Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A Support material

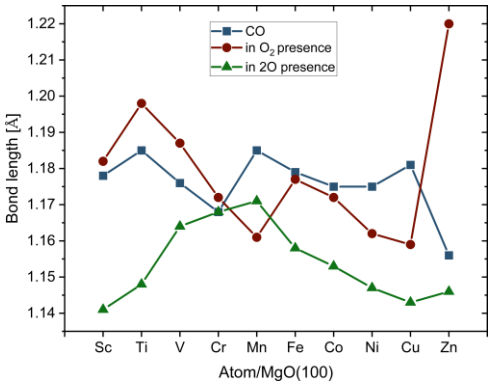

Fig. S2 CO bond length (blue) on M/MgO(100), (red) on M/MgO(100) in O_2 presence and (green) on M/MgO(100) in 2O presence

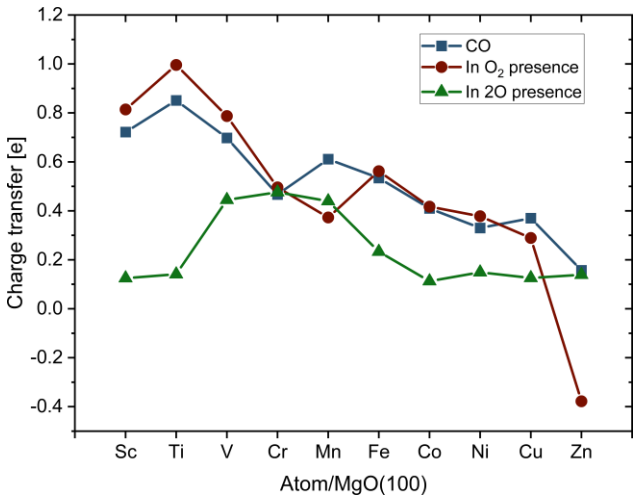

Fig. S1 Charge transfer towards CO from (blue) M/MgO(100), (red) in O_2 presence, and (green) on M/MgO(100) in 2O presence.

Table S1 Adsorption energy for atoms onto the surface using a four-layer slab $E_{ads}^{4-layers}$, and energies using our three-layer slab $E_{ads}^{3-layers}$.

Atom	$E_{ads}^{3-layers}$ [eV]	$E_{ads}^{4-layers}$ [eV]
Sc	-2.15	-2.15
Ti	-1.88	-1.95
V	-1.42	-1.42
Cr	-0.64	-0.64
Mn	-1.14	-1.14
Fe	-1.95	-1.95
Co	-1.91	-1.90
Ni	-2.22	-2.22
Cu	-1.26	-1.26
Zn	-0.21	-0.21

Table S2 Adsorption energy E_{ads}, charge transfer dQ and bond length B. L. Bold text indicate the system to which quantities correspond.

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Metal										
$E_{ads-bridge}$ [eV]	-1.67	-1.55	-1.03	-0.38	-0.67	-1.95	-1.77	-1.40	-1.26	-0.17
$E_{ads-top}$ [eV]	-2.15	-1.88	-1.42	-0.64	-1.14	-1.95	-1.92	-2.22	-1.26	-0.22
dQ_{tpp} [e]	-0.29	-0.16	-0.11	-0.04	-0.03	0.10	0.158	0.183	0.169	0.066
$E_{bridf-top}$ [ev]	0.48	0.33	0.46	0.27	0.48	0.67	0.52	0.81	0.52	0.05
E^{bulk} [ev]	2.47	4.16	4.60	3.80	3.45	3.85	4.25	3.30	2.76	1.49
O_2										
E_{ads} [eV]	-4.69	-5.23	-4.58	-3.82	-3.09	-3.20	-3.47	-2.76	-2.12	0.04
dQ [e]	11.50	1.30	1.17	1.16	1.13	0.98	0.83	0.69	0.67	0.81
B. L. [Å]	1.47	1.44	1.43	1.44	1.47	1.44	1.41	1.36	1.34	1.35
2O										
E_{ads} [eV]	-6.93	-9.82	-9.22	-7.50	-6.12	-5.91	-5.32	-3.81	-1.93	-1.24
dQ [e]	2.63	2.73	2.44	2.12	2.14	1.87	1.66	1.82	1.88	1.94
Only CO										
E_{ads} [eV]	-0.94	-2.00	-2.40	-1.84	-1.74	-2.45	-3.51	-3.60	-1.43	0.06
dQ [e]	0.722	0.85	0.70	0.47	0.61	0.53	0.41	0.33	0.37	0.16
B. L. [Å]	1.18	1.18	1.18	1.17	1.18	1.18	1.18	1.18	1.18	1.16
CO with O_2										
E_{ads} [eV]	-1.12	-1.37	-1.83	-0.84	-0.84	-1.20	-1.30	-0.55	-0.54	-2.62
dQ [e]	0.81	1.00	0.79	0.50	0.37	0.56	0.42	0.38	0.29	-0.38
B. L. [Å]	1.18	1.20	1.19	1.17	1.16	1.18	1.17	1.16	1.16	1.22
CO with 2O										
E_{ads} [eV]	-0.71	-0.35	-1.56	-1.62	-1.45	-0.88	-1.01	-0.32	-0.32	-0.34
dQ [e]	0.12	0.14	0.44	0.48	0.44	0.23	0.11	0.15	0.13	0.14
B. L. [Å]	1.14	1.15	1.16	1.17	1.17	1.16	1.15	1.15	1.14	1.15
CO with O										
E_{ads} [eV]	-0.97	-1.55	-2.84	-1.98	-2.04	-2.40	-1.98	-1.43	-1.47	-0.53
dQ [e]	0.76	0.83	0.69	0.59	0.64	0.43	0.33	0.31	0.22	0.13
B. L. [Å]	1.18	1.18	1.18	1.18	1.18	1.17	1.17	1.16	1.16	1.15
CO_2										
E_{ads} [eV]	-1.86	-1.89	-1.48	-0.56	-0.25	-0.46	-2.24	-1.95	-0.64	0.14
dQ [e]	1.52	1.34	1.22	0.88	0.67	0.66	0.61	0.53	0.52	0.54
Formation 1										
E_{on-top} [eV]	-0.54	-2.24	-3.14	-2.48	-1.20	-1.10	0.31	1.32	2.80	2.17
E_{bridge} [eV]	1.01	-1.33	-3.51	-2.46	-1.48	-0.96	0.08	1.68	2.52	2.98
Formation 2										
E_{on-top} [eV]	-1.76	-2.94	-2.82	-1.08	-0.06	-0.55	-0.93	0.09	1.53	1.24
E_{bridge} [eV]	-2.68	-3.45	-3.16	-1.69	-1.18	-1.29	-1.45	-0.30	0.69	1.86
	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**