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

Supporting Information

Combinatorial Selection of Two-dimensional 3*d*-TM–tetracyanoquinodimethane (TM–TCNQ) Monolayer as High-Activity Nanocatalysts for CO Oxidation

Qingming Deng[a,b], Tiantian Wu[b], Guibin Chen[a], Heine Anton Hansen[b]*, Tejs Vegge[b]*

[a.] *Physics department and Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaiyin Normal University, Huaian 223300, China.*
[b.] *Department of Energy Conversion and Storage, Technical University of Denmark, Fysikvej, 2800 Kgs. Lyngby, Denmark.*

	E_{diff}	Dist(TM-N)	Mag(μb)	Lattice(a)	Lattice(b)
Sc	-4.33	2.111	0	7.20	11.74
Ti	-3.31	2.064	1.506	7.22	11.54
V	-3.49	1.999	2.547	7.15	11.42
Cr	-3.56	1.978	3.395	7.11	11.40
Mn	-1.6	1.902	2.621	7.01	11.30
Fe	-2.61	1.842	1.586	6.93	11.20
Co	-2.52	1.822	0	6.88	11.19
Ni	-2.26	1.91	0.721	7.04	11.25
Cu	-2.18	1.974	0	6.92	11.15
Zn	-3.16	2.019	0	7.19	11.40

Table S1. Energy difference (E_{diff}) between embedding energy and cohesive energy in eV, distance (Dist) of TM and N atoms, magnetic moment (Mag) and lattice constant a and b of TM-TCNQ in Å.

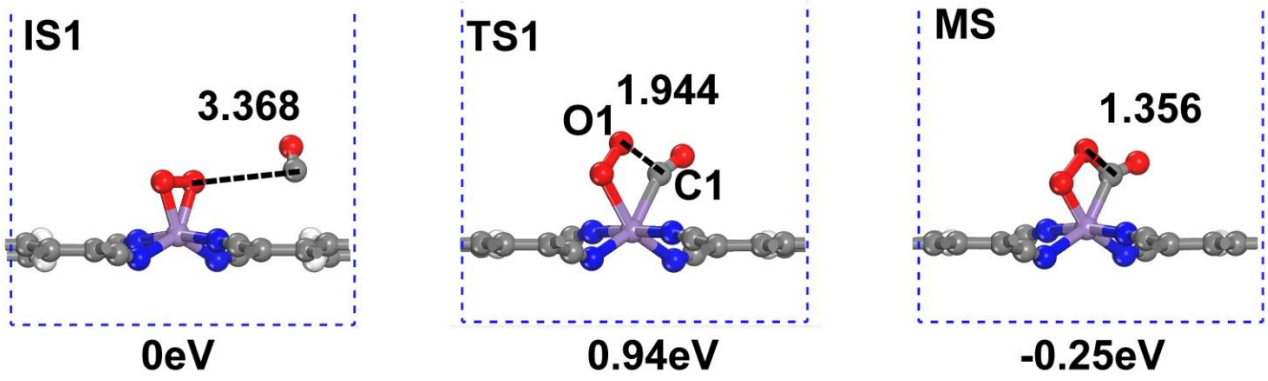

Figure S1. The configurations with DFT energy of the limiting step for CO oxidation reaction via LH mechanism on Mn-TCNQ.

On the Mn-TCNQ surface, the first activation energy of the rate-limiting step via ER mechanism is ca. 1.1 eV with CO_3 formation. While the barrier decreased to 0.94 eV via LH mechanism leading to OOCO formation as shown as in Fig.S2. By comparison of Sc-TCNQ, the structural parameter of the transition state (TS1) is quite different. The distance of labeled O1 and C1 (1.944Å) is longer than the one on Sc-TCNQ (1.352Å). When O1 and C1 forms a chemical bond (1.356 Å), the energy significantly decreases from 0.94eV to -0.25eV. Therefore, the configuration of TS1 on Mn-TCNQ is in between the IS1 and MS, but the one is quite similar with its TS1 on Sc-TCNQ.

