Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S1. Coordination of copper and palladium oxygen-bridged cation pairs to DS6 rings in the straight/zig-zag channel of ZSM-5 and relative stability for different Al positions.

Cation	Al site	M-Oz bonds, Å	M-O bonds, Å	∠MOM, deg	M-M distance, Å	ΔE, kJ mol^{-1}
$(Cu\text{-}O\text{-}Cu)^{2+}$	T7, T9'	1.934; 2.221 (Cu1)	1.747; 1.747	118.0	2.995	0.0
	-$AlO(SiO)_2$-Al-	1.931; 2.078; 2.696 (Cu2)				
	T9, T11'	1.969; 2.067; 2.635 (Cu1)	1.729; 1.730	156.6	3.387	-71.0
	-$AlO(SiO)_3$-Al-	1.999; 2.215 (Cu2)				
	T9, T11 [a]	1.964; 2.066 (Cu1)	1.730; 1.732	154.4	3.377	-49.0
	-$AlO(SiO)_2$-Al-	1.904 ; 2.249 (Cu2)				
	T9, T12'	1.983; 1.991; 2.686 (Cu1)	1.715; 1.715	154.7	3.348	-69.0
	-$AlO(SiO)_4$-Al-	1.883; 2.027(Cu2)				
	T11, T11'	1.959 ; 2.005 (Cu1)	1.749 ; 1.749	89.6	2.466	+76.0
	-$AlO(SiO)_2$-Al-	1.958 ; 2.003 (Cu2)				
$(Cu\text{-}O\text{-}Cu)^{2+}$	T7	1.956; 2.164; 2.982 (Cu1)	1.743; 1.744	120.0	3.021	
	-$AlO(SiO)_2$-Al-	2.008; 2.051; 2.808 (Cu2)				
$(Cu\text{-}OH\text{-}Cu)^{2+}$	T9, T11'	1.994; 2.024 (Cu1)	1.849; 1.860	127.5	3.326	
	-$AlO(SiO)_3$-Al-	1.931; 2.223 (Cu2)				
$(Pd\text{-}O\text{-}Pd)^{2+}$	T7, T9'	2.201; 2.230 (Pd1)	1.834; 1.861	128.7	3.331	0.0
	-$AlO(SiO)_2$-Al-	2.060; 2.263; 2.802 (Pd2)				
	T9, T11'	2.091; 2.140 (Pd1)	1.856; 1.866	114.2	3.125	-35.0

	-$AlO(SiO)_3$-Al-	2.049; 2.240 (Pd2)				
	T9, T11 [a]	2.089; 2.440; 2.905 (Pd1)	1.852; 1.858	114.3	3.116	97.0
	-$AlO(SiO)_2$-Al-	2.077; 2.157 (Pd2)				
	T9, T12’	2.092; 2.276 (Pd1)	1.880; 1.849	114.7°	3.140	55.0
	-$AlO(SiO)_4$-Al-	2.045; 2.219 (Pd2)				
	T11, T11’	2.129; 2.200 (Pd1)	1.869; 1.87	84.4	2.570	74.0
	-$AlO(SiO)_2$-Al-	2.130; 2.201 (Pd2)				
$(Pd\text{-}O\text{-}Pd)^{2+}$	T7	2.167; 2.159 (Pd1)	1.834; 1.843	130.9	3.344	
	-$AlO(SiO)_2$-Al-	2.203; 2.302; 2.749; 2.864 (Pd2)				
$(Pd\text{-}OH\text{-}Pd)^{2+}$	T8, T11’	2.195; 2.215 (Pd1)	1.979; 2.018	105.5	3.182	0.0
	-$AlO(SiO)_2$-Al-	2.128; 2.311 (Pd2)				
$(Pd\text{-}OH\text{-}Pd)^{2+}$	T9, T11’	2.135; 2.369; 2.750 (Pd1)	1.971; 2.016	119.6	3.445	-13.0
	-$AlO(SiO)_3$-Al-	2.115; 2.209 (Pd2)				

[a] – configurations at the 10MR of the straight channel

The relative energy in Table S1 is calculated by taking the ONIOM energy of the zeolite model with $(MOM)^{2+}$, where M=Cu, Pd and Al substitution is at sites T7,T9 as a reference zero. Only models with identical high and low-layer can be compared: the number and type of atoms should be the same, but their positions differ. The ONIOM energy is calculated as implemented in Gaussian 09:

$E_{ONIOM} = E(QM) + E(MM) + E(QM/MM)$,

where QM is the "high layer" of the ONIOM model, treated at quantum mechanical level, or DFT; the "low layer" is described by Molecular Mechanics, MM. The third term E(QM/MM) corresponds to the interaction between high layer and the low layer.

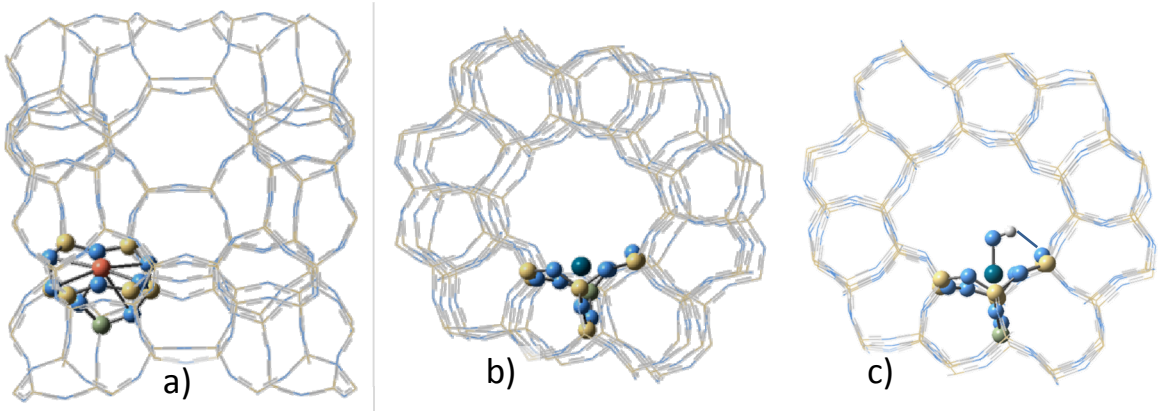


Figure S1. Coordination of cations in S6-1. a) Al at site T4 and Cu^{2+} seen from the direction of the sinusoidal channel. b) Al at site T7 and Pd^{2+} seen through the straight channel. c) Al at site T4 and $PdOH^{+}$ with the hydrogen bond denoted. Color legend: Oxygen atoms are blue balls, Si – brown, Al – green, Cu – red, Pd – dark blue-green, hydrogen atoms are small grey balls.

