

Theoretical Study of Nitric Oxide Adsorption and Dissociation on Copper-Exchanged Zeolites SSZ-13 and SAPO-34: The Impact of Framework Acid-Base Properties

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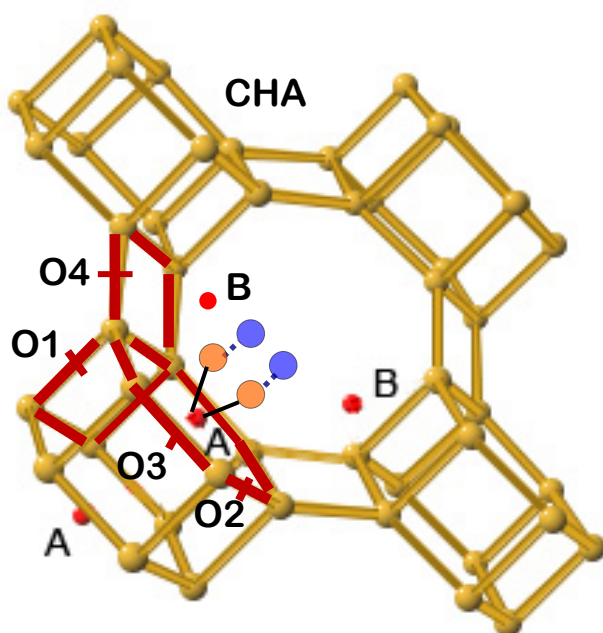


Figure 1S. The ONIOM model for adsorption of 2 NO molecules in Cu-SAPO-34 and Cu-SSZ-13. Framework oxygen and cation site notation follows refs. 14 and 21 (see main text). The high-layer, described by DFT is marked with red and the low layer is light brown; it is described by the semi-empirical PM6 method. Only tetrahedral framework atoms are displayed; the bridging framework oxygen atoms lie on the vertices connecting tetrahedral atoms.

Basis sets for the DFT-ONIOM and DFT-PBC calculations

Framework atoms (oxygen, silicon, aluminium, and for SAPO-34, also phosphorus) are described by the standard 6-31G(d) basis set. In terms of atomic orbitals, it reads as O [3s6p5d] Si, Al, P [4s9p5d]. Pure d-functions have been used. For the adsorption complex and the Brønsted acid site additional polarization functions were included and the basis set in terms of local atomic orbitals reads as Cu [9s15p15d14f9g], N, O [3s6p5d7f] and H[2s3p].

