Coordination and Activation of Nitrous Oxide by Iron Zeolites

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Iron-containing zeolites are heterogeneous catalysts that exhibit remarkable activity in the selective oxidation of inert hydrocarbons and catalytic decomposition of nitrous oxide (N₂O). The reduction of N₂O is critical to both of these functions, however direct experimental data tracking the iron active sites during N₂O binding and activation are limited. Here, the N₂O-ligated Fe(II) active site in iron-exchanged zeolite beta is isolated and characterised by variable-temperature Mössbauer, diffuse reflectance UV-Vis-NIR, and FTIR spectroscopy. N₂O is found to bind through the terminal nitrogen atom, with significant backbonding from the Fe(II) centre at low temperature. At higher temperatures the Fe-N₂O interaction is weakened, facilitating isomerization to the O-bound form which is competent in O-atom transfer. DFT calculations elucidate the geometric and electronic structure requirements for N₂O binding and activation. A geometric distortion imposed by the zeolite lattice plays an important role in activating N₂O. This highlights a mechanism for structural control over function in Fe-zeolite catalysts.

Introduction. N₂O is a potent and selective oxidant, but also a major cause of stratospheric ozone depletion and the third largest contributor to anthropogenic global warming.¹ It is generated in large quantities as a side product in the production of adipic acid and nitric acid, but it remains underutilised due to its high kinetic stability. Understanding the binding and activation of N₂O by transition metal catalysts is therefore of significant interest for the use of N₂O as an oxidant, and for its catalytic decomposition to environmentally benign O₂ and N₂. However, the N₂O ligand interacts only weakly both as a σ donor and as a π acceptor. Consequently only a handful of N₂O-ligated transition metal centres have been successfully isolated and characterised.^{2–6} Binding through the terminal nitrogen is generally preferred due to

backbonding effects.² Iron exchanged zeolites stabilize an S=2 square planar Fe(II) site (α -Fe(II)) that activates N₂O, forming a highly reactive Fe(IV)=O intermediate (α -O) active in the low-temperature hydroxylation of inert C-H bonds (e.g. methane, benzene),^{7,8} and catalytic decomposition of N₂O.^{9,10} Despite the large body of literature on N₂O activation and decomposition by Fe-zeolites, experimental spectroscopic data are limited,^{11–16} and no studies exist tracking the state of the α -Fe(II) active site over the course of N₂O binding and activation. In this study, N₂O ligated α -Fe(II) complexes are identified in Fe exchanged zeolite beta (Fe-*BEA) by diffuse reflectance spectroscopy (DR-UV-Vis-NIR), Fourier transform infrared spectroscopy (FTIR), and Mössbauer spectroscopy. The thermodynamics and kinetics of N₂O activation to form α -O are determined with operando DR-UV-Vis-NIR spectroscopy. DFT models of N₂O-ligated intermediates are evaluated against experimental data and used to interrogate the reaction coordinate for N₂O activation. They demonstrate the role of the ligand field from the zeolite lattice in tuning the thermodynamics and kinetics of N₂O binding and activation.

Spectroscopic Identification of an N₂O-bound Intermediate. We used room temperature ⁵⁷Fe Mössbauer spectroscopy to probe the state of the Fe sites during N₂O binding and activation (figure 1A-C). A sample containing >95% ⁵⁷Fe enriched α -Fe(II) (figure 1a – see figure S1 for full velocity range spectrum) was exposed to an atmosphere of 35 vol.% N₂O in He at room temperature. Upon exposure to N₂O the α -Fe(II) signal is no longer present, and a single new component appears with isomer shift δ =1.09 mm/s and quadrupole splitting $|\Delta E_Q|$ =1.53 mm/s (figure 1b), characteristic of high spin (S=2) Fe(II). We name this N₂O ligated high spin Fe(II) component ' α -N₂O'. After 30 min at 433 K the α -N₂O is fully converted to α -O, identified by Mössbauer spectroscopy (figure 1c).^{8,17,18} α -N₂O is therefore the Fe(II) precursor to the Fe(IV)=O α -O intermediate.

Figure 1. Room temperature Mössbauer spectra of **a)** α -Fe(II), **b)** α -N₂O (red component; some conversion to α -O is also observed – blue component), **c)** α -O formed from heating the sample of α -N₂O to 433 K for 30 min. **d)** Room temperature Mössbauer spectra of α -Fe(II) in the presence of atmospheres with increasing percentages of N₂O. The Mössbauer spectra exhibit change until the N₂O atmosphere $\geq 35\%$; further change upon increasing % N₂O is not observed. **e)** Temperature dependence of the Mössbauer spectra of the 35% α -N₂O sample. **f)** Low temperature (6K) Mössbauer spectra of α -Fe(II) with increasing % of N₂O in the atmosphere. These data show the conversion to a bis-N₂O bound form (α -(N₂O)₂ LT2'). (* indicates limited conversion to α -O).

To further identify α -N₂O, we collected Mössbauer data at various N₂O concentrations (figure 1d). The room temperature Mössbauer spectrum varies continuously between that of α -Fe(II) (low concentration limit), and that of α -N₂O (high concentration limit). Beyond 35 vol.% N₂O the active Fe sites are fully bound and no further spectral changes occur. The signals observed at intermediate N₂O concentrations may result from an equilibrium between α -Fe(II) and α -N₂O that exchanges rapidly relative to the $\sim 10^{-7}$ seconds lifetime of the ^{57}mFe 14.4 keV nuclear excited state probed by Mössbauer spectroscopy, yielding an averaged signal (See SI section S1.2).¹⁹ The fully bound sample (35 vol.% N₂O) was chosen to study the temperature dependence of the α -N₂O Mössbauer spectrum (figure 1e). With decreasing temperature down to 100K, both the isomer shift and the quadrupole splitting increase in magnitude. Further

cooling to 6K (figure 1f), induces no further increase and the Mössbauer parameters remain at $\delta=1.27$ mm/s and $|\Delta E_Q|=2.50$ mm/s. The temperature dependence of the quadrupole splitting ($\Delta|\Delta E_Q|=0.97$ mm/s) is characteristic of a temperature dependent structural change, e.g. the contraction of metal-ligand bonds at low temperature.²⁰ Interestingly, at 6K the Mössbauer spectra (figure 1f) show an additional species is present when the atmosphere exceeds 1 vol.% N₂O. From DFT calculations presented in figure S18 we assign this species, with $\delta=1.35$ mm/s and $|\Delta E_Q|=3.33$ mm/s, as a bis-N₂O-bound site and name it ' α -(N₂O)₂ LT2'.

To further probe the nature of the interaction between Fe-*BEA and N₂O we collected variable-

temperature Fourier transform infrared (FTIR) spectra at varied N₂O loadings. In the N₂O asymmetric stretch region two features appear upon dosing 44 equivalents N₂O per iron at room temperature (figure 2a). Only the feature at 2283 cm⁻¹ correlates with the presence of Fe(II). We assign the feature at 2235 cm⁻¹ to lattice adsorbed N₂O. In the symmetric stretch region (figure 2b), a single feature at 1340 cm⁻¹ is correlated with Fe(II). As these samples of Fe-*BEA contained >95% active Fe, we assign these features as the symmetric and antisymmetric stretches of the N₂O ligand of α -N₂O. A blue-shift of the N₂O symmetric stretch upon binding to α -Fe(II) (53 cm⁻¹) is characteristic of binding

Figure 2. **a)** Asymmetric and **(b)** symmetric N₂O stretches on H-*BEA and Fe-*BEA respectively exposed to 2.63 and 2.87 mmol N₂O per gram of zeolite at 298K. **c)** Asymmetric and **(d)** symmetric N₂O stretches on Fe-*BEA exposed to respectively 0.05, 0.14, 0.28, 0.86 and 2.08 mol N₂O per mol iron at 77K for spectra (1) to (5). * indicates lattice adsorbed N₂O. All spectra are relative to 550°C activated H-*BEA or Fe-*BEA.

through the N atom.¹⁵ Combined spectroscopic data therefore indicate α -N₂O is a single S=2 Fe(II) species containing an N₂O ligand bound through its terminal nitrogen atom.

At 77K (figures 2c/d), similar vibrational features are observed, and we assign these to the same α -N₂O site with $\nu_{\text{asym}} = 2287 \text{ cm}^{-1}$ and $\nu_{\text{sym}} = 1341 \text{ cm}^{-1}$. The similarity between the room temperature and low temperature frequencies indicates the N₂O ligand remains N-bound at low temperature. The blue-shift to 2287 and 1341 cm^{-1} at 77K may be explained by a contraction of the metal-ligand bond upon cooling which also explains the temperature dependent quadrupole splitting in figure 1e. Additional bands appear in the FTIR spectra of N₂O-dosed Fe-*BEA at 2204, 2295, 2310, 2334, and 2346 cm^{-1} that are not seen on H-*BEA and therefore correlate with Fe(II) (figures 2c and S5a). All of these saturate at low pN₂O with low relative intensity and do not relate to the majority α -Fe(II) site. At high pN₂O and low temperature, the mono-N₂O-bound complex transitioned into a bis-N₂O-bound complex (figure 1f). At a threshold pN₂O we similarly see the replacement of the 2287 and 1341 cm^{-1} bands by a 2253 cm^{-1} feature that may be connected to this bis-N₂O-bound α -(N₂O)₂ LT2 site (see figure S9). Full FTIR data and further discussion are presented in the SI section S1.3.

To understand the nature of the Fe(II)-N₂O interaction in α -N₂O, its 6K Mössbauer parameters are compared to those calculated from candidate models using periodic density functional theory (DFT). The calculations are run at the B3LYP-D3 level of theory, including dispersion to properly account for zeolite/adsorbate interactions.^{21,22} Starting from a spectroscopically-validated DFT model of α -Fe(II),^{8,23,24} two mono-N₂O-bound sites were optimised on the S=2 surface, with N₂O bound through either the terminal N atom or terminal O atom. Other binding modes (e.g. η^2 -O,N) did not yield stable minima, and the distribution of Al within the active site has only a limited effect on the binding and activation of N₂O (Tables S5). The calculated properties of the N- and O-bound models are presented in figure 3. Both models accurately model the experimental spectroscopic and thermodynamics parameters, with the N-bound

model giving closer agreement. The models confirm the assignment of the 2287 / 1341 cm^{-1} pair of vibrations in FTIR to the asymmetric and symmetric stretches of η^1 -N-bound N_2O on α -Fe(II). Particularly the blue-shifted symmetric stretch relative to gas phase N_2O (experimental $\nu_{\text{sym}} = 1285 \text{ cm}^{-1}$, computed at 1312 cm^{-1}) is a strong argument for the η^1 -N binding mode, both at 298K and at 77K. Parallel calculations performed on cluster models presented in S4 give similar results, although the N_2O molecule is found nearer the six membered-ring indicating influence of weak van der Waals interaction with the larger zeolite environment.

	experiment	DFT	
	α - N_2O	η^1 -O	η^1 -N
ΔE_{ads} (kcal/mol)	-4.8	-5.3	-8.2
δ (mm/s)	1.27	0.90	0.92
ΔE_{Q} (mm/s)	± 2.50	+2.06	+2.24
ν_{asym} (cm^{-1})	2287	2253	2303
ν_{sym} (cm^{-1})	1341	1196	1324
β HOMO	-	d_{z^2}	d_{xz}

Figure 3. Comparison of the geometric structures of the η^1 -N and η^1 -O N_2O -bound models evaluated by periodic DFT (top). In the table below, the calculated properties of these models (see also Tables S1 & S2) are compared to experimental data from α - N_2O collected at 6K (Mössbauer data) or 77K (vibrational data).

The 2.13 Å Fe-NNO bound is considerably shorter than the 2.34 Å Fe-ONN bond and this relates to their different calculated electronic structures. π backbonding is present in Fe-NNO but not in Fe-ONN. For π backbonding, an electron is promoted from the lowest energy doubly occupied d_{z^2} orbital of α -Fe(II) (responsible for the small $|\Delta E_{\text{Q}}|$ of α -Fe(II))⁸ into the d_{xz} orbital, resulting in a $(d_{xz})^2(d_{yz})^1(d_{z^2})^1(d_{xy})^1(d_{x^2-y^2})^1$ configuration. This promotion of a d_{z^2} electron into the $d\pi$ orbital enables π backbonding, and changes the electric field gradient at the ^{57}Fe nucleus, resulting in the larger $|\Delta E_{\text{Q}}|$ (relative to α -Fe(II)). For the O-bound intermediate, the Fe-ONN interaction is weak and the d_{z^2} orbital remains doubly occupied, resulting in the smaller calculated $|\Delta E_{\text{Q}}|$.^{8,25} The room temperature experimental N_2O binding enthalpy of -4.8 kcal/mol (*vide infra*) can be correlated with the room temperature Mössbauer and FTIR spectra (figures 1e and 2b) with $|\Delta E_{\text{Q}}| = 1.53 \text{ mm/s}$ and $\nu = 2283 \text{ cm}^{-1}$ (versus $|\Delta E_{\text{Q}}| = 2.50 \text{ mm/s}$ and $\nu = 2287$

cm⁻¹ at low temperature). DFT calculations on the cluster model for the N-bound form were also able to stabilize a local minimum ($\Delta H_{\text{bind}} = -3.4$ kcal/mol) geometry with a longer Fe-N bond length of 2.32 Å with limited backbonding and calculated $\Delta E_Q = -1.76$ mm/s (figure S18, η^1 -N' model). This may correlate to the weakened Fe-N bond for the room temperature α -N₂O that facilitates isomerization to the O-bound form on the intrinsic reaction coordinate for α -O formation (*vide infra*).