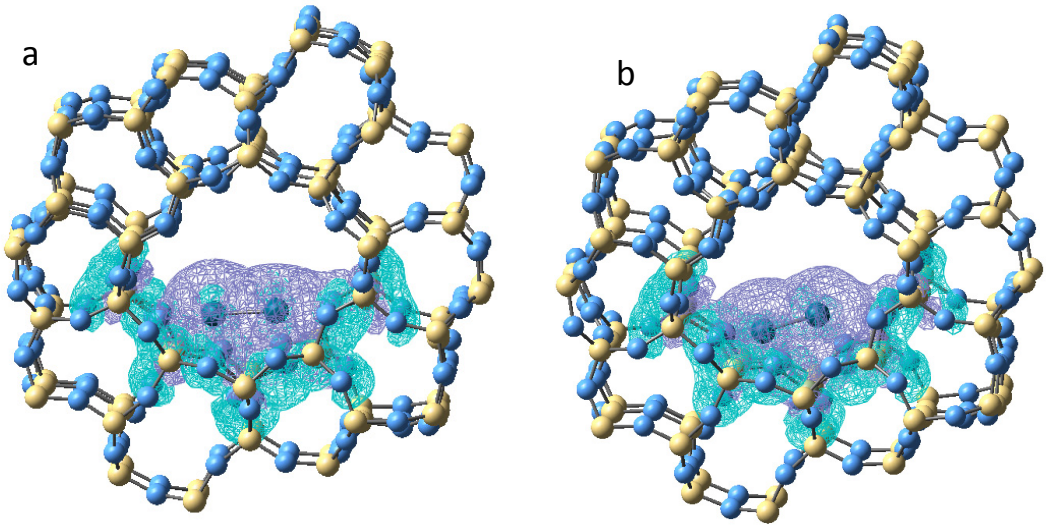


Figure S2. Deformation density maps of palladium cation dimers. a) Al positioned at T7; b) Al positioned at T11,T11'. Dark violet mesh describes regions of increased electron density; blue-green mesh describes regions of depleted electron density.

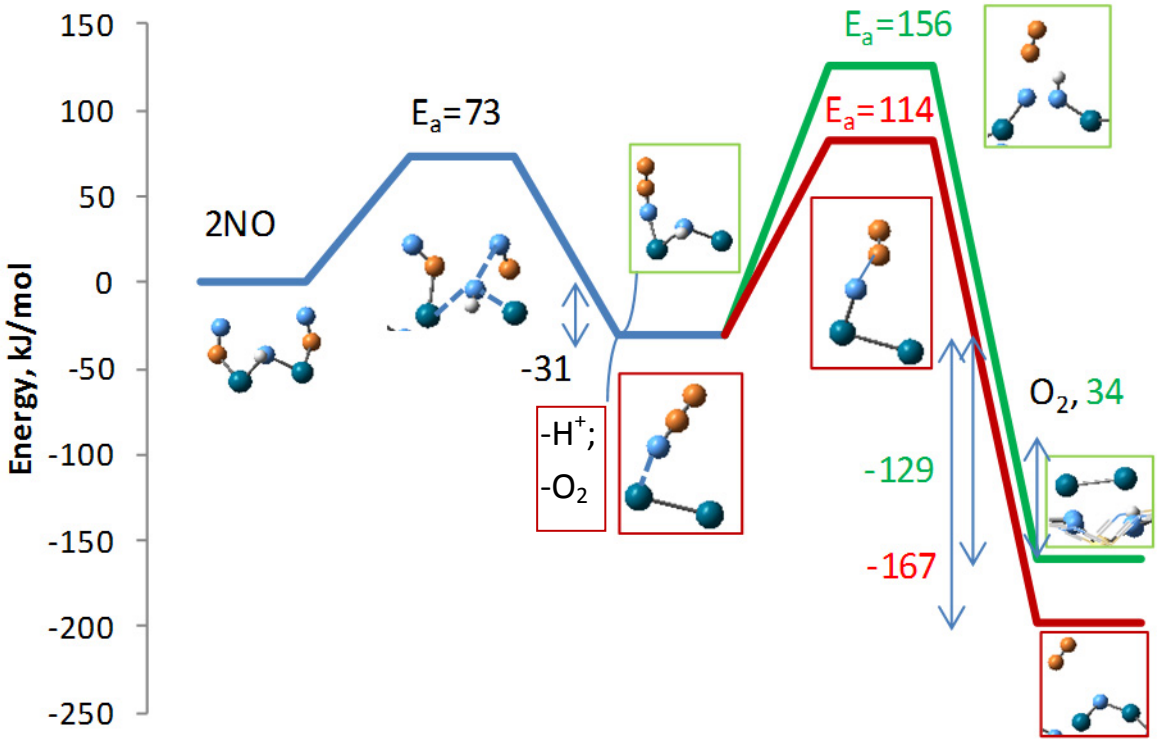
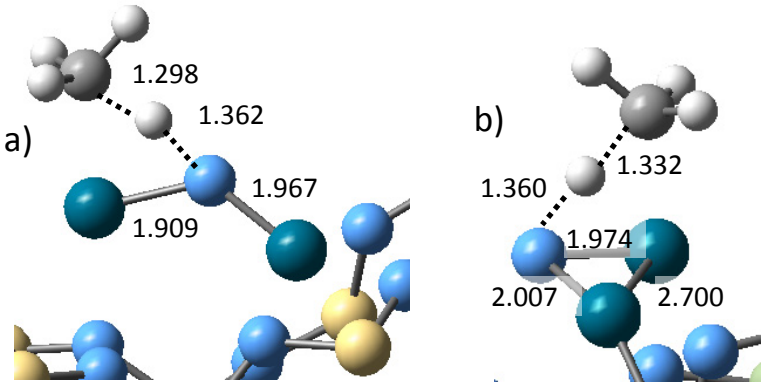


