Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

First Principle Studies of Mononuclear and Dinuclear Pacman Complexes for Electrocatalytic Reduction of CO_2

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Table S1: shows the charge on carbon of the adsorbed CO_2 on the mononuclear and dinuclear complexes.

X in complexes	M-X-Pac (charge on C in e)	Di-X-Pac (charge on C in e)
Cr	+0.75	+1.36
Mn	+0.61	+0.98
Fe	+0.49	+1.3
Co	+1.11	+1.5
Ni	+1.1	+1.8

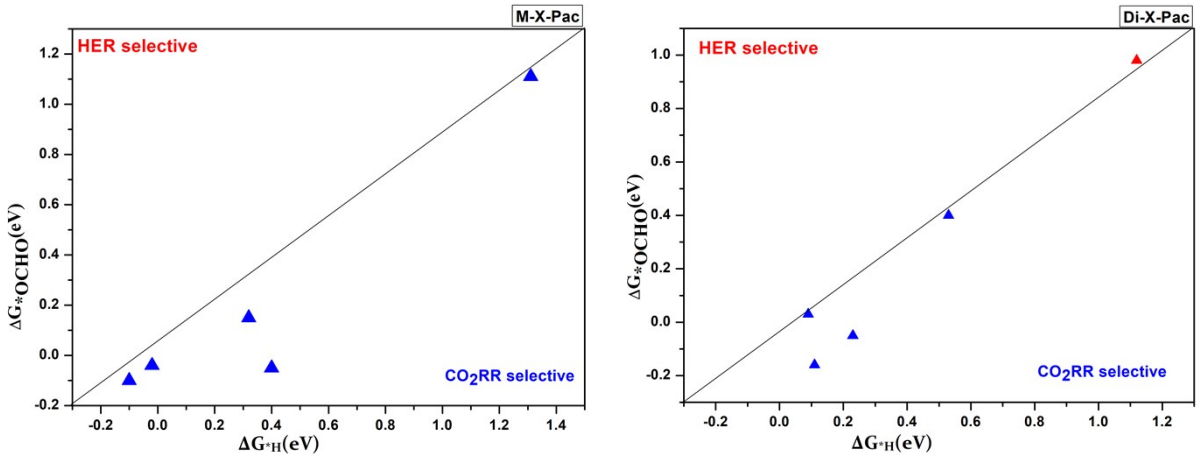

Fig. S1: Free energy for HER and the first hydrogenation step in CO_2RR for M-X-Pac and Di-X-Pac.