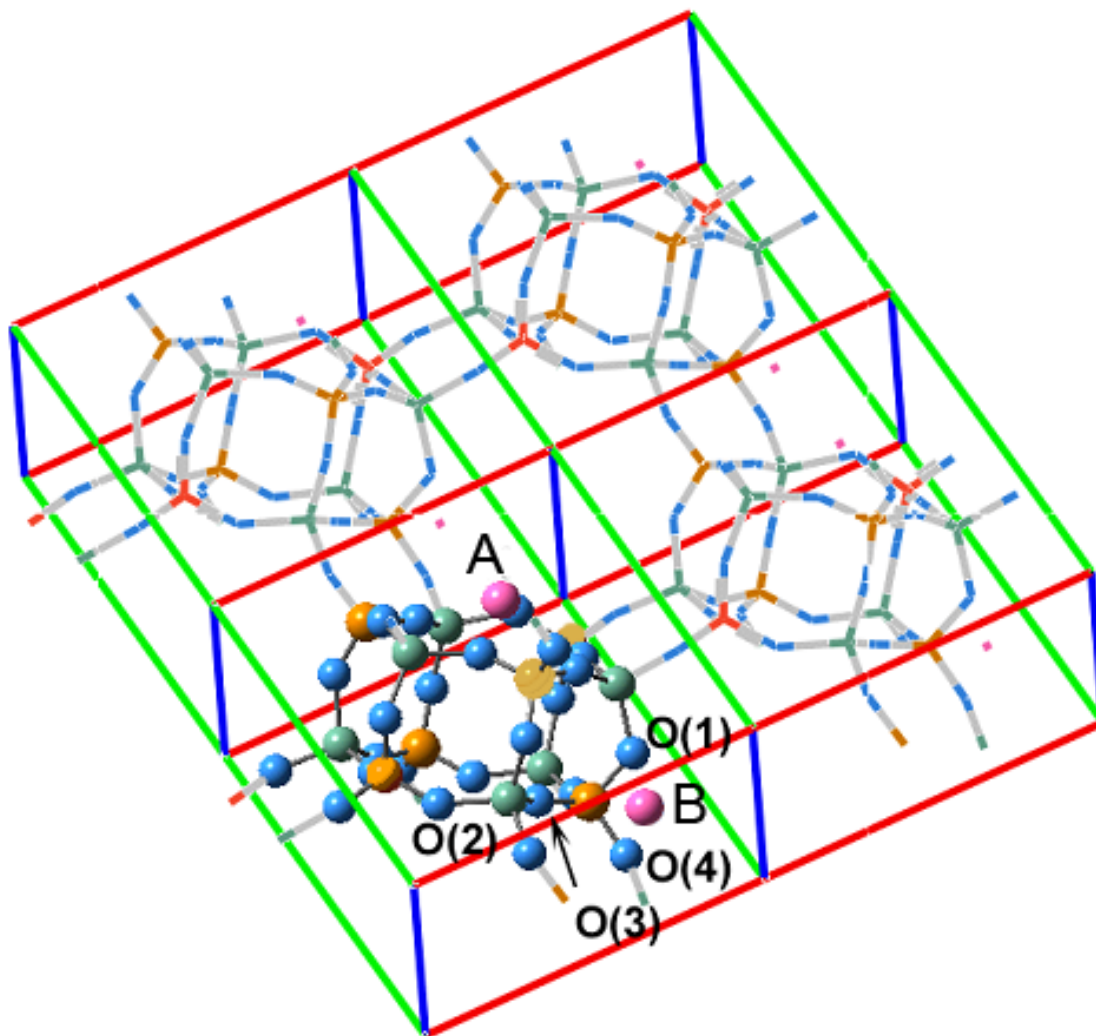


Figure 2S. The CHA unit cell with oxygen and cation site notation according to ref. 14, 21. The D6R of SAPO-34 with oxygen-bridged Si, Al and P atoms is outlined. Extraframework cations are denoted by pink large balls, Si atoms – light brown, Al – green, P – orange, oxygen atoms – blue.

The unit cell volume of Cu(II) and Cu(I) exchanged SSZ-13 is the same, 833.6 \AA^3 . Upon adsorption of dinitrosyls it increases to 844.4 \AA^3 for oxygen-end binding (hyponitrite) and to 846.7 \AA^3 for nitrogen-binding. For Cu-SAPO-34 unit cell volume is slightly larger, 845.3 \AA^3 and it increases by adsorption of dinitrosyls to 851.5 \AA^3 .