Thermodynamics of N₂O Binding and Activation. Site selective operando diffuse reflectance UV-Vis-NIR (DR-UV-Vis-NIR) spectroscopy was used to derive the enthalpy and entropy of N₂O binding to α -Fe(II) and of the transition state to α -O. The DR-UV-Vis-NIR spectrum of α -Fe(II) is characterised by a 15900 cm⁻¹ ligand field band (figure 4a, green spectrum).⁸ Upon exposing the sample to an atmosphere of 35 vol.% N₂O in He at room temperature, the 15900 cm⁻¹ absorption band is lost and a new absorption band appears at 11500 cm⁻¹, along with a weak absorption feature at 5000 cm⁻¹ (figure 4a, red trace). Reverting the atmosphere to 100 vol.% He restores the α -Fe(II) spectrum (figure S2). The new absorption features can be assigned to the α -N₂O intermediate identified by Mössbauer spectroscopy and are in agreement with DFT cluster models (see figure S18). After 30 min at 433K, the 11500 cm⁻¹ absorption band is lost and absorption bands at 6000 cm⁻¹, 16900 cm⁻¹, 20100 cm⁻¹ and 28000 cm⁻¹ appear (figure 4b), consistent with the DR-UV-Vis-NIR spectrum of α -O.⁸ Additional experiments in S2 show the analogous trends for α -O sites defined in Fe-*BEA and the α -O sites defined in Fe-ZSM-5 by other authors.^{7,26,27}

The thermodynamics of N₂O binding to α -Fe(II) was evaluated by the dependence of the equilibrium ratio of the 15900 cm⁻¹ and the 11500 cm⁻¹ absorption bands at different p_{N2O} and temperatures (figure 4c). The α -Fe(II) band gradually disappears with increasing p_{N2O} whereas the α -N₂O band gradually gains intensity and the presence of an isosbestic point at 13500 cm⁻¹

Figure 4. **a)** Comparison of DRS-UV-Vis-NIR spectra of Fe(II)-*BEA before (green) and after (red) introduction of a 35 vol.% N₂O in Helium atmosphere at room temperature. **b)** Comparison of DR-UV-Vis-NIR spectra collected before (red) and after (blue) heating at 433 K in a 35 vol.% N₂O in Helium atmosphere for 30 minutes. **c)** operando UV-Vis difference spectra of Fe-*BEA at 308 K after high temperature He treatment with p_{N2O} ranging from 0 to 0.05 atmosphere, showing the equilibrium between α-Fe(II) and α-N₂O. **d)** Van 't Hoff plot of data derived from the adsorption data from operando UV-Vis spectra analogous to those shown in figure 3A. **e)** Operando UV-Vis difference spectra of Fe-*BEA at 373 K following the transformation of α-N₂O to α-O over a time interval of 15 minutes in an atmosphere of 35 vol.% N₂O in He. **f)** Eyring plot of data derived from operando UV-Vis spectra analogous to those shown in figure 3C. Error bars in figures 4d and 4f indicate the 95% confidence interval of the linear regressions shown in section S3.

indicates the interchange between single species. The results were evaluated using the Langmuir adsorption model and the Van 't Hoff equation (see S3.1). The Van 't Hoff plot (figure 4d) yields an enthalpy of adsorption $\Delta H^\circ = -4.8 \pm 0.1$ kcal/mol and an entropy of adsorption $\Delta S^\circ = -7.1 \pm 0.4$ cal/mol/K. In ref. 28, an experimental $\Delta H^\circ = -12.7 \pm 0.5$ kcal was obtained. This study was, however, on Fe-ZSM-5 and did not directly observe the adsorption of N₂O onto α-Fe(II).

Next, the transformation of the α -N₂O adsorption complex into α -O was followed by operando UV-Vis-NIR spectroscopy at different temperatures. The gradual disappearance of the 11500 cm⁻¹ absorption band coincides with the growth of absorption bands at 16900 cm⁻¹ and 28000 cm⁻¹, with an isosbestic point at 14000 cm⁻¹ (figure 4e). The reaction therefore converts α -N₂O selectively into α -O.

The microkinetics are described by:

and the following parameters are defined, assuming a first order reaction (R2);

$$\text{N}_2\text{O adsorption equilibrium:} \quad K = \frac{k_a}{k_d} = \frac{[\alpha\text{-N}_2\text{O}]}{[\alpha\text{-Fe}]} \quad (1)$$

$$\text{Activation of N}_2\text{O:} \quad \frac{d[\alpha\text{-O}]}{dt} = k_r[\alpha\text{-N}_2\text{O}] \quad (2)$$

$$\text{Rate equation:} \quad \frac{d[\alpha\text{-O}]}{dt} = \frac{k_r K}{K P_{\text{N}_2\text{O}} + 1} P_{\text{N}_2\text{O}} ([\alpha\text{-Fe}]_0 - [\alpha\text{-O}]) \quad (3)$$

From the Eyring plot in figure 4f the enthalpy and entropy of the transition state (TS) are $\Delta H^\ddagger = 17.7 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -22.4 \pm 3.8$ cal/mol/K (see S3.2 for calculation details). The resulting apparent activation energy is 12.8 ± 1.5 kcal/mol. On Fe-ZSM-5 experimental values for the apparent activation energy of 10 kcal/mol, 15 kcal/mol and 16.7 kcal/mol have been reported,^{7,28,29} however these values were inferred indirectly without site selective monitoring of the active α -Fe(II) site.

Computational Evaluation of N₂O Activation. Cluster and periodic calculations with the B3LYP-D3 functional were performed to evaluate N₂O binding and activation by α -Fe(II). As recent studies highlight the potential importance of electrostatic confinement effects on the

197 metallozeolite reactivity,^{21,30} cluster and periodic calculations were then compared to understand
 198 how confining the reactants in the *BEA pore affects the barrier to O-atom transfer. Additional
 199 detail on this is presented in [section S4](#). Based on the small experimental N₂O binding enthalpy
 200 and entropy of binding, the calculated N₂O binding enthalpies were referenced to N₂O adsorbed
 201 on the zeolite lattice ($\Delta E_{\text{el,ads}} = -5.4$ kcal/mol, $\Delta H_{\text{ads,323K}} = -4.6$ kcal/mol from gas-phase N₂O). The
 202 N₂O binding enthalpies are more exothermic in the periodic models compared to the cluster
 203 models, especially in the N-bound case. (-6.0 vs. -4.1 kcal/mol for $\eta^1\text{-O}$ and -8.8 vs -3.8
 204 kcal/mol for $\eta^1\text{-N}$). Periodic models, or at least sufficiently large cluster models are therefore
 205 required to accurately model van der Waals interactions between the lattice and the N₂O ligand.

206 The reaction coordinate for O-atom transfer ([figure 5](#)) begins with N₂O binding to $\alpha\text{-Fe(II)}$. Only
 207 the O-bound intermediate can participate in O-atom transfer to Fe(II). Periodic calculations
 208 predict a binding enthalpy $\Delta H = -5.2$ kcal/mol for the O-bound intermediate, while cluster
 209 calculations predict $\Delta H = -4.1$ kcal/mol. Both methods are in good agreement with experiment (-
 210 4.8 kcal/mol). Proceeding from the O-bound intermediate, the Fe-ONN bond begins to contract
 211 and becomes collinear with the molecular z-axis, causing the β (spin down) electron on Fe(II) to
 212 be transferred from the d_{z^2} orbital into the βd_{xz} orbital (activated complex in [figure 5](#)). This
 213 enables π back donation from the Fe(II) centre into the empty $\beta\pi^*$ orbital of the N₂O ligand. As
 214 the N-O bond elongates, the Fe back donation increases. A transition state for N-O cleavage is
 215 found on the S=2 surface, with an activation enthalpy $\Delta H^\ddagger = 25.4$ kcal/mol for the cluster models
 216 (the S=1 transition state is destabilized by an additional 20 kcal/mol). The periodic model gives
 217 a comparable barrier and geometry (see [S4](#)). At the transition state, the N-O bond has
 218 elongated to 1.45 Å, the Fe-ONN bond has contracted to 1.83 Å, and the N₂O ligand is bent

Figure 5. Comparison of reaction profiles for N-O cleavage on the S=2 surface calculated with periodic and cluster models (black and grey values, respectively), both using the B3LYP-D3 functional. The reaction starts from unbound N₂O in a van der Waals complex with the zeolite lattice (left) and ends with α -O and liberated N₂ (right). The evolution of the β -HOMO leading up to the first electron transfer (red orbitals) is shown schematically, along with the evolution of the α -LUMO reflecting transfer of the second electron after the barrier (blue orbitals). The bond distances are taken from the cluster models, for which data on electronic structure are available.

($\angle \text{ONN}=138^\circ$). These geometric changes correlate to partial ($\sim 30\%$) transfer of the βd_{xz} electron into the π^* orbital of N₂O through back donation (red orbitals in figure 5). Proceeding past the transition state, the structure evolves into a transitory S=5/2 Fe(III) centre antiferromagnetically coupled to an N₂O[•] ligand radical. With further N-O elongation, the α -LUMO of the N₂O[•] ligand radical localizes on the terminal oxygen (blue orbitals in figure 5), the N-O bond is cleaved, and N₂ is released. This forms a transient Fe(III)-O[•] site with an Fe-O bond of 1.7-1.8 Å, and an O2p_x-derived LUMO. Finally, as the Fe-O bond continues to contract, a second electron is transferred from the Fe centre to its oxyl ligand, resulting in the experimentally-defined S=2 Fe(IV)=O ground state of α -O. The sequential two-electron reduction of N₂O is calculated to be exothermic by 3.9 kcal/mol when starting from the O-bound intermediate (1.9 kcal/mol from periodic calculations). From periodic calculations, it is endothermic by 1.0 kcal/mol when starting from the N-bound intermediate and exothermic by 11.7 kcal/mol starting from α -Fe(II) and gas-phase N₂O.

Periodic and cluster model calculations both predict an activation barrier of ~25 kcal/mol that exceeds the $\Delta H^\ddagger=17.7$ kcal/mol value from experiment. The predicted N-O cleavage barrier correlates strongly with the driving force for oxo transfer which was calculated by comparing functionals with varying amounts of Hartree Fock in Table S6. The B3LYP functional used here underestimates this driving force leading to an elevated predicted barrier. However, the electronic structure description of N-O cleavage is robust with respect to the DFT method (i.e. functional, periodic versus cluster). Cluster and periodic DFT calculations give comparable O-bound structures and predict similar energetics of N₂O activation in the O-atom reaction coordinate to form α -O. Still, different lattice topologies and different reactions may exhibit more pronounced confinement or long range solvation effects than O-atom transfer in *BEA,²¹ and in these cases periodic DFT is required.

Correlation of Structure to Function. as N₂O is a poor σ donor and π acceptor, N₂O-ligated transition metal complexes are rare, and N₂O tends to bind through its terminal N atom. This coordination mode enables backbonding, as the π^* acceptor orbitals of N₂O are polarized toward its terminal N atom.³¹ Only a handful of systems that bind N₂O have been experimentally characterised.³⁻⁶ A direct comparison can be made to the metal-organic framework Fe₂(dobdc), with high spin (S=2) square pyramidal Fe(II)O₅ centres that bind N₂O as mono-N- and mono-O-bound species in a 60:40 ratio at 10 K. Both binding modes feature long Fe-N₂O distances (2.4 Å) that indicate a lack of backbonding.⁶ In contrast, the square planar Fe(II)O₄ centres in Fe-*BEA only form a mono-N-bound species at low temperature, with a Mössbauer quadrupole splitting reflecting backbonding. At room temperature, a much smaller Mössbauer quadrupole splitting is observed, characteristic of a weaker Fe(II)-N₂O interaction with no backbonding. Therefore backbonding is favoured in Fe-*BEA, but not Fe₂(dobdc). A key structural difference between these S=2 Fe(II) sites is the presence/absence of an axial ligand. DFT calculations in figure S19 indicate backbonding is decreased by adding an axial ligand to α -N₂O. The axial

ligand anchors the Fe centre in the plane of the equatorial ligands, preventing the out-of-plane distortion required to form a short Fe-NNO interaction with backbonding.

Zeolite lattice constraints are known to enforce an ‘entatic state’ that activates α -O for H-atom abstraction from

methane.^{8,23,32} Cluster models show

lattice constraints similarly affect the

binding and activation of N₂O. In the

absence of lattice constraints on the β -

6MR ligand, α -Fe(II) is calculated to

assume a nearly planar structure (figure 6, left).³³ For this unconstrained DFT model, N₂O

binding through both the O and N atom is enthalpically disfavored. Placing α -Fe(II) in the *BEA

lattice (figure 6, right) constrains the O-Fe-O angle highlighted in yellow in figure 6 to 145°, and

renders N₂O binding enthalpically favorable. Distortion of the O-Fe-O angle results in a structure

resembling a trigonal bipyramidal site with a vacant equatorial position. This destabilizes α -

Fe(II) over the five-coordinate N₂O-ligated Fe(II) site and tunes up the driving force for N₂O

binding by 7.1 kcal/mol. This destabilization reduces the effective barrier for N₂O activation by

7.7 kcal/mol (figure 6).

Formation of α -O from the η^1 -O intermediate is the rate-determining step in selective

hydrocarbon oxidation,^{7,26} as well as a critical step in catalytic N₂O decomposition.⁷ This study

provides the first experimentally calibrated reaction coordinate for N₂O activation by an Fe-

zeolite. The electronic structure description of N-O cleavage given in figure 5 parallels the

activation of N₂O by the binuclear 2Cu(I) active site of Cu-ZSM-5 to form the [Cu₂O]²⁺ reactive

intermediate.³⁴ The experimental apparent barrier for N-O cleavage by Cu-ZSM-5 (E_a =2.5

kcal/mol)³⁴ is significantly lower than the barrier for Fe-*BEA (E_a =12.8 kcal/mol). The DFT

	unconstrained	BEA
$d(\text{Fe-O})_{\text{avg}}$	2.01 Å	1.99 Å
$\angle \text{O-Fe-O}$	173°	145°
$\Delta H_{\text{ads}}(\eta^1\text{-O})$	2.7	-4.4
$\Delta H_{\text{app}}^{\ddagger}$	29.1	21.4

Figure 6. Correlation of geometric structure with function for α -Fe(II) (left) in the absence of constraints, and with constraints from the BEA lattice (right). Distortion of the O-Fe-O angle highlighted in yellow promotes N₂O binding and activation. Enthalpies are given in kcal/mol.

282 reaction profiles for N₂O activation by Cu-ZSM-5 and Fe-*BEA are compared in figure 7. Note:
 283 the Fe-*BEA was recalculated here without dispersion to have the same level of theory as
 284 employed for Cu-ZSM-5 in ref. 34. The calculated binding enthalpy of oxygen-bound N₂O in Cu-
 285 ZSM-5 (-9 kcal/mol)³⁴ is about twice that of Fe-*BEA (-4.1 kcal/mol). This results in an ~4
 286 kcal/mol reduction of the apparent barrier. The activation barrier for N-O cleavage calculated for
 287 Cu-ZSM-5 ($\Delta H^\ddagger=11$ kcal/mol) is ~1/2 that of Fe-*BEA ($\Delta H^\ddagger=21$ kcal/mol). The Cu-ZSM-5
 288 reaction is also exothermic by an additional 40 kcal/mol due to a large ionic contribution to the
 289 product μ -oxo-Cu(II)₂ bonds. Correcting for this difference in driving force using Marcus theory,³⁵
 290 the intrinsic barriers for N-O cleavage by Cu-ZSM-5 (30 kcal/mol) and Fe-*BEA (25 kcal/mol)
 291 are found to be similar. The result is that the more stable [Cu₂O]²⁺ intermediate forms at room
 292 temperature, but reacts with methane only at elevated temperatures;³⁶ while the less stable α -O
 293 intermediate forms at elevated temperatures, but reacts with methane at room temperature.⁷

Figure 7. Comparison of the DFT reaction profiles for N₂O binding and activation by the reduced 2Cu(I) active site of Cu-ZSM-5 (blue, values reproduced from ref. 34), and α -Fe(II) (red, using the same DFT method as ref. 34). Mulliken charges of the produced metal-oxo complexes are compared at the right of the figure.

The comparison of N₂O activation by α -Fe(II) and this 2Cu(I) site highlights the balancing act between the stability and reactivity of the metal-oxo product.