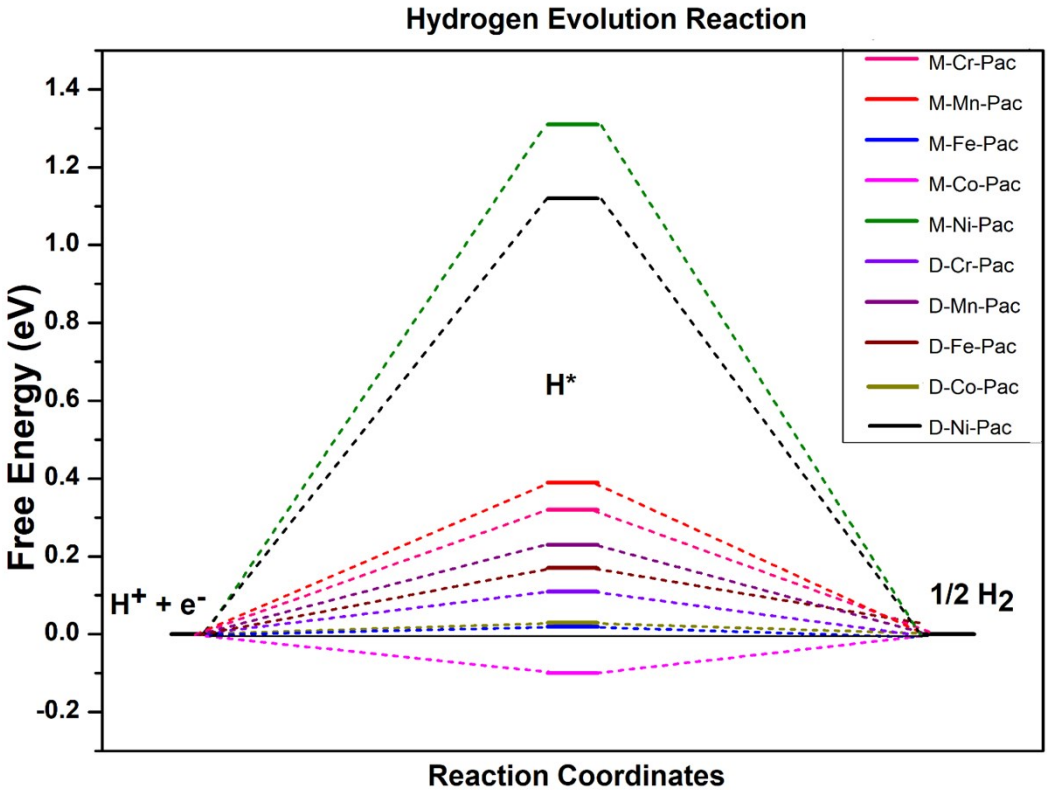

Fig. S2: The free energy diagram for HER (Hydrogen evolution reaction) on the surface of the M-X-Pac and Di-X-Pac.

Table S2: The calculated zero-point energies and entropy corrections of various adsorbed intermediates where * indicates the catalyst.

Adsorbed intermediates	E_{ZPE} (eV)	TS (eV)
*CO_2	0.30	0.39
*OCHO	0.60	0.23
*COOH	0.60	0.26
*OCHOH	0.91	0.35
*CHO	0.43	0.21
*CH_2O	0.73	0.32
*CHOH	0.76	0.21
*CH_3O	1.09	0.20
*CH_2OH	1.07	0.24
*CH_3OH	1.39	0.30

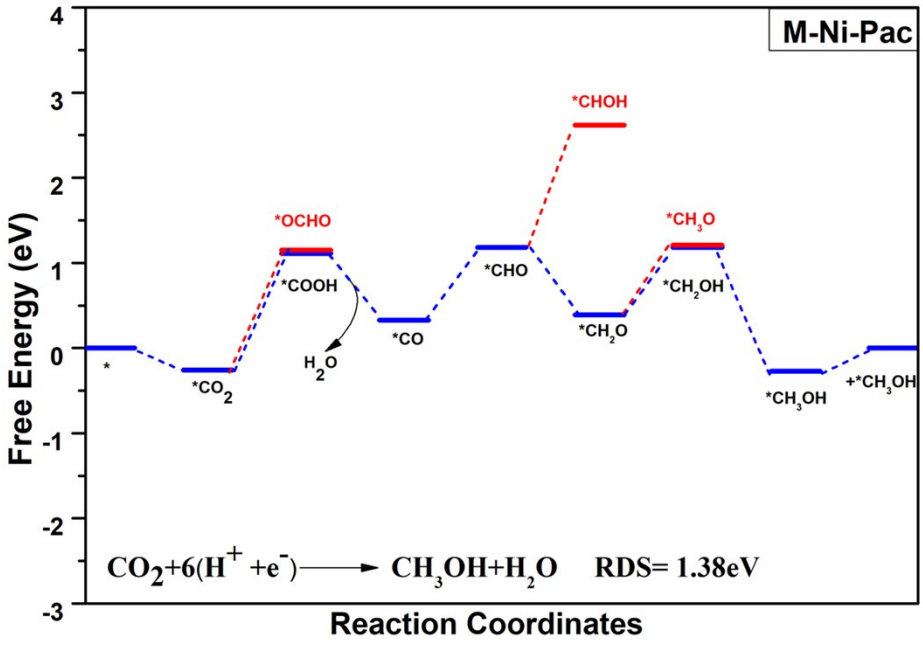

Fig. S3: Free energy diagram for the electrocatalytic reduction of CO_2 to CH_3OH using mononuclear Pacman complexes M-Ni-Pac

