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Supplementary Information

Comparison of the Mechanisms of deNOx and deN$_2$O Processes on Bimetallic Cu-Zn and Monometallic Cu-Cu Dimers in Clinoptilolite Zeolite - a DFT Study Simulating Industrial Conditions

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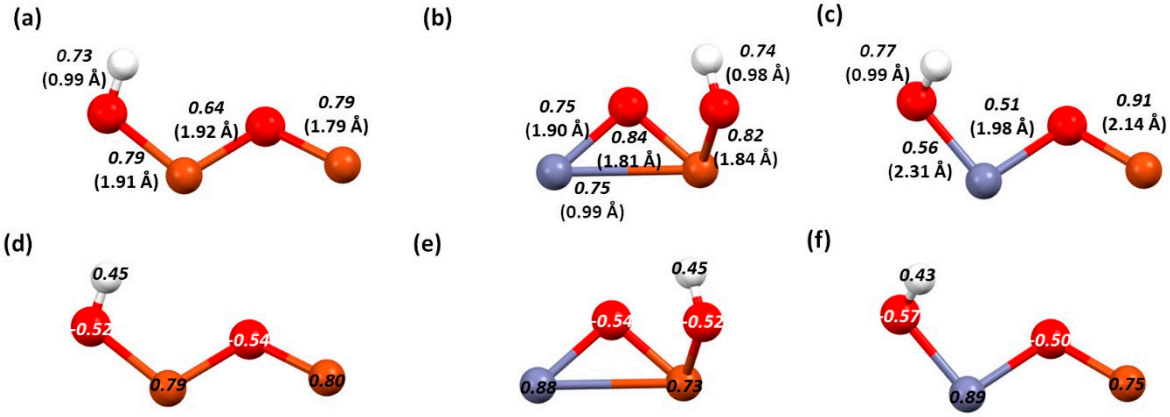

Figure S1. Bond order and length (in brackets) for zeolite clinoptilolite structures: a) Cu-O-Cu dimer with OH group on copper, b) Cu-O-Zn dimer with OH group on copper, c) Cu-O-Zn dimer with OH group on zinc and ionicity for: d) Cu-O-Cu dimer with OH group on copper, e) Cu-O-Zn dimer with OH group on copper, f) Cu-O-Zn dimer with OH group on zinc. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

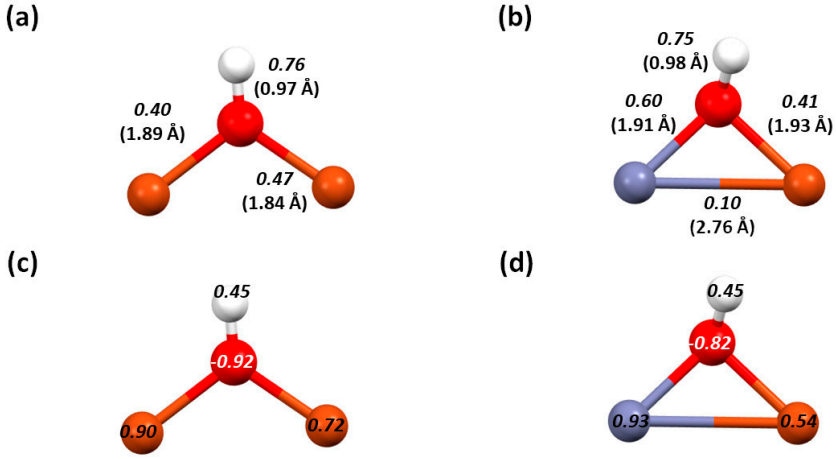

Figure S2. Bond order and lenght (in brackets) for zeolite clinoptilolite structures: a) Cu-O-Cu dimer with OH group on oxygen bridge, b) Cu-O-Zn dimer with OH group on oxygen bridge and ionicity: c) Cu-O-Cu dimer with OH group on oxygen bridge, d) Cu-O-Zn dimer with OH group on oxygen bridge. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

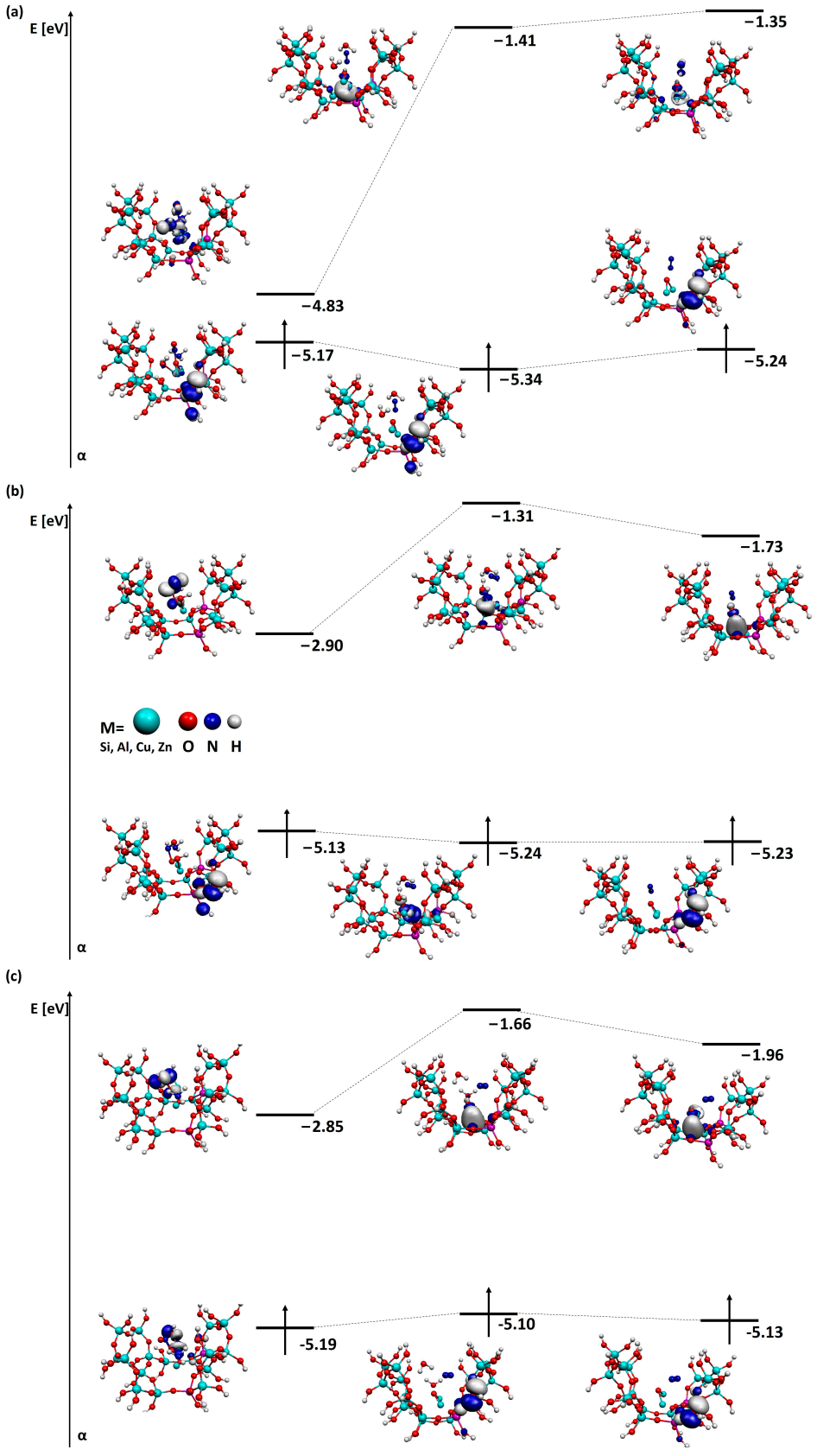

Figure S3. SOMO and LUMO orbitals for three most important steps in deNOx mechanism for a) Cu-O-Cu with OH group on copper; b) for Cu-O-Zn with OH group on copper and c) for Cu-O-Zn with OH group on zinc.