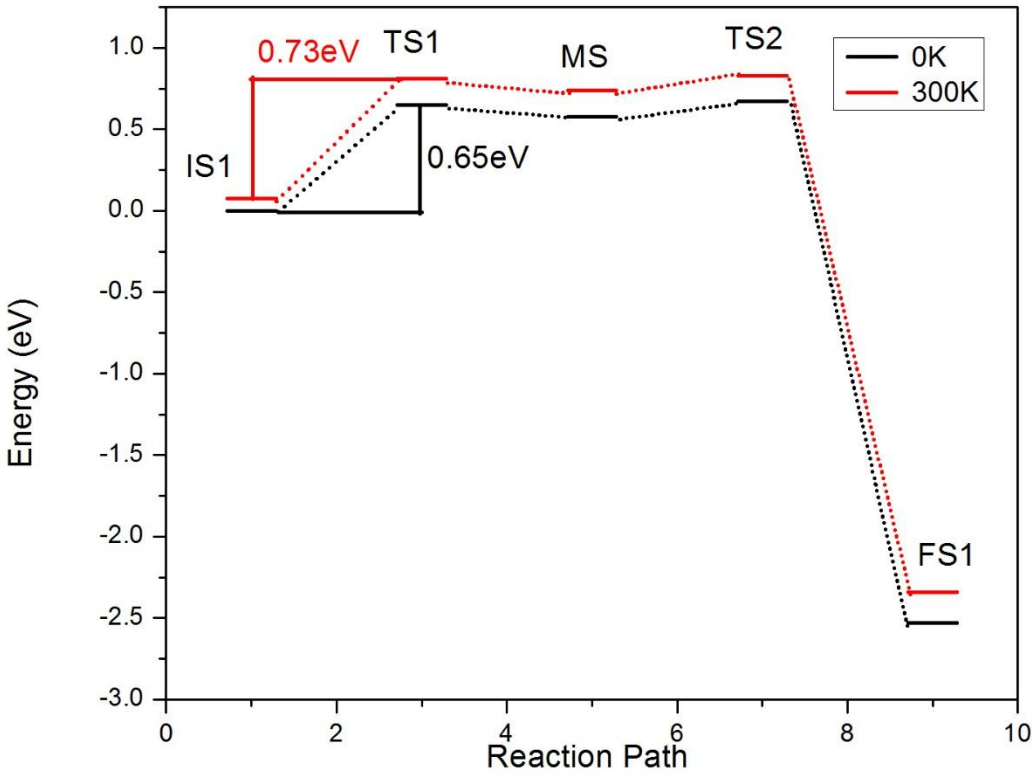

Figure S2. Reaction free energy profiles for CO oxidation catalyzed for the first by Sc-TCNQ via the LH mechanisms at 0 and 300K.

The coordination of Sc-TCNQ

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_cell_angle_beta            90.0362451130867
_cell_angle_gamma           89.9897918373574
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loop_
_symmetry_equiv_pos_as_xyz
x,y,z

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_occupancy
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
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N3  N  1.0000  0.69336  0.60448  0.12642  0.0000
N4  N  1.0000  0.26903  0.35651  0.12836  0.0000
Sc1  Sc  1.0000  0.48140  0.48036  0.12792  0.0000
C1  C  1.0000  0.82226  0.66807  0.12614  0.0000
C2  C  1.0000  0.98134  0.73407  0.12606  0.0000
C3  C  1.0000  0.14033  0.66797  0.12656  0.0000
C4  C  1.0000  0.14902  0.92106  0.12692  0.0000
C5  C  1.0000  0.98157  0.85941  0.12628  0.0000
C6  C  1.0000  0.81421  0.92117  0.12614  0.0000
C7  C  1.0000  0.82238  0.29254  0.12854  0.0000
C8  C  1.0000  0.98153  0.22653  0.12815  0.0000
C9  C  1.0000  0.14038  0.29272  0.12827  0.0000
C10  C  1.0000  0.14910  0.03941  0.12750  0.0000
C11  C  1.0000  0.98170  0.10117  0.12746  0.0000
C12  C  1.0000  0.81428  0.03950  0.12669  0.0000
H1  H  1.0000  0.28109  0.87525  0.12705  0.0000
H2  H  1.0000  0.68209  0.87546  0.12569  0.0000
H3  H  1.0000  0.28127  0.08506  0.12800  0.0000
H4  H  1.0000  0.68213  0.08522  0.12651  0.0000
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