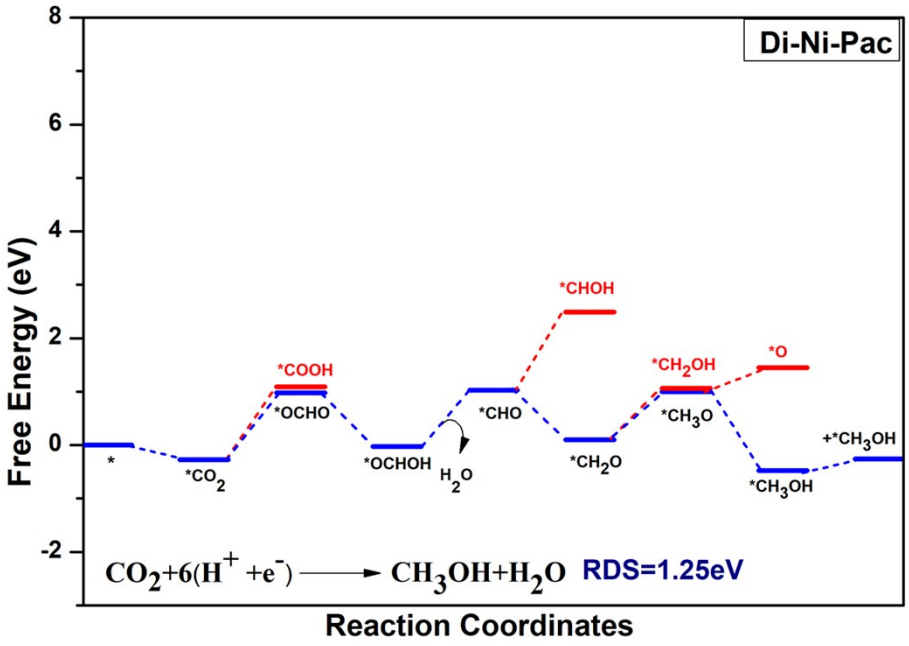

Fig. S4: Free energy diagram for the electrocatalytic reduction of CO_2 to CH_3OH using Dinuclear Pacman complexes Di-Ni-Pac.

