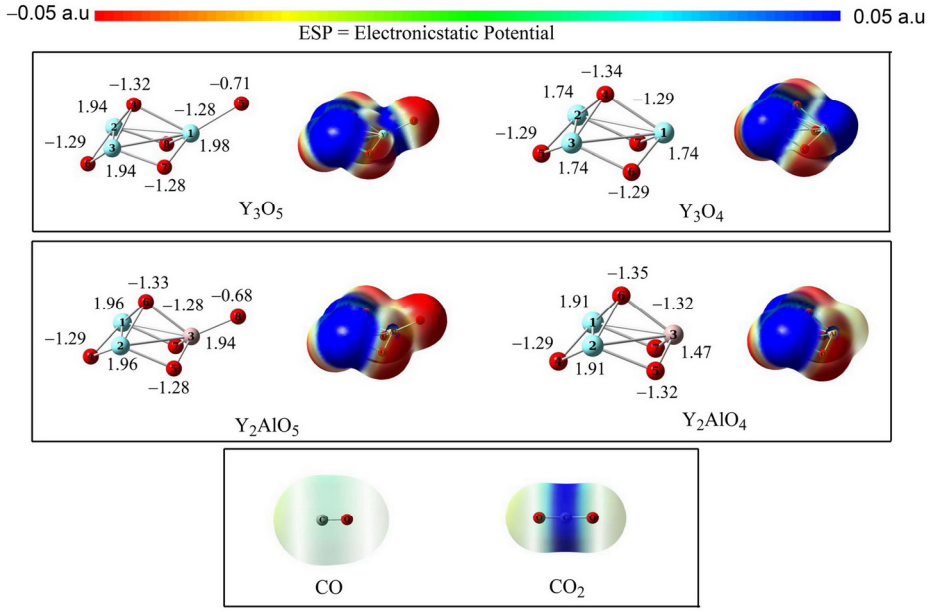


Fig. S11

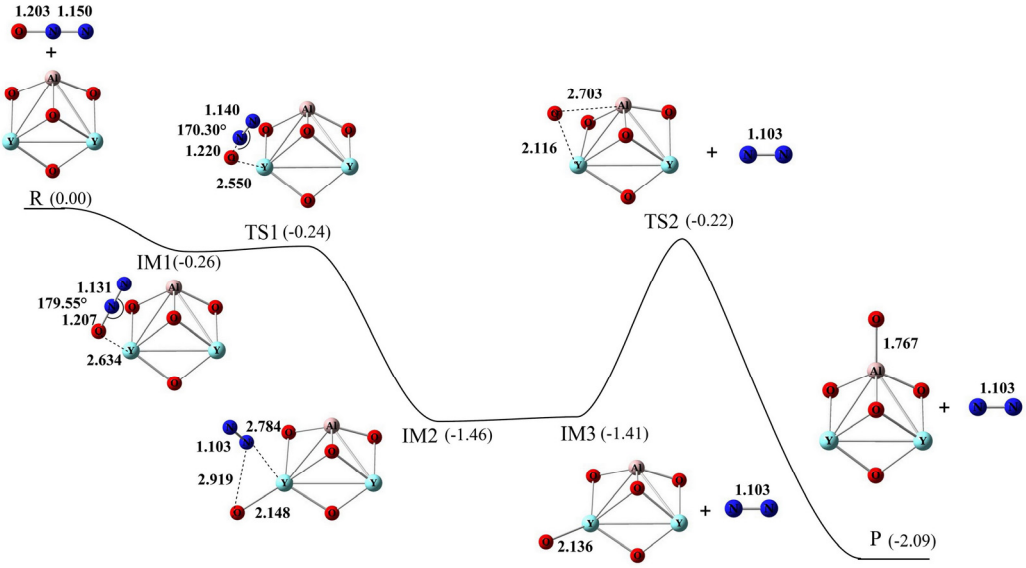


Fig. S12

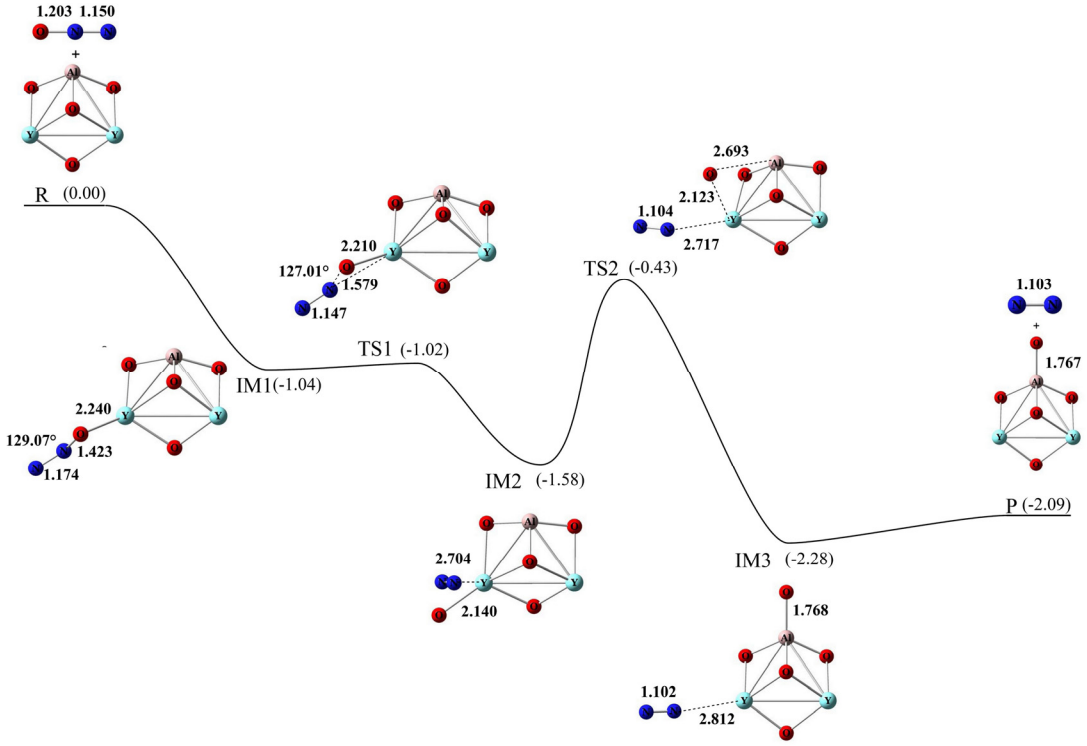

1.203 1.150
R (0.00)
2.210
127.01°
1.579
1.147
TS1 (-1.02)
2.693
2.123
1.104
2.717
TS2 (-0.43)
1.103
1.767
P (-2.09)
IM1(-1.04)
2.240
129.07°
1.423
1.174
IM2 (-1.58)
2.704
2.140
IM3 (-2.28)
1.768
1.102
2.812

Table S1

	State	BP86[a,b]	CCSD(T)[a,c]
Y_2AlO_4	(C_s, ^{2}A')	0.00	0.00
	(C_{2v}, $^2A_1$)	0.02	0.12
Y_2AlO_5	(C_s, ^{2}A")	0.00	0.00
	(C_{2v}, $^2B_2$)	0.08	0.23
	(C_s, ^{2}A')	0.12	0.08

[a] All energies are in eV.

[b] At the BP86/Y/Stuttgart+2*f*1*g*/O/Al/aug-cc-pVTZ level.

[c] Single point CCSD(T) energy using BP86 results within 0.20 eV .

Table S2

Y_3O_4 C_{3v} ($^2A_1$ 0.00 eV)

Y	0.000000	1.832621	0.068639
Y	-1.587097	-0.916311	0.068639
Y	1.587097	-0.916311	0.068639
O	-1.664655	0.961089	-0.747240
O	1.664655	0.961089	-0.747240
O	0.000000	-1.922178	-0.747240
O	0.000000	0.000000	1.237876

Y_3O_5 C_s (^{2}A" 0.00 eV)

Y	0.649603	1.553103	0.000000
Y	-0.413401	-1.035704	1.576317
Y	-0.413401	-1.035704	-1.576317
O	0.992287	-0.730349	0.000000
O	2.312744	2.924094	0.000000
O	-1.614386	-1.589437	0.000000
O	-0.413401	0.961215	-1.739572
O	-0.413401	0.961215	1.739572

Y_3O_5 C_s (^{2}A' 0.11 eV)

