Theoretical Design of Transition Metal-Doped TiO_2 for the Selective Catalytic Reduction of NO with NH_3 by DFT Calculations

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Supporting Information

Table S1. Imaginary frequencies for transition states of every elementary step on M-TiO_2 (M=V, Cr, Mn, Fe, Co, Mo, and Ce) and TiO_2.

/cm^{-1}	TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8	TS9
TiO_2	502.62	/	148.61	/	/	/	/	/	90.49
V	768.60	/	605.81	/	/	/	512.90	/	111.44
Cr	746.89	/	312.28	/	31.86	211.54	180.16	/	148.06
Mn	948.90	/	610.12	/	/	/	197.28	/	226.32
Fe	945.09	/	/	32.43	83.54	118.41	1343.86	/	247.50
Co	941.49	/	/	37.46	/	122.39	/	/	157.93
Mo	382.51	38.21	705.82	138.36	119.14	512.14	1050.20	109.13	663.71
Ce	1366.40	/	181.45	109.08	623.00	/	/	/	103.95

Table S2. Imaginary frequencies for transition states of TS1 (NH_3 dissociation) and TS7 (NH_2 dissociation) on M-TiO_2 (M = 3d and 4d transition metals and Ce).

/cm^{-1}	Sc	TiO_2	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
TS1	1341.39	502.62	768.60	746.89	948.90	945.09	941.49	1062.70	1160.75	1093.17	
TS7	175.36	/	512.90	180.16	197.28	1343.86	/	100.74	1033.58	/	
/cm^{-1}	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ce
TS1	1408.07	265.00	557.22	382.51	869.59	1085.76	933.50	1244.73	1169.61	1222.32	1366.40
TS7	199.44	/	536.85	1050.20	1280.93	165.66	172.81	616.99	/	1060.48	/

Table S3. Reaction energies and energy barriers of every step for N_2 formation M-TiO_2 (M=V, Cr, Mn, Fe, Co, Mo, and Ce) and TiO_2 (correspond to Fig. 3-4).

/eV	TiO_2	V	Cr	Mn	Fe	Co	Mo	Ce
NH_3*	-1.16	-1.24	-1.28	-1.38	-0.84	-0.93	-1.5	-0.88
TS1	1.31	1.43	1.34	0.97	1.35	0.65	1.39	1.26
NH_2*	0.99	0.93	0.64	0.66	1.06	0.18	0.73	0.87
TS2	/	/	/	/	/	/	0.087	/
NH_2NO	-1.03	-1.37	-1.98	-2.18	-2.81	-1.8	-0.69	-1.65
NH_2NO*	-0.44	-0.52	-0.53	-0.33	-0.47	-0.49	-0.51	-0.39
TS3	0.61	0.41	0.44	0.53	/	/	0.55	0.62
HNNOH	0.57	0.37	0.44	0.4	0.4	0.52	0.5	0.52
TS4	/	/	/	/	0.43	0.43	0.68	0.75
HNNOH’	0.85	0.73	0.78	0.29	0.42	0.42	0.63	0.2
TS5	/	/	0.004	/	0.014	/	0.29	0.2
N_2	-2.51	-2.92	-2.74	-1.85	-2.44	-2.23	-3.13	-2.01
TS6	/	/	0.007	/	0.01	0.022	0.067	/
H_2O	-0.65	/	-0.19	-0.82	-0.25	-0.47	-0.06	-0.45
H*	0.8	0.87	0.94	0.71	0.69	0.68	1.13	1.05

Table S4. Reaction energies and energy barriers of every step for N_2O formation on M-TiO_2 (M = 3d and 4d transition metals and Ce) (correspond to Fig. 5).

/eV	NH_3*	TS1	NH_2*	TS7	NH*	TS8	NHNO*	TS9	N_2O
TiO_2	-1.16	1.31	0.99	/	1.56	/	-2.25	0.27	-0.08
V	-1.24	1.43	0.93	1.04	0.96	/	-1.84	0.03	-0.19
Cr	-1.28	1.34	0.64	1.63	1.07	/	-2.81	0.74	-0.18
Mn	-1.38	0.97	0.66	1.33	0.97	/	-3.04	0.19	-0.73
Fe	-0.84	1.35	1.06	1.14	0.36	/	-2.84	0.31	-0.79
Co	-0.93	0.65	0.18	/	0.76	/	-2.92	0.56	-0.50
Mo	-1.50	1.39	0.73	1.29	0.73	0.04	-1.40	0.73	0.29
Ce	-0.88	1.26	0.87	/	1.42	/	-3.71	0.81	0.68

Table S5. Reaction energies and energy barriers of NH_3 and NH_2 dissociation on M-TiO_2 (M = 3d and 4d transition metals and Ce) (correspond to Fig. 7).