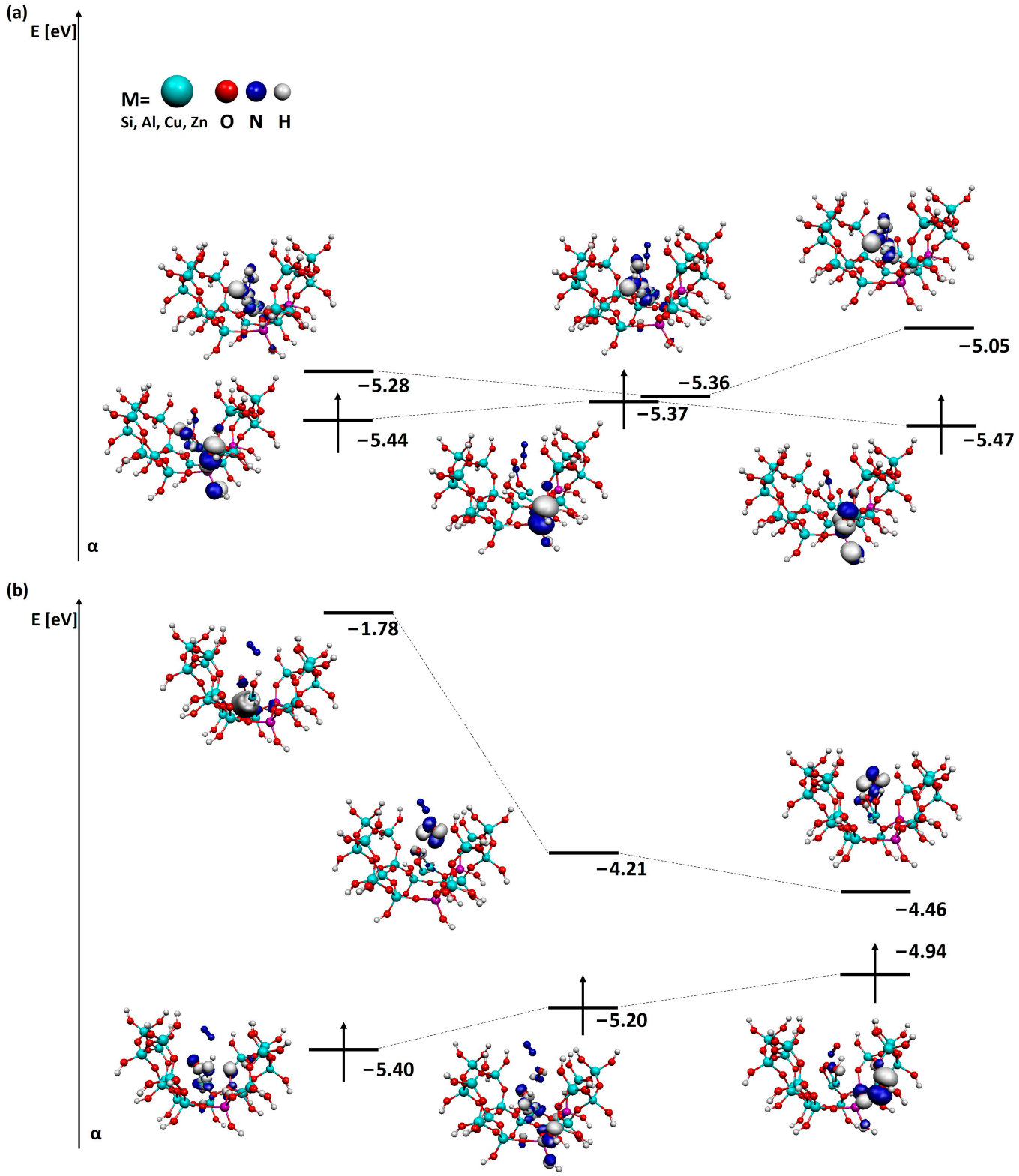

Figure S4. SOMO and LUMO orbitals for three most important steps in deN_2O mechanism for Cu-O-Cu with OH group on copper: a) starts with NO; b) starts with N_2O.

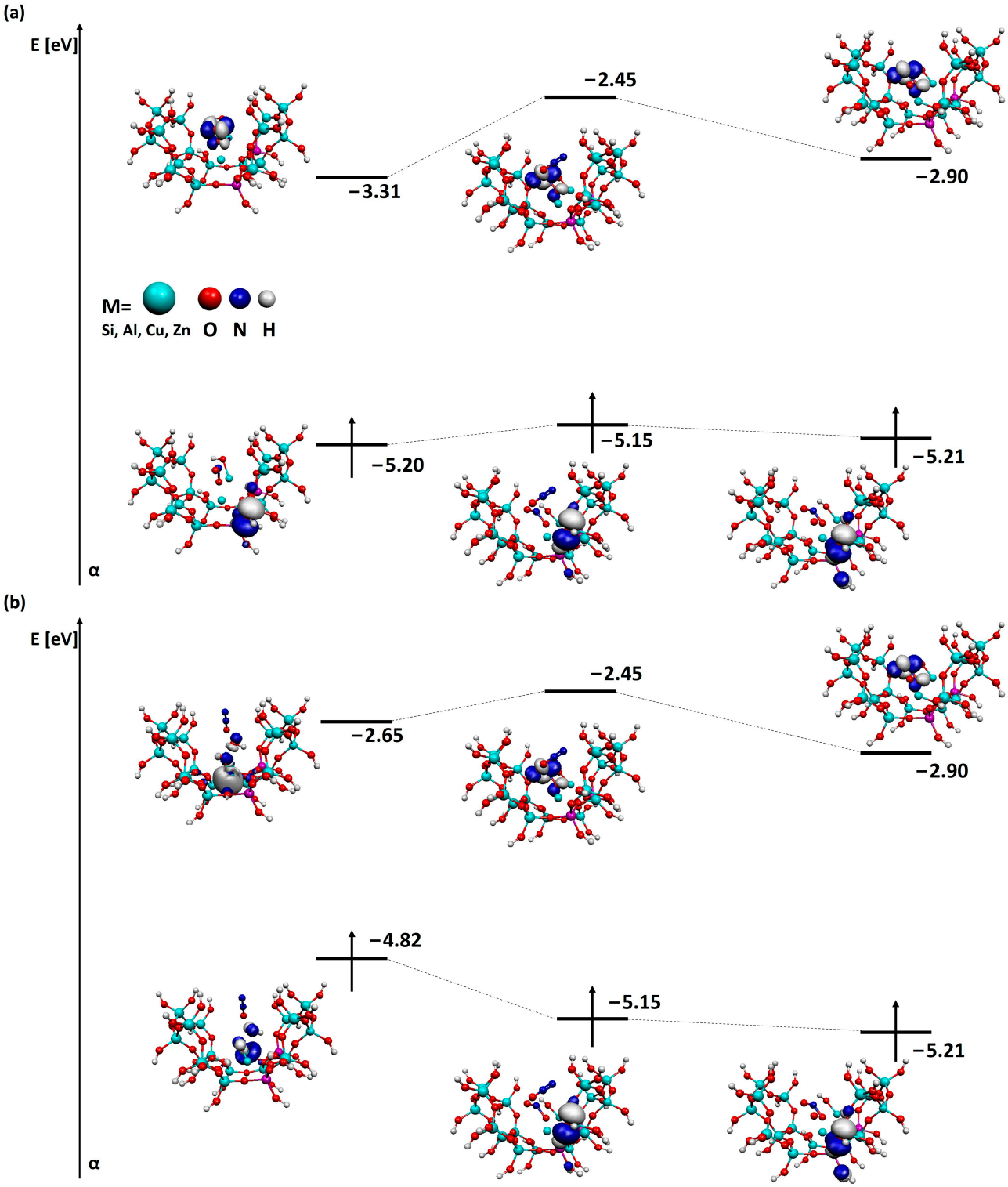

Figure S5. SOMO and LUMO orbitals for three most important steps in deN_2O mechanism for Cu-O-Zn with OH group on copper: a) starts with NO; b) starts with N_2O.

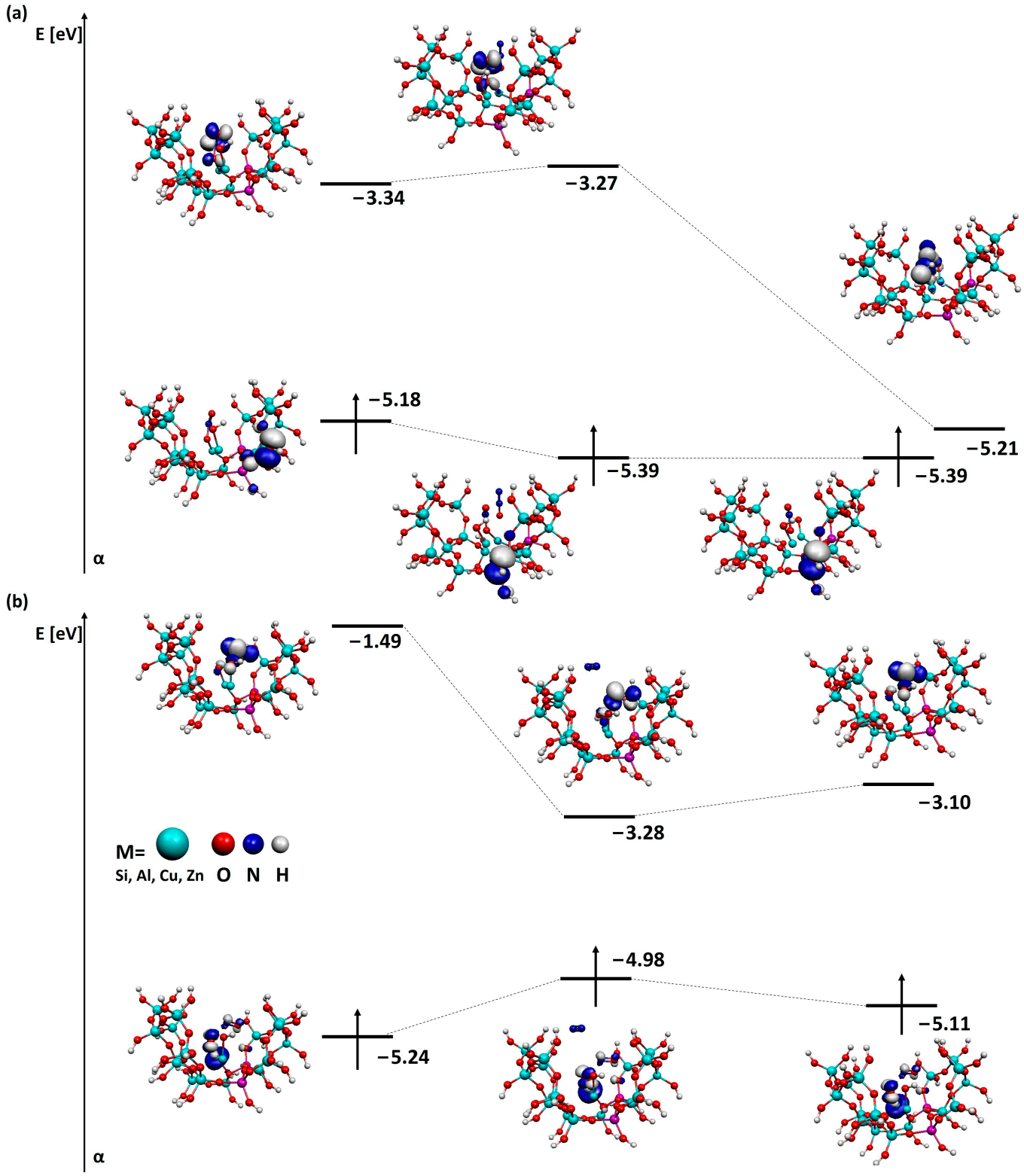

Figure S6. SOMO and LUMO orbitals for three most important steps in deN_2O mechanism for Cu-O-Zn with OH group on zinc: a) starts with NO; b) starts with N_2O.

