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Reduction of N_2 to NH_3 by TiO_2-supported Ni cluster catalysts: A DFT study

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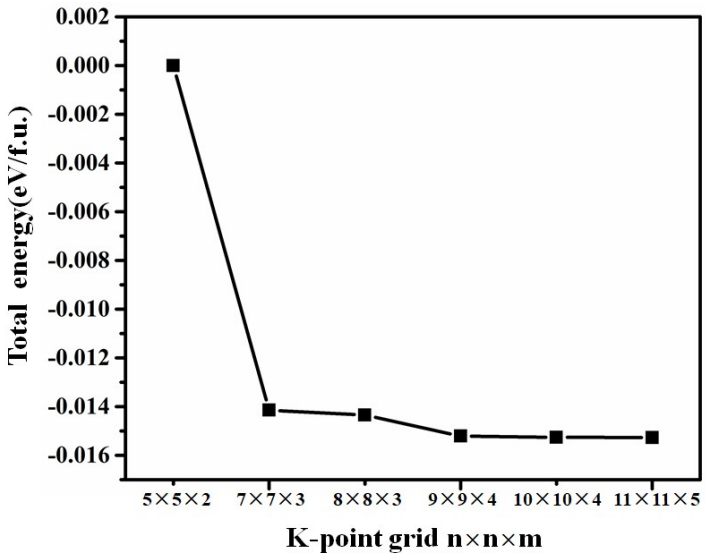

Figure S1. Convergence test of the k-point grid for the total energy (eV/formula-unit) of TiO_2 unit cell. Convergence at 9×9×4 k-point grid is within 0.5 meV/atom.

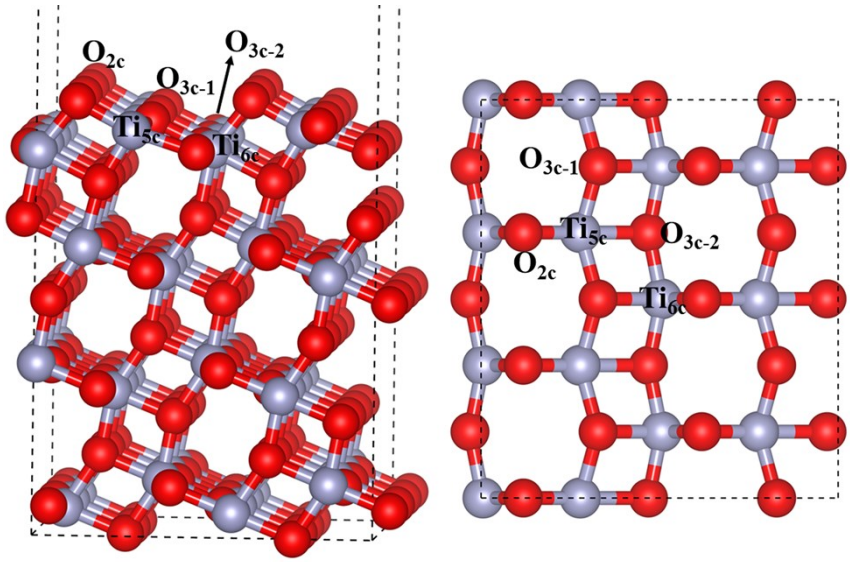

Figure S2. Side (left) and top (right) views of the optimized TiO_2 (101) surface. Red and silver balls are O and Ti atoms, respectively. The characters O_{2c}, O_{3c-1}, O_{3c-2}, Ti_{5c} and Ti_{6c} respectively represent the surface two-coordinated O atoms, three-coordinated O atoms, five-coordinated and six coordinated Ti atoms.