Figure S3. Energy barriers and reaction enthalpies for NO reduction to N_2O on $[Pd(OH)Pd]^{2+}$ in ZSM-5 and subsequent reduction to N_2. $-H^+$ denotes a proton transfer back to a Brønsted acid site in Pd-H-ZSM-5. Arrows denote the reaction enthalpies and the oxygen desorption energy. The red line marks a spin-forbidden path of N_2O reduction on a reduced $[Pd\text{-}Pd]^{2+}$

site; the green line marks a spin-allowed reaction by adsorption of N_2O on a "fresh" $[Pd(OH)Pd]^{2+}$ site.

In the first reaction step of 2NO reduction to N_2O on $[Pd(OH)Pd]^{2+}$ an energy barrier of 73 kJ mol^{-1} was calculated, as shown in Figure S2 and it is weakly exothermic by 31 kJ mol^{-1}. Molecular dynamics simulations indicate that the oxygen release and restoration of a Brønsted acid site proceed simultaneously with N_2O formation and the N_2O molecule remains adsorbed on a $(Pd\text{-}Pd)^{2+}$ dimer. There are two possible routes for the reduction of N_2O, which is the rate-determining step: (i) direct reduction with oxygen transfer to $(Pd\text{-}Pd)^{2+}$ dimer; (ii) reduction on another $(Pd\text{-}OH\text{-}Pd)^{2+}$ site. The first reaction proceeds with lower energy barrier of 114 kJ mol^{-1}, but it is spin-forbidden. Spin-forbidden processes rely on the spin-orbit coupling which is stronger in heavy metal cations. Due to strong interaction with framework oxygen atoms, spin density and charges of Pd cation dimers are more delocalized than they are for copper cations. Thus it is more likely that the palladium cations in ZSM-5 allow the lower energy path, than the copper cations. For the spin-allowed route on a fresh $(Pd\text{-}OH\text{-}Pd)^{2+}$ site a higher energy barrier of 156 kJ mol^{-1} is calculated, the reaction is less exothermic, and additional energy of 34 kJ mol^{-1} is needed for O_2 desorption.



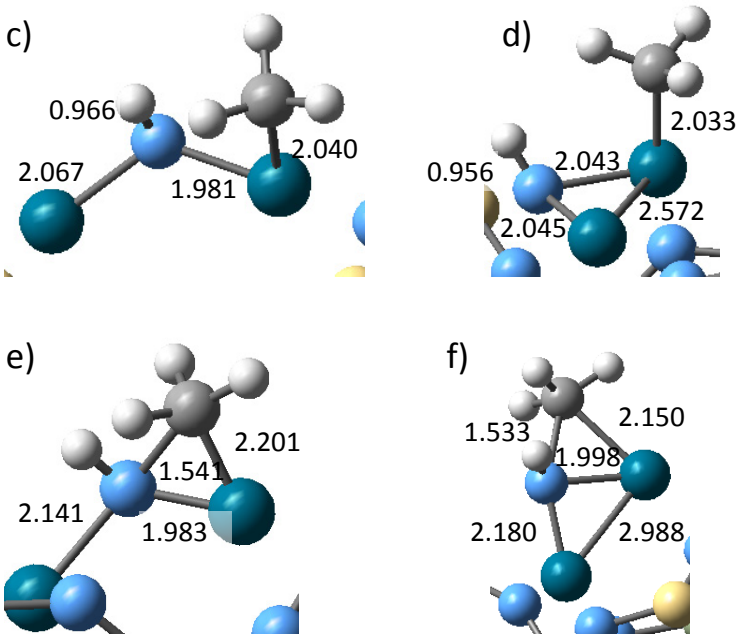
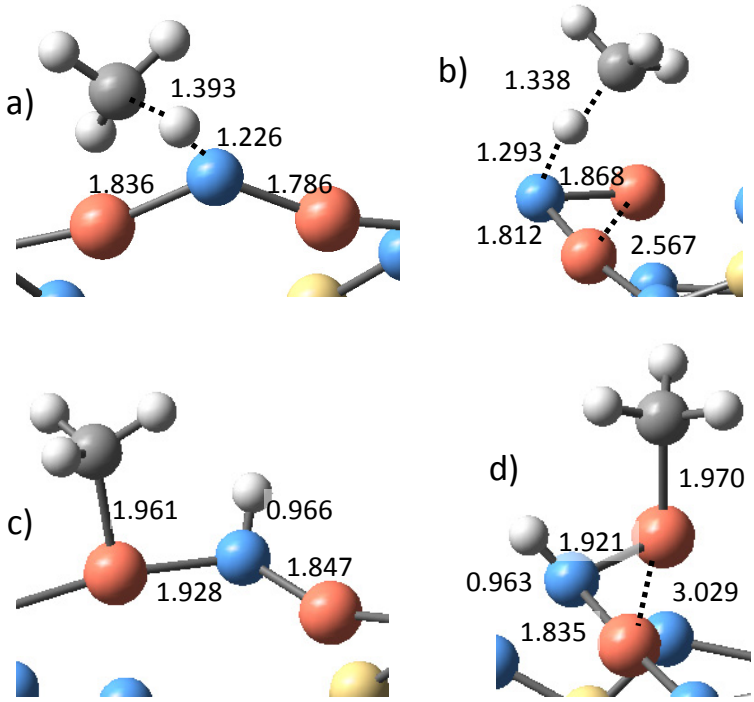


Figure S4. Transition states and reaction intermediates in the methane to methanol reaction on Pd-ZSM-5. a) transition state structure for T9T11' Al substitution, broad Pd-O-Pd angle; b) transition state structure for T11T11' Al substitution, narrow Pd-O-Pd angle; c) and e) reaction intermediates for broad Pd-O-Pd angle; d) and f) reaction intermediates for narrow Pd-O-Pd angle.