Table S1. Energies for different structure and considered multiplicities for deNOx process.

Structure	Multiplicity	Energy [H]
A1	**1**	**-14593.383**
	3	-14593.382
	5	-14593.417
	7	-14593.324
	9	-14593.195
A2	1	-14722.707
	3	-14722.715
	5	-14722.739
	7	-14722.708
	9	-14722.609
A3	1	-14779.355
	3	-14779.376
	5	-14779.364
	7	-14779.323
A4	1	-14779.291
	3	-14779.279
	5	-14779.310
	7	-14779.296
	9	-14779.171
A5	1	-14702.853
	3	-14702.791
	5	-14702.875
	7	not converged
	9	-14702.710

Structure	Multiplicity	Energy [H]	Structure	Multiplicity	Energy [H]
B1	2	-14592.774	C1	2	-14592.774
	4	-14592.780		4	-14592.780
	6	-14592.780		6	-14592.780
	8	-14592.675		8	-14592.675
B2	1	-14668.610	C2	1	-14668.543
	3	-14668.610		3	-14668.591
	5	-14668.624		5	-14668.587
	7	-14668.602		7	-14668.586
	9	-14668.462		9	-14668.473
B3	2	-14855.155	C3	2	-14855.140
	4	-14855.158		4	-14855.157
	6	-14855.169		6	-14855.109
	8	-14855.151		8	-14855.066
	10	-14854.967		10	-14855.030
B4	2	not converged	C4	2	-14855.119
	4	-14855.223		4	-14855.068
	6	-14855.226		6	-14855.216
	8	-14855.075		8	-14854.995
	10	-14854.977		10	-14854.970
B5	2	-14702.311	C5	2	-14702.315
	4	-14702.334		4	-14702.325
	6	-14702.335		6	-14702.333
	8	-14702.239		8	-14702.136
	10	-14702.084		10	-14702.023

Table S2. Energies for different structure and considered multiplicities for deN$_2$O process.

Structure	Multiplicity	Energy [H]	Structure	Multiplicity	Energy [H]
D1	2	-14592.774	E1	1	-14593.383
	4	-14592.780		3	-14593.382
	6	-14592.780		5	-14593.417
	8	-14592.675		7	-14593.324
D2	2	-14777.477		9	-14593.195
	4	-14777.491	E2	1	-14722.707
	6	-14777.503		3	-14722.715
	8	-14777.401		5	-14722.739
	10	-14777.351		7	-14722.708
D3	1	-14907.470		9	-14722.609
	3	-14907.478	E3	1	not converged
	5	-14907.478		3	not converged
	7	-14907.431		5	-14907.434
	9	-14907.365		7	not converged
D4	1	not converged		9	not converged
	3	-14797.885	E4	1	-14797.828
	5	-14797.892		3	-14797.882
	7	-14797.876		5	-14797.864
	9	-14797.852		7	-14797.877
				9	-14797.831

Structure	Multiplicity	Energy [H]	Structure	Multiplicity	Energy [H]
F1	1	-14668.610	G1	1	-14668.610
	3	-14668.610		3	-14668.610
	5	-14668.624		5	-14668.624
	7	-14668.602		7	-14668.602
	9	-14668.462		9	-14668.462
F2	1	-14853.318	G2	2	-14798.560
	3	-14853.332		4	-14798.571
	5	-14853.353		6	-14798.575
	7	-14853.332		8	-14798.544
	9	-14853.288		10	-14798.448
F3	2	-14983.280	G3	2	-14983.269
	4	-14983.283		4	-14983.287
	6	-14983.287		6	-14983.298
	8	not converged		8	-14983.260
	10	-14983.208		10	-14983.164
F4	2	-14873.691	G4	2	-14873.712
	4	not converged		4	-14873.727
	6	-14873.709		6	-14873.733
	8	-14873.719		8	-14873.724
	10	-14873.635		10	-14873.649
	12	-14873.477			

Structure	Multiplicity	Energy [H]	Structure	Multiplicity	Energy [H]
H1	1	-14668.543	I1	1	-14668.543
	3	-14668.591		3	-14668.591
	5	-14668.587		5	-14668.587
	7	-14668.586		7	-14668.586
	9	-14668.473		9	-14668.473
H2	1	-14853.289	I2	2	-14798.554
	3	-14853.304		4	-14798.558

	5	-14853.308		6	-14798.554
	7	-14853.305		8	-14798.514
	9	-14853.277		10	-14798.434
H3	2	-14983.213	I3	2	-14983.267
	4	-14983.259		4	not converged
	6	-14983.252		6	not converged
	8	-14983.214		8	-14983.182
	10	-14983.173		10	-14983.162
H4	2	-14873.750	I4	2	not converged
	4	-14873.748		4	-14873.730
	6	-14873.742		6	-14873.732
	8	-14873.718		8	-14873.631
	10	-14873.621		10	-14873.593

Energy difference between stages in mechanism with bridged OH group were calculated as follows:

A. Energy for deNOx process on Cu-O-Cu dimer with OH group on bridged oxygen (same for B diagram):

1. Energy difference between stage A1 and A0:

$$E_{diff} = E_{A1} - E_{A0} - 2E_{NO2}\ [eV]$$

2. Energy difference between stage A1' and A1 (transition state):

$$E_{diff} = E_{A1'} - E_{A1}\ [eV]$$

3. Energy difference between stage A1'' and A1':

$$E_{diff} = E_{A1''} - E_{A1'}\ [eV]$$

4. Energy difference between stage A3 and A2:

$$E_{diff} = E_{A3} - E_{A2} - E_{NH3}\ [eV]$$

5. Energy difference between stage A4 and A3:

$$E_{diff} = E_{A4} - E_{A3}\ [eV]$$

6. Energy difference between stage A5 and A4:

$$E_{diff} = E_{A5} - E_{A4} + E_{H2O}\ [eV]$$

7. Energy difference between stage A1 and A5:

$$E_{diff} = E_{A1} - E_{A5} + E_{N2}\ [eV]$$

B. Energy for deNOx process on Cu-O-Cu dimer with OH group on one of the metal atom in dimer:

1. Energy difference between stage C2 and C1 (same for D and E diagrams):

$$E_{diff} = E_{C2} - E_{C1} - E_{NO} - E_{NH3}\ [eV]$$

2. Energy difference between stage C3 and C2 (same for D and E diagrams):

$$E_{diff} = E_{C3} - E_{C2}\ [eV]$$

3. Energy difference between stage C4 and C3 (same for D and E diagrams):

$$E_{diff} = E_{C4} - E_{C3} + 2E_{H2O}\ [eV]$$

4. Energy difference between stage C5 and C4 (same for D and E diagrams):

$$E_{diff} = E_{C5} - E_{C4} + E_{N2}\ [eV]$$

C. Energy for deN₂O process on Cu-O-Cu dimer with OH group on bridged oxygen (start with NO adsorption):

1. Energy difference between stage A1 and A0:

$$E_{diff} = E_{A1} - E_{A0} - 2E_{NO2}\ [eV]$$

2. Energy difference between stage A1' and A1 (transition state):

$$E_{diff} = E_{A1'} - E_{A1}\ [eV]$$

3. Energy difference between stage A1'' and A1':

$$E_{diff} = E_{A1''} - E_{A1'}\ [eV]$$

4. Energy difference between stage F3 and F2 (same for G diagram):

$$E_{diff} = E_{F3} - E_{F2} - E_{N2O}\ [eV]$$

5. Energy difference between stage F4 and F3 (same for G diagram):

$$E_{diff} = E_{F4} - E_{F3} + E_{N2}\ [eV]$$

6. Energy difference between stage F1 and F4 (same for G diagram):

$$E_{diff} = E_{F1} - E_{F4} + E_{NO2}\ [eV]$$

D. Energy for deN₂O process on Cu-O-Cu dimer (start with N₂O adsorption):

1. Energy difference between stage H2 and H1 (same for I diagram):

$$E_{diff} = E_{H2} - E_{H1} - E_{N2O}\ [eV]$$

2. Energy difference between stage H3 and H2 (same for I diagram):

$$E_{diff} = E_{H3} - E_{H2} - E_{NO}\ [eV]$$

3. Energy difference between stage H4 and H3 (same for I diagram):

$$E_{diff} = E_{H4} - E_{H3} + E_{N2}\ [eV]$$

4. Energy difference between stage H5 and H4 (same for I diagram):

$$E_{diff} = E_{H5} - E_{H4} + E_{NO2}\ [eV]$$

E. Energy for deN₂O process on Cu-O-Cu dimer with OH group on one of the metal atom in dimer (start with NO adsorption):

1. Energy difference between stage J2 and J1 (same for L and M diagrams):

$$E_{diff} = E_{J2} - E_{J1} - E_{NO}\ [eV]$$

2. Energy difference between stage J3 and J2 (same for L and M diagrams):

$$E_{diff} = E_{J3} - E_{J2} - E_{N2O}\ [eV]$$

3. Energy difference between stage J4 and J3 (same for L and M diagrams):

$$E_{diff} = E_{J4} - E_{J3} + E_{N2}\ [eV]$$

4. Energy difference between stage J5 and J4 (same for L and M diagrams):

$$E_{diff} = E_{J5} - E_{J4} + E_{NO2}\ [eV]$$

F. Energy for deN₂O process on Cu-O-Cu dimer with OH group on one of the metal atom in dimer (start with N₂O adsorption):