Conclusion. In this study, we define the interaction between N₂O and the α -Fe(II) active site in Fe-*BEA using spectroscopic results coupled to DFT calculations. These data suggest that, at low temperature, an η^1 -N species is observed with backbonding from the Fe(II) centre into the N₂O ligand. At room temperature, the Fe(II)-N₂O interaction is weakened, turning off backbonding, and enabling formation of an O-bound intermediate that performs O-atom transfer to Fe(II). Using DR-UV-Vis-NIR spectroscopic handles of the α -Fe(II)/ α -N₂O/ α -O species, we quantified the thermodynamics of N₂O binding and the barrier for N-O bond cleavage. Cluster and periodic DFT calculations provide a unified electronic structure description of the N-O cleavage reaction, where at the transition state $\sim 1/2$ of an electron is transferred from the Fe centre into an empty π^* orbital of the N₂O ligand. The close agreement between cluster and periodic calculations indicate that long-range electrostatics do not contribute to this reaction coordinate in the *BEA lattice. Short-range interactions (van der Waals) between the adsorbate and zeolite lattice do contribute, however, and can be accurately modelled with a sufficiently large cluster model. Finally, we have correlated the structure of the Fe(II) active site to its function. We find both Fe(II) out-of-plane distortions due to zeolite lattice constraints and the vacant *trans* axial position tune the thermodynamics of N₂O binding and activation. Comparing Fe(II) and Cu₂(I) active sites in zeolites, we find there is a balance between the driving force for N-O cleavage, and the H-atom abstraction reactivity of the resulting metal-oxo intermediate. Together, these results highlight potential mechanisms for structural control of function in metallozeolite catalysts.

Methods

Sample preparation and treatment. Fe-*BEA (Fe/Al=0.04; 0.3 wt.% Fe) was prepared from calcined (O₂, 823 K) commercial NH₄-beta (*BEA) zeolite (Si/Al=12.5, CP814E, Zeolyst International) by diffusion impregnation of ⁵⁷Fe(acac)₃ (acac = acetylacetonate) in toluene solution (2.33 mM; 0.25 ml g⁻¹ zeolite). The solution is decanted and calcined at 823 K to remove organics. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 3300 DV) was performed for elemental analysis. Low iron loadings (0.3 wt.%), an organic complex with a protected single iron ion, and the absence of water during preparation were used to ensure a high dispersion of iron and to avoid the formation of oligomers and other spectator species. The sample was pelletized between 250 and 125 µm, transferred into a quartz tube (~1.5 g of sample) and heated to 1173 K at a heating ramp of 10 K/min in a He flow of 20 ml/min. The sample was kept at 1173 K for two hours. Subsequently the sample was treated in a 20 ml/min flow of H₂ for one hour at 973 K, and another hour in a He flow of 20 ml/min at the same temperature. The H₂ treatment step had only minor effects on the iron speciation. Finally, the sample was cooled down to room temperature and either transferred to another quartz sample holder for operando UV-Vis spectroscopy or treated in the original piece of quartz glassware for non-operando in situ UV-Vis-NIR and Mössbauer. N₂O and He gas flows were controlled with calibrated mass flow controllers (Brooks Instrument 0154) and temperature was monitored with a thermocouple. Helium flows were oxygen and moisture filtered to avoid contamination. Caution was taken to minimize contamination of gas tubing and glassware entrances and exits by air or other contaminants. For reference, a sample was also prepared leaving the Fe(acac)₃ out of the preparation.

UV-Vis-NIR spectroscopy. Non-operando diffuse reflectance (DR) UV-Vis-NIR spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer at room temperature against a halon white reflectance standard in the range 4000–50000 cm⁻¹.

Operando UV-Vis spectroscopy was recorded using an AvaSpec-2048L fibre-optic spectrometer in combination with a DH-2000 deuterium halogen light source (Top Sensor Systems), a FCB-UV400 ME fibre optic cable and a FCBUV400G-0.1-XHT high temperature probe. The probe was positioned at a 90° angle to the sample holder (measuring specular reflection). The raw spectra were recorded against a BaSO₄ reference. Each spectrum is an average of 49 measurements with an individual integration time of 10.1803 ms.

FTIR spectroscopy. FTIR spectra of N₂O on self-supported zeolite pellets (21.28 mg for Fe-BEA and 19.82 mg for H-BEA with an area of 2 cm²) were recorded using a Nicolet Magna 550 - FTIR spectrometer (4 cm⁻¹ optical resolution and 128 scans) equipped with an MCT detector. Prior to the adsorption measurements, samples were activated under vacuum (10⁻⁶ torr) for 5 hours at 450°C and another hour at 550°C. After cooling, spectra were collected at 77K. Small doses of N₂O were added into the sample chamber's vacuum by sequentially exposing it to volumes of 2.1 cm³ containing specified pressures of N₂O at room temperature (see S1.3 for more details). During adsorption the sample was kept at 77K. Spectra were baselined and analysed using the Omnic software of Thermo Fischer.

Mössbauer spectroscopy. ⁵⁷Fe Mössbauer spectra were recorded with a See Co.W302 resonant gamma ray spectrometer in horizontal geometry with zero external field using a 1.85 GBq source (Be window, Rh matrix). Data were collected from samples enriched with 100% ⁵⁷Fe. Isomer shifts are given relative to α -iron (in this case α -iron does not refer to α -Fe(II)) foil at room temperature. Spectra were collected with 1024 points and summed up to 512 points before analysing, and then fit with Lorentzian doublets using the Vinda software package for Microsoft Excel.

Cluster model static calculations. Cluster models were generated from crystallographic coordinates of BEA polymorph A, as outlined in refs. 8,23 but with capping hydrides at 1.42 Å instead of capping hydroxyls to reduce computation times (see SI S5 for coordinates). To model

α -Fe(II), two Si atoms in a β -type six membered ring were substituted for Al atoms. Such Al configuration was shown to be representative for α -Fe(II) in the different (experimentally indistinguishable) β -type exchange sites found in *BEA polymorphs A and B.²³ Spin-unrestricted DFT calculations were performed with Gaussian 09 (revision D.01)³⁷ using the B3LYP functional with the D3 dispersion correction of Grimme.³⁸ The 6-311G* basis set was used for Fe, for atoms directly coordinated to Fe, and for N₂O. The 6-31G* basis set was used for all other atoms. For geometry optimisations, the six T-sites of the β -6MR ligand were allowed to relax, and all other atoms were frozen at their crystallographic positions. Enthalpy changes were derived from single point calculations performed on optimised structures, but using a larger basis (6-311+G* on Fe, coordinating atoms, and N₂O; and 6-311G* on all others). Thermal contributions to the enthalpy were calculated from vibrational analysis on optimised structures. For the N-O cleavage reaction coordinates, the N-O cleavage transition state was verified to contain a single imaginary frequency corresponding to motion along the reaction coordinate. Mössbauer quadrupole splittings were calculated using the B3LYP functional, with the TZVP basis set on Fe and coordinating O atoms, and 6-31G* on all other atoms. Isomer shifts were calculated with the ORCA computational package (version 303)³⁹ using the B3LYP functional. The CP(PPP) basis set⁴⁰ was used on Fe, with 6-311G* on coordinating O atoms and 6-31G* on all others. A calibration curve was generated by relating the DFT-calculated electron densities at the iron nucleus ($|\psi_0|^2$) to the experimental isomer shifts for a test set of 23 structurally defined Fe complexes. The isomer shift values were then estimated from the value of $|\psi_0|^2$ calculated for each cluster model.

Static calculations with periodic boundary conditions. Static spin-polarized DFT calculations have been performed on a periodically extended unit cell of BEA polymorph A⁴¹, containing an α -Fe(II) site in the plane of the six-membered ring and two Al substitutions for charge compensation. N₂O adsorption energies are determined using the hybrid B3LYP

functional^{42,43} with additional Grimme D3 dispersion corrections³⁸ in a two-level approach. First, a geometry optimisation at the PBE-D3 level of theory⁴⁴ is carried out using the VASP software package.^{45–47} A partial Hessian vibrational analysis is performed on the adsorbate and a 14T cluster around the acid sites of the optimised structures to verify the true nature of the stationary states and to derive the thermal enthalpy contributions.^{48,49} The geometries are further refined by a second optimisation at the B3LYP-D3 level of theory using the CP2K software package⁵⁰ to obtain more accurate energy estimates. For the N-O cleavage reaction, transition states were localized with the improved dimer method.^{51,52} The corresponding reactant and product state were found by following the intrinsic reaction coordinate and minimization via the conjugate gradient algorithm. More details on the computational methodology are given in SI Section S4.

Data availability. The data that support the findings of this study are available from the authors on reasonable request, see author contributions for specific data sets.

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417 Author Contributions

418 M.L.B, B.E.R.S, B.F.S., E.I.S. and R.A.S. designed the experiments. M.L.B., B.E.R.S., and
419 H.M.R. performed the experiments. G.F. performed the FTIR experiments. B.E.R.S. performed
420 the cluster DFT calculations. P.C. and V.V.S. performed the periodic DFT calculations. M.L.B,
421 B.E.R.S., H.M.R, P.C., V.V.S., B.F.S, and E.I.S. analysed the data. M.L.B, B.E.R.S., and H.M.R.
422 wrote the manuscript with guidance from R.A.S, E.I.S. and B.F.S.

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586

Coordination and Activation of Nitrous Oxide by Iron Zeolites — Supplementary Information

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S1: Supplementary Spectroscopy

S1.1 Supplementary data and figures

Figure S1. Full velocity range (± 12 mm/s) Mössbauer spectra and fits for data in figure 1A-C. IS = isomer shift, $|\Delta E_Q|$ = quadrupole splitting – values in mm/s.

Figure S2: Difference UV-Vis spectra (relative to the spectrum of Fe(II)-*BEA after He 1173 K) before introduction of a 35 vol.% N₂O atmosphere (blue), after introduction of the N₂O atmosphere (orange) and after subsequent removal of the N₂O atmosphere at 308 K (grey).

Figure S3: Stacked DRS-UV-Vis-NIR spectra of H-*BEA dried in He at 923 K and subsequently exposed to 35 vol.% N₂O in He at room temperature and heated in 35 vol.% N₂O in He atmosphere at 433 K.

S1.2: lifetime of α -N₂O in equilibrium vs 14.4 keV ⁵⁷Fe excited state

The average lifetimes of the α -Fe(II) bound N₂O_{ads} in equilibrium with the unbound N₂O can be calculated from the adsorption enthalpy and entropy derived in S3.1 for the temperatures used in the Mössbauer experiment in figure 1e, and are given by the following table:

T (K)	100	150	200	250	280
average lifetime N ₂ O _{ads} (s)	4.5x10 ⁻⁴	9.2x10 ⁻⁸	1.2x10 ⁻⁹	8.7x10 ⁻¹¹	2.7x10 ⁻¹¹

The Mössbauer spectrum at 100K shows a single doublet despite the N₂O_{ads} lifetime being much longer than the ~10⁻⁷ seconds lifetime of the ⁵⁷mFe 14.4 keV nuclear excited state probed by Mössbauer spectroscopy. However, we know the spectrum already completely converted to the low temperature species (same as the spectrum at 6K) and the spectrum is no longer an average. At 150K the N₂O_{ads} lifetime is of the same order of magnitude as the Mössbauer measurement. In this case an average is seen together with some broadening on the inner side of the strongest doublet. For the higher temperature spectra an average is observed.

S1.3: FTIR Spectroscopy

Unless specified otherwise, difference spectra are shown in this section from which the spectra of the 550°C vacuum pre-treated sample were subtracted. Before the 550°C treatment the samples had been treated in He flow at 900°C. N₂O was loaded onto the samples at 77K, and the spectra were measured at 77K. The dosages of N₂O loaded onto Fe-*BEA (with 0.33 wt.% Fe) can be converted from mmol N₂O per gram zeolite to mol N₂O per mol Fe using Table S1.

Table S1. Overview of the FTIR measurements at 77K on H-*BEA and Fe-*BEA. The 298K measurements were taken after the 77K measurements on the samples with highest N₂O doses.

H ⁺ -BEA		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	μmol _{N₂O} /g	3	7	10	19	28	37	54	72	101	129	188	250	313	397	517	805	1355	2867
Fe ⁺ -BEA		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
	μmol _{N₂O} /g	3	5	8	16	25	33	51	69	96	123	178	233	316	424	691	1202	2627	
	mol _{N₂O} /mol _{Fe}	0.05	0.09	0.14	0.28	0.42	0.56	0.86	1.17	1.62	2.08	3.01	3.94	5.35	7.18	11.7	20.34	44.46	

After the N₂O loading at 77K, the sample was warmed up to 298K in the same N₂O atmosphere and another measurement was taken. The total area under the asymmetric N₂O stretching region (2400 to 2150 cm⁻¹) was measured for all samples and plotted against the total N₂O exposure in figure S4. Analysis of this plot reveals a much larger area under the 298K spectra. This indicates N₂O has difficulty to penetrate into the zeolite at 77K. The adsorption of N₂O also proceeds with more difficulty on H-*BEA than on Fe-*BEA. A direct quantitative comparison between the H-*BEA and Fe-*BEA samples exposed to similar amounts of N₂O at 77K as overlaid in figure S8 is therefore not appropriate. On H-*BEA, the area rises monotonically with increasing exposure to N₂O, as is also evident from the original spectra in figure S5. On Fe-*BEA the total area takes an upward jump at a p_{N₂O} threshold between samples (6) and (7), and a downward jump going from sample (10) to (11). The upward jump is easily observed from the spectra in figure S6 and the downward jump is best shown by the spectra in figure S9. For samples (7) to (10) and (11) to (14) the area remains stable despite the addition of N₂O. This does not mean the zeolite is saturated with N₂O, but more likely indicates a kinetic barrier to further uptake of N₂O. For the 298K FTIR spectra, the integrated spectral intensity corrected for N₂O loading from 2150 cm⁻¹ to 2400 cm⁻¹ differs by < 2% for H-*BEA and Fe-*BEA, so for these experiments a quantitative comparison as done in the main text is justified. We can thus safely state that the ~2235 cm⁻¹ band is more intense on H-*BEA than on Fe-*BEA at 298K, and the 2283 cm⁻¹ feature in Fe-*BEA fully comes at the expense of ~2235 cm⁻¹ intensity.

Figure S4: Area under the 2400 – 2150 cm⁻¹ spectral region measured at 77K corresponding to the N₂O asymmetric stretch region plotted against the cumulative amount of N₂O added to the vacuum at 77K. On the right an enlargement is shown of the lower amounts of N₂O. The numbers on the curves correspond to the measurements listed in Table S1.

Figure S5: FTIR spectra of different amounts of N₂O loaded onto H-*BEA at 77K.

Figure S7: FTIR spectra of different amounts of N₂O loaded onto Fe-*BEA at 77K. The N₂O loading indicated on the right applies to the full line spectra. The full line spectra are copied as broken lines to allow easy comparison to the spectrum upon the next addition of N₂O.

Figure S8: FTIR spectra of a selection of N₂O loadings onto Fe-*BEA in black compared to a selection on H-*BEA in red

The features at ~2236 and 2287 cm⁻¹ grow gradually with p_{N₂O} up to 0.123 mmol_{N₂O}/g (figure S7). At 3.01 mmol_{N₂O}/g they both disappear along with a feature at 2351 cm⁻¹ and they are replaced by a single feature at 2253 cm⁻¹. Also the 1341 cm⁻¹ feature disappears along with the 2287 cm⁻¹ feature (see figure S9 for detail). Further increase in p_{N₂O} does not alter the 2253 cm⁻¹ feature but does bring back features at 2231 cm⁻¹. Possibly the mono-N₂O bound α-Fe(II) sites are preferred up to a certain p_{N₂O}, above which multiple N₂O are bound to the α-Fe(II) sites, in agreement with the appearance of the α-(N₂O)₂ LT2 site in low temperature Mössbauer. However, because of the different method of N₂O loading (slow cooling from room temperature in dilute N₂O atmosphere for Mössbauer spectroscopy versus exposure to pulses of N₂O at 77K for FTIR) we do not claim a definite connection between the 2253 cm⁻¹ band and α-(N₂O)₂ LT2. Moreover, we calculate $\nu_{\text{asym}} = 2385 \text{ cm}^{-1}$ and $\nu_{\text{asym}} = 2401 \text{ cm}^{-1}$ respectively for the O/O and N/N bound bis-N₂O complexes, quite different from the experimental value of 2253 cm⁻¹. The new ν_{asym} happens to coincide exactly with the ν_{asym} calculated for the η¹-O bound complex (see

figure 3), and is also similar in energy to lattice adsorbed N₂O asymmetric stretches observed on H-*BEA (figure S5).