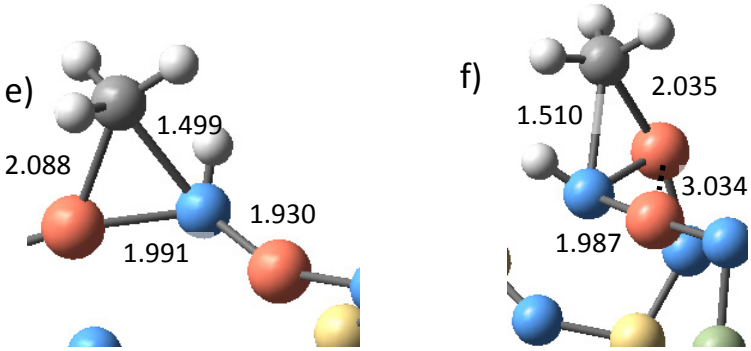


Figure S4. Transition states and reaction intermediates in the methane to methanol reaction on Cu-ZSM-5. a) transition state structure for T9T11' Al substitution, broad Cu-O-Cu angle; b) transition state structure for T11T11' Al substitution, narrow Cu-O-Cu angle; c) and e) reaction intermediates for broad Cu-O-Cu angle; d) and f) reaction intermediates for narrow Cu-O-Cu angle.

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Optimized structure of Pd cation dimer in ZSM-5