/eV	NH_3*	TS1(E_{app-1})	NH_{2*}	TS7	NH*	E_{app-2}
Sc	-1.04	0.89	-0.27	1.48	1.44	1.21
TiO_2	-1.16	1.31	0.99	/	1.53	2.55
V	-1.24	1.43	0.93	1.04	0.96	1.97
Cr	-1.28	1.34	0.64	1.63	1.07	2.27
Mn	-1.38	0.97	0.66	1.33	0.97	1.99
Fe	-0.84	1.35	1.06	1.14	0.36	2.20
Co	-0.93	0.65	0.18	/	0.76	0.94
Ni	-1.22	0.68	0.44	0.27	0.09	0.71
Cu	-1.03	0.68	-0.06	0.40	0.14	0.68
Zn	-0.77	0.62	-0.10	0	-0.30	0.62
Y	-1.01	0.71	-0.12	1.05	0.98	0.92
Zr	-1.41	1.26	0.93	/	2.00	2.93
Nb	-0.59	1.25	0.88	1.06	0.82	1.94
Mo	-1.50	1.39	0.73	1.29	0.73	2.02
Tc	-1.63	1.23	0.82	1.02	0.72	1.84
Ru	-1.88	1.25	0.70	0.79	0.76	1.49
Rh	-1.89	1.12	0.33	1.29	1.28	1.62
Pd	-2.00	0.90	0.42	1.45	1.38	1.87
Ag	-0.88	0.75	0.16	/	0.44	0.75
Cd	-0.76	0.72	-0.15	0.42	-0.1	0.72
Ce	-0.88	1.26	0.87	/	1.42	2.29

Table S6. Oxygen vacancy formation energy of $O_{2c\text{-}1}$ ($E_{VO\text{-}1}$), $O_{2c\text{-}2}$ ($E_{VO\text{-}1}$), and the sum of $O_{2c\text{-}1}$ and $O_{2c\text{-}2}$ ($E_{VO\text{-}1}$), doping energy, Bader charge transfer of doping metal, $O_{2c\text{-}1}$ and $O_{2c\text{-}2}$ after doping on M-TiO_2 (M = 3d and 4d transition metals and Ce) (correspond to Fig. 9-10).

/eV	$E_{VO\text{-}1}$	Doping energy	Bader charge transfer of doping metal/*e*	Bader charge transfer of $O_{2c\text{-}1}$/*e*	Bader charge transfer of $O_{2c\text{-}2}$/*e*	$E_{VO\text{-}2}$	$E_{VO\text{-}sum}$
Sc	1.19	-0.25	-2.17	1.01	0.9058	1.48	2.67
Ti	3.49	0	-2.02	0.92	0.9196	3.57	7.06
V	2.8	2.06	-1.91	0.86	0.9207	3.44	6.24
Cr	1.87	2.21	-1.80	0.82	0.9178	2.35	4.22
Mn	0.6	5.09	-1.76	0.85	0.9222	2.04	2.64
Fe	1.04	4.41	-1.72	0.80	0.9215	2.31	3.35
Co	0.14	5.97	-1.53	0.72	0.9124	2.20	2.34
Ni	-0.94	6.90	-1.31	0.63	0.9125	0.29	-0.7
Cu	-1.39	8.86	-1.21	0.62	0.9082	-0.13	-1.5
Zn	-1.67	8.83	-1.29	0.59	0.9055	-0.26	-1.9
Y	1.06	0.60	-2.27	1.05	0.9108	1.43	2.49
Zr	4.75	-2.0	-2.36	1.01	0.9228	3.50	8.25
Nb	4.60	-2.82	-2.78	1.03	0.9223	3.44	8.04
Mo	3.54	2.51	-1.99	0.91	0.92	3.45	6.99
Tc	3.75	1.22	-1.79	0.86	0.9199	3.45	7.20
Ru	2.77	2.70	-1.59	0.80	0.9178	3.42	6.19
Rh	1.89	4.45	-1.42	0.72	0.9183	2.56	4.45
Pd	0.69	7.84	-1.31	0.76	0.9172	1.46	2.15
Ag	-0.56	10.44	-1.18	0.63	0.9027	0.69	0.13
Cd	-1.51	10.65	-1.31	0.62	0.8954	-0.22	-1.70
Ce	2.28	-1.43	-2.32	0.96	0.9246	3.45	5.73

Table S7. Electronic energies and Gibbs free energies (at 150 and 250 ℃) for reaction energies and barriers of every step for N_2 formation on Mn-TiO_2 (correspond to Fig. 3-4).

