Supporting Information

Silicon Nanocages for Selective Carbon Dioxide Conversion under Visible Light

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S1. Computational details for search of global minimum structures

The ground state structures of neutral VSi_n (n = 12-16) and MSi_{12} (M is 3*d* transition metal atom) clusters were searched independently by a homemade comprehensive genetic algorithm (CGA) code,[1] combined with the DMol^3 program based on density functional theory (DFT).[2] The essential details and validity of this CGA-DFT scheme can be found in our previous review article.[1] For each cluster size, every independent CGA search was lasted for at least 3000 iterations retaining 16 members in the population. The mutation rate was set as 30% to ensure the diversity of the population. The resulting child clusters were optimized by DMol^3 using the double numerical basis including *d*-polarization function (DND) and the Perdew-Burke-Enzerhof (PBE) functional within the generalized gradient approximation (GGA).[3]

Table S1. HOMO-LUMO gap of spin up (↑) and spin down (↓) electrons of VSi_n (n = 12-16) clusters calculated by different methods including the VASP code using PAW potentials with the PBE functional and HSE06 hybrid functional, respectively, and the Gaussian09 program using the aug-cc-pvdz all-electron basis set with the PBE and HSE06 functionals, respectively. The gap values are given in unit of eV. These two DFT codes give nearly identical gap values by using the HSE06 functional

Method	VSi_{12}		VSi_{13}		VSi_{14}		VSi_{15}		VSi_{16}	
	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓
VASP-PBE	1.50	0.37	0.67	1.62	1.74	0.28	1.11	0.88	0.68	1.98
VASP-HSE06	2.54	1.03	1.70	2.25	2.44	0.90	1.70	1.45	1.45	2.57
Gaussian-PBE	3.28	1.73	2.51	3.06	3.15	1.57	2.40	2.12	2.16	3.30
Gaussian-HSE06	2.57	1.02	1.78	2.37	2.45	0.89	1.71	1.43	1.47	2.62

Table S2. HOMO and LUMO levels for spin up (↑) and spin down (↓) electrons of VSi_n (n = 12-16) clusters calculated by VASP and Gaussian09 programs, respectively, both using the HSE06 hybrid functional. The energies (in unit of eV) are relative to vacuum

Method	Property	VSi_{12}	VSi_{13}	VSi_{14}	VSi_{15}	VSi_{16}
VASP	$HOMO^{\uparrow}$	–6.08	–5.48	–6.23	–5.57	–4.85
	$LUMO^{\uparrow}$	–3.54	–3.78	–3.79	–3.87	–3.40
	$HOMO^{\downarrow}$	–6.09	–5.89	–6.20	–6.10	–6.07
	$LUMO^{\downarrow}$	–5.06	–3.64	–5.30	–4.65	–3.50
Gaussian09	$HOMO^{\uparrow}$	–6.08	–5.50	–6.24	–5.58	–4.83
	$LUMO^{\uparrow}$	–3.51	–3.72	–3.79	–3.87	–3.36
	$HOMO^{\downarrow}$	–6.13	–5.96	–6.21	–6.14	–6.11
	$LUMO^{\downarrow}$	–5.11	–3.59	–5.34	–4.71	–3.49

Table S3. Adsorption energy (in unit of eV) of CO_2 molecule on VSi_n (n = 12-16) clusters calculated by various methods, including HSE06 functional with planewave basis and D3 correction by VASP program, PBE functional with DND basis and D2 correction by DMol^3 program, HSE06 functional with aug-cc-pvdz basis set by Gaussian09 program, respectively. The results obtained by VASP and Dmol^3 programs without dispersion correction are also presented

Method	VSi_{12}	VSi_{13}	VSi_{14}	VSi_{15}	VSi_{16}
VASP, HSE06-D3	–0.43	–0.31	–0.21	0.04	0.22
VASP, HSE06	–0.33	–0.21	–0.10	0.15	0.33
DMol, PBE-D2	–0.41	–0.33	–0.20	0.07	0.24
DMol, PBE	–0.31	–0.23	–0.12	0.15	0.32
Gaussian, HSE06	–0.15	–0.05	0.06	0.37	0.51