Si           -6.031751   -7.282926    6.098042
 Si           -6.024020    7.346752    6.037349
 Si           -6.013112   -4.192947    5.854877
 Si           -6.008648    4.254844    5.819830
 O            -5.741352   -5.713005    6.312441
 O            -5.735280    5.778358    6.264767
 O            -8.059134    0.016805    2.167325
 Si           -8.280078   -6.323312    1.611377
 Si           -8.273379    6.352321    1.558790
 Si           -8.183970   -1.512890    1.678830
 Si           -8.182356    1.542526    1.666155
 O            -6.537647   -7.533665    4.590754
 O            -6.529658    7.585511    4.528030
 O            -6.580314   -4.179159    4.348150
 O            -6.575870    4.229155    4.313267
 O            -7.478179   -7.614398    2.138682
 O            -7.470114    7.646890    2.075368
 O            -7.485306   -4.985765    2.019251
 O            -7.480020    5.017366    1.977752
 O            -7.114250   -2.420110    2.468157
 O            -7.111674    2.455133    2.447931
 O            -8.408597   -6.393062    0.006875
 O            -8.401832    6.408892   -0.046235
 O            -4.681768   -8.119436    6.363580
 O            -4.673153    8.184009    6.295943
 Si           -6.470770   -8.311302    3.183284
 Si           -6.461964    8.351372    3.114157
 Si           -6.555354   -3.901515    2.763939
 Si           -6.551211    3.938350    2.731415
 O            -4.634051   -3.362431    5.919119
 O            -4.630465    3.423433    5.890967
```

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O	-7.488888	4.060480	-0.778109
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O	-8.493120	5.691793	-2.582359
Si	-7.651593	-5.595001	-1.169977
Si	-7.645677	5.600295	-1.216422
O	-8.265252	-2.195103	-2.438121
O	-8.262934	2.190640	-2.456315
Si	-7.372811	-2.494118	-1.130205
Si	-7.370180	2.499528	-1.150927
Si	-3.133005	-8.283787	5.958861
Si	-3.124218	8.343360	5.889881
O	-4.972199	-8.247389	2.603661
O	-4.963465	8.281068	2.535090
O	-5.045242	-4.021034	2.217762
O	-5.040977	4.051738	2.184270
Si	-3.046704	-3.549581	5.732897
Si	-3.042922	3.607354	5.703206
O	-8.446390	-0.008088	-3.882351
O	-1.954202	0.035885	7.544010
O	-2.584073	-4.922676	6.432120
O	-2.578837	4.985713	6.391013
O	-2.212793	-7.458876	6.992735
O	-2.204874	7.526083	6.930568
O	-2.273273	-2.311578	6.408727
O	-2.270797	2.374183	6.389288
Si	-8.235138	-6.001588	-4.094189
Si	-8.228805	5.983221	-4.143910
Si	-1.742951	-5.957615	7.332172
Si	-1.736617	6.027194	7.282451
Si	-7.965473	-1.543971	-3.882146
Si	-7.963850	1.527235	-3.894887
Si	-1.473285	-1.499998	7.544216
Si	-1.471662	1.571208	7.531474
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O	-2.898781	7.756784	4.406701
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O	-6.187783	6.243986	-1.451699
O	-2.698867	-3.603657	4.161497
O	-2.695035	3.648022	4.131413
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O	-2.509110	7.688569	1.810958
Si	-1.753239	-4.254284	3.031177
Si	-1.748725	4.288248	2.995738
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Si	1.070505	-5.921218	5.996499
Si	1.076792	5.976744	5.947138
Si	-5.119333	-1.552783	-5.168198
Si	-5.117707	1.522373	-5.180961
Si	1.372854	-1.508811	6.258164
Si	1.374479	1.566342	6.245406
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Si	0.988805	8.360924	3.986698
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Si	-5.533114	3.506337	-7.544830
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Si	0.959074	3.550310	3.881531
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Si	3.447150	-5.610017	8.042852
Si	3.453116	5.680020	7.996014
Si	-2.920263	-2.570362	-3.276751
Al	-2.853915	2.494755	-3.269340
Si	3.655361	-2.518754	8.133338
Si	3.658061	2.589396	8.112147
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O	-1.643995	-6.325572	-3.797571
O	-1.637322	6.302689	-3.849962
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O	2.275083	3.569446	2.952349
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O	5.127076	2.101211	7.666316
Si	3.464157	-7.302965	2.477297
Si	3.471888	7.326713	2.416604
Si	-2.819819	-4.255675	-8.858578
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Si	3.676833	4.236088	2.532736
O	3.423455	-5.735287	2.108951
O	3.429527	5.756077	2.061278
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Si	-0.321312	6.321825	-4.779142
Si	6.164177	-6.309835	6.699806
Si	6.170875	6.365798	6.647219
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Si	-0.303334	1.502346	-4.910045