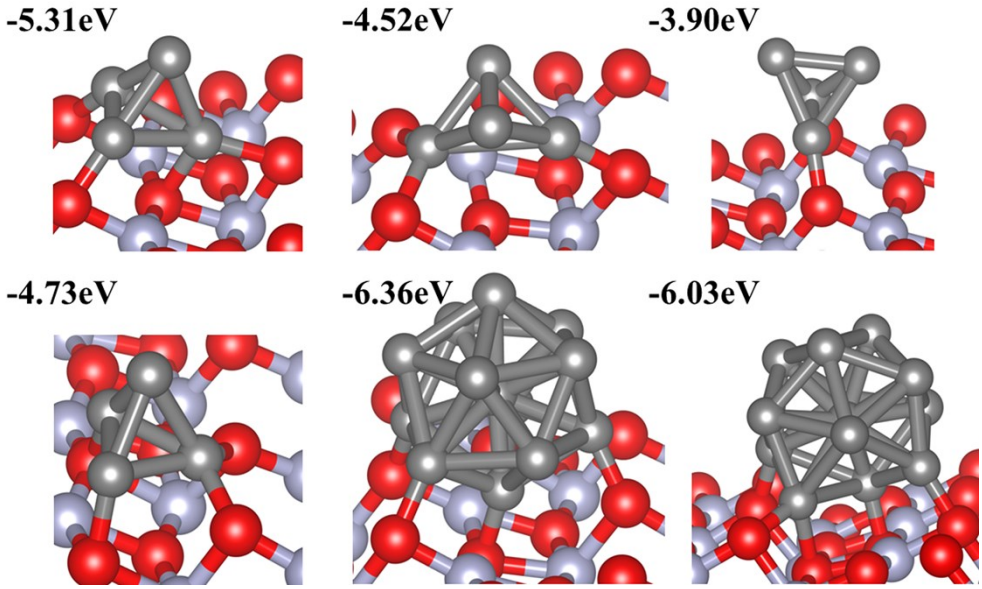

Figure S3. The optimized configurations and corresponding adsorption energies for Ni_4 and Ni_{13} clusters anchoring on TiO_2 surface. Dark grey, red and silver balls are Ni, O and Ti atoms, respectively.

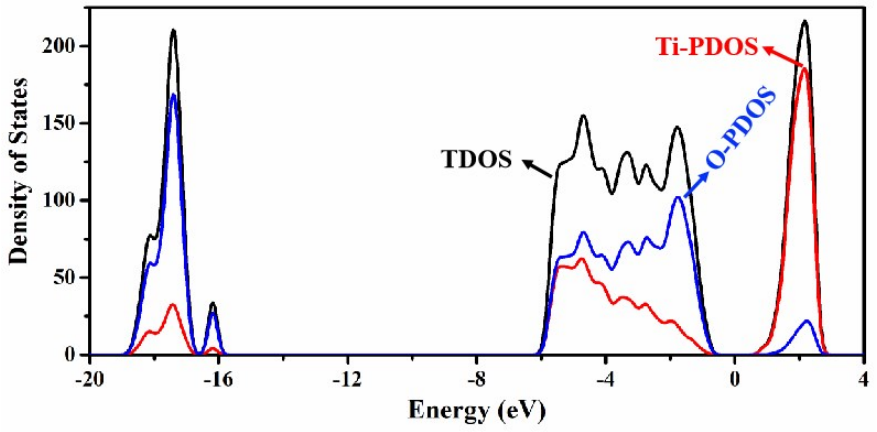

Figure S4. PDOS of pristine TiO_2 (101) surface.

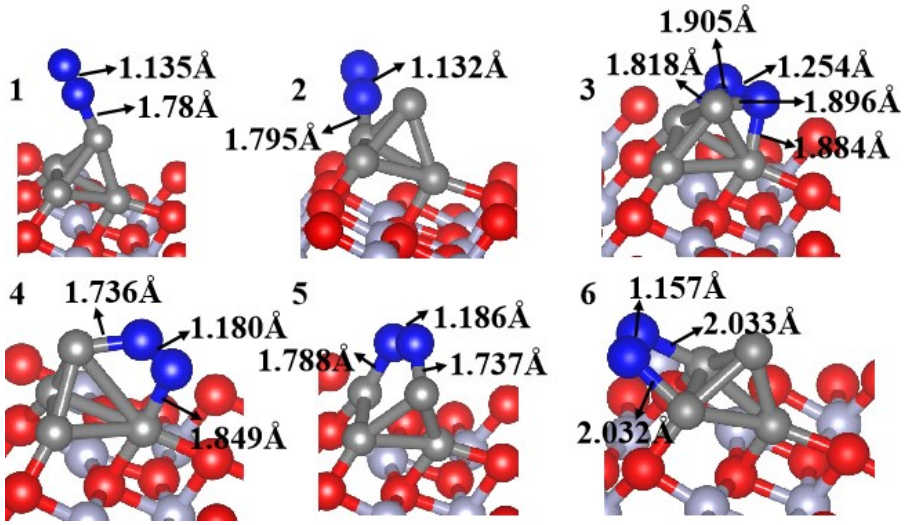

Figure S5. The optimized configurations and corresponding adsorption energies for N_2 adsorption on Ni_4-TiO_2 (101). Dark grey, blue, red and silver balls are Ni, N, O and Ti atoms, respectively.