Figure S9: detail on the spectral changes at 77K in Fe-*BEA going from 0.9 N₂O/Fe to 3.0 N₂O/Fe in the asymmetric stretching region (left) and the symmetric stretching region (right).

S2: Supplementary Reactivity Studies

Test experiments were carried out on the α -O site in Fe-*BEA to demonstrate its similar properties to the α -O sites in Fe-ZSM-5, the material in which these active sites were originally defined. The α -O site in Fe-*BEA is identified by absorption bands at 6000 cm⁻¹, 16900 cm⁻¹, 20100 cm⁻¹ and 28000 cm⁻¹ and a room temperature Mössbauer doublet with $\delta=0.30$ and $|\Delta E_Q|=0.50$.⁸ In Fe-ZSM-5, similar features are observed and linked to reactivity (figure S10, right). The work in this paper was continued with Fe-*BEA because a higher α -Fe(II) site purity could be obtained, as was established in ref. 33.

The α -O site in Fe-ZSM-5 is known to only be formed with N₂O, and not O₂.⁷ This is also the case for the α -O site defined in Fe-*BEA, as shown in figure S10. The α -Fe(II) absorption feature at 15900 cm⁻¹ is unaffected by treatment in O₂ at temperatures as high as 923 K. Meanwhile, reaction in N₂O atmosphere at 433 K causes the dissipation of the 15900 cm⁻¹ feature and results in the α -O absorption spectrum. The α -O site in Fe-ZSM-5 was shown to be stable up to 573 K, above which a recombination of α -O to form gas phase O₂ occurs.⁷ In figure S11, a similar behaviour is shown for α -O in the Fe-*BEA materials. The α -O material releases O₂ at 678 K in a helium flow and the absorption spectrum shows the restoration of the α -Fe(II) precursor after O₂ desorption.

The active site was shown to be reactive in the room temperature activation of methane to form methanol,⁸ and in the room temperature activation of benzene to form phenol,⁵³ features which are strong identifiers of α -O.^{7,26} In figures S12-S14 we add spectroscopic evidence of CO oxidation by the α -O sites in Fe-*BEA to form CO₂, paralleling earlier studies on α -O in Fe-ZSM-5.⁷ The difference spectra in figure S12 show the dissipation of the α -O 16900 cm⁻¹ absorption band alongside the appearance of new features which are most likely linked to CO adsorbed at the iron site. A helium flush at room temperature shows the restoration of the α -Fe(II) site as indicated by the 15900 cm⁻¹ absorption feature. Temperature programmed desorption after the CO reaction results in the desorption of CO₂ from the material at 412 K (figure S14).

Figure S10: Left: DR-UV-Vis-NIR spectra of Fe-*BEA after treatment in He at 1173 K (orange), after treatment in O₂ at 923 K and cooling in O₂ atmosphere to room temperature (blue), after N₂O reaction as done in the main paper to form α -O (grey). **Right:** DR-UV-Vis-NIR spectra of Fe-ZSM-5 (Si/Al=15, 0.76 wt.% Fe) showing similar absorption features to Fe-*BEA after He treatment at 1173 K and H₂ treatment at 973 K (blue), subsequent heating in N₂O at 433 K (orange), and reaction with CH₄ at room temperature (grey).

Figure S11: Left: TPD experiment in helium from of the α -O sample showing the recombination of surface oxygen to form O_2 at 678 K (405 °C). Right: DR-UV-Vis-NIR spectra of the sample after He treatment at 1173 K (blue), after subsequent formation of α -O and before the TPD experiment (orange) and after the TPD experiment, showing the recovery of the α -Fe(II) spectrum (grey).

Figure S12: DR-UV-Vis-NIR difference spectra showing the changes occurring upon CO interaction with α -O at room temperature. The difference spectrum shows the disappearance of the α -O feature and the appearance of features that can be linked to the adsorption of CO on the α -Fe(II) sites (orange). The sample is then flushed with helium to partially desorb CO and to regenerate the α -Fe(II) feature (blue). The underlying (non-difference) spectra are shown in figure S13.

Figure S13: Raw DR-UV-Vis-NIR spectra underlying the difference spectra shown in figure S12. Spectrum after treatment in He at 1173 K (blue), after N_2O reaction to form $\alpha\text{-O}$ (orange), after CO interaction (grey) and after a helium flush at room temperature (yellow).

Figure S14: TPD experiment in helium flow after the reaction of $\alpha\text{-O}$ with CO at room temperature showing the signal of $m/z=44$ corresponding to CO_2 . The contribution of N_2O to the signal has been removed by removing the portion of the signal that correlates to the signal of $m/z=30$.

S3: Calculation of experimental adsorption thermodynamics and reaction kinetics

Two consecutive reaction take place:

For the equilibrium reaction (R1) an equilibrium constant K is defined as the ratio of the forward reaction (adsorption reaction) constant k_a and the backward reaction (desorption reaction) constant k_d :

$$[\alpha\text{-N}_2\text{O}]_{\text{eq}} = \frac{k_a}{k_d} P_{\text{N}_2\text{O}} [\alpha\text{-Fe}]_{\text{eq}} \quad \text{Or} \quad [\alpha\text{-N}_2\text{O}]_{\text{eq}} = K P_{\text{N}_2\text{O}} [\alpha\text{-Fe}]_{\text{eq}}$$

For the activated reaction, the reaction constant k_r is defined and first order kinetics are assumed:

$$\frac{d[\alpha\text{-O}]}{dt} = k_r [\alpha\text{-N}_2\text{O}]$$

Assuming the equilibrium condition between $\alpha\text{-N}_2\text{O}$ and $\alpha\text{-Fe}$ holds ($[\alpha\text{-Fe}] = [\alpha\text{-Fe}]_{\text{eq}}$ and $[\alpha\text{-N}_2\text{O}] = [\alpha\text{-N}_2\text{O}]_{\text{eq}}$), and stating the balance of the α -sites as:

$$[\alpha\text{-Fe}] = [\alpha\text{-Fe}]_0 - [\alpha\text{-N}_2\text{O}] - [\alpha\text{-O}]$$

where $[\alpha\text{-Fe}]_0$ is the initial concentration of $\alpha\text{-Fe}$ sites, the following rate equation can be derived:

$$\frac{d[\alpha\text{-O}]}{dt} = \frac{k_r k_a}{k_a P_{\text{N}_2\text{O}} + k_d} P_{\text{N}_2\text{O}} ([\alpha\text{-Fe}]_0 - [\alpha\text{-O}])$$

$$\frac{d[\alpha\text{-O}]}{dt} = \frac{k_r K}{K P_{\text{N}_2\text{O}} + 1} P_{\text{N}_2\text{O}} ([\alpha\text{-Fe}]_0 - [\alpha\text{-O}])$$

S3.1: Thermodynamics of the equilibrium reaction

The equilibrium of the N₂O adsorption onto the α -Fe sites (R1) was monitored at different partial pressure of N₂O and at various temperatures by operando UV-Vis spectroscopy (figure 4c) as described in the methods section in the main text. For each data point, a UV-Vis spectrum was recorded, and this data was converted to coverage (θ):

$$\theta = \frac{[\alpha\text{-N}_2\text{O}]}{\Sigma[\alpha\text{-sites}]} = \frac{\int (|\Delta A_{10}|)}{\int (|\Delta A_{10}|)_{\max}}$$

Where $\int (|\Delta A_{10}|)$ is the area under the difference UV-Vis absorption spectrum obtained by subtracting the UV-Vis absorption spectrum of the α -Fe sample before exposure to N₂O. The spectral range used was 12000 – 19000 cm⁻¹, including the 15900 cm⁻¹ d-d band and part of the 11500 cm⁻¹ d-d band of α -Fe(II) and α -N₂O respectively. $\int (|\Delta A_{10}|)_{\max}$ is the area obtained at full N₂O coverage and is obtained by linearization of the Langmuir plot shown in figure S15. From the coverage data Langmuir isotherms at various temperatures are constructed and the equilibrium constants are determined for the different temperatures (figure S16). The linearity of

the plots indicates that the Langmuir adsorption model is well applicable in this case.

Figure S15: Langmuir isotherms and equilibrium constants derived from the absorption spectroscopy data for the adsorption of N₂O on α -Fe.

The temperature dependence of the equilibrium constant can now be used to derive the temperature independent standard state adsorption enthalpy (ΔH°) and adsorption entropy (ΔS°) from the Van 't Hoff equation:

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

With R the gas constant and T temperature. The Van 't Hoff plot is shown in figure 4d of the main text. The resulting values are $\Delta H^\circ = -4.8 \pm 0.1$ kcal/mol and $\Delta S^\circ = -7.1 \pm 0.4$ cal/mol/K. The numerical errors are calculated for a 95% confidence interval.

S3.2: Kinetics of the activated reaction

To evaluate the kinetics of the activated reaction (R2) the activated complex theory is considered, which is expressed by the Eyring equation:

$$k_r = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

$$\ln \frac{k_r}{T} = \frac{-\Delta H^\ddagger}{RT} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}$$

With k_r the reaction constant, R the gas constant, T temperature, h Planck's constant, k_B the Boltzmann constant, $\Delta H^\ddagger$ the enthalpy of the transition state ('activation enthalpy') and $\Delta S^\ddagger$ the entropy of the transition state ('activation entropy'). $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are assumed temperature independent in this model.

The conversion is assessed at different temperatures by following the UV-Vis absorption over time with operando UV-Vis spectroscopy (figure 4e) as described in the methods section of the main text. The conversion of α -sites into α -O at time t ($X_{\alpha,t}$) is derived from the absorption data through:

$$X_{\alpha,t} = \frac{\int (|\Delta A_{10}|)_t}{\int (|\Delta A_{10}|)_f}$$

Where $\int (|\Delta A_{10}|)_t$ is the area under the difference UV-Vis absorption spectrum (range 10000 – 40000 cm^{-1} , including the 11500 cm^{-1} d-d band of α -N₂O and the 16900 cm^{-1} , 20100 cm^{-1} and 28000 cm^{-1} bands of α -O) at time t obtained by subtracting the UV-Vis absorption spectrum at the time ($t=0$) where the N₂O flow and temperature are stabilized. $\int (|\Delta A_{10}|)_t$, and thus $X_{\alpha,t}$ is proportional to $[\alpha\text{-O}]$, and $(1 - X_{\alpha,t})$ is proportional to $[\alpha\text{-Fe}] + [\alpha\text{-N}_2\text{O}]$, and to $[\alpha\text{-Fe}]$ and $[\alpha\text{-N}_2\text{O}]$ through an adsorption term (*vide infra*). $\int (|\Delta A_{10}|)_f$ is the area obtained at full conversion ($X_{\alpha,f}=1$), when the spectrum becomes stable in time. Assuming first order kinetics, the conversion data at different temperatures can be related to the rate constant k_{obs} by:

$$\frac{dX_{\alpha,t}}{dt} = k_{\text{obs}}(1 - X_{\alpha,t}) \quad (4)$$

764

$$\ln(1 - X_{\alpha,t}) = -k_{obs}t$$

Figure S16: plots of $k_{obs}t$ versus time and the derived rate constants k_{obs} .

765

766 Plotting $\ln(1 - X_{\alpha,t})$ versus time thus yields a $-k_{obs}t$ vs t plot from which the values of k_{obs} can be
 767 obtained (figure S16).

768 The linearity of the $k_{obs}t$ vs t plots is in agreement with the assumption of a first order
 769 reaction. Diffusion limitation was excluded by ensuring that the N₂O adsorption on the α -sites
 770 reached equilibrium in a timescale significantly shorter than the progress of the activated
 771 reaction for the probed temperature range. This was monitored by the growth of the 11500 cm⁻¹
 772 absorption band and the disappearance of the 15900 cm⁻¹ absorption band.

773 We have now derived reaction constants for the rate equation (4). Of more interest are
 774 the rate constants k_r corresponding to rate equation (2). We therefore combine the Van 't Hoff
 775 and Eyring equations with the reaction equation (3) to derive the following:

$$\frac{d[\alpha\text{-O}]}{dt} = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \cdot \frac{P_{N_2O} \cdot e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}}{1 + P_{N_2O} \cdot e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}} \cdot (1 - X_{\alpha,t})$$

From this equation follows that:

$$k_{obs} = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \cdot \frac{P_{N_2O} \cdot e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}}{1 + P_{N_2O} \cdot e^{-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}}$$

And k_r , as defined in R1, can be derived by dividing the obtained k_{obs} by the absorption term in this equation, which is fully determined by the experimental conditions and the values of ΔH° and ΔS° . In this case the absorption term ≈ 1 and the difference between k_{obs} and k_r is very small, because at the used P_{N_2O} , $[\alpha\text{-}N_2O] \gg [\alpha\text{-}Fe]$.

Plotting an Eyring plot (figure 4f) reveals the temperature dependence of the real reaction constants k_r . In its linear form, the Eyring equation then allows the derivation of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Subsequently, the Gibbs free energy of the activated complex can be derived:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

For known T and with $\Delta H^\ddagger = 17.7 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -22.4 \pm 3.8$ cal/mol/K. The numerical errors are calculated for a 95% confidence interval. The resulting apparent activation energy corresponding to rate equation (5) is 12.8 ± 1.5 kcal/mol.

$$\frac{d[\alpha\text{-O}]}{dt} = k_{app} P_{N_2O} [\alpha\text{-}Fe] \quad (5)$$

S4: Supplementary DFT Calculations

S4.1: periodic DFT calculations

S4.1.1: Computational details for periodic DFT calculations

A hybrid functional was used to estimate the N_2O adsorption energies. To keep the computational procedure within reach, a two-step procedure was followed, wherein the

796 geometries were first optimised at the PBE-D3 level of theory using VASP. Thermal corrections
797 were derived from the normal modes of the optimised geometry calculated with VASP at the
798 PBE-D3 level of theory. Afterwards, these structures were re-optimised with the more accurate
799 hybrid B3LYP-D3 functional using the CP2K software and adsorption enthalpies were derived.

800 Periodic calculations were performed on a unit cell of Fe-BEA,⁴¹ containing 64 T atoms, an α -
801 Fe(II) active site located near the plane of the six-membered ring and two Al substitutions in the
802 six-membered ring at the T6 position for charge compensation. Such Al substitution is
803 representative for the β -type six-membered rings that host α -Fe(II).²³ The optimal cell volume of
804 the unit cell of Fe-BEA was calculated by a least squares fit to the Birch Murnaghan equation of
805 state curve.⁵⁴ This led to a cell volume of 4280.99 Å³ (and cell parameters: a=12.69 Å, b=12.67
806 Å, c=26.63 Å, α =90.00°, β =89.98°, γ =90.00°). During all calculations, the unit cell parameters
807 are kept fixed.