Si	6.139529	-1.500230	6.554728
Si	6.141144	1.555185	6.542053
O	4.500805	-7.543256	3.684913
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O	6.012090	-2.415560	5.237034
O	6.014666	2.459684	5.216809
O	0.984735	-6.413796	-3.794405
O	0.991500	6.388158	-3.847516
O	3.929905	-8.145464	1.186565
O	3.938520	8.157981	1.118928

Si	5.746665	-8.312908	4.352471
Si	5.755470	8.349767	4.283344
Si	-0.443191	-3.944474	-6.812225
Si	-0.439026	3.895390	-6.844753
Si	6.049014	-3.900500	4.614136
Si	6.053157	3.939365	4.581612
O	4.320410	-3.386138	1.345416
O	4.323996	3.399726	1.317264
O	1.021990	-1.441081	-4.183693
O	1.222568	1.530390	-4.378787
O	2.091016	-4.071194	-4.209771
O	2.095309	4.041034	-4.243436
O	3.119714	-5.702594	-2.419435
O	3.125732	5.686133	-2.466683
Si	2.380578	-5.611410	-3.846917
Si	2.386490	5.583889	-3.893357
O	3.032797	-1.967670	-2.493660
O	3.138670	2.184025	-2.676690
Al	2.468967	-2.483803	-4.096383
Si	2.511840	2.502619	-4.168570
Si	5.070958	-8.312577	0.064270
Si	5.079745	8.314570	-0.004710
O	0.799461	-4.065804	-7.829168
O	0.803728	4.006968	-7.862657
Si	5.293591	-3.577447	0.078262
Si	5.297377	3.579489	0.048567
O	7.291649	-4.021831	3.597194
O	7.295915	4.050940	3.563703
O	4.432239	0.030168	-1.687118
O	4.934317	-4.956110	-0.669094
O	4.939552	4.952280	-0.710200
O	4.651183	-7.496742	-1.260256
O	4.659102	7.488217	-1.322423
O	5.104880	-2.345947	-0.939304
O	5.107356	2.339794	-0.958734
Si	4.595158	-5.999042	-1.846355
Si	4.601491	5.985767	-1.896075
Si	4.589823	-1.521632	-2.163557
Si	4.588575	1.554347	-2.201079
O	3.326199	-6.262034	-4.977223
O	3.332797	6.224114	-5.029023
O	6.821713	-3.623530	0.584172
O	6.825545	3.628150	0.554088
O	3.534289	-2.155938	-5.286605
O	3.536543	2.115360	-5.304318
Si	2.370282	-3.908077	-8.147898
Si	2.374379	3.844941	-8.180062
Si	8.862469	-3.864104	3.278463
Si	8.866566	3.888914	3.246299
O	3.349747	-0.026500	-6.817848
O	2.840125	-2.406817	-7.808462
O	2.842636	2.346053	-7.828179
O	3.211404	-4.943016	-7.247846
O	3.216599	4.886423	-7.288625
Si	3.674035	-6.316110	-6.548624
Si	3.680683	6.264782	-6.600817
O	5.672572	-5.844657	-3.033489
O	5.678737	5.820399	-3.081883
O	5.599532	-1.618313	-3.419389
O	5.601227	1.591051	-3.432702
Si	3.760335	-1.581893	-6.774583

Si	3.761981	1.528772	-6.787490
Si	8.278924	-4.270691	0.354251
Si	8.283438	4.271841	0.318811
O	9.126470	-4.168758	1.719385
O	9.130882	4.180343	1.684747
O	5.261382	-6.503260	-6.734845
O	5.268226	6.448703	-6.788578
Si	7.182685	-5.964176	-3.579666
Si	7.188972	5.933786	-3.629026
Si	7.098101	-1.554385	-3.999008
Si	7.099727	1.520775	-4.011767
O	5.309099	-1.746254	-7.179305
O	5.310914	1.688126	-7.193554
O	9.035928	-3.472630	-0.822602
O	9.039594	3.463244	-0.851376
O	8.112637	-4.879927	-2.834977
O	8.117781	4.854770	-2.875363
O	8.105510	-2.251295	-2.954409
O	8.107876	2.225244	-2.972979
O	7.527174	-0.017911	-4.215460
O	7.207644	-5.686532	-5.163876
O	7.213631	5.642981	-5.210878
O	7.164978	-2.332026	-5.406481
O	7.167419	2.286624	-5.425642
Si	8.907409	-3.542380	-2.427103
Si	8.911141	3.519814	-2.456401
O	6.368683	-4.152687	-7.128167
O	6.373041	4.093777	-7.162378
Si	6.640443	-5.672745	-6.670603
Si	6.646410	5.617292	-6.717441
Si	6.659082	-2.582766	-6.913768
Si	6.661781	2.525384	-6.934960
Pd	1.098580	-0.613402	-2.253661
Pd	-1.284484	0.344823	-2.110258

Optimized structure of copper cation dimer in ZSM-5

Si	-6.116244	-7.227263	6.076056
Si	-6.227868	7.399206	5.784182
Si	-6.118205	-4.141420	5.784475
Si	-6.182661	4.304517	5.615935
O	-5.843146	-5.651752	6.271337
O	-5.930824	5.837090	6.042075
O	-8.124583	-0.007539	1.990832
Si	-8.282089	-6.357236	1.530931
Si	-8.378803	6.315616	1.278041
Si	-8.227000	-1.545702	1.524203
Si	-8.250312	1.509043	1.463245
O	-6.589766	-7.505873	4.563155
O	-6.705124	7.609985	4.261515
O	-6.655209	-4.156062	4.266732
O	-6.719364	4.250407	4.098979
O	-7.480300	-7.633007	2.094438
O	-7.596742	7.624934	1.789963
O	-7.506696	-5.006721	1.933335
O	-7.583019	4.994215	1.733764
O	-7.165863	-2.431276	2.348905
O	-7.203061	2.442898	2.251640
O	-8.377868	-6.453180	-0.074506

O	-8.475546	6.345966	-0.329916
O	-4.765002	-8.047935	6.381597
O	-4.889396	8.251933	6.056330
Si	-6.488306	-8.304837	3.169768
Si	-6.615440	8.354182	2.837334
Si	-6.600814	-3.903036	2.679139
Si	-6.660631	3.935109	2.522727
O	-4.747598	-3.298233	5.863002
O	-4.799374	3.486143	5.727618
O	-7.905911	-1.647710	-0.049883
O	-7.930338	1.553064	-0.113754
O	-7.466907	-4.116182	-0.844400
O	-7.528803	3.994286	-1.006247