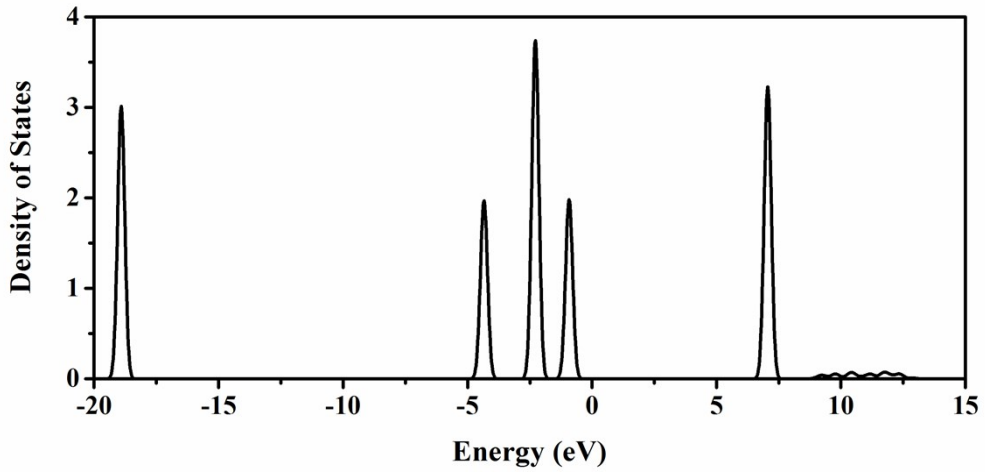

Figure S6. PDOS for N atoms of gas N_2 molecule. The PDOS plots for two N atoms overlap completely.

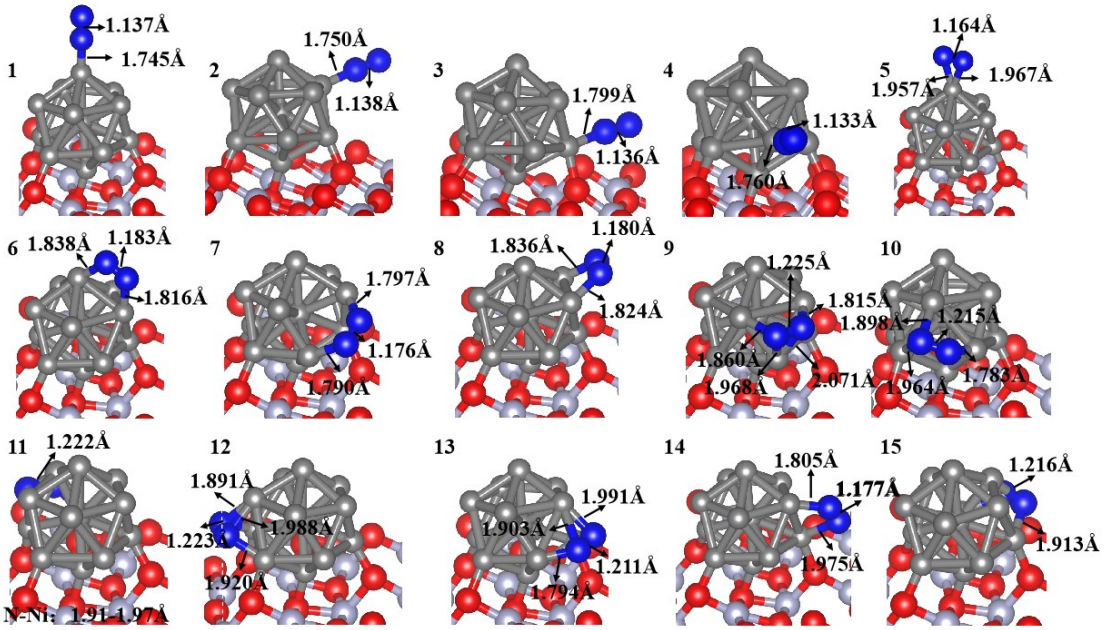

Figure S7. The optimized configurations and corresponding adsorption energies for N_2 adsorption on Ni_{13}-TiO_2 (101). Dark grey, blue, red and silver balls are Ni, N, O and Ti atoms, respectively.