808 Spin polarized geometry optimisations were performed with the VASP software package (VASP
809 5.4),^{45–47,55} using the Projector Augmented Wave (PAW) approach.^{56,57} As level of theory, the
810 PBE functional⁴⁴ was applied together with Grimme D3 dispersion corrections.³⁸ The
811 recommended GW PAW potentials were used.⁵⁸ In addition, a plane wave basis set was
812 employed with a kinetic energy cut-off of 600 eV. Sampling of the Brillouin zone was restricted
813 to the Γ -point only. An ionic energy criterion of 10⁻⁴ eV and an electronic convergence criterion
814 of 10⁻⁵ eV were applied for all relaxations. The local minima were optimised using the conjugate
815 gradient algorithm. Transition states were localized with the improved dimer method^{51,52} and
816 refined with a quasi-Newton algorithm. The corresponding reactant and product states were
817 optimised from geometries that were slightly displaced along the imaginary normal mode
818 corresponding to the transition state motion. The nature of each stationary state was verified by
819 analysing the normal modes. To obtain the normal modes, a partial Hessian vibrational analysis
820 (PHVA)^{59–61} on the adsorbate, the Fe active site and a 14T cluster of the framework, centred

around the two acid sites, was conducted. To calculate adsorption enthalpies at 50°C, thermal contributions to the enthalpy were estimated based on the harmonic oscillator (HO) approximation using the TAMkin software package.⁴⁹

To obtain more reliable estimates for the electronic energy, the obtained stationary states are refined by a further geometry optimisation with a hybrid functional using the CP2K software package (CP2K 6.1).⁵⁰ Spin polarized geometry optimisations were carried out at the B3LYP level of theory^{42,43} with additional Grimme D3 dispersion corrections.³⁸ A mixed basis set approach with a combination of both Gaussian type orbitals (GTO) and plane waves (PW).^{62,63} For the plane waves basis set, an energy cut-off of 320 Ry is used. As Gaussian basis set, the DZVP-MOLOPT-SR-GTH basis⁶⁴ is used for all elements in conjunction with GTH pseudopotentials.⁶⁵ The self-consistent field (SCF) convergence criterion was set to 10^{-6} Ha. Cell parameters are kept fixed. The conjugate gradient algorithm was chosen to find the stationary states.

S4.1.2: N₂O adsorption at the Fe active site

Static periodic DFT calculations were performed to evaluate the energy difference between the η^1 -N and η^1 -O coordination of N₂O. To this end, five distinctly different configurations of each type were optimised. Table S2 compares the electronic adsorption energies from both methods for all configurations. Also, the resulting adsorption energies from a single-point energy calculation at the B3LYP-D3 level of theory are included. The single-point results largely differ from the adsorption energies obtained with the PBE functional. Also, a large spread on the single-point adsorption energies is found, depending on the configuration. This result clearly indicates that in order to obtain accurate results, a full geometry optimisation with a hybrid functional (B3LYP) should be performed instead of a simple energy refinement. Table S3 lists two key geometry characteristics of the optimised N₂O configurations for both DFT methods. This comparison shows a remarkable resemblance between the PBE-D3 geometries from

VASP and the B3LYP-D3 geometries from CP2K. The most stable η^1 -O and η^1 -N models are marked in blue in Tables S2 and S3. For these two models, the entropy changes from static calculations relative to gas-phase N₂O were -101.3 J/mol/K for the adsorption of N₂O to the BEA lattice, -121.8 J/mol/K for the η^1 -N model A, and -115.7 J/mol/K for the η^1 -O model E.

Table S2. Comparison of electronic N₂O adsorption energies in Fe-BEA for 5 different η^1 -N bound and η^1 -O bound configurations, obtained from a geometry optimisation at the PBE-D3 level of theory in VASP, a single-point energy calculation at the B3LYP-D3 level of theory in CP2K or a geometry optimisation at the B3LYP-D3 level of theory in CP2K. Reference level: empty Fe-BEA framework and N₂O in gas phase. The most stable models are marked in blue.

		$\Delta E_{\text{el,ads}}$ (kJ/mol)		
		VASP	CP2K	
		opt-PBE-D3	sp-B3LYP-D3	opt-B3LYP-D3
η^1 -N	A	-56.6	-170.5	-56.1
	B	-49.3	-115.5	-43.4
	C	-57.6	-160.1	-50.5
	D	-54.2	-135.8	-47.3
	E	-52.2	-147.1	-50.6
η^1 -O	A	-29.7	-138.9	-29.0
	B	-29.4	-133.5	-33.9
	C	-29.0	-112.3	-30.2
	D	-27.5	X	X
	E	-30.5	-143.2	-44.1

Table S3. Comparison of some key geometry characteristics (Fe-N₂O bond distance and Fe-N₂O bond angle) for 5 different configurations of η^1 -N bound and η^1 -O bound N₂O adsorbed in Fe-BEA, obtained from the optimised geometries at the PBE-D3 level of theory in VASP or at the B3LYP-D3 level of theory in CP2K. The most stable models are marked in blue.

		VASP – PBE-D3		CP2K – B3LYP-D3	
		d(Fe-N) (Å)	<(Fe-N-N) (°)	d(Fe-N) (Å)	<(Fe-N-N) (°)
η^1 -N	A	2.03	161.3	2.13	160.1
	B	2.06	156.9	2.12	154.9
	C	2.01	171.1	2.11	168.8
	D	2.02	150.5	2.10	151.6
	E	2.03	147.3	2.14	148.8

		d(Fe-O) (Å)	<(Fe-O-N) (°)	d(Fe-O) (Å)	<(Fe-O-N) (°)
$\eta^1\text{-O}$	A	2.38	133.3	2.39	133.0
	B	2.54	122.9	2.57	121.8
	C	2.66	136.9	2.63	139.5
	D	2.67	131.2	2.66	127.3
	E	2.34	127.1	2.33	128.0

S4.1.3: N_2O binding and activation

The static energy profile for the N-O cleavage on the S=2 surface was evaluated at the B3LYP-D3 level of theory in CP2K. Since the $\eta^1\text{-N}$ bound configuration is the most stable state, it first needs to rotate and rearrange into the $\eta^1\text{-O}$ bound configuration before the cleavage reaction can occur. Table S4 contains the geometrical parameters as well as the electronic energy of the reactant, product and transition state, with respect to the gas phase N_2O reactant and empty Fe-BEA framework. The reactant and product states were optimised by following the intrinsic reaction coordinate from the optimised transition state. Figure S17 displays snapshots of the stationary states along the reaction pathway. To calculate the adsorption enthalpies, thermal corrections were obtained from the normal mode calculation on the optimised geometries in VASP since normal mode calculations in CP2K were proven to be less reliable. These thermal corrections were added to the B3LYP-D3 electronic energies. The contribution of these thermal corrections to the overall enthalpy is less than 5 kJ/mol for all states. Given the similarities between the optimised geometries that are obtained with PBE and B3LYP (see Table S3), it seems reasonable to assume that the thermal corrections will be very similar for both methods.

Table S4. Key geometry characteristics (Fe-ON₂ bond distance, O-N₂ bond distance and Fe-O-N₂ bond angle), electronic energies, and adsorption enthalpies at 323 K (with respect to the empty Fe-BEA framework and N_2O in gas phase) of the transition state and corresponding reactant and product minima for the N-O cleavage reaction in Fe-BEA, obtained from the geometry optimisations at the B3LYP-D3 level of theory in CP2K.

	d(Fe-O) (Å)	d(O-N) (Å)	<(Fe-O-N) (°)	$\Delta E_{\text{el,B3LYP-D3}}$ (kJ/mol)	$\Delta H_{323\text{K,B3LYP-D3}}$ (kJ/mol)
--	----------------	---------------	------------------	---	---

Reactant	2.27	1.21	142	-38.2	-35.0
TS	1.82	1.56	135	66.9	62.0
Product	1.61	3.03	133	-52.3	-49.0

Figure S17: Snapshots of the optimised geometries of (a) the most stable $\eta^1\text{-N}$ bound configuration, (b) the most stable $\eta^1\text{-O}$ bound configuration, (c) the reactant state, (d) the transition state and (e) the product state of the N-O cleavage reaction.

	$\eta^1\text{-O}$	$\eta^1\text{-N}$	$\eta^1\text{-N}'$	$\eta^1\text{-O,O}$	$\eta^1\text{-O,N}$	$\eta^1\text{-N,N}$
$\Delta H_{\text{binding}}$ (kcal/mol)	-4.1	-3.8	-3.4	-8.3	-7.9	-6.2
LF band (cm ⁻¹)	12300	6300	11600	10400 6100	6500	none
ΔE_Q (mm/s)	-1.63	2.39	-1.76	2.50	3.02	4.15
β HOMO	d_{z^2}	d_{xz}	d_{z^2}	d_{z^2}/d_{xz}	d_{z^2}/d_{xz}	d_{xy}

Figure S18: Comparison of the geometric structures of the three possible mono-N₂O-bound models (top), and bis-N₂O-bound models (bottom) evaluated by cluster DFT calculations. (Note that cluster calculations were used in this comparison due to the difficulty of predicting Mössbauer parameters by periodic calculations.) (It is not possible to bind additional N₂O ligands to the sterically protected *trans* axial positions of these sites.) In the table below, the predicted properties of these models are compared. DFT calculations predict S=2 ground states for all six models. Based on their predicted quadrupole splittings, the $\eta^1\text{-O,O}/\eta^1\text{-O,N}$ models are potential structural models of the $\alpha\text{-(N}_2\text{O)}_2$ LT2 species observed at low temperature and high N₂O concentrations (see figure 1f).

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889

890 **Table S5.** Key geometric and electronic structural parameters of the $\eta^1\text{-N}$ (A) and $\eta^1\text{-O}$ (B) bound active
891 sites, as well as the N-O cleavage transition state (C) from cluster models. The associated electronic
892 energies of N₂O adsorption and activation included at the right of each table. $Q_{\text{TS}}(\text{N}_2\text{O})$ quantifies the
893 extent of charge transfer from the Fe centre into the N₂O ligand at the N-O cleavage transition state. Note
894 that the results of the T3/T3', T5/T5', and T7/T7' sites parallel those of the T4/T4', T6/T6', and T8/T8'
895 sites, respectively. A comparison of this is shown in D.

A. $\eta^1\text{-N}$	d(Fe-N) (Å)	β homo	ΔE_Q (mm/s)	ΔE_{ads} (kcal/mol)
T4/T4'	2.12	d_{xz}	+2.22	-10.1
T6/T6'	2.21	d_{xz}	+2.39	-3.9
T8/T8'	2.14	d_{xz}	+2.30	-11.5

B. $\eta^1\text{-O}$	d(Fe-O) (Å)	β homo	ΔE_Q (mm/s)	ΔE_{ads} (kcal/mol)
T4/T4'	2.22	$d_{z^2}/d_{x^2-y^2}$	+2.45	-8.1
T6/T6'	2.35	d_{z^2}	-1.63	-3.9
T8/T8'	2.22	$d_{z^2}/d_{x^2-y^2}$	+2.11	-9.4

C. TS	d(Fe-O) (Å)	d(Fe-N) (Å)	$Q_{\text{TS}}(\text{N}_2\text{O})$	ΔE_{act} (kcal/mol)
T4/T4'	1.81	1.50	-0.26	27.4
T6/T6'	1.83	1.46	-0.29	27.9
T8/T8'	1.80	1.54	-0.22	30.9

D. $\eta^1\text{-O}$	d(Fe-ONN) (Å)	d(Fe-O) _{avg} (Å)	<O-Fe-O _{avg}	<Fe-O-NN
T4/T4'	2.22	2.07	144°	135°
T7/T7'	2.21	2.08	146°	137°
T6/T6'	2.35	2.03	147°	128°
T5/T5'	2.35	2.03	148°	128°
T8/T8'	2.22	2.08	140°	140°
T3/T3'	2.22	2.08	142°	141°

S4.2: Evaluation of the B3LYP Functional for O-atom Transfer

As presented in Table S6, the driving force and activation barrier associated with the O-atom transfer reaction are very sensitive to the amount of Hartree-Fock (HF) exchange included in the DFT functional. As the level of HF exchange is decreased, the driving force for O-atom transfer increases. Adjusting for this difference in driving force using Marcus theory,^{66,67} the resulting intrinsic barriers are similar across the three functionals, indicating each predicts similar electronic structure contributions to the N-O cleavage barrier. Indeed, all predict a transition state electronic structure that is well-described as involving transfer of $\sim\frac{1}{2}$ of a spin-down electron from the Fe d_{xz} orbital into a vacant π^* orbital of N_2O . This analysis suggests that, while B3LYP functional used in this study under-predicts the driving force for O-atom transfer,

resulting in a calculated barrier that is higher than experimental value (17.7 kcal/mol), it correctly describes the orbital interactions contributing to N-O cleavage.

Table S6. Effect of Hartree-Fock exchange on the predicted energetics (ΔE , in kcal/mol) of the N-O cleavage reaction. The three functionals predict different driving forces for O-atom transfer, but similar intrinsic barriers. †B3LYP is a hybrid functional that already includes 20% HF exchange. The intrinsic barriers are calculated by using a Marcus Theory correction.

functional	α -N ₂ O	N-O TS	α -O	intrinsic barrier
BP86 with 30% HF exchange added	0	31.2	7.7	27.2
†B3LYP (contains 20% HF exchange)	0	23.8	-6.4	26.9
BP86 with 15% HF exchange added	0	13.3	-24.4	24.0

S4.3: Additional cluster DFT calculations

Figure S19: A) toy model of the N-bound Fe^{II} species, in which the 6-membered ring ligand is capped with hydrogens and allowed to freely geometry optimise, B) geometry optimised structure including an axial amine ligand, and C) structure in which the axial amine ligand is deleted, and the coordinates of the N₂O ligand are re-optimised (i.e. the Fe^{II} and 6-membered ring ligand are frozen). For each model, the out-of-plane distortion of the iron atom is quantified by the average distortion of the O-Fe-O angle ($\delta\text{OFeO}_{\text{avg}}$), and the doubly-occupied orbital is indicated.

S5: Cartesian coordinates of the model structures used in this work

Table S7 gives a full overview of the models used in this study. Cartesian coordinates are given below for the structures used for the main text figures. The others can be reproduced from the computational methods or can be made available upon reasonable request.