Table S4. Zero-point energy (ZPE) and entropic correction (*TS*) at T = 298 K for the molecules and intermediate species involved in the CO_2 hydrogenation reaction, obtained by calculating their vibrational frequencies. The entropy values of molecules are taken from the NIST-JANAF thermodynamics table.[4] Since the (ZPE – *TS*) values of each reaction intermediate on various VSi_n clusters are very similar, here we used the data of VSi_{12} throughout the calculations as presented in the Table. The reaction intermediates are indicated by *, while the formula without * represents a free molecule

Species	ZPE (eV)	*TS* (eV)	ZPE−*TS* (eV)
H_2	0.29	0.41	−0.12
H_2O	0.60	0.59	0.01
CO	0.14	0.62	−0.48
CO_2	0.31	0.67	−0.35
CH_2O	0.72	0.68	0.04
HCOOH	0.92	1.02	−0.10
CH_3OH	1.39	0.79	0.60
CH_4	1.20	0.58	0.61
CO_2*	0.32	0.13	0.19
HCOO*	0.59	0.20	0.39
COOH*	0.65	0.14	0.51
CO*	0.20	0.13	0.07
HCOOH*	0.91	0.22	0.69
HCO*	0.48	0.15	0.33
HCOH*	0.81	0.14	0.67
H_2COH*	1.08	0.11	0.97
CH_2*	0.67	0.07	0.60
CH_3*	0.97	0.15	0.82

Table S5. Magnetic moment (M), adsorption energy of CO_2 molecule (ΔE_{CO2*}), kinetic barriers for CO_2 chemisorption (E_a^{CO2}) and H_2 dissociation (E_a^{H2}) for various transition metal doped Si_{12} clusters

property	Ti	V	Cr	Mn	Fe	Co	Ni
M (μ_B)	0	0.56	0	1.28	0	0.37	0
ΔE_{CO2*} (eV)	–0.40	–0.43	0.06	0	–0.10	–0.67	–0.58
E_a^{CO2} (eV)	0.59	0.60	1.14	1.10	0.86	0.71	0.78
E_a^{H2} (eV)	0.86	0.55	1.69	1.61	1.53	1.54	1.40