O	-8.423212	-5.797709	-2.628482
O	-8.510107	5.588518	-2.855696
S	-7.604047	-5.667183	-1.248537
S	-7.689466	5.525657	-1.471892
O	-8.220182	-2.292917	-2.582248
O	-8.253645	2.091866	-2.669747
Si	-7.351683	-2.563782	-1.252270
Si	-7.389786	2.428786	-1.351898
Si	-3.207142	-8.205342	6.010423
Si	-3.334006	8.418156	5.678698
O	-4.979004	-8.237182	2.619138
O	-5.105115	8.287649	2.289381
O	-5.079131	-4.018162	2.165075
O	-5.140725	4.052838	2.004017
Si	-3.155352	-3.474687	5.711383
Si	-3.209958	3.680678	5.568596
O	-8.390375	-0.130396	-4.064201
O	-2.128930	0.147894	7.486947
O	-2.695518	-4.832665	6.441299
O	-2.771118	5.073551	6.243618
O	-2.314652	-7.356513	7.049228
O	-2.428986	7.625158	6.750266
O	-2.405841	-2.219689	6.382805
O	-2.441593	2.465044	6.289321
Si	-8.125536	-6.124450	-4.176986
Si	-8.216979	5.857729	-4.416093
Si	-1.864090	-5.846160	7.374162
Si	-1.955533	6.136019	7.135055
Si	-7.896917	-1.661917	-4.030138
Si	-7.920350	1.408614	-4.091411
Si	-1.635472	-1.383627	7.521010
Si	-1.658905	1.686904	7.459737
O	-2.956072	-7.652771	4.518329
O	-3.074080	7.810397	4.209759
O	-6.137239	-6.305372	-1.439157
O	-6.232507	6.178037	-1.688266
O	-2.775677	-3.550364	4.148267
O	-2.831007	3.699723	4.003590
O	-5.811578	-2.196513	-1.541232
O	-5.844164	2.073830	-1.626446
Si	-3.891254	-8.321610	1.434961
Si	-4.018419	8.341356	1.102448
Si	-3.979465	-3.873158	0.997320
Si	-4.038619	3.878159	0.842641
O	-4.440797	-7.544212	0.138183
O	-4.555643	7.504552	-0.162118
O	-4.740798	-0.033170	-0.509440
O	-4.036080	-2.385347	0.386610

O	-4.072345	2.366477	0.291786
O	-4.286368	-4.937247	-0.169816
O	-4.361366	4.890035	-0.365921
O	-6.550000	-5.958297	-4.466854
O	-6.639003	5.704200	-4.699581
Si	-4.619233	-6.330456	-0.902274
Si	-4.715224	6.247675	-1.153274
O	-0.288554	-5.680006	7.084294
O	-0.377558	5.982490	6.851567
O	-6.309504	-1.724137	-4.292534
O	-6.333991	1.484526	-4.356563
O	-0.048059	-1.445848	7.258613
O	-0.072546	1.762818	7.194584
Si	-4.504824	-1.605063	-0.898536
Si	-4.524396	1.534339	-0.966663
Si	-1.880567	-7.306145	3.372270
Si	-1.993063	7.434777	3.078112
O	-2.514814	-7.643801	1.929973
O	-2.631949	7.704912	1.623687
Si	-1.802270	-4.210483	3.047416
Si	-1.867449	4.330174	2.876985
O	-2.513403	-4.147970	1.604260
O	-2.577106	4.199299	1.437689
O	-1.507371	-5.742282	3.440308
O	-1.596073	5.880748	3.208368
O	-0.552424	-8.187822	3.597605
O	-0.678595	8.344901	3.267691
O	-3.619319	-6.533236	-2.146632
O	-3.718140	6.415885	-2.405034
Si	-5.286289	-6.084888	-5.456825
Si	-5.377069	5.810463	-5.694199
Si	0.975157	-5.806598	6.094323
Si	0.884376	6.088754	5.856949
Si	-5.025621	-1.666508	-5.259003
Si	-5.049097	1.407997	-5.320348
Si	1.235831	-1.388211	6.292141
Si	1.212367	1.686267	6.230790
O	-3.302920	-1.739424	-2.023744
O	-3.339422	1.625639	-2.098475
O	-0.412324	-3.397102	3.010017
O	-0.465244	3.537249	2.871641
O	1.036786	-7.300732	5.495844
O	0.923386	7.558591	5.199323
O	-5.438590	-5.028234	-6.663164
O	-5.512865	4.704327	-6.857379
O	0.822855	-4.749944	4.887984
O	0.748581	4.982617	4.693768
O	-5.371065	-2.397774	-6.651000
O	-5.405221	2.077783	-6.740311
O	0.890380	-2.119484	4.900147
O	0.856225	2.356073	4.810837
O	-4.632518	-0.131207	-5.541974
O	1.628926	0.147083	6.009177
O	-3.932018	-5.774089	-4.646400
O	-4.018463	5.552939	-4.872432
O	2.329428	-5.495798	6.904747
O	2.242985	5.831229	6.678714
O	-3.787065	-2.414916	-4.554711
O	-3.822281	2.202678	-4.646867
O	2.474370	-2.136637	6.996444
O	2.439130	2.481001	6.904298

Si	0.943312	-8.237624	4.190515
Si	0.816027	8.441128	3.857687
Si	-5.379507	-3.709555	-7.582213
Si	-5.433391	3.351090	-7.723109
Si	0.881939	-3.431265	3.968935
Si	0.828055	3.629380	3.828039
O	-2.726647	-4.188735	-2.929222
O	-2.789607	4.055930	-3.093728
O	3.534803	-3.910443	8.621924
O	3.471884	4.334211	8.457400
Si	-2.953750	-5.721385	-3.368766
Si	-3.039872	5.566176	-3.594020
Si	3.307694	-5.443095	8.182382
Si	3.221552	5.844465	7.957136
Si	-2.838977	-2.639751	-3.309158
Si	-2.875106	2.490378	-3.419904
Si	3.488568	-2.349126	8.228096
Si	3.449593	2.757903	8.126184
O	1.975907	-7.711082	3.073848
O	1.856875	7.886275	2.762599
O	-1.539209	-6.387352	-3.744198
O	-1.635562	6.238138	-3.996144
O	4.722236	-6.109062	7.806951
O	4.625884	6.516429	7.555006
O	-4.044993	-3.741063	-8.484267
O	-4.099238	3.366943	-8.626109
O	2.216453	-3.462773	3.066881
O	2.162208	3.645233	2.925039
O	-1.294951	-2.173774	-3.651445
O	-1.371654	2.026122	-3.795603
O	4.962782	-1.860753	7.799984
O	4.931217	2.275388	7.717446
Si	3.450121	-7.222709	2.645735
Si	3.338498	7.403759	2.353861