Table S7. Overview of the models used in this study

Solid State Models			
VASP PBE-D3		CP2K B3LYP-D3	
Empty α -Fe(II) in BEA + gas-phase N ₂ O		Empty α -Fe(II) in BEA + gas-phase N ₂ O	
N ₂ O adsorbed on zeolite away from α -Fe(II)		N ₂ O adsorbed on zeolite away from α -Fe(II)	
η^1 -N bound A		η^1 -N bound A	
η^1 -N bound B		η^1 -N bound B	
η^1 -N bound C		η^1 -N bound C	
η^1 -N bound D		η^1 -N bound D	
η^1 -N bound E		η^1 -N bound E	
η^1 -O bound A		η^1 -O bound A	
η^1 -O bound B		η^1 -O bound B	
η^1 -O bound C		η^1 -O bound C	
η^1 -O bound D		η^1 -O bound D	
η^1 -O bound E		η^1 -O bound E	
		α -O + N ₂ product	
		η^1 -O bound reactant state	
		Transition state	
Cluster Models (B3LYP-D3, unless specified otherwise)			
Adsorption complexes & Reaction coordinate	Different Al configurations	Different Hartree-Fock Exchange	Other
Empty α -Fe(II) in BEA + gas-phase N ₂ O	T4T4' η^1 -N bound	η^1 -O (BP86, 15% HF)	Empty α -Fe(II) in BEA + gas-phase N ₂ O (method fig 6)
N ₂ O adsorbed on zeolite without α -Fe(II)	T8T8' η^1 -N bound	η^1 -O (BP86, 30% HF)	η^1 -O (method fig 6)
η^1 -N bound	T3T3' η^1 -O bound	TS (BP86, 15% HF)	α -O + N ₂ product (method fig 6)
η^1 -O bound	T4T4' η^1 -O bound	TS (BP86, 30% HF)	Transition state (method fig 6)
η^1 -N' bound	T5T5' η^1 -O bound	α -O (BP86, 15% HF)	α -Fe(II) Toy model fig 5
η^1 -N,N bound	T7T7' η^1 -O bound	α -O (BP86, 30% HF)	η^1 -N bound fig S6
η^1 -O,O bound	T8T8' η^1 -O bound		η^1 -N bound + axial amine fig S6
η^1 -O,N bound	T4T4' Transition state		η^1 -N bound, amine deleted and reoptimised fig S6
α -O product	T8T8' Transition state		
S=1 Transition state (no dispersion)			
S=2 Transition state			

927

928 **S5.1: Solid state models**929 **Table S8.** CP2K Empty α -Fe(II) in BEA

atom	x	y	z
Fe	6.353564	6.730672	13.31266
Al	4.154358	5.82348	11.77172
Al	8.547722	5.821399	14.85541
Si	8.476812	10.00988	25.09748
Si	4.220206	2.536525	11.78183
Si	10.14656	4.218768	18.43281
Si	2.650241	8.484991	5.097252
Si	5.788269	4.21373	8.202684
Si	6.848931	8.479229	21.46918
Si	8.446764	6.795594	25.14399
Si	6.926634	4.219546	18.42755
Si	5.85119	8.479965	5.15702

Si	6.020444	1.751895	16.64391
Si	1.734955	6.739581	9.968247
Si	10.89617	6.002692	23.32911
Si	6.010077	10.89974	23.26825
Si	6.689003	1.75379	9.980795
Si	10.9695	6.739072	16.65542
Si	1.801803	6.004282	3.294485
Si	5.998273	6.698483	16.62668
Si	6.70406	6.698564	10.00002
Si	6.010126	6.007633	23.2834
Si	10.94407	1.728512	16.63642
Si	1.756408	1.729743	9.991272
Si	10.94478	10.90019	23.32716
Si	0.550679	2.560243	14.77547
Si	2.581248	12.14716	8.058258
Si	10.11369	0.56529	21.4898
Si	0.582286	10.08739	25.18183
Si	12.14141	2.555977	11.85799
Si	10.11821	12.14612	18.56783
Si	2.586867	0.567464	5.136552
Si	0.548021	5.779519	14.77875
Si	5.786264	12.13552	8.090628
Si	6.901091	0.55864	21.45236
Si	0.552009	6.870087	25.16283
Si	12.16107	5.774304	11.83841
Si	6.913729	12.13527	18.53526
Si	5.79931	0.558805	5.17327
Si	3.677801	2.557914	14.8264
Si	2.600382	9.020406	8.157112
Si	10.11442	3.670558	21.48413
Si	3.68243	10.04721	25.10075
Si	9.020817	2.558801	11.80008
Si	10.10015	9.019353	18.4687
Si	2.586244	3.672505	5.14186
Si	3.661432	5.74917	14.93471
Si	5.761493	9.016263	8.220196
Si	6.910055	3.682478	21.45985
Si	3.655988	6.853322	25.06662
Si	9.044028	5.749492	11.69096
Si	6.939051	9.016082	18.40581
Si	5.790566	3.682497	5.16677
Si	8.482499	2.534949	14.84359
Si	2.562723	4.216855	8.194623
Si	10.05021	8.485022	21.52918
Si	12.12567	10.08291	1.460542
Si	12.13884	6.865617	1.453855
Si	9.020939	10.04805	1.525317
Si	9.040095	6.853923	1.559333
Si	4.222703	10.01075	1.528804
Si	4.252924	6.796425	1.481267
Si	6.690707	10.89996	3.356958
Si	6.68787	6.007935	3.343197
Si	1.756992	10.9018	3.302528
O	10.5712	10.51998	1.607622
O	0.035433	10.54092	0.023139
O	0.28817	10.78322	2.639194
O	12.27412	8.475393	1.605616
O	10.59543	6.395036	1.623001
O	12.658	6.400413	-0.0174
O	0.341268	6.196575	2.624403
O	8.144718	10.83572	2.637474
O	8.940629	8.453842	1.796368
O	8.406657	10.34722	0.052384
O	8.180026	6.118742	2.717796
O	8.414277	6.477081	0.106369
O	5.534857	10.6093	2.252745
O	4.177385	8.400167	1.731872
O	2.88147	10.67164	2.153963
O	5.598336	6.201792	2.152395
O	2.944291	6.109421	2.143387

O	2.111494	2.155583	14.92263
O	2.179427	10.58448	8.183089
O	10.53583	2.116947	21.67045
O	2.135106	10.5215	25.01676
O	10.5831	2.154277	11.70047
O	10.52042	10.58357	18.44309
O	2.164576	2.119027	4.955489
O	12.65661	2.0969	13.33216
O	2.1294	0.036611	6.600783
O	10.57073	0.035467	20.02522
O	12.40172	1.81674	15.93641
O	1.820331	0.312948	9.208497
O	10.80164	12.37668	22.68023
O	12.40804	10.78334	24.00502
O	0.300234	1.816773	10.69678
O	10.8796	0.311189	17.41754
O	1.89927	12.37943	3.945777
O	0.39264	4.171989	14.92338
O	4.184362	12.3383	8.263839
O	8.505458	0.395634	21.59319
O	0.425468	8.481006	25.02106
O	12.30859	4.166403	11.69369
O	8.515367	12.33955	18.36214
O	4.194874	0.396848	5.032937
O	2.116528	6.192898	14.92146
O	6.197284	10.576	8.269142
O	6.486339	2.120823	21.57966
O	2.0975	6.397792	25.00559
O	10.59174	6.191086	11.7054
O	6.503011	10.57561	18.35695
O	6.213965	2.120895	5.046218
O	0.031522	6.210711	13.29862
O	6.232888	12.64088	6.618493
O	6.466739	12.64062	20.00729
O	12.42565	6.537035	15.94899
O	6.55923	0.336207	9.207016
O	6.156881	12.3741	22.6105
O	12.35852	6.196406	23.9913
O	0.279526	6.537024	10.67201
O	6.139971	0.332921	17.41763
O	6.542889	12.37401	4.015201
O	4.549895	1.801535	15.95767
O	1.716368	8.177247	9.205871
O	10.87419	4.550428	22.6096
O	4.556995	10.83514	23.9882
O	8.155304	1.797272	10.66996
O	10.98438	8.175997	17.41978
O	1.82526	4.552861	4.016596
O	3.826636	4.156905	15.10495
O	4.177975	8.861178	8.540497
O	8.510005	3.832145	21.67248
O	3.759438	8.452748	24.82952
O	8.87345	4.158036	11.52101
O	8.522516	8.860535	18.08537
O	4.190631	3.833138	4.953383
O	4.258322	2.170532	13.36831
O	2.341307	8.409668	6.677359
O	10.52766	4.198584	20.0071
O	4.295531	10.3462	26.57404
O	8.441728	2.170974	13.25771
O	10.35885	8.409561	19.94886
O	2.175409	4.197903	6.620736
O	4.465293	6.480474	16.13756
O	6.565173	8.18054	9.363637
O	6.145359	4.544047	22.59644
O	4.516594	6.117941	23.90779
O	8.238028	6.481373	10.48878
O	6.135909	8.180544	17.26216
O	6.554374	4.544372	4.029984
O	4.394392	6.207446	13.52778

O	6.114795	8.401958	6.756162
O	6.505518	4.266272	19.99346
O	4.28497	6.476399	26.51864
O	8.312708	6.208197	13.099
O	6.585505	8.401546	19.86981
O	6.196502	4.264343	6.633385
O	7.14819	1.887354	15.49797
O	1.998286	5.577131	8.849249
O	10.62156	7.147452	22.21662
O	7.165478	10.60901	24.37296
O	5.553393	1.890718	11.12081
O	10.71129	5.576633	17.7748
O	2.077549	7.148255	4.40795
O	8.520081	4.121143	15.04545
O	4.180074	4.08257	8.355597
O	8.443229	8.58776	21.77041
O	8.52224	8.399616	24.89395
O	4.180587	4.122983	11.58178
O	8.53154	4.092884	18.27341
O	4.25699	8.587697	4.85609
O	9.783982	1.812254	15.50686
O	1.899567	2.931706	8.912218
O	10.78241	9.78982	22.15408
O	9.817872	10.67136	24.47303
O	2.918639	1.812735	11.11937
O	10.801	2.930114	17.71554
O	1.920446	9.790902	4.47424
O	6.926968	6.55339	15.2613
O	6.227457	5.602627	8.917793
O	6.235913	7.151	22.1515
O	7.100457	6.201459	24.47354
O	5.775653	6.554078	11.36494
O	6.472533	5.601546	17.70936
O	6.463736	7.151674	4.47457
O	9.820785	6.706172	15.54831
O	6.548881	2.968065	8.903182
O	6.130942	9.797759	22.07867
O	9.75495	6.108693	24.48116
O	2.881581	6.707792	11.07761
O	6.211016	2.955019	17.72415
O	6.568866	9.798266	4.546799

930

931 **Table S9.** CP2K gas-phase N₂O

atom	x	y	z
O	5.77728	9.019009	13.72949
N	3.884508	9.76474	14.88351
N	4.804776	9.400489	14.32058

932

933 **Table S10.** CP2K N₂O adsorbed on zeolite away from α -Fe(II)

atom	x	y	z
Fe	6.439935	6.818707	6.47556
Al	4.247674	5.922335	4.93491
Al	8.620667	5.899569	8.032393
Si	8.56391	10.12569	18.25695
Si	4.334177	2.642284	4.960699
Si	10.24884	4.324331	11.60694
Si	2.783238	8.55677	24.89021
Si	5.832778	4.360019	1.368358
Si	6.914646	8.558517	14.62918
Si	8.56425	6.928305	18.2543
Si	7.024066	4.332377	11.58566
Si	5.984666	8.560482	24.96043
Si	6.102295	1.855223	9.811676
Si	1.789749	6.814901	3.124547
Si	11.01846	6.089734	16.48662

Si	6.094213	10.98758	16.44881
Si	6.772279	1.879586	3.13683
Si	11.07203	6.816719	9.841112
Si	1.862313	6.096882	23.09227
Si	6.067726	6.803648	9.795994
Si	6.79734	6.815824	3.161677
Si	6.086163	6.112261	16.43546
Si	11.01952	1.831656	9.80019
Si	1.852972	1.849301	3.152307
Si	11.01735	11.00237	16.49078
Si	0.648	2.67868	7.930819
Si	2.657215	12.24461	1.25693
Si	10.20591	0.654212	14.6472
Si	0.657931	10.17293	18.35661
Si	12.23363	2.685483	5.012142
Si	10.19858	12.23678	11.71567
Si	2.65868	0.656125	24.95611
Si	0.639432	5.892085	7.940548
Si	5.8691	12.24883	1.241561
Si	7.003708	0.646102	14.64739
Si	0.658148	6.94887	18.3532
Si	12.24007	5.897379	5.026392
Si	6.99796	12.23548	11.70692
Si	5.87465	0.649352	24.93742
Si	3.770933	2.653368	7.997591
Si	2.688477	9.116352	1.333546
Si	10.204	3.754905	14.65767
Si	3.766705	10.14747	18.26129
Si	9.108895	2.648459	4.948728
Si	10.18451	9.108582	11.63301
Si	2.675248	3.762875	24.91961
Si	3.753721	5.867591	8.082464
Si	5.853229	9.128449	1.395336
Si	7.006979	3.770422	14.63349
Si	3.76349	6.955748	18.26598
Si	9.119829	5.859353	4.885164
Si	7.024894	9.117955	11.565
Si	5.873165	3.775812	24.94631
Si	8.547579	2.612286	7.991187
Si	2.613094	4.326525	1.340153
Si	10.12443	8.548471	14.70122
Si	12.21651	10.17283	21.25198
Si	12.21372	6.949843	21.24905
Si	9.117603	10.14069	21.31817
Si	9.120088	6.955647	21.31241
Si	4.28368	10.14054	21.30396
Si	4.284571	6.925388	21.30415
Si	6.769348	10.98935	23.12887
Si	6.77682	6.117265	23.14204
Si	1.864636	11.01001	23.09916
O	10.66407	10.61883	21.40282
O	0.123057	10.65215	19.81755
O	0.400173	10.85073	22.42915
O	12.31007	8.561943	21.38885
O	10.66769	6.475649	21.39482
O	0.114289	6.477402	19.81147
O	0.398844	6.283533	22.42857
O	8.232202	10.92772	22.42378
O	9.038081	8.547541	21.59119
O	8.507259	10.42958	19.84272
O	8.230087	6.192982	22.42377
O	8.508351	6.623568	19.84256
O	5.623393	10.67843	22.02328
O	4.113599	8.534177	21.50227
O	2.983629	10.86894	21.93434
O	5.616877	6.390645	22.03956
O	2.973911	6.202165	21.91682
O	2.202832	2.253797	8.093438
O	2.266149	10.68002	1.4194
O	10.62537	2.203299	14.82986