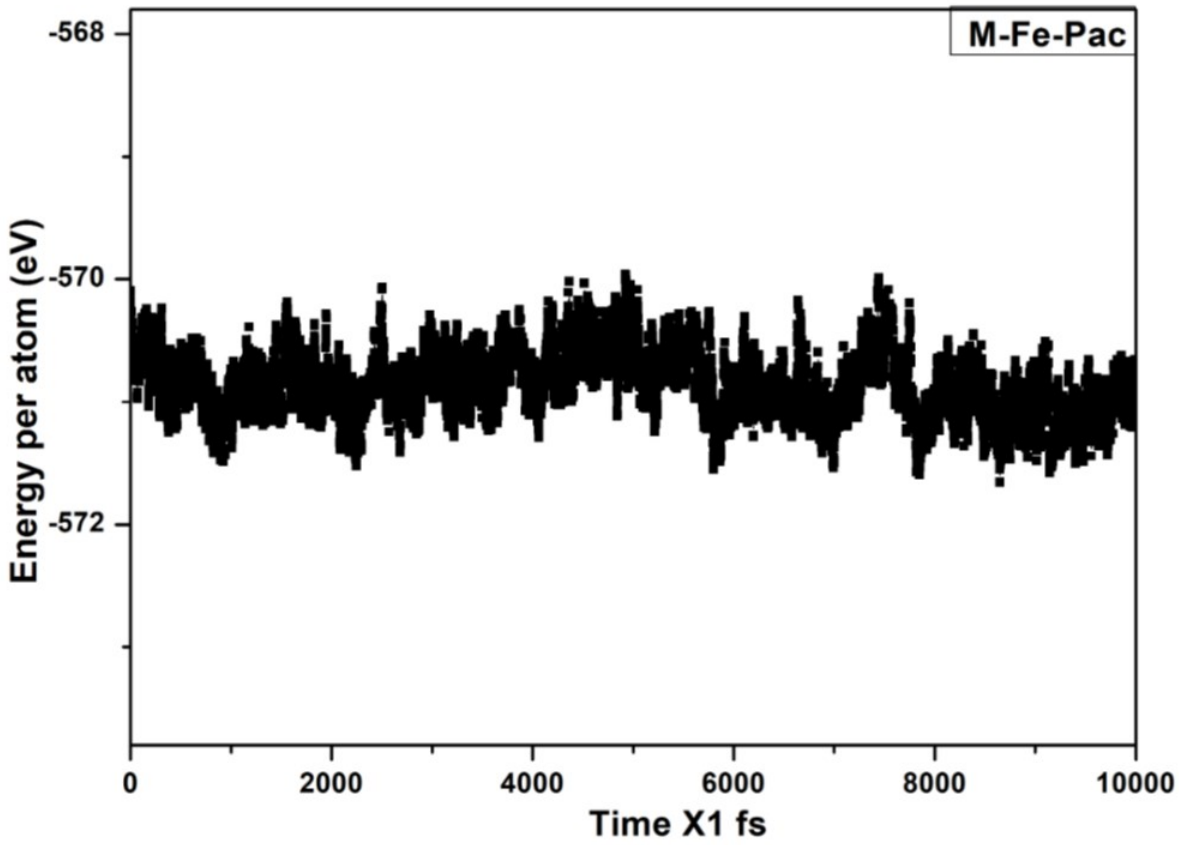

Fig. S5: Variation of energy per atom against the time for AIMD simulations for mononuclear iron pacman (M-Fe-Pac) complex. The simulation is run under 400K for 10ps with a time step of 1 fs.

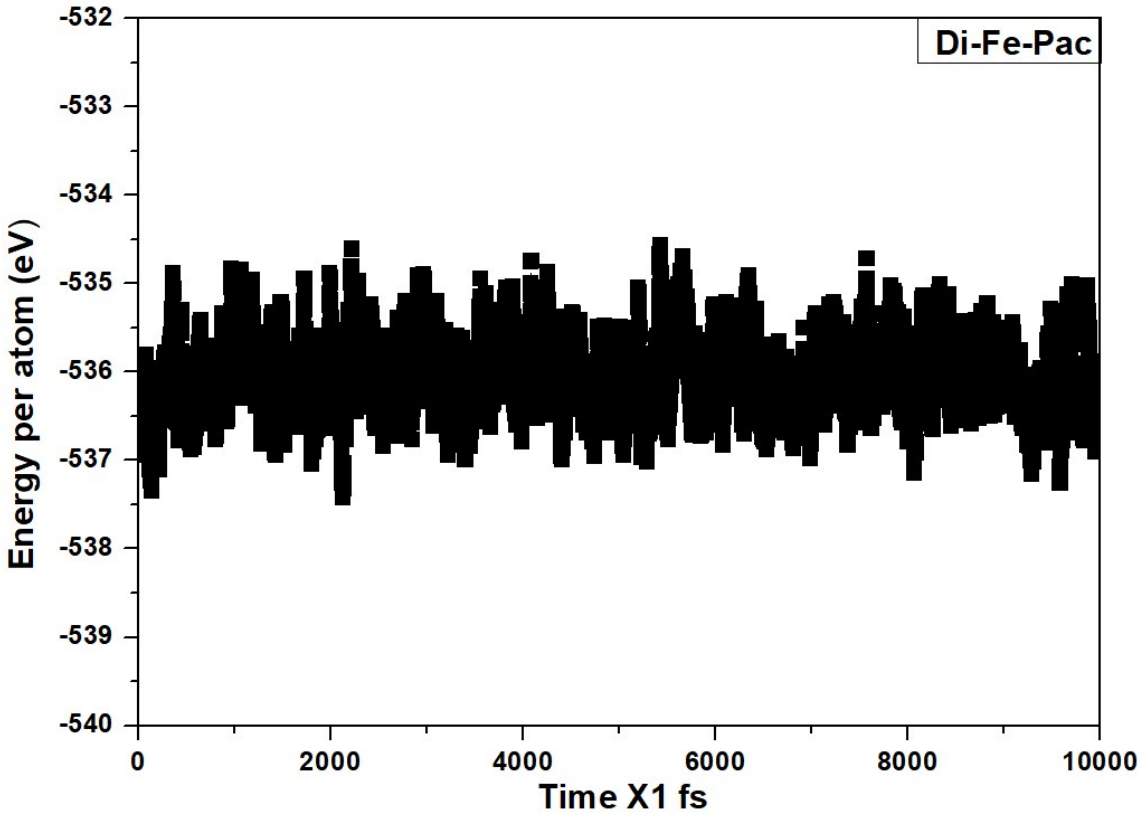

Fig. S6: Variation of energy per atom against the time for AIMD simulations for dinuclear iron pacman (Di-Fe-Pac) complex. The simulation is run under 400K for 10ps with a time step of 1 fs.