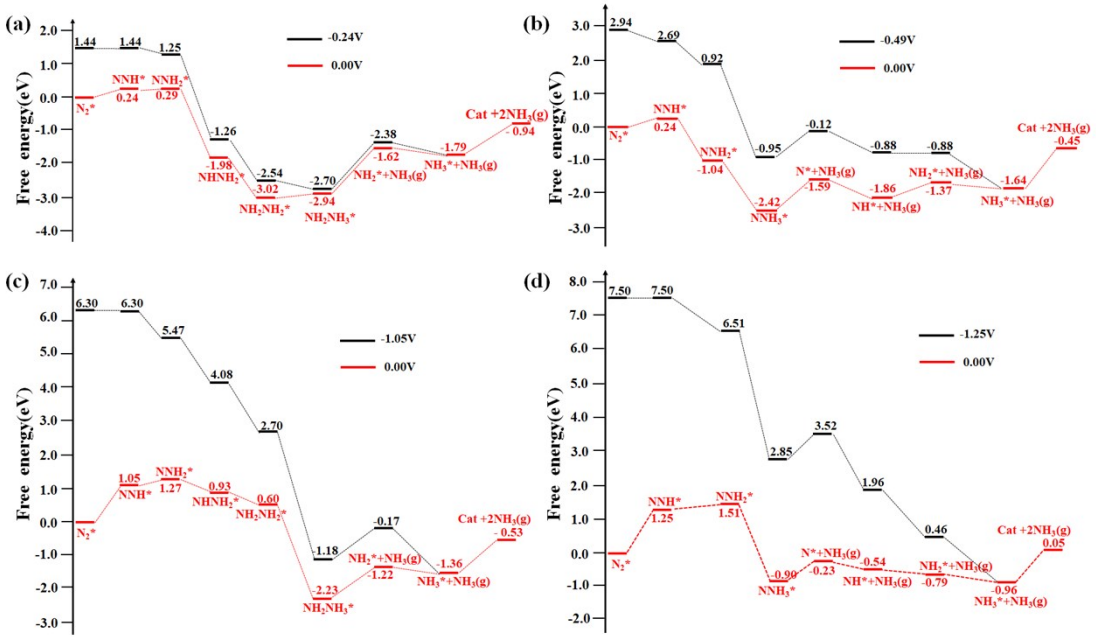

Figure S8. The Gibbs free energies for the nitrogen reduction reaction (NRR) on Ni_4/Ni_{13}-TiO2(101) catalyst at no energy input as well as limiting potential is shown in red and black line, respectively: (a) N_2 adsorbed on Ni_4-TiO_2(101) in side-on configuration (Configuration 3); (b) N_2 adsorbed on Ni_{13}-TiO_2(101) in side-on configuration (Configuration 9); (c) N_2 adsorbed on Ni_4-TiO_2(101) in end-on configuration (Configuration 1); (d) N_2 adsorbed on Ni_{13}-TiO_2(101) in end-on configuration (Configuration 1).

Table S1. N-N bond length (L_{N-N}) for each intermediate in NRR process on TiO_2(101) supported Ni clusters.

	Configuration	intermediate	L_{N-N}(Å)		Configuration	intermediate	L_{N-N}(Å)
Ni_4-TiO_2	1 (end-on)	N_2*	1.135	Ni_{13}-TiO_2	1 (end-on)	N_2*	1.137
		NNH*	1.213			NNH*	1.205
		NNH_2*	1.277			NNH_2*	1.278
		NHNH*	1.276			NHNH*	1.278
		NNH_3*	1.488			NHNH2*	1.366
		$NHNH_2$*	1.372		9 (side-on)	N_2*	1.225
		NH_2NH_2*	1.454			NNH*	1.332
	3 (side-on)	N_2*	1.254			NHNH*	1.387
		NNH*	1.345				
		NNH_2*	1.441				
		NHNH*	1.397				

Table S2. ZPE and TS (T=300K) values for NRR process of N_2*on Ni_4-TiO_2(101) in configuration 1 and 3.