Table 1S: Selected Bond Lengths (Å) in Cu-SAPO-34 and Cu-SSZ-13 with Brønsted acid sites at Different Oxygen Atoms (O1, O2, O3, O4, as shown in Figure 2S); Relative Stability of the Acid Sites.

Acid Site	R _{Al-O} , Å	R _{Si-O} , Å	R _{O-H} , Å	ΔE, kJ mol ⁻¹
SAPO-34	PBC			
Cu ⁺ in 6MR				
O1H	1.859	1.780	0.977	0.0
O2H	1.862	1.780	0.980	8.0
O3H	1.847	1.812	1.011	47.8
O4H	1.875	1.777	0.982	13.4
SAPO-34	ONIOM			
Cu ⁺ in 6MR				
O1H	1.886	1.773	0.988	0.0
O2H	1.898	1.775	0.994	9.7
O3H	1.876	1.791	1.065	65.8
O4H	1.887	1.761	0.998	12.6
SSZ-13				
Cu ⁺ in 6MR				
PBC				
O1H AlO(SiO)Al ^a	1.875	1.747	0.978	0.0
O1H AlO(SiO)2Al	1.878	1.750	0.979	7.5
O2H AlO(SiO)2Al	1.880	1.750	0.981	50.2
O2H AlO(SiO)Al	1.883	1.748	0.983	57.8
O3H	1.869	1.759	0.990	142.8
O4H	1.881	1.762	0.987	118.0
SSZ-13				
Cu ⁺ in 6MR				
ONIOM				
O1H	1.949	1.733	0.966	0.0