1. Energy difference between stage K2 and K1 (same for N and O diagrams):

$$E_{diff} = E_{K2} - E_{K1} - E_{N2O}\ [eV]$$

2. Energy difference between stage K3 and K2 (same for N and O diagrams):

$$E_{diff} = E_{K3} - E_{K2} - E_{NO}\ [eV]$$

3. Energy difference between stage K4 and K3 (same for N and O diagrams):

$$E_{diff} = E_{K4} - E_{K3} + E_{N2}\ [eV]$$

4. Energy difference between stage K5 and K4 (same for N and O diagrams):

$$E_{diff} = E_{K5} - E_{K4} + E_{NO2}\ [eV]$$

Electron analysis

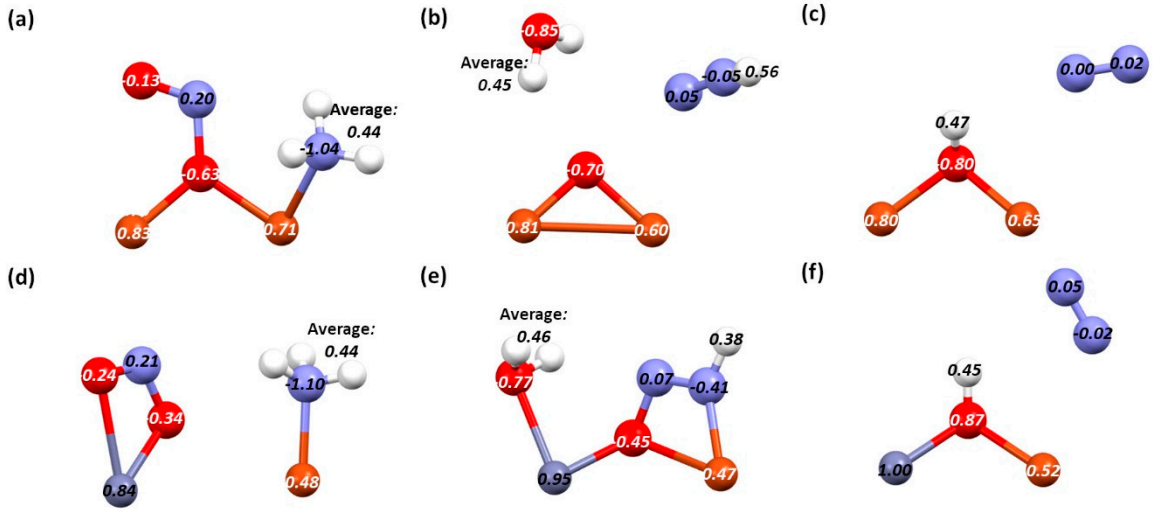

Figure S7. Ionicity for zeolite clinoptilolite structures from deNOx process: dimer Cu-O-Cu with OH group on bridged oxygen – a) step A3, b) step A4, c) step A5; dimer Cu-O-Zn with OH group on bridged oxygen – d) step B3, e) step B4, f) step B5. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

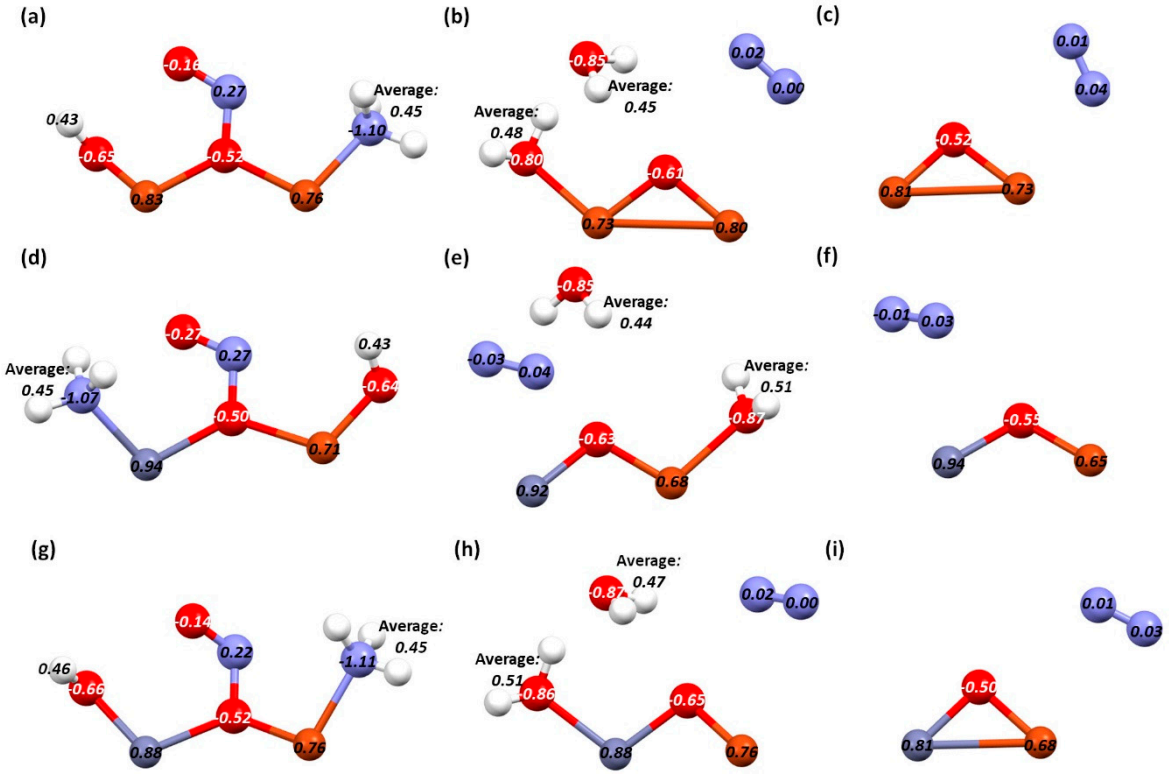

Figure S8. Ionicity for zeolite clinoptilolite structures from deNOx process: dimer Cu-O-Cu with OH group on copper – a) step C2, b) step C3, c) step C4; dimer Cu-O-Zn with OH group on copper – d) step D2, e) step D3, f) step D4 and dimer Cu-O-Zn with OH group on zinc – g) sstep E2, h) step E3 and i) step E4. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

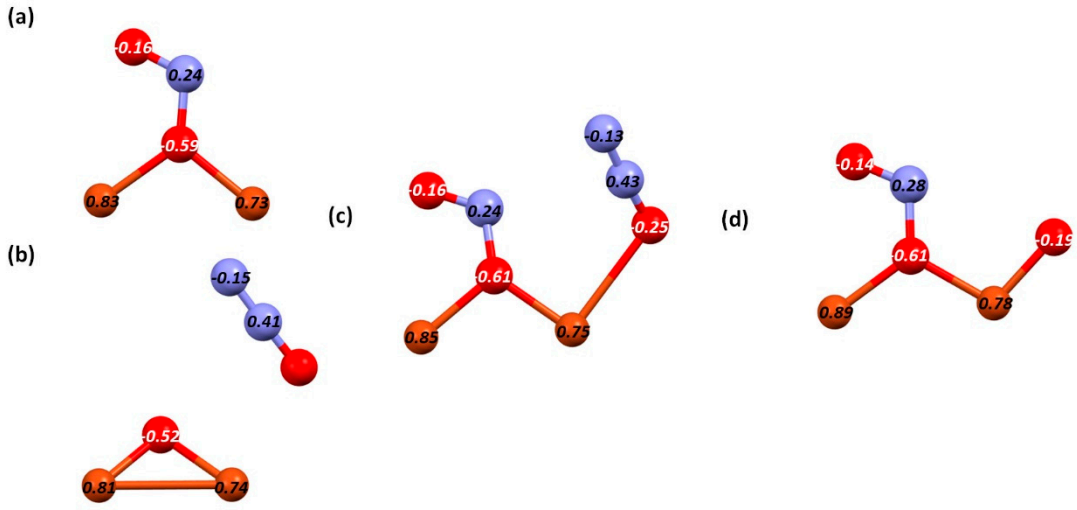

Figure S9. Ionicity for zeolite clinoptilolite structures from deN_2O process: dimer Cu-O-Cu with OH group on copper – a) step F2, b) step H2, c) step F3 (H3), d) step F4 (H4). The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen.