Y	0.686435	1.529567	0.000000
Y	-0.433297	-1.024520	1.579013
Y	-0.433297	-1.024520	-1.579013
O	0.990778	-0.719381	0.000000
O	2.378372	2.908171	0.000000
O	-1.624280	-1.588585	0.000000
O	-0.433297	0.966115	-1.722040
O	-0.433297	0.966115	1.722040

Y_3O_5 C_s (^{2}A' 0.21 eV)

Y	0.229440	-0.828589	1.505504
Y	0.229440	-0.828589	-1.505504
Y	-0.689824	1.820390	0.000000
O	-1.253061	-0.206738	0.000000
O	1.677724	-0.682444	0.000000
O	0.242312	-2.462883	0.000000
O	0.229440	1.278202	1.745314
O	0.229440	1.278202	-1.745314

Y_2AlO_4 C_s (^{2}A' 0.00 eV)

Y	0.000000	1.509314	-0.533837
Y	0.000000	-1.509314	-0.533837
Al	0.000000	0.000000	2.394290
O	-1.346215	0.000000	-0.880541
O	1.346215	0.000000	-0.880541
O	0.000000	-1.509716	1.537634
O	0.000000	1.509716	1.537634

Y_2AlO_4 C_{2v} ($^2A_1$ 0.02 eV)

Y	-0.113324	-0.477844	1.575410
Y	-0.113324	-0.477844	-1.575410
Al	0.791409	1.744819	0.000000
O	-0.113324	1.541741	1.527950
O	-1.266194	-1.107841	0.000000
O	-0.113324	1.541741	-1.527950
O	1.311712	-0.151989	0.000000

Y_2AlO_5 C_s ($^2A''$ 0.00 eV)

Y	-0.240640	-0.654302	1.572057
Y	-0.240640	-0.654302	-1.572057
Al	0.667247	1.571726	0.000000
O	-1.395315	-1.298018	0.000000
O	-0.240640	1.355313	-1.517925
O	1.166973	-0.351300	0.000000
O	-0.240640	1.355313	1.517925
O	1.971583	2.764082	0.000000

Y_2AlO_5 C_{2v} ($^2B_2$ 0.08 eV)

Y	0.000000	1.510745	-0.785597
Y	0.000000	-1.510745	-0.785597
Al	0.000000	0.000000	2.128669
O	-1.343799	0.000000	-1.127560
O	1.343799	0.000000	-1.127560
O	0.000000	-1.499763	1.285964
O	0.000000	1.499763	1.285964
O	0.000000	0.000000	3.883672

Y_2AlO_5 C_s (^{2}A' 0.12 eV)

Y	-0.263241	-0.631011	1.576272
Y	-0.263241	-0.631011	-1.576272
Al	0.703892	1.542968	0.000000
O	-1.403161	-1.289491	0.000000
O	-0.263241	1.367731	-1.493074
O	1.171941	-0.345683	0.000000
O	-0.263241	1.367731	1.493074
O	2.180483	2.544748	0.000000

Y_2AlO_5 C_{2v} (^{2}B$_1$ 0.31 eV)

Y	0.000000	1.511646	-0.790424
Y	0.000000	-1.511646	-0.790424
Al	0.000000	0.000000	2.167482
O	-1.344735	0.000000	-1.144942
O	1.344735	0.000000	-1.144942
O	0.000000	-1.477930	1.272313
O	0.000000	1.477930	1.272313
O	0.000000	0.000000	3.929737

Table S3

Cartesian coordinates for the reaction of Y_3O_5 with CO as shown in Fig. 5

IM1

Y	-1.300913	-0.000021	0.290210
Y	1.496036	-1.573361	-0.032044
Y	1.495994	1.573382	-0.032053
O	0.850426	0.000008	1.239131
O	-2.965060	0.000044	1.700273
O	2.329900	0.000011	-1.066102
O	-0.436025	1.752324	-0.542542
O	-0.435990	-1.752347	-0.542527
C	-3.698746	-0.000023	-0.949144
O	-4.813389	-0.000025	-1.178675

TS1

Y	1.294041	-0.114906	0.155965
Y	-1.414383	1.629968	0.054903
Y	-1.602369	-1.511324	-0.030571
O	-0.771529	-0.020985	1.236784
O	3.021160	-0.290117	1.502080
O	-2.418039	0.139357	-0.950399
O	0.275937	-1.776944	-0.681823
O	0.478523	1.702442	-0.592789
C	3.813943	0.115153	-0.752926
O	4.951707	0.141661	-0.828106