Si	-2.630450	-4.407030	-8.859699
Si	-2.694906	4.038907	-9.028239
Si	3.630995	-4.128740	2.691449
Si	3.566539	4.317197	2.522909
O	3.403886	-5.661391	2.251907
O	3.316208	5.827451	2.022645
O	-0.884208	-0.097630	-5.307584
O	5.629437	0.183136	6.285919
Si	-0.204695	-6.418860	-4.646252
Si	-0.301409	6.253992	-4.899141
Si	6.056751	-6.140570	6.904896
Si	5.960037	6.532282	6.652007
Si	-0.375467	-1.593760	-4.892265
Si	-0.364454	1.459209	-4.925954
Si	5.995377	-1.334211	6.683316
Si	5.972065	1.720534	6.622358
O	4.464319	-7.435198	3.877387
O	4.348961	7.680661	3.575747
O	-1.652184	-4.354326	-7.582065
O	-1.716339	4.052144	-7.749816
O	4.609261	-4.076036	3.969084
O	4.545107	4.330433	3.801331
O	6.048309	-7.452351	5.973684
O	5.931866	7.805589	5.669208
O	-0.145613	-5.100181	-5.565300
O	-0.221933	4.900755	-5.764871
O	6.115834	-4.821891	5.985847

O	6.039511	5.179045	5.786277
O	-0.359562	-2.549394	-6.173158
O	-0.396718	2.324775	-6.270415
O	5.901903	-2.271102	5.377987
O	5.864706	2.603072	5.280722
O	1.089568	-6.453022	-3.687333
O	0.991890	6.346122	-3.942742
O	3.948554	-8.081285	1.378010
O	3.824161	8.218584	1.052743
Si	5.702859	-8.183623	4.581690
Si	5.575724	8.475395	4.249256
Si	-0.297901	-4.043527	-6.771640
Si	-0.357741	3.794618	-6.928052
Si	5.963532	-3.765237	4.779508
Si	5.903715	4.072908	4.623096
O	4.296561	-3.316890	1.469314
O	4.244792	3.467484	1.333935
O	1.081103	-1.505948	-4.166635
O	1.099296	1.326624	-4.284291
O	2.184635	-4.107853	-4.117652
O	2.122816	4.002586	-4.279539
O	3.190649	-5.702155	-2.281578
O	3.103758	5.684072	-2.508795
Si	2.479501	-5.639641	-3.724718
Si	2.394050	5.553194	-3.948033
O	3.052753	-1.889484	-2.432866
O	3.070468	1.886462	-2.523216
Al	2.542534	-2.511917	-4.038792
Al	2.492529	2.409000	-4.134588
Si	5.113196	-8.256168	0.281424
Si	4.986332	8.367330	-0.050302
O	0.965798	-4.170119	-7.761610
O	0.904203	3.900881	-7.922669
Si	5.296445	-3.519653	0.224981
Si	5.241953	3.635729	0.082117
O	7.227244	-3.891828	3.789537
O	7.165649	4.179172	3.628479
O	4.570492	0.018283	-1.547935
O	4.963613	-4.912878	-0.507502
O	4.888002	4.993336	-0.705179
O	4.713324	-7.464778	-1.063928
O	4.598990	7.516893	-1.362890
O	5.118102	-2.305941	-0.815544
O	5.082152	2.378774	-0.908881
Si	4.656708	-5.976967	-1.674637
Si	4.565265	6.005213	-1.913743
Si	4.643922	-1.500700	-2.054868
Si	4.621359	1.531670	-2.121242
O	3.452920	-6.299761	-4.825584
O	3.357649	6.183650	-5.074694
O	6.814482	-3.544752	0.761841
O	6.759153	3.705336	0.617161
O	3.633313	-2.197327	-5.195619
O	3.600666	2.073136	-5.280910
Si	2.541334	-4.003965	-8.051479
Si	2.482179	3.747352	-8.206158
Si	8.802780	-3.725674	3.499669
Si	8.743625	4.025643	3.344990
O	3.461935	-0.093812	-6.763756
O	2.991894	-2.493611	-7.726545
O	2.955638	2.258219	-7.821370

O	3.372762	-5.017460	-7.118615
O	3.297764	4.809821	-7.314721
Si	3.832595	-6.375438	-6.388700
Si	3.736604	6.202694	-6.639699
O	5.756374	-5.831963	-2.842392
O	5.667371	5.830534	-3.075119
O	5.656233	-1.612916	-3.296451
O	5.631786	1.595677	-3.360519
Si	3.884382	-1.644800	-6.687747
Si	3.860668	1.465123	-6.749759
Si	8.281291	-4.182942	0.571220
Si	8.216112	4.357715	0.400790
O	9.100455	-4.052415	1.951165
O	9.036752	4.294854	1.784593
O	5.424842	-6.551892	-6.540318
O	5.326020	6.397229	-6.798721
Si	7.278057	-5.947089	-3.356456
Si	7.187277	5.948263	-3.593830
Si	7.165551	-1.545298	-3.847081
Si	7.142088	1.529224	-3.908435
O	5.442246	-1.802190	-7.058914
O	5.416042	1.631438	-7.127432
O	9.055111	-3.396945	-0.602811
O	9.002191	3.537406	-0.741187
O	8.183940	-4.843404	-2.610651
O	8.109665	4.889157	-2.804867
O	8.157543	-2.217118	-2.771755
O	8.123388	2.258435	-2.861064
O	7.586194	-0.008770	-4.079229
O	7.332453	-5.694063	-4.944049
O	7.246009	5.632965	-5.170082
O	7.267010	-2.344253	-5.240471
O	7.231770	2.273387	-5.332617
Si	8.959333	-3.492889	-2.208247
Si	8.905449	3.567756	-2.349144
O	6.520390	-4.198372	-6.948654
O	6.457470	4.046282	-7.113178
Si	6.795449	-5.708705	-6.461792
Si	6.709307	5.578855	-6.687038
Si	6.793488	-2.622862	-6.753373
Si	6.754513	2.484166	-6.855285
Cu	0.626809	-1.751941	-2.224991
Cu	2.228226	0.030492	-3.032598

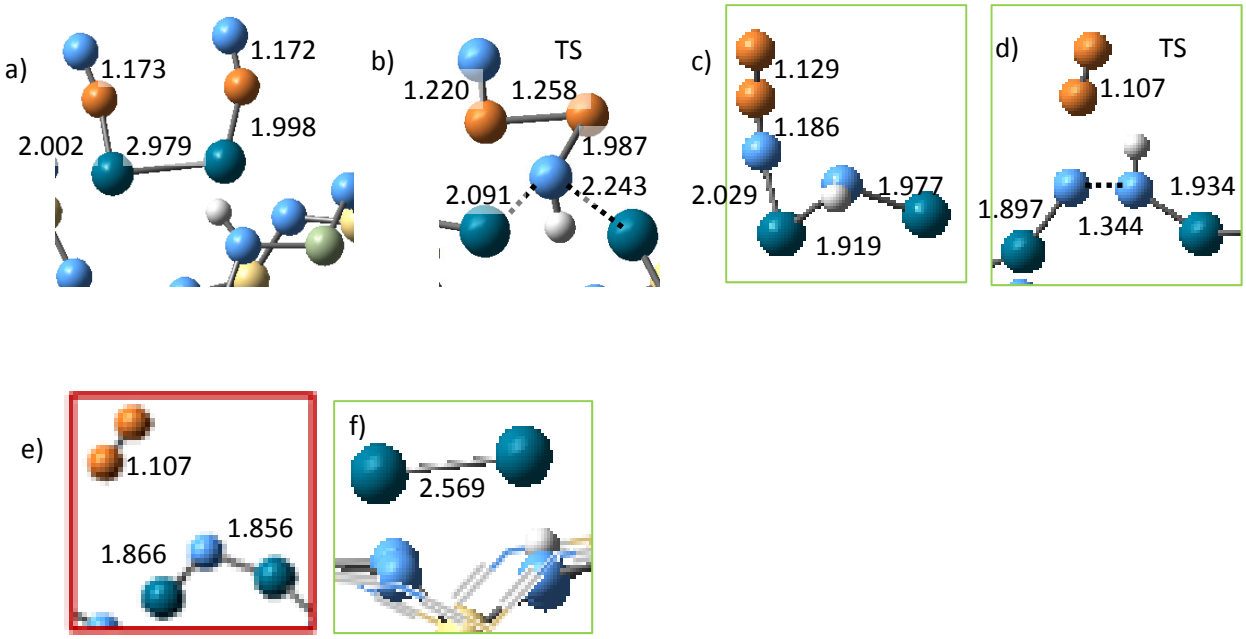

Figure S5. Reaction intermediates in NO decomposition. a) adsorption of 2NO molecules on $[Pd\text{-}Pd]^{2+}$; b) transition state to N_2O formation; c) oxygen-bonded N_2O (after reorientation); d) N_2 release and hydro-peroxide formation e) restored active site in a spin-forbidden reaction; f) restored active site in a spin-allowed reaction