AIO(SiO)Al				
O1H	1.950	1.730	0.967	4.2
AIO(SiO)2Al				
O2H	1.951	1.731	0.969	62.3
AIO(SiO)2Al				
O2H	1.953	1.734	0.968	65.1
AIO(SiO)Al				
O3H	1.950	1.743	0.974	137.1
O4H	1.961	1.737	0.970	92.4

^a – ordering of the framework negative charges within the unit cell, which corresponds to a single D6R: Al-O-Si-O-Al (closely spaced); Al-O-Si-O-Si-O-Al (maximum separation).

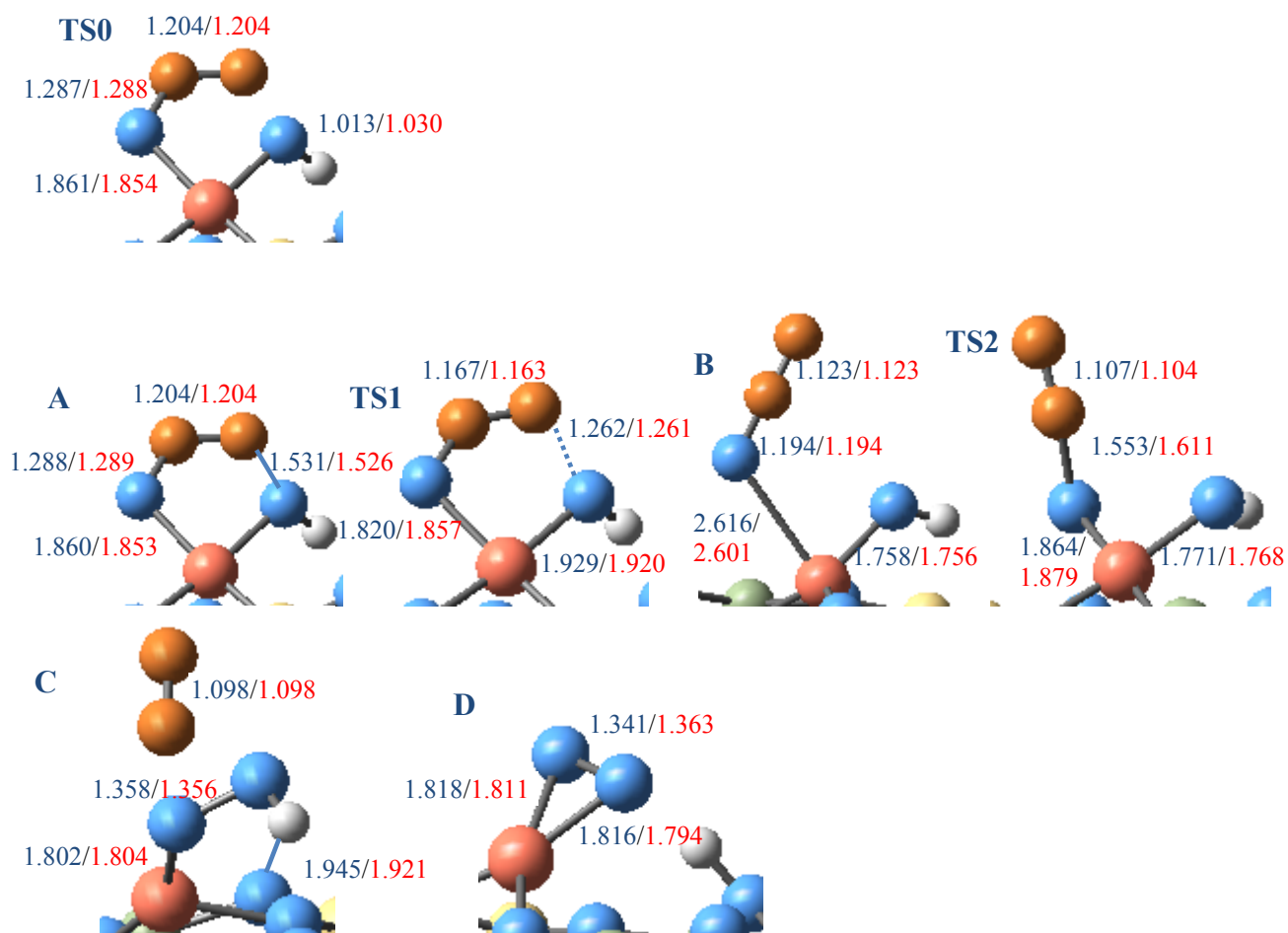


Figure 3S. Geometries of intermediates and transition states along the reaction path denoted on Figure 7: the transition state TS0 for proton transfer to the dinitrosyls from a Brønsted acid site. A, the equilibrium protonated adsorption complex. The transition state TS1 to N_2O formation. B, N_2O adsorbed at hydroxylated copper cation. C, nitrogen desorption and surface copper hydroperoxide. D, Surface peroxide and a restored Brønsted acid site. The blue labels are for SAPO-34 and the red labels for SSZ-13.