IM2

Y	-1.269968	-0.000001	-0.248737
Y	1.501327	-1.574069	0.137954

Y	1.501326	1.574070	0.137955
O	0.517868	0.000000	1.194188
O	-3.137306	-0.000009	1.126627
O	2.598255	0.000001	-0.597849
O	-0.217463	1.704522	-0.884551
O	-0.217463	-1.704523	-0.884552
C	-3.892374	0.000001	0.099125
O	-5.071447	0.000007	-0.160671

TS2

Y	-1.231733	-0.261615	0.376416
Y	1.241099	1.708002	-0.144821
Y	1.689350	-1.410767	-0.245804
O	0.383676	0.020180	-1.168254
O	-3.289831	-1.010884	-0.349990
O	2.623344	0.291317	0.413896
O	0.108720	-1.786289	0.927416
O	-0.353122	1.541077	1.041623
C	-3.819384	0.154356	-0.311938
O	-4.889484	0.655183	-0.561467

IM3

Y	-1.287401	-0.000009	-0.436042
Y	1.456506	-1.572273	0.124858
Y	1.456495	1.572274	0.124859
O	0.410764	-0.000003	1.116723
O	-4.498431	0.000016	1.578628
O	2.600341	0.000005	-0.539511
O	-0.192377	1.696408	-1.011228

O	-0.192365	-1.696419	-1.011227
C	-3.667984	0.000004	0.702037
O	-3.608196	-0.000002	-0.569129

TS3

Y	0.260811	1.537600	0.000000
Y	-0.814703	-0.993262	1.591096
Y	-0.814703	-0.993262	-1.591096
O	0.627564	-0.605410	0.000000
O	2.762490	1.744278	0.000000
O	-1.959290	-1.588664	0.000000
O	-0.814703	1.058211	-1.677889
O	-0.814703	1.058211	1.677889
C	3.431879	0.748273	0.000000
O	4.296632	-0.039327	0.000000

IM4

Y	1.038307	-0.000020	-1.250796
Y	-1.154115	1.594777	0.412616
Y	-1.154138	-1.594758	0.412641
O	0.301674	0.000002	0.795655
O	3.209833	-0.000008	0.158650
O	-2.435921	0.000018	0.358711
O	-0.127225	-1.672481	-1.372084
O	-0.127200	1.672456	-1.372111
C	3.076795	0.000004	1.339229
O	3.062232	0.000016	2.501260

Cartesian coordinates for the reaction of Y_2AlO_5 with CO as shown in Fig. 6

IM1

Y	-1.460099	-1.353735	-0.247119
Y	-0.695908	1.709327	-0.109700
Al	1.089306	-0.395117	0.564051
O	-2.285157	0.457963	0.247058
O	0.722375	1.208951	1.219843
O	0.067428	-0.070600	-1.041038
O	0.023993	-1.719447	1.061138
O	2.811503	-0.853676	0.309400
C	3.566917	-0.027068	-0.378161
O	4.725084	-0.094334	-0.689872

TS1

Y	1.945713	-0.848974	0.098356
Y	0.042791	1.722751	0.071907
Al	-0.845885	-0.971463	-0.112884
O	1.839694	1.047395	-0.648623
O	-1.467877	0.547038	-0.796200
O	0.204277	-0.149649	1.183405
O	0.435900	-1.950730	-0.766383
O	-2.550164	-1.593656	0.348901
C	-3.248795	-0.578067	0.053370
O	-4.344624	-0.147884	-0.007722

IM2

Y	2.061034	-0.577122	0.012468
Y	-0.241124	1.646378	0.107655
Al	-0.674706	-1.305730	0.138918

O	1.517309	1.250587	-0.774502
O	-1.717175	0.120494	-0.651451
O	0.240945	-0.129034	1.202327
O	0.710868	-2.004360	-0.621442
O	-2.405501	-1.721565	0.400462
C	-2.854231	-0.579641	-0.159312
O	-3.981437	-0.172200	-0.247255