/eV	ΔE(el)	ΔG(150℃)	ΔG(250℃)
NH_3*	-1.38	-0.44	-0.50
TS1	0.97	0.85	0.81
NH_2*	0.66	0.56	0.55
TS2	/	/	/
NH_2NO	-2.18	-2.02	-2.05
NH_2NO*	-0.33	-0.34	-0.36
TS3	0.53	0.47	0.49
HNNOH	0.40	0.41	0.41
TS4	/	/	/
HNNOH’	0.29	0.23	0.21
TS5	/	/	/
N_2	-1.85	-1.98	-1.99
TS6	/	/	/
H_2O	-0.82	-0.77	-0.70
H*	0.71	0.14	0.20

Table S8. Electronic energies and free energies (at 150 and 250 ℃) for reaction energies and barriers of every step for N_2O formation on Mn-TiO_2 (correspond to Fig. 5).

/eV	NH_3*	TS1	NH_2*	TS7	NH*	TS8	NHNO*	TS9	N_2O
ΔE(el)	-1.38	0.97	0.66	1.33	0.97	/	-3.04	0.19	-0.73
ΔG(150℃)	-0.44	0.85	0.56	1.26	0.89	/	-2.93	0.24	-0.68
ΔG(250℃)	-0.50	0.81	0.55	1.27	0.88	/	-2.98	0.24	-0.69

Table S9. Electronic energies and free energies (at 150 and 250 ℃) for reaction energies and barriers of every step for NH_3 and NH_2 dissociation on M-TiO_2 M=V, Cr, Mn, Fe, Co, Mo, and Ce) and TiO_2 (correspond to Fig. 5).

/eV		NH_3	TS1(E_{app-1})	NH_2	TS7	NH	E_{app-2}
	ΔE(el)	-1.16	1.31	0.99	/	1.53	2.55
TiO_2	ΔG(150℃)	-0.23	1.19	1.03	/	1.42	2.45
	ΔG(250℃)	-0.28	1.19	1.01	/	1.41	2.42
	ΔE(el)	-1.24	1.43	0.93	1.04	0.96	1.97
V	ΔG(150℃)	-0.33	1.33	0.90	0.90	0.89	1.80
	ΔG(250℃)	-0.39	1.35	0.91	0.92	0.88	1.83
	ΔE(el)	-1.28	1.34	0.64	1.63	1.07	2.27
Cr	ΔG(150℃)	-0.32	1.20	0.53	1.61	0.98	2.14
	ΔG(250℃)	-0.38	1.21	0.52	1.63	0.97	2.15
	ΔE(el)	-1.38	0.97	0.66	1.33	0.97	1.99
Mn	ΔG(150℃)	-0.44	0.85	0.56	1.26	0.89	1.82
	ΔG(250℃)	-0.50	0.81	0.55	1.27	0.88	1.82
	ΔE(el)	-0.84	1.35	1.06	1.14	0.36	2.20
Fe	ΔG(150℃)	0.074	1.26	0.96	1.15	0.32	2.11
	ΔG(250℃)	0.0073	1.29	0.95	1.19	0.33	2.14
	ΔE(el)	-0.93	0.65	0.18	/	0.76	0.94
Co	ΔG(150℃)	-0.051	0.61	0.21	/	0.68	0.89
	ΔG(250℃)	-0.12	0.64	0.23	/	0.69	0.92
	ΔE(el)	-1.50	1.39	0.73	1.29	0.73	2.02
Mo	ΔG(150℃)	-0.56	1.28	0.69	1.19	0.71	1.88
	ΔG(250℃)	-0.62	1.29	0.68	1.21	0.71	1.89
	ΔE(el)	-0.88	1.26	0.87	/	1.42	2.29
Ce	ΔG(150℃)	0.060	1.10	0.71	/	1.43	2.14
	ΔG(250℃)	0.019	1.09	0.67	/	1.43	2.10