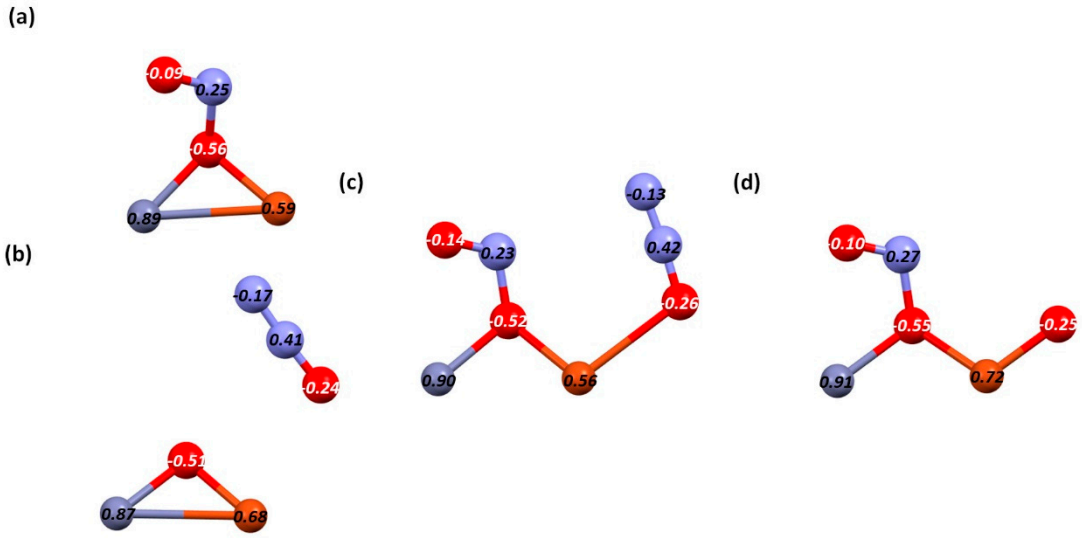

Figure S10. Ionicity for zeolite clinoptilolite structures from deN_2O process: dimer Cu-O-Zn with OH group on bridged oxygen– a) step G2, b) step I2, c) step G3 (I3), d) step G4 (I4). The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen.

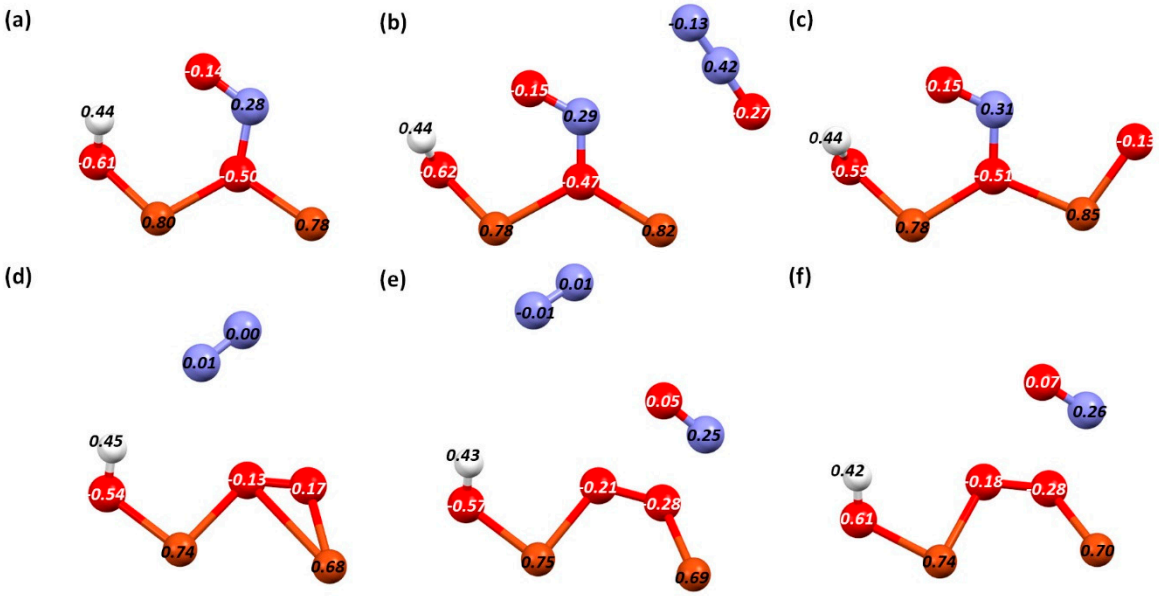

Figure S11 Ionicity for zeolite clinoptilolite structures from deN_2O process: dimer Cu-O-Cu with OH group on copper – a) step J2, b) step J3, c) step J4 when NO is first, d) step K2, e) step K3 and f) step K4 when N_2O is first. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

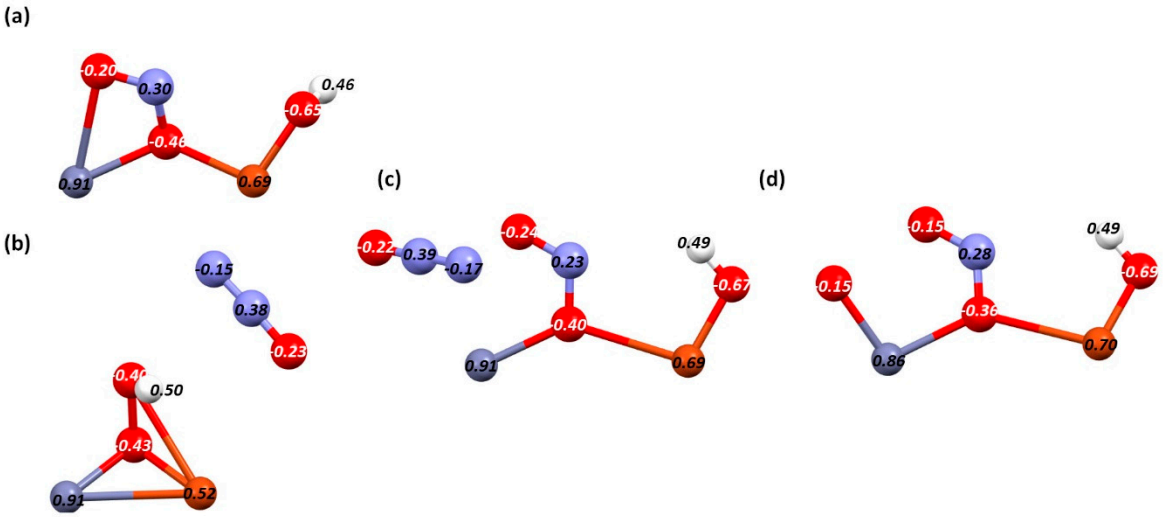

Figure S12. Ionicity for zeolite clinoptilolite structures from deN2O process: dimer Cu-O-Zn with OH group on copper – a) step L2, b) step N2, c) step L3 (N3) and d) step L4 (N4). The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

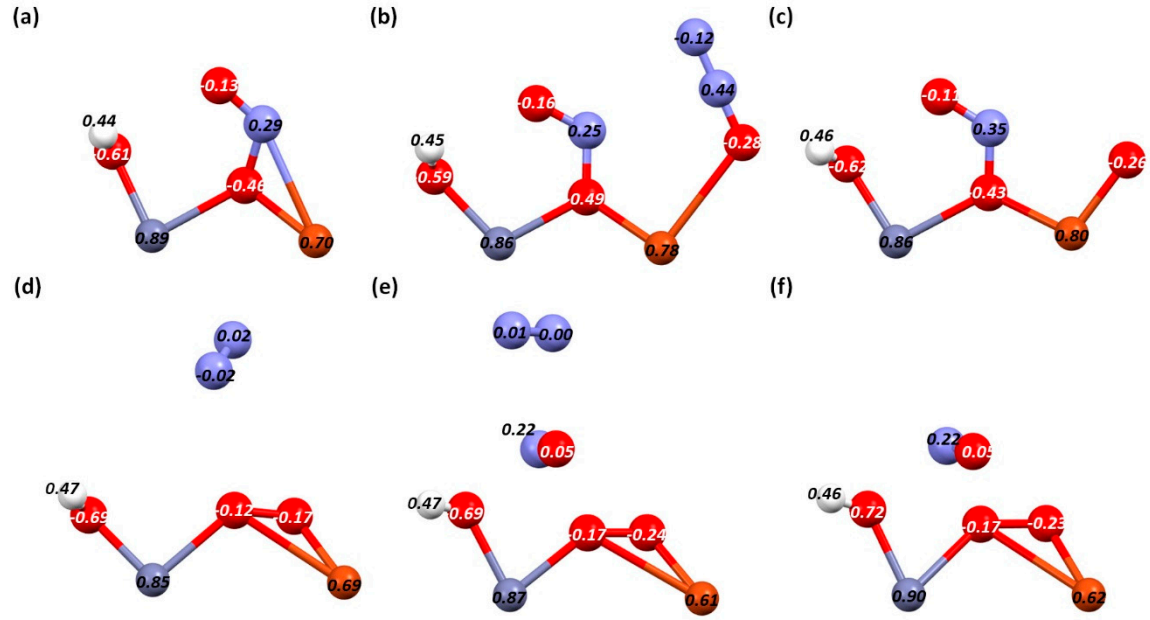

Figure S13. Ionicity for zeolite clinoptilolite structures from deN2O process: dimer Cu-O-Zn with OH group on zinc – a) step M2, b) step M3, c) step M4 when NO is first, d) step O2, e) step O3 and f) step O4 when N2O is first. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

Another important analysis to understand the mechanisms of the processes in more detail was the analysis of bond lengths and orders as well as charges. Bond lengths and orders are presented below (Fig. S14-S21).

Figure S14 summarises bond orders and length of the interacting NO2 molecules with metal dimers.

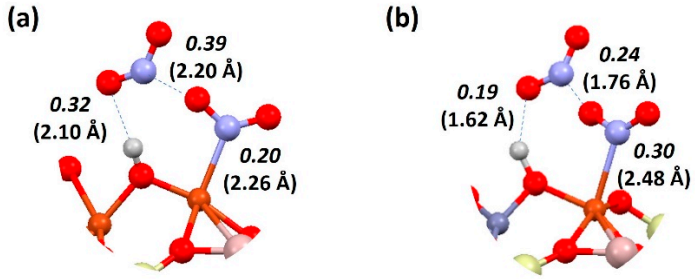

Figure S14. Bond order and length (in brackets) for the zeolite clinoptilolite structures from two molecule NO_2 adsorption: a) step A1 (see Figure 4), b) step B1 (see Figure 4). The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

Figure S15. shows a comparison of the most relevant steps in the deNOx process for systems with an OH group on bridged oxygen.