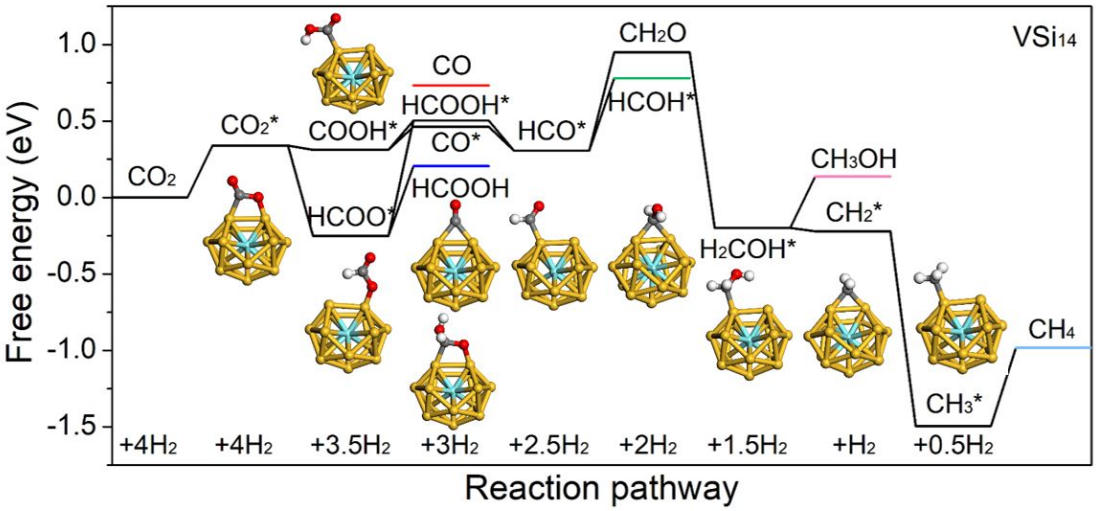

Figure S1. Free energy diagram of CO_2 hydrogenation on VSi_{14} cluster. The colored line segments indicate the formation of various products. The atomic structures of reaction intermediates are presented for each step. The H, C, O, Si and V atoms are shown in white, grey, red, yellow and cyan colors, respectively.

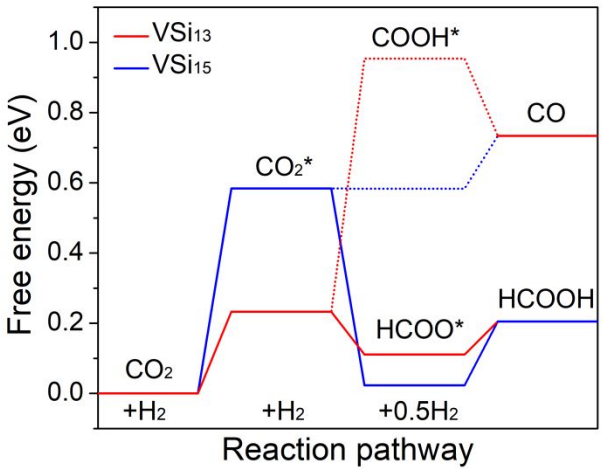

Figure S2. Free energy diagram of CO_2 hydrogenation on VSi_{13} and VSi_{15} clusters. The solid and dotted lines show the HCOO* path and COOH* path, respectively.

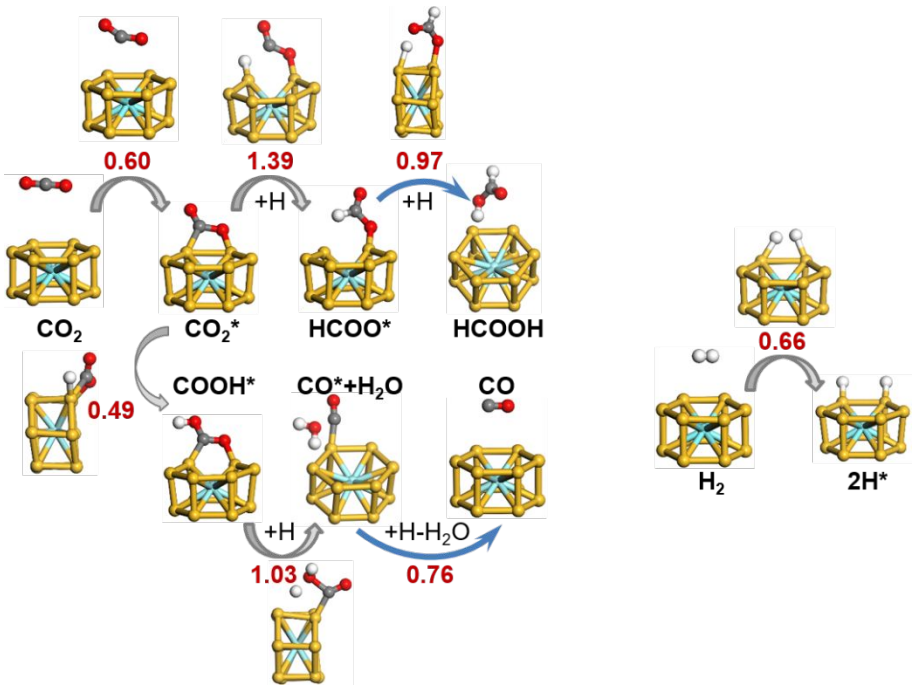

Figure S3. Atomic structures of reactants and products for the elemental steps of CO_2 hydrogenation to form CO_2 and HCOOH (left panel), as well as H_2 dissociation (right panel). The red numbers and the structure next to them show the kinetic barrier (in eV) and transition state for each step, respectively. The H, C, O, Si and V atoms are shown in white, grey, red, yellow and cyan colors, respectively.