Configuration **1**	ZPE (eV)	TS (eV)	Configuration **3**	ZPE (eV)	TS (eV)
N_2*	0.21	0.15	N_2*	0.20	0.08
NNH*	0.47	0.19	NNH*	0.52	0.07
NHNH*	0.80	0.21	NHNH*	0.85	0.08
NNH_2*	0.81	0.19	NNH_2*	0.87	0.08
$NHNH_2$*	1.12	0.22	$NHNH_2$*	1.09	0.15
NH_2NH_2*	1.48	0.26	NNH_3*	1.16	0.13
NH_2NH_3*	1.75	0.20	$NHNH_3$*	1.42	0.18
NNH_3*	1.13	0.21	NH_2NH_2*	1.45	0.12
N*	0.07	0.11	NH_2NH_3*	1.76	0.18
NH*	0.36	0.06	N*	0.12	0.02
NH_2*	0.70	0.07	NH*	0.40	0.03
NH_3*	1.02	0.18	NH_2*	0.70	0.07
			NH_3*	1.05	0.11

Table S3. The energy barriers ($E_{barrier}$) of rate-determining step in NRR process.

This work		$E_{barrier}$ (eV)	Reported work	$E_{barrier}$ (eV)
Ni_4-TiO_2(101)	Configuration 1	0.73	FeN_4 [1]	0.85
	Configuration 3	0.32	MnO [2]	1.88
Ni_{13}-TiO_2(101)	Configuration 1	1.66	C-doped TiO_2/C [3]	0.64
	Configuration 9	0.51	MoS_2 [4]	0.68
			TiO_2 (101)/$Ti_3C_2T_x$ [5]	0.40
			electron-deficient Cu nanoparticles [6]	1.60
			Au_1/C_3N_4 [7]	1.33
			N-C@NiO/GP [8]	1.23

Table S4. ZPE and TS (T=300K) values for NRR process of N_2*on Ni_{13}-TiO_2(101) in configuration 1 and 9.

Configuration **1**	ZPE (eV)	TS (eV)	Configuration **3**	ZPE (eV)	TS (eV)
N_2*	0.20	0.21	N_2*	0.18	0.11
NNH*	0.47	0.47	NNH*	0.50	0.09
NHNH*	0.81	0.21	NHNH*	0.83	0.09
NNH_2*	0.80	0.20	NNH_2*	0.81	0.09
$NHNH_2$*	1.14	0.21	$NHNH_2$*	1.06	0.14
$NHNH_3$*	1.42	0.21	NNH_3*	1.14	0.15
NNH_3*	1.14	0.17	$NHNH_3$*	1.40	0.19
N*	0.10	0.02	NH_2NH_2*	1.41	0.14
NH*	0.38	0.04	NH_2NH_3*	1.73	0.25
NH_2*	0.70	0.08	N*	0.10	0.02
NH_3*	1.04	0.15	NH*	0.39	0.03
			NH_2*	0.70	0.07
			NH_3*	1.04	0.11

Table S5. Computed frequencies for each intermediate structures in NRR process of adsorbed N_2 in configuration 1 on Ni_4 -TiO_2 (101) catalyst.

Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)
N_2*	66.373611	$NHNH_2$*	106.561040	NH_2NH_3*	47.652733	NH_2*	103.696434
	11.037772		103.110487		44.899527		101.121580
	8.996761		99.575185		36.348894		44.580160
	8.651273		48.239377		22.966354		20.558257
	2.671124		43.145378		22.529673		19.854807
	2.466002		35.272318		20.075969		18.370221
NNH*	94.457163		34.999001		19.981173		16.122828
	52.155676		21.603991		18.682670		12.361258
	32.839154		13.936664		15.276501		4.232470
	16.016818		13.119399		14.154425	NH_3*	103.442272
	15.119209		9.655198		11.919058		103.296612
	9.340287		5.937369		5.549476		100.679046
	5.808344		4.411993		5.229605		48.353819
	2.318402		2.601207		4.183259		47.868596
	0.983892		1.403684		2.092944		35.888090
NHNH*	96.246750	NH_2NH_2*	104.225166	NNH_3*	99.718320		18.214774
	92.316598		102.021041		98.442398		17.599372
	45.131108		101.346293		91.511597		10.471807
	42.741338		99.192051		47.444998		3.340028
	39.653067		48.835078		46.670856		2.101497
	30.940970		48.087011		40.700379		1.653625
	15.058249		39.804537		30.246401		
	13.015273		37.126560		29.776817		
	7.505012		33.582196		21.816061		
	3.115836		31.569718		17.19082		
	2.385300		25.062278		8.331983		
	1.005224		18.625560		6.768291		
NNH_2*	101.888639		10.617313		4.785697		
	98.004936		7.244151		1.758863		
	47.678371		3.654317		1.446667		
	41.651991		2.597983	N*	27.290455		
	35.976563		2.400130		3.036654		
	18.319095		1.207084		1.559696		
	15.709908	NH_2NH_3*	102.860222	NH*	95.754715		
	15.021463		102.771221		22.860446		
	8.035964		102.426766		20.03443		
	5.258421		100.629157		19.346373		
	2.842582		100.117225		14.300271		
	1.306419		48.239819		3.660941		

Table S6. Computed frequencies for each intermediate structures in NRR process of adsorbed N_2 in configuration 3 on Ni_4 -TiO_2 (101) catalyst.

Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)
N2*	42.030493	**$NHNH_2$***	103.467568	**NNH3***	24.346190	**NH_2NH_3***	18.941959
	13.946754		101.382406		23.427832		18.264414
	13.025423		99.982626		21.485554		14.796869
	10.595273		45.845598		16.934416		13.628680
	9.877396		23.970775		12.179112		12.742424
	6.627987		23.144141		11.251599		6.243197
NNH*	99.653101		22.049158		9.303302		5.500248
	36.142967		20.030327		5.557533		5.012818
	33.965184		20.030327		2.940922		2.760025
	21.318246		16.823711	**NHNH3***	103.593091	**N***	25.029467
	16.357932		15.900454		102.962562		16.127661
	14.892892		14.369173		100.458453		15.061739
	12.777228		11.236524		98.503917	**NH***	100.396509
	10.907468		5.078300		48.197073		23.468374
	7.624935		1.640303		47.672367		22.932780
NHNH*	99.164783	**NH_2NH_2***	103.129150		36.260482		18.466632
	98.638550		103.058600		22.374804		17.261462
	41.369031		101.101747		20.830515		12.074383
	37.365656		100.801616		20.463851	**NH_2***	103.548049
	31.453344		45.696793		19.818798		101.264478
	24.913428		45.534389		16.716584		44.619053
	20.870408		24.513992		14.640365		20.745144
	15.342554		22.912388		12.949751		19.983611
	14.020996		22.292246		6.554100		18.361945
	12.328181		21.318154		5.682058		16.432165
	10.084386		20.548478		4.082367		12.189586
	7.086324		19.860561		2.727673		4.283590
NNH_2*	101.612516		17.632137	**NH_2NH_3***	102.419884	**NH_3***	104.307713
	99.244839		17.031815		101.772994		102.909025
	46.756071		12.768628		101.195606		99.122604
	35.252543		12.025212		100.161871		48.279025
	32.292721		5.377287		99.794719		47.951568
	25.197789		4.332088		48.348913		36.488377
	21.861760	**NNH3***	104.172786		47.715008		21.136471
	16.711071		102.682480		44.735705		19.812275
	14.338509		91.078265		37.922363		11.139363
	13.918281		48.418889		23.911752		7.519373
	8.563626		47.673862		23.305559		5.687167
	5.304044		37.295859		20.626617		3.603594

Table S7. Computed frequencies for each intermediate structures in NRR process of adsorbed N_2 in configuration 1 on Ni_{13} -TiO_2 (101) catalyst.

Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)
N_2*	66.129920	NNH_2*	41.647681	$NHNH_3$*	35.775791	NH*	100.439568
	12.141324		35.656237		22.051307		21.410353
	9.366344		17.533109		21.624176		20.621858
	9.100778		15.225087		19.112788		17.380185
	0.705870		13.560093		18.486082		12.996618
	0.703226		6.467371		17.352954		12.583395
NNH*	95.055757		5.373016		13.253029	NH_2*	103.792163
	54.504710		3.251519		12.037089		101.554315
	29.914206		1.033085		11.362295		44.921522
	14.951513	$NHNH_2$*	106.026018		4.734518		20.472440
	10.478474		102.219455		2.668658		19.734825
	9.579061		101.099980		1.503674		18.718272
	7.617110		47.830917	NNH_3*	104.516513		14.563843
	2.946185		43.150724		104.033506		10.191477
	1.932160		35.714612		101.493513		3.640899
NHNH*	96.364245		34.879499		48.633492	NH_3*	103.640602
	94.250363		21.521715		48.540548		103.523957
	45.343331		19.244408		35.752993		101.236650
	42.453697		14.876302		18.999383		48.388365
	39.663387		11.156787		18.784253		48.203042
	31.375973		7.067243		17.610344		35.839301
	14.551344		3.558871		16.759664		18.905240
	14.167144		2.881129		15.200664		18.387773
	7.069492		1.154130		10.676834		11.891922
	3.893493	$NHNH_3$*	104.339455		5.696931		5.482874
	1.766707		103.774452		3.379973		3.071496
	1.137951		101.081225		2.761643		2.256824
NNH_2*	101.506522		99.542959	N*	18.088372		
	98.112857		48.581995		16.714061		
	48.148630		48.205222		15.886668		

Table S8. Computed frequencies for each intermediate structures in NRR process of adsorbed N_2 in configuration 9 on Ni_{13} -TiO_2 (101) catalyst.

Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)	Structure	Frequency (THz)
N_2*	46.076984	$NHNH_2$*	103.914362	NNH3*	21.511034	NH_2NH_3*	18.085361
	12.264056		100.888467		20.181132		17.801626
	11.302827		99.298164		19.325598		14.913265
	7.579236		44.883659		16.529627		11.676204
	6.614807		22.608057		11.418972		11.401770
	4.294890		20.982547		10.547923		4.962074
NNH*	99.128913		20.286864		6.928376		4.435595
	36.715415		19.858942		4.694874		2.810851
	34.174444		18.406344		3.802253		1.001094
	19.902830		15.796546	NHNH3*	104.073655	N*	19.683172
	14.742159		15.203059		102.553914		16.683177
	13.817695		10.775387		98.413071		12.133879
	9.623988		10.299728		97.652792	NH*	100.699496
	8.494814		4.481872		48.273282		22.175308
	6.593340		3.666753		48.042108		20.789586
NHNH*	99.987294	NH_2NH_2*	103.420061		35.360496		17.542370
	99.584720		102.932264		20.167680		14.835456
	41.066329		100.744371		19.956492		13.092284
	36.914569		100.113680		19.095973	NH_2*	103.249647
	31.313303		45.217001		18.130681		100.460975
	22.642062		44.672839		15.867613		44.598058
	20.376315		22.615109		15.052113		21.322149
	14.197648		21.887518		11.482612		20.588123
	13.057888		21.302253		8.727793		19.271543
	9.413289		20.010661		5.216415		15.223782
	7.802834		19.555510		3.925675		11.550115
	7.015488		19.177672		2.907481		3.720477
NNH_2*	104.206321		15.455280	NH_2NH_3*	103.722825	NH_3*	103.912119
	101.663056		14.819534		103.326238		102.328655
	44.936800		11.620448		103.278052		90.000304
	20.873190		10.101209		100.961903		48.397866
	20.375771		4.912740		100.321247		47.356418
	20.065861		3.754114		48.319889		37.353623
	17.867678	NNH3*	103.448070		48.152583		21.707731
	16.605657		102.083820		44.526213		19.888795
	15.177800		98.395050		35.530045		12.378780
	14.986976		48.405084		21.132055		8.908488
	10.433108		47.925558		20.366897		6.462117
	4.373095		37.592801		18.760908		2.754420

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