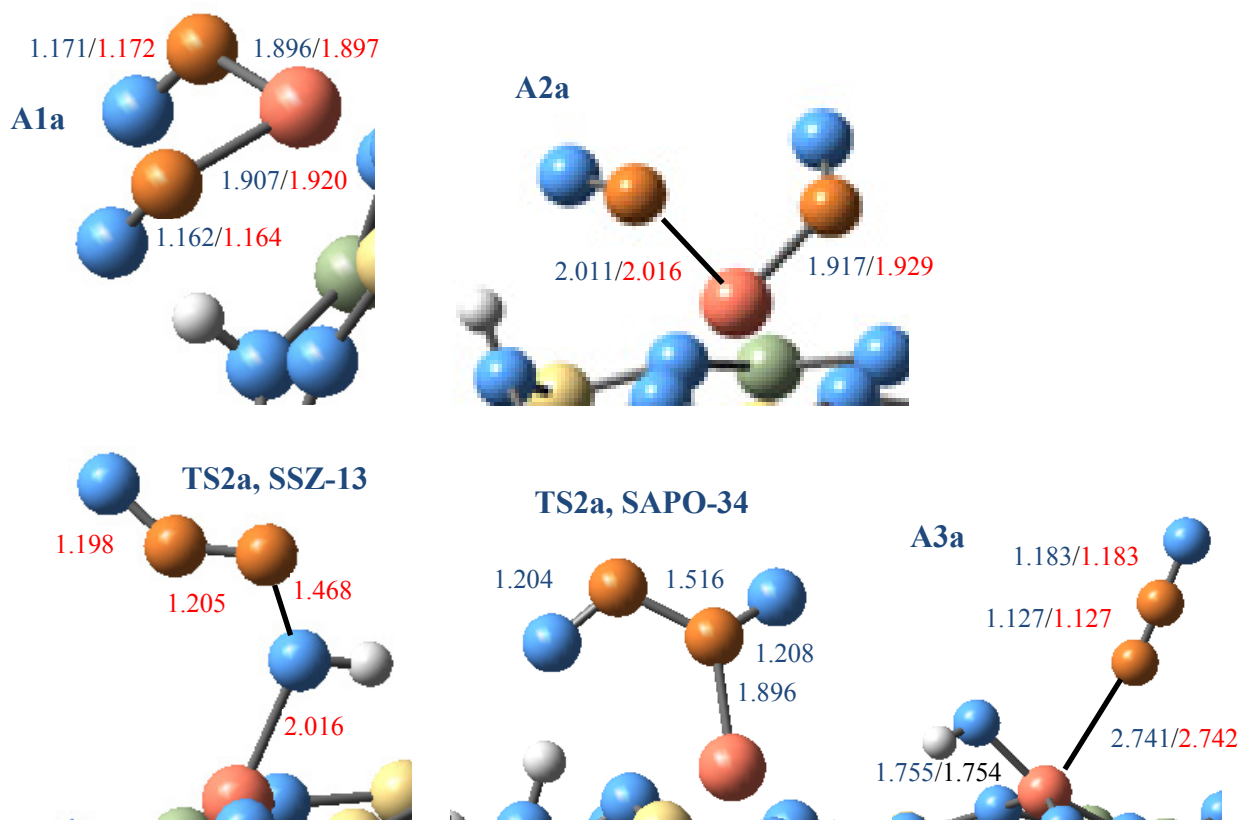


Figure 4S. Geometries of intermediates and transition states along the reaction path 1a-3a denoted on Figure 8: A1a, N-bonded dinitrosyl. A2a, reversal of one nitrosyl group. TS2a, transition state to N_2O formation in SSZ-13 and in SAPO-34. A3a, N_2O adsorbed. The blue labels are for SAPO-34 and the red labels for SSZ-13.

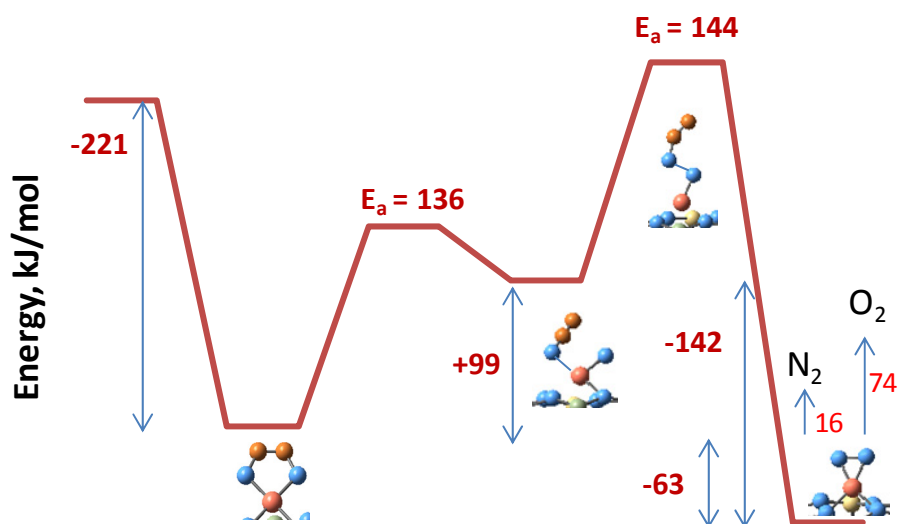


Figure 5S. Elementary steps in the reaction path for proton-assisted nitric oxide dissociation from hyponitrite $Cu(ON)_2$ adsorption complex in SSZ-13, with energy barriers and heat effects denoted. Endothermic heat effects are denoted as negative. Bond lengths in the reaction intermediates are displayed in Figure 6S.