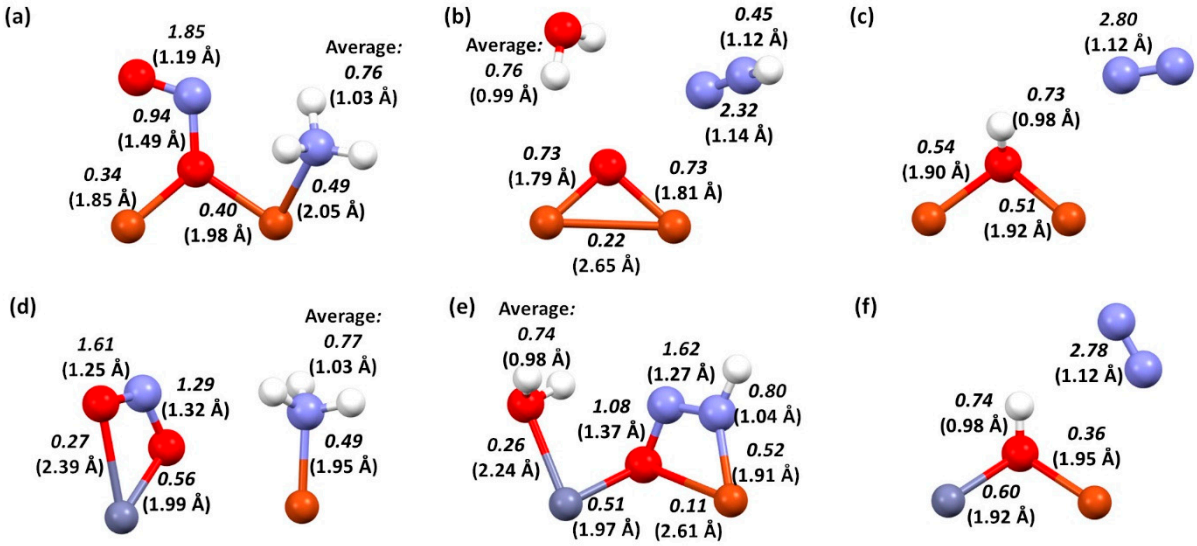

Figure S15. Bond order and length (in brackets) for the zeolite clinoptilolite structures from deNOx process: dimer Cu-O-Cu with OH group on bridged oxygen – a) step A3, b) step A4, c) step A5; dimer Cu-O-Zn with OH group on bridged oxygen – d) step B3, e) step B4, f) step B5. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

The stages shown are the coadsorption of NO and NH_3, the transformation and the desorption of the water molecule. Already at the first stage a significant change in the coadsorption mechanism takes place. In the case of the monometallic system (Fig. S15a), NO adsorbs on bridged oxygen, NH_3 on copper and the dimer structure is not disrupted. In contrast to the bimetallic system (Fig. S15d), where the attachment of NO and NH_3 causes Cu to dissociate from the bridging oxygen, additionally a bond is also formed between the oxygen with NO and zinc. In the next step, a water molecule and a nitrogen molecule with an additional hydrogen atom are formed in both cases. In the first case (Fig. S15b), both H_2O and -N=NH are detached and the copper atoms approach each other and form a bond, and the bonds of the copper atoms with oxygen are also shortened (from 1.85 Å and 1.98 Å to 1.79 Å and 1.81 Å, respectively). In the case of the bimetallic dimer (Figure S15e), neither the water nor the diazenyl (N=NH) molecule detaches from the catalyst. At binding zinc to water, the bonding order is relatively low (0.26) while a higher bonding order is formed by copper and oxygen bridging with the diazenyl molecule (0.52 and 1.08, respectively). This is shown in the energy that is released during the desorption

of water in the next step. The first system gives off more of it than the second one. In the final stage, the two systems show complete similarity.

In the next visualisation (Fig. S16), the analysis of the three most important steps in the deNOx process for systems with an OH group on one of the metals can be followed.

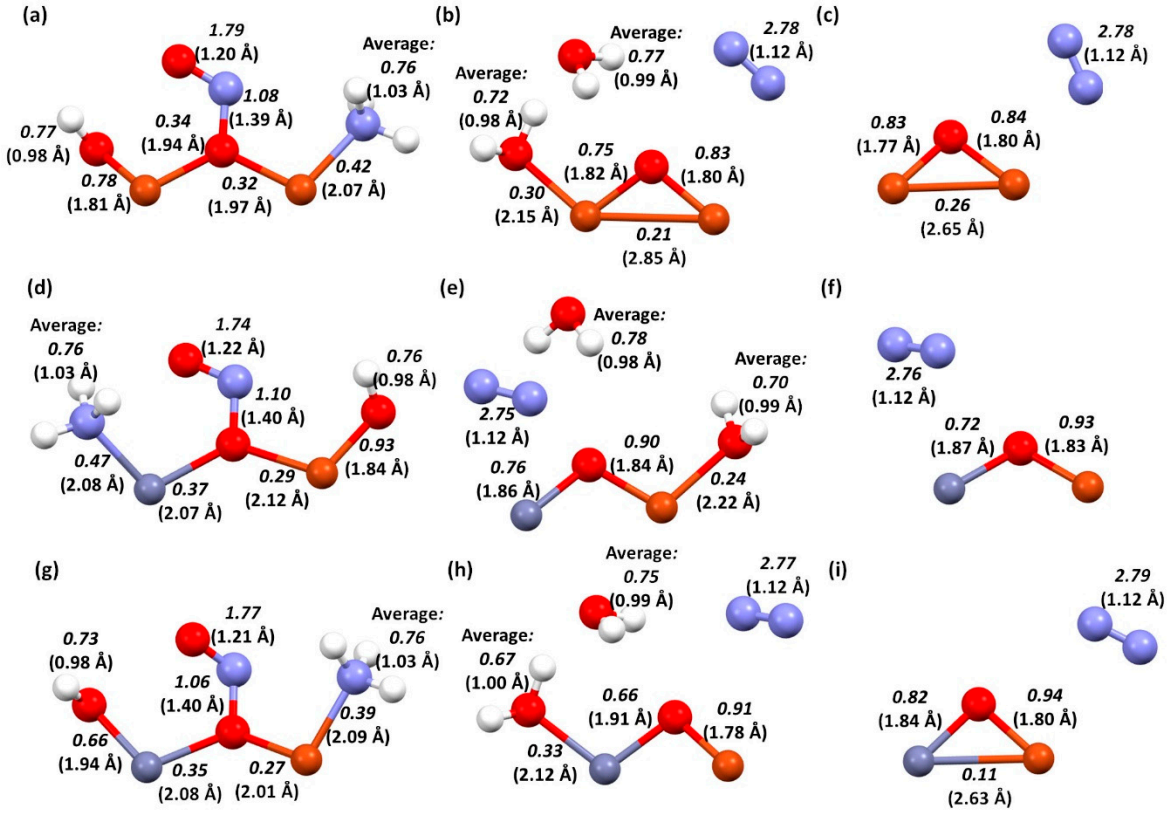

Figure S16. Bond order and length (in brackets) for the zeolite clinoptilolite structures from deNOx process: dimer Cu-O-Cu with OH group on copper – a) step C2, b) step C3, c) step C4; dimer Cu-O-Zn with OH group on copper – d) step D2, e) step D3, f) step D4 and dimer Cu-O-Zn with OH group on zinc – g) step E2, h) step E3, and i) step E4. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

NO adsorbs on bridged oxygen, while NH_3 locates on a metal that is free of an OH group. The order of bonding is very similar in all cases for nitrogen bonding with NO and bridged oxygen. Differences are apparent for the OH bond (the strongest for Cu-O-Zn with an OH group on copper 0.93, the weakest for Cu-O-Zn with an OH group on zinc 0.66). In the next step, the differences are not very significant. In each case, the N_2 molecule and the H_2O molecule break away, and one H_2O molecule (the one formed with the help of the OH group) is still adsorbed on the catalyst. In the case of the system with a bridged OH group on Cu-O-Cu, the two copper atoms also come together and form a bond. After the desorption of water molecules, a similar pattern for the Cu-O-Zn structure with an OH group on zinc was observed.

The most relevant steps for the deN_2O process were then analysed. Here, the adsorption step of one NO or N_2O molecule was considered first, followed by the coadsorption and desorption of the N_2 molecule (Fig. S17-S21).

As mentioned earlier, the adsorption of the N_2O molecule initially has little effect on the structure, only causing the formation of a bond between the copper atoms (Fig. S17b).