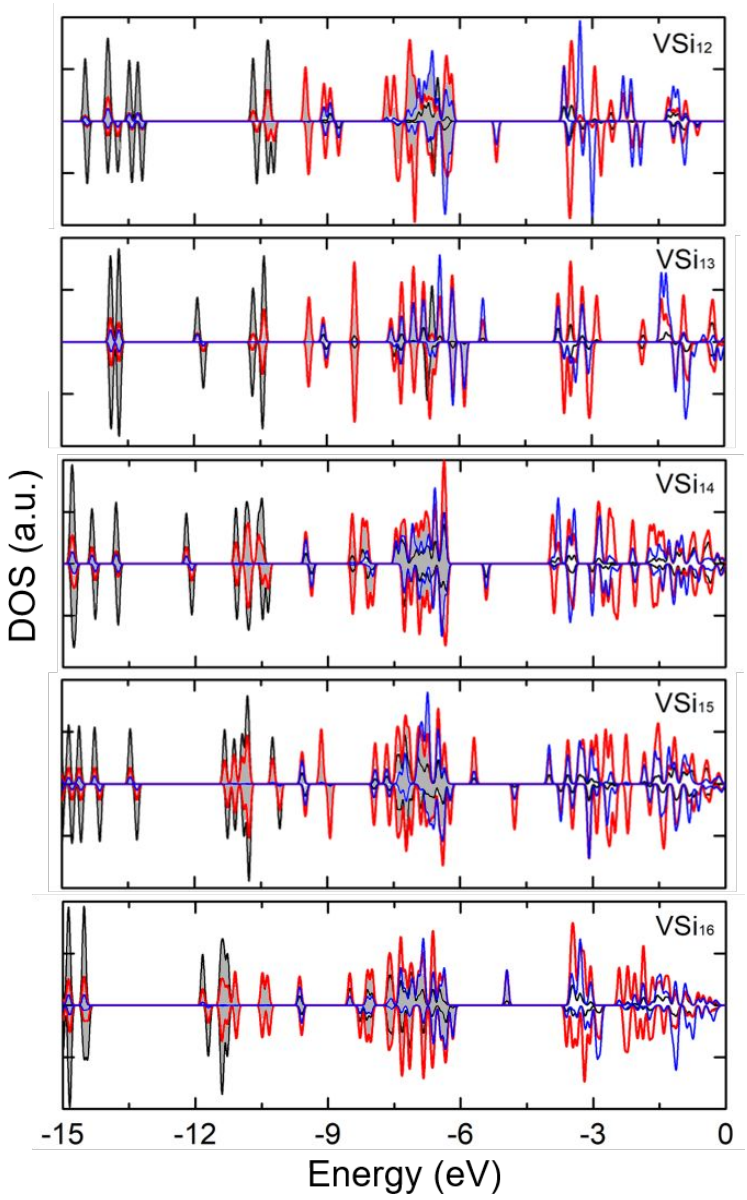

Figure S4. Spin-polarized density of states (DOS) of VSi_n (n = 12-15) clusters. The black and red lines show the local DOS from Si atoms projected on the *s* and *p* orbitals, respectively. The blue lines show the local DOS from V atoms. The energy is relative to vacuum. The occupied states are shadowed.

References

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(2) Delley, B. From Molecules to Solids with the $DMol^3$ Approach. *J. Chem. Phys.* **2000,** *113*, 7756–7764.

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(4) Chase, M. W. *NIST-JANAF Thermochemical Tables,* 4th ed; American Chemical Society and American Institute of Physics Press: New York, **1998**.