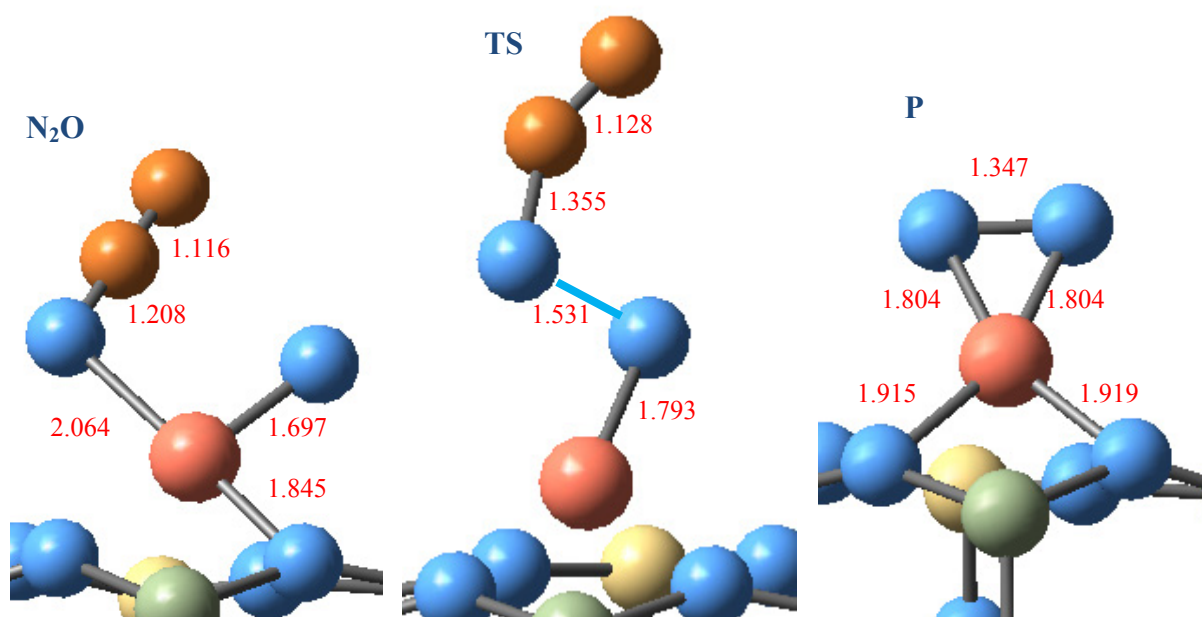


Figure 6S. Geometries of intermediates and transition states along the reaction path denoted on Figure 5S (without proton transfer): N_2O – the direct N_2O formation together with $ZCuO$ from $ZCu(ON)_2$; TS – transition state of N_2O decomposition; P – the peroxide $ZCu(O_2)$ remaining after N_2 desorption.

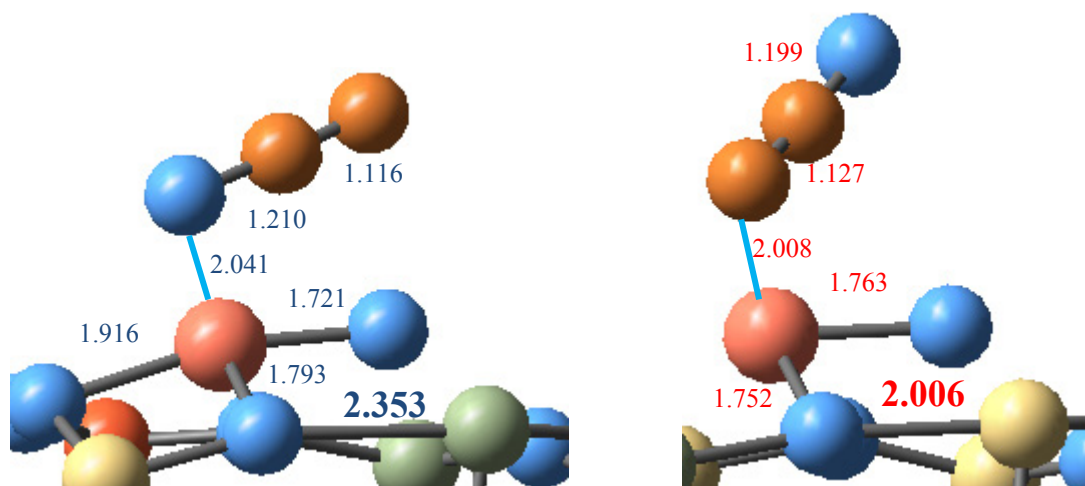


Figure 7S. Structural distortion in (A) Cu-SAPO-34, upon N_2O formation from $ZCu(ON)_2$ without protonation. (B) Cu-SSZ-13, upon N_2O formation from $ZCu(ON)_2$ without protonation or presence of a Brønsted acid site. The blue labels are for SAPO-34 and the red labels for SSZ-13. The distorted bonds are emphasized: Al-O = 2.352 Å in SAPO-34 and Si-O = 2.006 Å in SSZ-13.