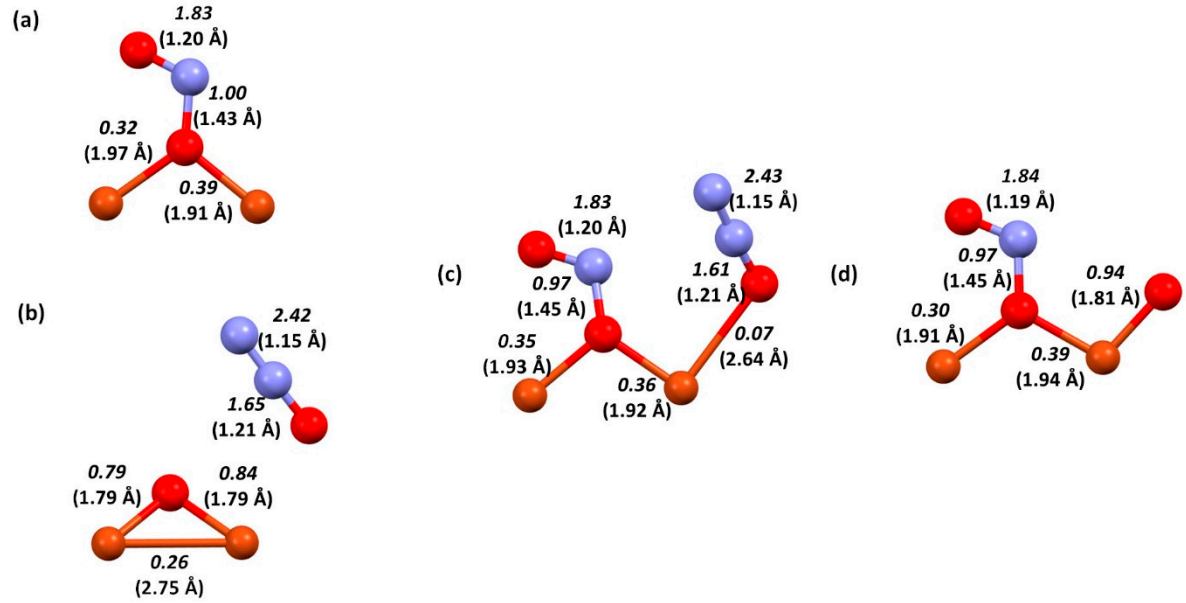

Figure S17. Bond order and length (in brackets) for the zeolite clinoptilolite structures from deN_2O process: dimer Cu-O-Cu with OH group on bridged oxygen – a) step F2, b) step H2, c) step F3 (H3), d) step F4 (H4). The atoms color: orange – copper, gray – zinc, pink – aluminum, yellow – silica, red – oxygen.

In contrast, the coadsorption of NO and N_2O results in the attachment of both molecules, which leads to the conclusion that the order does not matter in the case of the Cu-O-Cu structure with an OH group on bridged oxygen. In the next step, N_2 desorbs from the catalyst surface with the need to deliver energy to the system.

Next, a bimetallic system with an OH group on bridged oxygen was analysed. Here, as in the previous case, the presence of N_2O in the catalytic system is not important until NO is attached to the catalyst structure (Figure S18). This type of solution can be very advantageous for industrial applications due to the fact that the gas containing both NO and N_2O can successfully flow. This type of catalyst also performs well in the deNOx processes, making this type of catalyst quite universal in nitrogen oxide reduction processes.

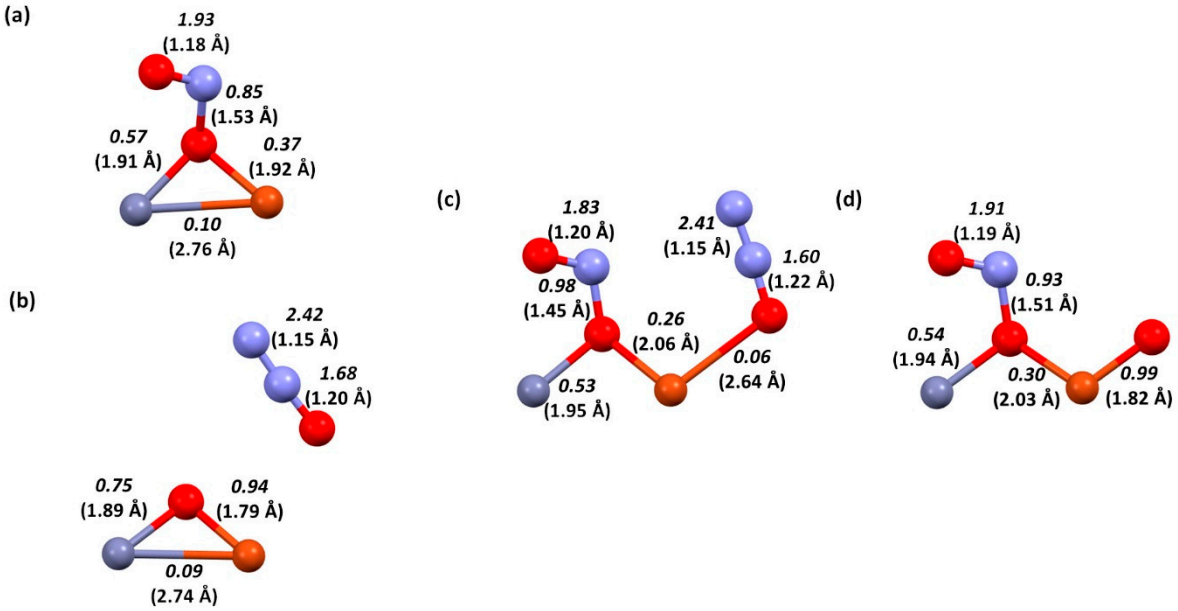

Figure S18. Bond order and length (in brackets) for zeolite clinoptilolite structures from deN_2O process: dimer Cu-O-Zn with OH group on bridged oxygen– a) step G2, b) step I2, c) step G3 (I3), d) step G4 (I4). The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen.

In the case of this system, the desorption of N_2 and NO_2 requires an energy effort, which makes it appear unfavourable; however, this effort is not very large and the benefit of being able to use it successfully in the deNOx and deN_2O processes may significantly overweigh the costs associated with the additional energy spent during the desorption of the nitrogen molecule.

The next system analysed is a monometallic dimer with an OH group on copper (Figure S19). The order of adsorption of NO and N_2O has a significant effect on the mechanism. After NO adsorbs on bridged oxygen, N_2O does not adsorb at all. This may be due to the competition of NO and N_2O for space on the bridging oxygen (Fig 19d). The affinity of NO for the structure is much higher than that of N_2O, so it adsorbs first and blocks the adsorption of N_2O. If there is no nitric oxide molecule in the system, it can be seen that N_2O adsorbs on the surface, dissociates the N_2 molecule, and the oxygen atom enters between one of the copper atoms and the bridging oxygen to form bonds with both the bridging oxygen and the two copper atoms.

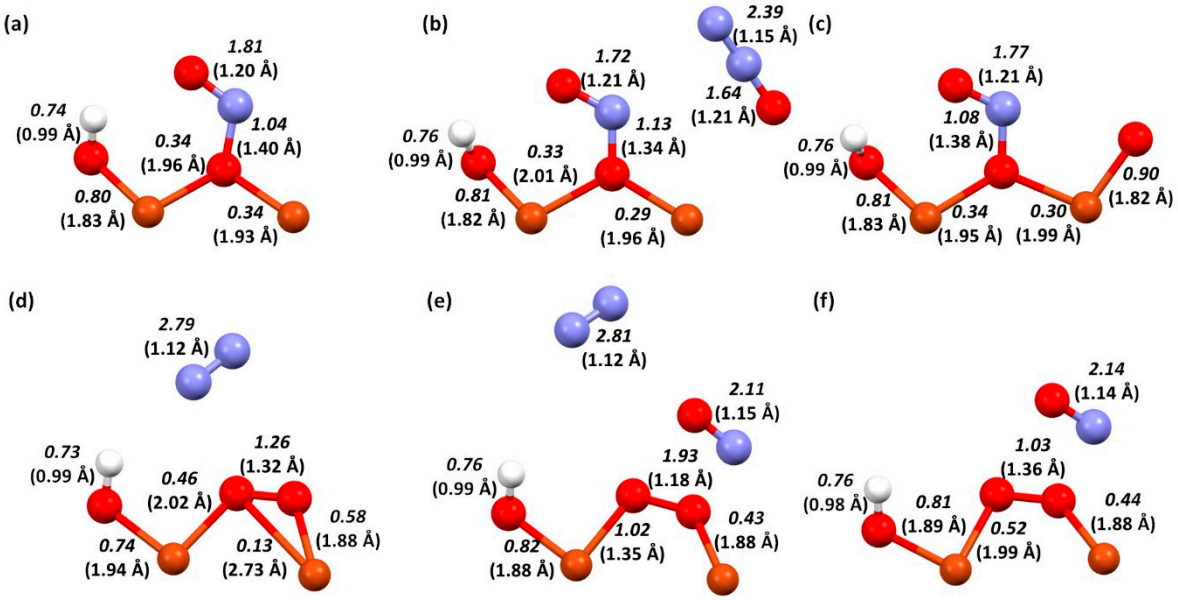

Figure 19. Bond order and length (in brackets) for the zeolite clinoptilolite structures from deN_2O process: dimer Cu-O-Cu with OH group on copper – a) step J2, b) step J3, c) step J4 when NO is first, d) step K2, e) step K3 and f) step K4 when N_2O is first. The atoms color: orange – copper, gray – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

The deN_2O process is very favorable on a monometallic system with the OH group on the copper atom, but the fact that it absolutely requires contact with N_2O before NO can be problematic in manufacturing processes where these gases occur equivalently.

The next system is a Cu-O-Zn bimetallic structure with an OH group on copper. In the case of the NO adsorption, we can observe a similarity to the system where NO and NH_3 adsorb on the bimetallic structure; however, in this case there is no bond breaking between the bridged oxygen and copper (Fig. S20a).