TS2

Y	2.092867	0.061079	-0.122191
Y	-0.776147	-1.283618	-0.048632
Al	-0.232379	1.795961	-0.063565
O	1.105589	-1.544609	0.703094
O	-1.313134	0.630526	1.022722
O	0.174140	0.257875	-1.161514
O	1.380912	1.771320	0.684797
O	-2.598314	1.825597	-0.370919
C	-2.432096	0.711524	0.171802
O	-2.966516	-0.432909	-0.070974

IM3

Y	-2.163187	-0.003450	-0.174161
Y	0.757980	-1.159649	0.251987
Al	-0.058291	1.800051	0.604333
O	-0.883811	-1.405818	-0.946717
O	2.862571	-0.691278	-0.283150
O	-0.612311	0.113250	1.338907
O	-1.433465	1.842083	-0.525912
O	1.357933	0.945341	-0.226948

C	2.751031	0.618854	-0.340290
O	3.590912	1.477310	-0.462405

TS3

Y	2.101969	0.098267	-0.603367
Y	-0.658170	-1.085438	0.357094
Al	0.117163	1.653105	0.778365
O	1.332570	-1.619250	0.193288
O	-0.805497	0.424733	1.698680
O	0.019466	0.565670	-0.858053
O	1.900449	1.540361	0.802167
O	-3.972854	1.513702	-0.801391
C	-3.506515	0.456015	-0.683626
O	-3.073158	-0.641061	-0.586239

IM4

Y	1.727850	0.719583	-0.581190
Y	-0.790073	-1.179948	-0.355570
Al	0.502573	0.017590	1.930995
O	0.949542	-0.965655	-1.442241
O	-0.289144	-1.543719	1.568459
O	-0.239372	0.829819	0.286299
O	2.171569	0.245794	1.331190
O	-2.871591	2.438506	0.248161
C	-2.856274	1.330201	-0.099083
O	-2.967141	0.213300	-0.488717

Cartesian coordinates for the reaction of Y_3O_4 with N_2O as shown in Fig. 8

IM1

Y	-0.703555	-1.263743	1.572152
Y	-0.703555	-1.263743	-1.572152
Y	0.397977	1.313840	0.000000
O	-1.900022	-1.829165	0.000000
O	-0.703555	0.736972	1.698239
O	-0.703555	0.736972	-1.698239
O	0.710495	-0.970808	0.000000
N	3.907065	2.400645	0.000000
N	2.739531	2.242899	0.000000
O	1.700390	3.179448	0.000000

TS1

Y	1.719274	-1.319569	0.393000
Y	1.074457	1.745367	0.054436
Y	-1.226862	-0.417148	-0.502121
O	2.572428	0.395823	-0.349956
O	0.242899	-1.900399	-0.828533
O	-0.442357	1.417097	-1.206320
O	0.282831	0.077378	1.142358
N	-4.409241	0.683421	1.301616
N	-3.483946	0.316618	0.734325
O	-3.387751	-0.907102	-0.272409

IM2

Y	1.860467	-1.056664	0.534867
Y	0.752061	1.804185	-0.157997
Y	-1.178726	-0.752800	-0.488202
O	2.446624	0.667897	-0.419349
O	0.520164	-2.007235	-0.611021

O	-0.692661	1.124889	-1.365741
O	0.224232	0.177512	1.124960
N	-4.082742	1.192262	1.461800
N	-3.174481	0.792715	0.979297
O	-3.138079	-1.674184	-0.322065

Cartesian coordinates for the reaction of Y_2AlO_4 with N_2O as shown in Fig. 9

IM1

Y	-1.100591	1.573271	-0.056118
Y	-1.100536	-1.573300	-0.056093
Al	1.229765	0.000032	0.504647
O	0.868184	1.496608	-0.408000
O	-1.942708	-0.000039	-1.075217
O	0.868238	-1.496570	-0.407975
O	-0.575503	0.000005	1.298261
O	2.345031	0.000076	1.897002
N	4.572385	-0.000053	-1.179407
N	3.620627	0.000065	-0.622990

Cartesian coordinates for CO, CO_2, N_2O and N_2

CO

C	0.000000	0.000000	-0.650176
O	0.000000	0.000000	0.487632

CO_2

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.172549
O	0.000000	0.000000	-1.172549

N_2O

N	0.000000	0.000000	-1.209493
N	0.000000	0.000000	-0.071388
O	0.000000	0.000000	1.120772

N_2

N	0.000000	0.000000	0.551597
N	0.000000	0.000000	-0.551597