O	2.211365	10.60067	18.17305
O	10.67957	2.255048	4.853659
O	10.60457	10.67428	11.5992
O	2.257037	2.209563	24.74274
O	0.122052	2.237418	6.459816
O	2.193761	0.128804	26.42312
O	10.62529	0.133096	13.17248
O	12.47022	1.964176	9.089877
O	1.912943	0.397333	2.43387
O	10.96629	12.45021	15.77289
O	12.47955	10.8505	17.16859
O	0.398434	1.96998	3.849624
O	10.9695	0.406739	10.57379
O	1.919684	12.46521	23.80221
O	0.481473	4.286344	8.080824
O	4.266331	12.44326	1.421836
O	8.604573	0.482882	14.82885
O	0.50746	8.561832	18.26658
O	12.3893	4.293332	4.863258
O	8.597028	12.43419	11.51934
O	4.266435	0.481266	24.82907
O	2.207105	6.290409	8.081015
O	6.280443	10.69034	1.440008
O	6.574421	2.209018	14.74653
O	2.207232	6.494933	18.17285
O	10.66496	6.291764	4.941028
O	6.589504	10.67729	11.50836
O	6.300479	2.212724	24.82856
O	0.125081	6.364083	6.472896
O	6.324444	0.054872	26.38095
O	6.571227	0.053738	13.19585
O	12.51755	6.636917	9.112879
O	6.638617	0.472236	2.347189
O	6.298602	12.47538	15.84141
O	12.47616	6.282463	17.16379
O	0.330597	6.63971	3.830646
O	6.227123	0.441256	10.59117
O	6.5727	12.48465	23.72967
O	4.606098	1.915788	9.181713
O	1.804042	8.255079	2.366797
O	10.9712	4.63804	15.77171
O	4.629375	10.93438	17.14124
O	8.273624	1.913077	3.761367
O	11.06798	8.268091	10.58045
O	1.911534	4.641665	23.79921
O	3.927461	4.267585	8.186606
O	4.269412	8.955384	1.700543
O	8.603063	3.917475	14.85102
O	3.90565	8.55236	17.99121
O	8.949331	4.261811	4.758853
O	8.607123	8.951243	11.2447
O	4.276877	3.919944	24.72697
O	4.350818	2.243529	6.541784
O	2.443807	8.52451	26.4685
O	10.6118	4.2825	13.18244
O	4.369189	10.5014	19.72824
O	8.527781	2.237808	6.404375
O	10.43751	8.503055	13.11801
O	2.265808	4.311183	26.38805
O	4.535617	6.619779	9.290427
O	6.658961	8.308875	2.549944
O	6.235952	4.640479	15.76399
O	4.63071	6.188465	17.14032
O	8.328143	6.570459	3.655647
O	6.218733	8.287558	10.42244
O	6.647222	4.646212	23.81927
O	4.474183	6.36547	6.681771
O	6.225029	8.507252	26.56354
O	6.642658	4.354373	13.15855
O	4.371477	6.57697	19.72545

O	8.40265	6.363673	6.286394
O	6.667805	8.500975	13.0266
O	6.23493	4.357155	26.42356
O	7.191337	1.976791	8.62381
O	1.992112	5.658838	1.992276
O	10.78418	7.241856	15.37214
O	7.205937	10.68101	17.58768
O	5.681026	1.989233	4.324726
O	10.87693	5.671067	10.98748
O	2.158504	7.242136	24.20194
O	8.600448	4.197361	8.192272
O	4.227092	4.263075	1.535738
O	8.512053	8.580655	14.94447
O	8.690503	8.52612	17.99379
O	4.284636	4.226492	4.761166
O	8.631952	4.268082	11.41024
O	4.390131	8.580938	24.64917
O	9.83429	1.900968	8.695321
O	1.98417	3.011693	2.030199
O	10.79229	9.866446	15.35937
O	9.86137	10.86169	17.62579
O	3.031002	1.973654	4.254868
O	10.87704	3.024836	10.88662
O	2.152411	9.894306	24.23982
O	7.006275	6.630145	8.440905
O	6.313004	5.754606	2.048962
O	6.231396	7.2477	15.28299
O	7.205917	6.364363	17.58499
O	5.864813	6.646971	4.52239
O	6.490812	5.695174	10.88648
O	6.662221	7.250152	24.30341
O	9.904678	6.726251	8.759786
O	6.562483	3.117024	2.099754
O	6.230709	9.89554	15.24778
O	9.862751	6.198238	17.62479
O	2.945694	6.729752	4.220909
O	6.31684	3.062134	10.88
O	6.656097	9.900263	24.33431
O	6.411917	3.83389	20.37671
N	8.059242	3.311114	18.80283
N	7.25673	3.564236	19.56857

934

935 **Table S11.** CP2K η^1 -N bound A

atom	x	y	z
Fe	6.425809	6.999756	13.49667
Al	4.272236	5.875542	11.8917
Al	8.584893	5.863469	15.02261
Si	8.535033	10.07014	25.25463
Si	4.301632	2.593258	11.92891
Si	10.21486	4.281355	18.58371
Si	2.730109	8.517354	5.215039
Si	5.806499	4.3091	8.353067
Si	6.922412	8.506639	21.62389
Si	8.548097	6.865139	25.27045
Si	7.002233	4.298032	18.59487
Si	5.931803	8.551836	5.279052
Si	6.093505	1.83241	16.77875
Si	1.760214	6.760831	10.10938
Si	10.98332	6.028071	23.4797
Si	6.066201	10.9253	23.42426
Si	6.737329	1.82212	10.12587
Si	11.07888	6.759832	16.80522
Si	1.87402	6.033799	3.418935
Si	6.047557	6.749174	16.84207
Si	6.793017	6.773513	10.11178
Si	6.090971	6.050628	23.43548
Si	10.99548	1.782778	16.77877

Si	1.832654	1.788611	10.12473
Si	10.99233	10.9585	23.48404
Si	0.616547	2.665509	14.92255
Si	2.649156	12.19233	8.208716
Si	10.1857	0.604893	21.61789
Si	0.637297	10.13469	25.32581
Si	12.20986	2.668551	11.98042
Si	10.18437	12.19385	18.69349
Si	2.62915	0.610472	5.289496
Si	0.64847	5.873395	14.92405
Si	5.854006	12.21877	8.202902
Si	6.967216	0.595867	21.61793
Si	0.632919	6.913055	25.31454
Si	12.20571	5.873778	11.99402
Si	6.976809	12.21768	18.68338
Si	5.851335	0.625616	5.280462
Si	3.736593	2.641857	14.98233
Si	2.679311	9.059561	8.298257
Si	10.18847	3.703208	21.65692
Si	3.736024	10.09437	25.23206
Si	9.08226	2.640189	11.93562
Si	10.16602	9.054492	18.6058
Si	2.635781	3.705107	5.267969
Si	3.768504	5.840512	15.05714
Si	5.84098	9.090089	8.344697
Si	7.009461	3.702539	21.6641
Si	3.734738	6.910432	25.20524
Si	9.070864	5.856549	11.88179
Si	6.997494	9.088394	18.55988
Si	5.832226	3.722303	5.299297
Si	8.53742	2.576555	14.95495
Si	2.58328	4.28503	8.320781
Si	10.11982	8.508372	21.68545
Si	12.17177	10.13658	1.582531
Si	12.19999	6.913433	1.594623
Si	9.071339	10.09327	1.674
Si	9.099812	6.909063	1.702643
Si	4.283311	10.08505	1.657042
Si	4.312831	6.872483	1.632297
Si	6.75033	10.96709	3.481988
Si	6.755858	6.074992	3.481937
Si	1.816139	10.95888	3.427234
O	10.61832	10.58057	1.715063
O	0.058433	10.59501	0.142746
O	0.35603	10.85376	2.735473
O	12.30179	8.526126	1.705061
O	10.65599	6.460987	1.793655
O	0.064338	6.456344	0.140691
O	0.417606	6.218757	2.734988
O	8.219098	10.8721	2.8055
O	8.967176	8.502463	1.978275
O	8.435112	10.40981	0.210776
O	8.23857	6.12327	2.824113
O	8.499998	6.565645	0.232693
O	5.609255	10.67357	2.365361
O	4.185962	8.476449	1.885199
O	2.962221	10.7776	2.289946
O	5.671495	6.299346	2.293697
O	3.029893	6.127291	2.281323
O	2.17048	2.241468	15.10603
O	2.267731	10.62556	8.369147
O	10.63413	2.151302	21.76386
O	2.188872	10.58196	25.18722
O	10.65165	2.256396	11.79617
O	10.54748	10.62523	18.54245
O	2.17622	2.15667	5.139895
O	0.053678	2.252467	13.4574
O	2.176937	0.04039	6.741216
O	10.63504	0.041176	20.16543
O	12.43751	1.903597	16.0489

O	1.899033	0.350787	9.375989
O	10.89104	12.4173	22.79234
O	12.45567	10.8502	24.16862
O	0.390388	1.902932	10.85646
O	10.95942	0.340873	17.52942
O	1.910926	12.41745	4.122582
O	0.480863	4.271516	15.10745
O	4.252636	12.43846	8.358279
O	8.576539	0.465936	21.76347
O	0.499048	8.524109	25.19901
O	12.37941	4.272781	11.79623
O	8.581096	12.43516	18.54393
O	4.241532	0.483455	5.139651
O	2.22263	6.287447	15.01373
O	6.225311	10.65971	8.450154
O	6.551554	2.152777	21.76515
O	2.177617	6.460748	25.11323
O	10.6253	6.274521	11.96488
O	6.587171	10.65478	18.4557
O	6.302453	2.176181	5.142364
O	0.098906	6.291948	13.45328
O	6.306188	0.021792	6.716598
O	6.501998	0.036229	20.16134
O	12.5546	6.626953	16.11903
O	6.645387	0.426524	9.303979
O	6.239408	12.40355	22.78235
O	12.43338	6.208743	24.16874
O	0.279021	6.633516	10.7875
O	6.226028	0.404623	17.53616
O	6.568849	12.44821	4.106774
O	4.603827	1.900262	16.13398
O	1.818	8.21395	9.368416
O	10.97125	4.569664	22.7761
O	4.593251	10.86308	24.09507
O	8.228796	1.909894	10.76724
O	11.04563	8.220277	17.53759
O	1.897439	4.577582	4.124707
O	3.915395	4.244798	15.20076
O	4.261116	8.90146	8.644774
O	8.598206	3.832275	21.9468
O	3.835276	8.504482	24.92608
O	8.892438	4.254444	11.79271
O	8.580857	8.899288	18.25694
O	4.237256	3.826937	5.047833
O	4.286245	2.237553	13.51963
O	2.421341	8.485935	6.800193
O	10.52615	4.268539	20.17484
O	4.356912	10.41155	0.071014
O	8.523786	2.166369	13.37764
O	10.43794	8.481589	20.10119
O	2.248134	4.273622	6.735119
O	4.523245	6.561483	16.30209
O	6.663605	8.254607	9.466534
O	6.23041	4.576478	22.77906
O	4.608313	6.133848	24.08525
O	8.332569	6.555961	10.60906
O	6.150926	8.260759	17.43803
O	6.578594	4.63359	4.196919
O	4.529289	6.294099	13.6546
O	6.200045	8.499289	6.875347
O	6.672398	4.265697	20.1778
O	4.345118	6.570606	0.0423
O	8.320796	6.359511	13.27701
O	6.657667	8.489178	20.02694
O	6.198936	4.275175	6.782892
O	7.191105	1.927541	15.59718
O	1.909525	5.593079	8.974655
O	10.71658	7.169436	22.35838
O	7.186545	10.61352	24.55546
O	5.632359	1.890378	11.30743

O	10.89182	5.594809	17.94039
O	2.155262	7.169583	4.541246
O	8.593869	4.161013	15.12713
O	4.197172	4.276775	8.537229
O	8.514433	8.580329	21.9342
O	8.685444	8.467605	25.02019
O	4.291544	4.173792	11.70556
O	8.602599	4.277289	18.34506
O	4.337644	8.595104	4.960132
O	9.832543	1.885092	15.65789
O	1.985231	2.944596	8.997259
O	10.80416	9.814983	22.34803
O	9.83971	10.78351	24.61511
O	2.99874	1.900489	11.24123
O	10.8106	2.939839	17.90436
O	2.003067	9.807935	4.55797
O	7.020548	6.563279	15.54151
O	6.374336	5.679192	9.002333
O	6.303694	7.16493	22.2716
O	7.191508	6.297307	24.60218
O	5.844237	6.632315	11.44329
O	6.407761	5.682234	17.99539
O	6.571446	7.238625	4.597821
O	9.930228	6.643026	15.7056
O	6.485026	3.042902	9.086808
O	6.212369	9.818052	22.2466
O	9.830232	6.122705	24.61769
O	2.903976	6.634285	11.21714
O	6.312944	3.035475	17.85359
O	6.634744	9.883891	4.685456
O	5.693334	10.96379	15.20956
N	6.207057	9.05757	13.99533
N	5.951425	9.988941	14.59836

936

937 **Table S12.** CP2K η^1 -O bound E

atom	x	y	z
Fe	6.419427	6.909332	13.31786
Al	4.211836	5.831903	11.8232
Al	8.55643	5.809528	14.90103
Si	8.501095	10.03456	25.15284
Si	4.250027	2.54726	11.82568
Si	10.20092	4.228809	18.48396
Si	2.668714	8.486764	5.137669
Si	5.806938	4.216447	8.253687
Si	6.860664	8.492493	21.50586
Si	8.495735	6.823972	25.18038
Si	6.982328	4.253002	18.448
Si	5.867741	8.485065	5.193711
Si	6.063703	1.787113	16.67354
Si	1.773494	6.74784	10.01675
Si	10.93094	6.010821	23.39851
Si	6.034669	10.91025	23.3151
Si	6.716006	1.758109	10.03107
Si	11.008	6.727458	16.70212
Si	1.824297	6.011656	3.32238
Si	6.02744	6.724036	16.67314
Si	6.756271	6.703604	10.03224
Si	6.046087	6.01822	23.3179
Si	10.9883	1.737615	16.6891
Si	1.783023	1.739482	10.03021
Si	10.97183	10.91364	23.37578
Si	0.596463	2.581588	14.82908
Si	2.593959	12.15181	8.110132
Si	10.14419	0.570394	21.53154
Si	0.620988	10.10163	25.23598
Si	12.18436	2.583555	11.89489
Si	10.1564	12.15054	18.61392

Si	2.610311	0.577923	5.18901
Si	0.587356	5.786458	14.83889
Si	5.807526	12.13989	8.139857
Si	6.931287	0.564303	21.50135
Si	0.604757	6.872768	25.22176
Si	12.19953	5.786813	11.88604
Si	6.953268	12.15837	18.57989
Si	5.822906	0.556265	5.221028
Si	3.719745	2.576349	14.88012
Si	2.602113	9.028255	8.200975
Si	10.12688	3.690574	21.54292
Si	3.708398	10.07111	25.13879
Si	9.062317	2.571605	11.82973
Si	10.13143	9.014832	18.5181
Si	2.621963	3.6878	5.182482
Si	3.722053	5.777943	14.96428
Si	5.771352	9.021495	8.256936
Si	6.9349	3.688139	21.49604
Si	3.68834	6.884825	25.10468
Si	9.068807	5.773268	11.73983
Si	6.962215	9.031302	18.45048
Si	5.812007	3.688671	5.204149
Si	8.531544	2.536461	14.88219
Si	2.58545	4.231684	8.243582
Si	10.07469	8.489121	21.5761
Si	12.15517	10.09578	1.481876
Si	12.16288	6.879966	1.491982
Si	9.043895	10.07613	1.577566
Si	9.052679	6.895807	1.608031
Si	4.272179	10.02321	1.568061
Si	4.26487	6.824064	1.53458
Si	6.723854	10.91327	3.401344
Si	6.701022	6.01202	3.376957
Si	1.801166	10.91769	3.338557
O	10.60073	10.52594	1.621939
O	0.02849	10.58062	0.04314
O	0.344786	10.78324	2.64572
O	12.29855	8.488739	1.607404
O	10.61153	6.452718	1.697306
O	0.027125	6.400707	0.042475
O	0.368137	6.195026	2.644212
O	8.192866	10.85511	2.71495
O	8.938776	8.488491	1.884555
O	8.420265	10.4017	0.107662
O	8.183869	6.121376	2.730852
O	8.425158	6.554444	0.148075
O	5.600854	10.60971	2.270139
O	4.185247	8.420265	1.815911
O	2.946605	10.69868	2.205536
O	5.598211	6.206241	2.202368
O	2.951692	6.116889	2.158888
O	2.155087	2.171751	15.01168
O	2.184716	10.59289	8.262931
O	10.54316	2.131574	21.6737
O	2.166787	10.57772	25.10674
O	10.62835	2.173952	11.70621
O	10.52942	10.58445	18.45528
O	2.177981	2.133993	5.045852
O	0.046144	2.159191	13.36166
O	2.154526	0.034626	6.647547
O	10.61594	0.027354	20.07605
O	12.42925	1.810215	15.95471
O	1.835457	0.308028	9.274062
O	10.87451	12.38433	22.6996
O	12.4257	10.78045	24.07122
O	0.344733	1.812543	10.76522
O	10.89961	0.308122	17.44432
O	1.898405	12.38694	4.015781
O	0.412301	4.183847	15.01478
O	4.201579	12.3493	8.266682