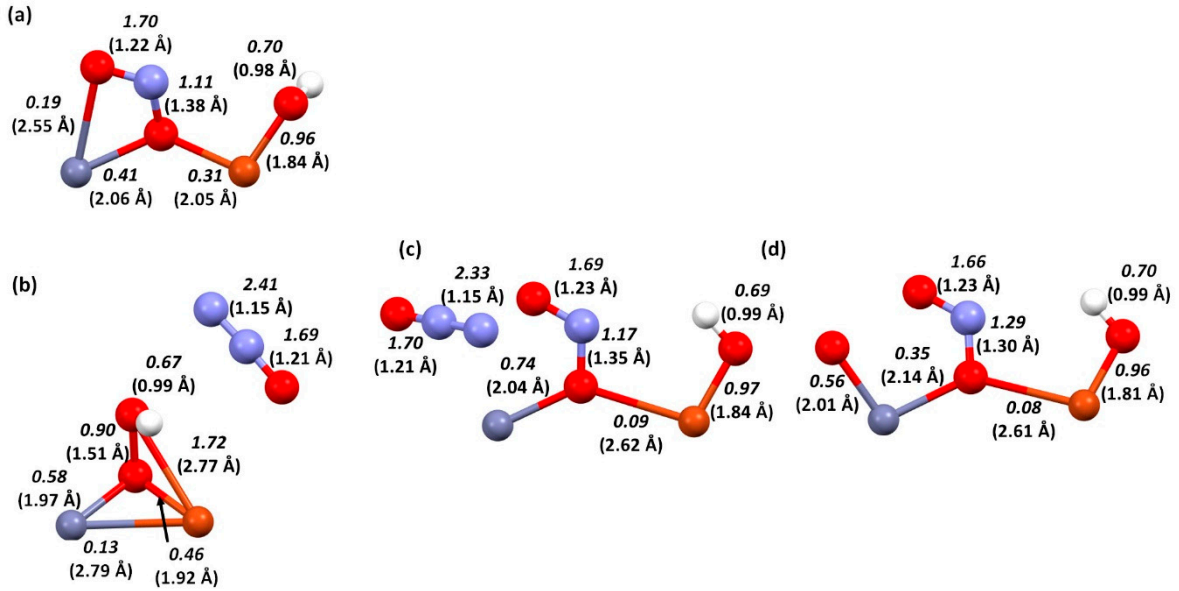

Figure S20. Bond order and length (in brackets) for the zeolite clinoptilolite structures from deN2O process: dimer Cu-O-Zn with OH group on copper – a) step L2, b) step N2, c) step L3 (N3) and d) step L4 (N4). The atoms color: orange – copper, gray – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

What is important here is that the presence of N_2O interacts with the structure, causing displacement of the OH group and its additional attachment to the bridging oxygen. With the addition of NO, the system further lowers its energy and N_2O does not attach after NO adsorption, thus it was decided to combine these steps. The order of adsorption for this structure is not important, and desorption of N_2 requires energy investment.

The last system shown is a bimetallic dimer with an OH group on zinc (Figure S21). In contrast to the previous system, the order is very important in how the system reacts.

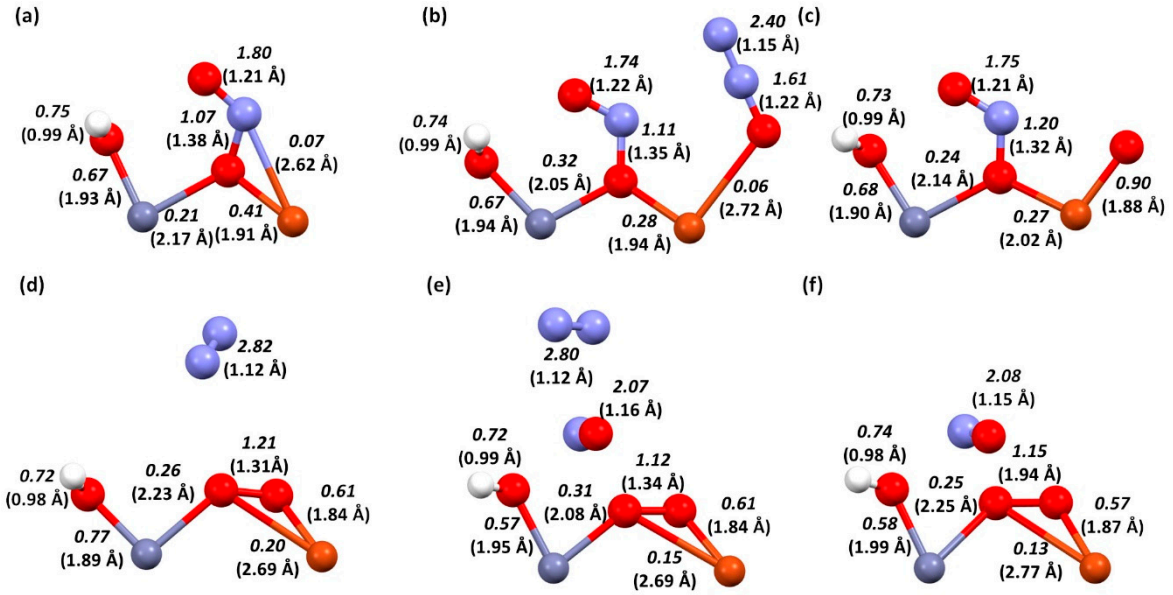

Figure S21. Bond order and length (in brackets) for the zeolite clinoptilolite structures from deN2O process: dimer Cu-O-Zn with OH group on zinc – a) step M2, b) step M3, c) step M4 when NO is first, d) step O2, e) step O3 and f) step O4 when N_2O is first. The atoms color: orange – copper, gray-blue – zinc, pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.

In the case of NO adsorption, first N_2O adsorbs on the copper and then the nitrogen molecule detaches. Apart from the NO adsorption, the remaining steps are endothermic. In the case of N_2O adsorption, the N_2 molecule detaches first, and the oxygen from the N_2O binds to the entire system between the zinc and the bridging oxygen. Despite the relatively energetically favourable deN_2O process, where N_2O adsorbs first, the fact that NO has a significantly higher affinity for the catalyst effectively excludes it from use in industrial processes.

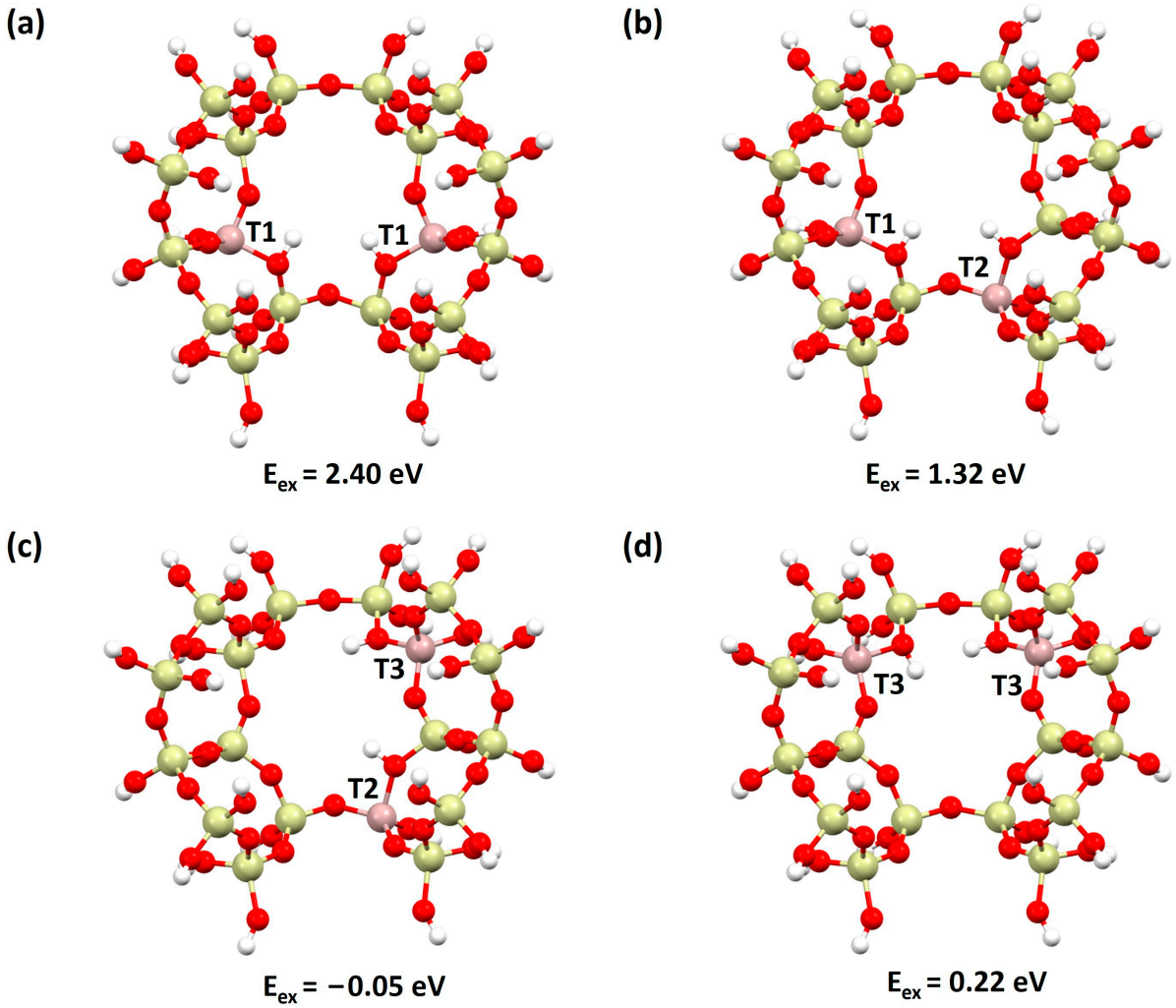

Figure S22. Clinoptilolite structure with two aluminium atom in different T-position with exchange energy below structure: a) aluminium on T1-T1, b) aluminium on T1-T2, c) aluminium on T2-T3 and d) aluminium on T3 and T3. The atoms color: pink – aluminum, yellow – silica, red – oxygen, white – hydrogen.