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通过 g-C_3N_4 担载 MNi_{12} (Fe, Co, Cu, Zn)纳米团簇调节甲烷化反应性能

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Tunable Reactivity of MNi_{12} (M = Fe, Co, Cu, Zn) Nanoparticles Supported on Graphitic Carbon Nitride in Methanation

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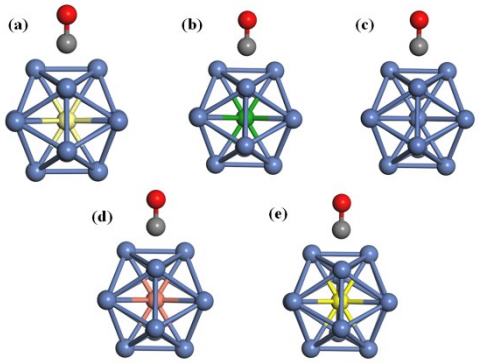

Fig. S1 Six initial adsorption models of MNi_{12} NPs on g-C_3N_4 substrate.

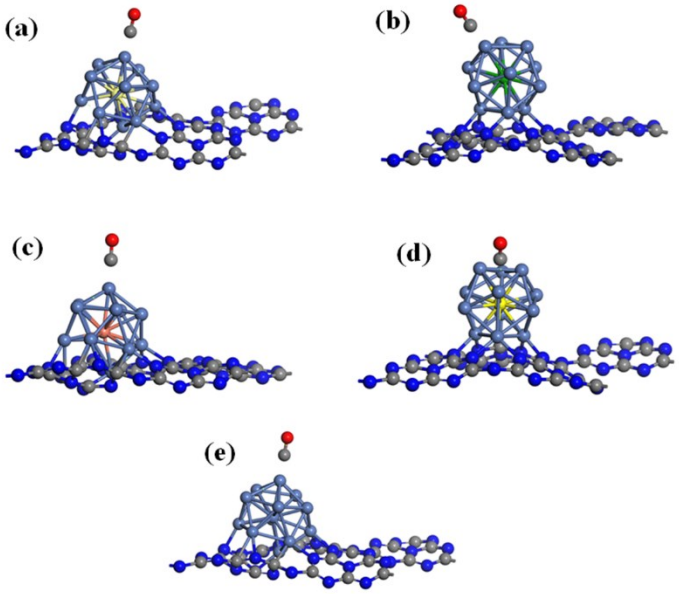

Fig. S2 The most stable configurations of CO adsorbed on isolated MNi_{12} NPs.

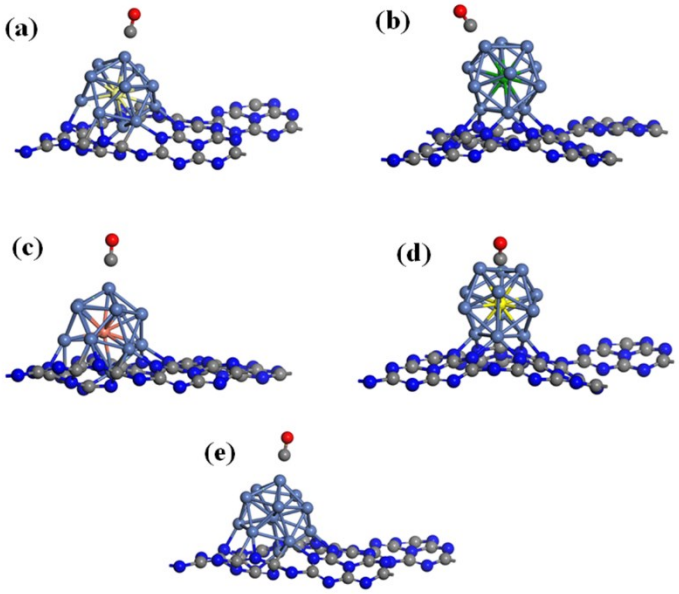

Fig. S3 The most stable configurations of CO adsorbed on MNi_{12} NPs-C_3N_4 composites.

Table S1 Total energy test for k-point accuracy. The energy is shown in Ha.

	E_{tot}/Ha
3 × 3 × 1	−2664.6178535
4 × 4 × 1	−2664.6178535
5 × 5 × 1	−2664.6178535
6 × 6 × 1	−2664.6178535

Table S2 Total energy test for vaccum accuracy. The energy is shown in Ha.

Vaccum/nm	E_{tot}/Ha
1.2	−5180.430002
1.3	−5180.429727
1.4	−5180.429497
1.5	−5180.4292845
1.6	−5180.429119
1.7	−5180.428958
1.8	−5180.428811

Table S3 Binding energy E_b, C—O bond length d_{C-O} of all the possible adsorption behaviors CO adsorbed on isolated MNi_{12} NPs and MNi_{12} NPs-C_3N_4 composites.

Sample	O attach to catalysts			C point to catalysts		
	E_b/eV	d_{C-O}/nm	d_{Ni-O}/nm	E_b/eV	d_{C-O}/nm	d_{Ni-C}/nm
CO-$FeNi_{12}$	−0.50	0.1165	0.1858	−2.54	0.1210	0.1942
CO-$FeNi_{12}$-C_3N_4	−0.29	0.1161	0.1860	−2.30	0.1167	0.1716
CO-$CoNi_{12}$	−0.53	0.1165	0.1858	−2.59	0.1210	0.1942
CO-$CoNi_{12}$-C_3N_4	−0.37	0.1161	0.1895	−2.29	0.1168	0.1724
CO-Ni_{13}	−0.56	0.1165	0.1851	−2.59	0.1211	0.1940
CO-Ni_{13}-C_3N_4	−0.39	0.1165	0.1864	−2.45	0.1167	0.1714
CO-$CuNi_{12}$	−0.53	0.1165	0.1856	−2.63	0.1209	0.1943
CO-$CuNi_{12}$-C_3N_4	−0.36	0.1162	0.1864	−2.44	0.1167	0.1713
CO-$ZnNi_{12}$	−0.46	0.1165	0.1856	−2.68	0.1209	0.1945
CO-$ZnNi_{12}$-C_3N_4	−0.31	0.1161	0.1888	−2.41	0.1204	0.1932

Table S4 The total energy of the MNi_{12} NPs with different spin configurations (high spin states and low spin states), and the energy difference between them (ΔE).

MNi_{12}	High spin/Ha	Low spin/Ha	ΔE/eV
Fe	−2465.25	−2465.23	−0.47
Co	−2488.83	−2488.82	−0.40
Ni	−2515.48	−2515.47	−0.37
Cu	−2544.45	−2544.43	−0.40
Zn	−2576.33	−2576.32	−0.33