O	8.535493	0.398663	21.67058
O	0.506878	8.488423	25.11087
O	12.37637	4.184829	11.70446
O	8.554291	12.36211	18.45251
O	4.217159	0.397893	5.048045
O	2.162879	6.189418	14.93456
O	6.201078	10.58047	8.357857
O	6.49916	2.126624	21.59191
O	2.143508	6.394432	25.01868
O	10.62376	6.189031	11.78412
O	6.563474	10.59861	18.3584
O	6.223755	2.123185	5.125875
O	0.047686	6.20787	13.3627
O	6.284474	12.62834	6.664417
O	6.482277	12.6308	20.05977
O	12.48261	6.541777	16.02508
O	6.561816	0.329623	9.281608
O	6.218866	12.39418	22.68967
O	12.38999	6.199913	24.06947
O	0.306807	6.538982	10.69927
O	6.217876	0.369079	17.44187
O	6.553027	12.39747	4.031125
O	4.573413	1.813377	16.02749
O	1.731876	8.199957	9.277047
O	10.8831	4.555629	22.68453
O	4.566811	10.85048	24.00607
O	8.199756	1.812457	10.6882
O	10.98537	8.181713	17.43693
O	1.886031	4.557791	4.034258
O	3.909424	4.17991	15.11554
O	4.185396	8.863003	8.545167
O	8.525327	3.835037	21.76364
O	3.759015	8.480881	24.83045
O	8.882696	4.17622	11.59873
O	8.547123	8.844011	18.17545
O	4.219335	3.829662	4.955561
O	4.269426	2.165791	13.41334
O	2.343692	8.420605	6.716964
O	10.53263	4.250899	20.07414
O	4.356924	10.34097	26.60609
O	8.515662	2.165423	13.29542
O	10.4293	8.41781	20.00161
O	2.245475	4.254861	6.656805
O	4.475818	6.524252	16.20869
O	6.572736	8.176306	9.390722
O	6.147058	4.56122	22.60855
O	4.574262	6.121977	23.989
O	8.306636	6.534771	10.51016
O	6.143614	8.21995	17.29829
O	6.563856	4.53885	4.044602
O	4.435245	6.270768	13.56226
O	6.13057	8.41667	6.791897
O	6.584399	4.267257	20.01729
O	4.307556	6.557829	26.56802
O	8.331308	6.217431	13.15076
O	6.583104	8.423744	19.90934
O	6.196155	4.26995	6.679824
O	7.175694	1.899538	15.50925
O	2.001465	5.587511	8.88794
O	10.63101	7.157019	22.29143
O	7.175247	10.60442	24.42981
O	5.600895	1.903695	11.19133
O	10.79262	5.584206	17.84896
O	2.07601	7.163384	4.435123
O	8.595737	4.114592	15.10637
O	4.1998	4.095929	8.443948
O	8.461213	8.5846	21.78256
O	8.593151	8.426328	24.92431
O	4.185155	4.13206	11.61312
O	8.587508	4.101528	18.27183

O	4.274147	8.577661	4.900344
O	9.811759	1.817537	15.58305
O	1.90347	2.941903	8.945006
O	10.78681	9.799087	22.20973
O	9.831249	10.69721	24.51107
O	2.969485	1.819216	11.12855
O	10.87869	2.939283	17.77738
O	1.983954	9.809054	4.508818
O	6.956594	6.555215	15.31857
O	6.306409	5.587443	8.961949
O	6.235061	7.169297	22.18757
O	7.177999	6.20981	24.47149
O	5.833478	6.545579	11.39845
O	6.500439	5.655346	17.78476
O	6.480817	7.156069	4.510934
O	9.861653	6.640836	15.59773
O	6.551468	2.954475	8.939241
O	6.145451	9.811489	22.12012
O	9.819301	6.114967	24.57646
O	2.947557	6.715006	11.10119
O	6.228749	3.020799	17.72205
O	6.573927	9.81262	4.590359
O	5.778445	9.09135	13.82354
N	3.837179	9.806571	14.93195
N	4.768574	9.455018	14.39815

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939 **Table S13.** CP2K η^1 -O bound reactant state

atom	x	y	z
O	10.59298	10.52025	1.623605
Si	9.036283	10.06591	1.586019
O	8.408237	10.35116	0.113799
O	8.181847	10.85913	2.712327
Si	6.711258	10.92156	3.395737
O	6.571186	9.827153	4.590694
Si	5.879113	8.493881	5.197169
O	6.551822	7.176023	4.548184
Si	6.702907	6.033878	3.403522
O	6.560023	4.577586	4.10541
Si	5.782042	3.687262	5.209069
O	6.131634	4.260615	6.684564
Si	5.788001	4.214491	8.260281
O	6.554293	2.96251	8.944651
Si	6.719762	1.761171	10.03079
O	5.602618	1.897657	11.19065
Si	4.245454	2.532771	11.82108
O	2.960887	1.813225	11.1248
Si	1.769375	1.733591	10.03138
O	1.896473	2.933725	8.943977
Si	2.575907	4.226635	8.246826
O	4.185572	4.091851	8.473369
O	4.267057	2.16069	13.41085
Si	3.706745	2.561434	14.87568
O	3.851522	4.165214	15.10631
Si	3.72613	5.761425	14.93616
O	4.481316	6.205616	13.53293
Al	4.202527	5.813237	11.77952
O	2.873728	6.643341	11.12461
Si	1.73626	6.734025	10.01178
O	1.984462	5.586953	8.874532
Fe	6.418247	6.82577	13.31576
O	6.388036	9.09333	13.25992
N	6.67195	10.07127	13.92169
N	6.926389	11.01217	14.49468
Al	8.582319	5.809927	14.90154
O	9.917059	6.6456	15.53374
Si	11.0145	6.7325	16.68722
O	10.72352	5.592624	17.82214

Si	10.16304	4.232072	18.46998
O	10.80987	2.936714	17.7537
Si	10.97055	1.735177	16.67417
O	9.821243	1.80917	15.53768
Si	8.526796	2.53598	14.87282
O	8.599686	4.112984	15.10414
O	8.32194	6.193898	13.13811
Si	9.059855	5.750651	11.72148
O	8.273854	6.479716	10.50406
Si	6.741032	6.700105	10.00154
O	5.781144	6.542131	11.32099
O	7.019222	6.563782	15.36586
Si	6.049757	6.724829	16.67748
O	6.48118	5.666496	17.81844
Si	6.955117	4.254789	18.45825
O	6.216182	3.023792	17.72004
Si	6.058026	1.791131	16.67179
O	7.176804	1.900543	15.5124
O	4.183617	4.111512	11.60481
O	10.52709	4.251654	20.05301
Si	10.13055	3.693354	21.52898
O	8.532725	3.836417	21.76169
Si	6.940063	3.708372	21.51313
O	6.568943	4.254265	20.02845
O	8.553791	4.099451	18.27194
O	6.299293	5.606661	8.904105
O	6.108164	8.435817	6.799863
Si	5.778393	9.027048	8.277294
O	6.641399	8.189492	9.371086
O	4.290669	8.563289	4.857241
Si	2.689635	8.476063	5.129545
O	1.995023	9.803094	4.515699
Si	1.790415	10.92385	3.359092
O	1.889089	12.39049	4.033171
O	2.425394	8.396849	6.720064
Si	2.62676	9.014043	8.210269
O	4.198373	8.863045	8.632636
O	2.067393	7.160443	4.432352
Si	1.79487	6.000407	3.328765
O	1.825315	4.543598	4.039659
Si	2.596406	3.686484	5.178623
O	2.247225	4.252986	6.658835
O	6.214446	0.377076	17.44134
O	4.568566	1.812005	16.02546
O	0.26377	6.541953	10.69005
O	1.731819	8.192546	9.276588
O	6.569809	0.334229	9.28017
O	8.205488	1.799571	10.68706
Si	9.060504	2.567275	11.82638
O	8.488171	2.17088	13.28456
O	12.49901	6.543489	16.03294
O	10.98028	8.181485	17.43788
Si	10.1126	9.018094	18.51054
O	10.35856	8.421616	20.00006
Si	10.02658	8.48819	21.57742
O	10.70589	9.809718	22.21474
Si	10.93291	10.92669	23.36921
O	9.812482	10.76367	24.53483
Si	8.491655	10.05197	25.15019
O	8.604925	8.450249	24.9031
Si	8.474187	6.851982	25.16626
O	9.766671	6.112684	24.52604
Si	10.90899	6.013642	23.3736
O	10.62513	7.160024	22.26433
O	7.15337	10.61287	24.4364
Si	6.014068	10.94627	23.32314
O	6.143621	9.887071	22.09742
Si	6.822866	8.535982	21.51498
O	6.146409	7.245658	22.20972
Si	6.009864	6.068818	23.32207

O	7.114696	6.294273	24.492
O	6.570008	8.466356	19.91627
Si	6.947776	9.049051	18.45097
O	6.138904	8.222725	17.30558
O	8.420055	8.57591	21.8154
O	12.38478	6.212589	24.00857
O	10.88453	4.549691	22.67884
O	6.162238	12.43641	22.69676
O	4.547009	10.86022	24.01011
Si	3.690574	10.06299	25.13245
O	4.299047	10.34926	26.60974
O	0.335822	6.14716	2.639273
O	2.945267	6.108641	2.188039
Si	4.238531	6.847376	1.554797
O	5.588648	6.283257	2.244385
O	4.532502	6.488054	16.13928
O	6.193557	4.625209	22.61134
O	4.534158	6.107948	23.99176
Si	3.674277	6.892481	25.11615
O	4.285178	6.560322	26.58765
O	12.41877	1.816722	15.95669
O	10.89393	0.310426	17.44202
O	1.814989	0.298349	9.278544
O	0.32774	1.823632	10.76585
O	10.81251	12.39376	22.70144
O	12.41315	10.77169	24.01084
O	2.145857	2.158139	15.01397
Si	0.594605	2.587201	14.8363
O	0.414195	4.194657	15.01247
Si	0.594696	5.801118	14.83075
O	0.042068	6.265757	13.36695
O	0.065109	2.146221	13.36993
O	2.174163	6.200729	14.91994
O	2.186816	10.57664	8.18934
Si	2.590673	12.14361	8.125785
O	4.189407	12.34305	8.355905
Si	5.789267	12.14292	8.159157
O	6.217618	12.63204	6.672548
O	6.200119	10.58813	8.359699
O	10.54252	2.13484	21.67061
Si	10.11821	0.581634	21.52216
O	8.510885	0.410088	21.66946
Si	6.906482	0.596424	21.5177
O	6.489812	2.156934	21.66886
O	10.60992	0.033129	20.07421
O	2.134664	10.51617	25.09239
Si	0.572826	10.09971	25.22004
O	0.40763	8.491622	25.11032
Si	0.555976	6.881185	25.20619
O	2.112109	6.461723	25.02024
O	3.81757	8.479592	24.82152
O	10.6291	2.172131	11.7765
Si	12.18758	2.586475	11.91939
O	12.37575	4.193762	11.78231
Si	12.18691	5.801083	11.90372
O	10.6077	6.186653	11.78669
O	8.886046	4.160029	11.52292
O	10.5272	10.58523	18.45439
Si	10.1512	12.15238	18.61295
O	8.549537	12.36331	18.45364
Si	6.946428	12.1793	18.58792
O	6.475905	12.70547	20.05114
O	6.559407	10.61872	18.36213
O	8.529824	8.854344	18.16428
O	2.162622	2.13212	5.04721
Si	2.599491	0.581598	5.203344
O	4.202946	0.405195	5.045897
Si	5.805929	0.562556	5.218211
O	6.219703	2.127759	5.12404
O	2.164274	0.051728	6.672575

O	4.192917	3.826134	4.942119
O	8.929929	8.481201	1.896866
Si	9.038646	6.892369	1.603686
O	8.428144	6.563087	0.132064
O	10.59705	6.454999	1.698439
Si	12.14803	6.872663	1.491554
O	12.30477	8.483336	1.608551
Si	12.15258	10.09563	1.497878
O	8.172027	6.109407	2.722703
O	4.101869	8.446234	1.814025
Si	4.238722	10.04767	1.572879
O	2.940878	10.77086	2.219678
O	5.592095	10.60889	2.257518
O	6.55004	12.40732	4.031779
O	0.314531	10.77198	2.702975
O	-0.01328	6.3934	0.030421
O	0.016009	10.585	0.04808

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941 **Table S14.** CP2K Transition state

atom	x	y	z
Fe	6.473151	6.86066	13.31518
Al	4.218526	5.802628	11.80141
Al	8.576779	5.791555	14.91644
Si	8.499019	10.03746	25.14848
Si	4.249167	2.528954	11.82475
Si	10.16319	4.217762	18.47047
Si	2.690896	8.475914	5.130828
Si	5.792322	4.195769	8.259582
Si	6.823768	8.529054	21.51642
Si	8.466561	6.832792	25.17615
Si	6.955857	4.253154	18.46161
Si	5.876848	8.484766	5.194004
Si	6.06026	1.789329	16.67509
Si	1.760382	6.733404	10.01889
Si	10.88936	5.997703	23.40175
Si	6.016515	10.93886	23.31682
Si	6.720371	1.747189	10.03749
Si	11.00897	6.730557	16.69893
Si	1.793722	6.000448	3.33303
Si	6.043674	6.729031	16.68935
Si	6.76365	6.670564	10.00466
Si	5.998834	6.064449	23.3255
Si	10.97552	1.724641	16.66758
Si	1.776606	1.73087	10.0292
Si	10.93718	10.91572	23.37969
Si	0.601601	2.590391	14.83718
Si	2.589076	12.14213	8.109588
Si	10.11436	0.579217	21.5441
Si	0.58005	10.0983	25.22037
Si	12.19638	2.582962	11.91884
Si	10.15214	12.15738	18.63052
Si	2.599236	0.58113	5.19621
Si	0.599763	5.801904	14.83422
Si	5.796365	12.13375	8.140929
Si	6.903195	0.594139	21.52073
Si	0.55746	6.875349	25.22338
Si	12.20046	5.801305	11.90502
Si	6.94673	12.17746	18.5914
Si	5.805091	0.548955	5.20056
Si	3.721671	2.576112	14.87922
Si	2.629426	9.013704	8.212378
Si	10.12218	3.677522	21.54728
Si	3.686357	10.05669	25.13458
Si	9.075082	2.554089	11.82656
Si	10.11878	9.014996	18.52978
Si	2.595164	3.685754	5.180749
Si	3.747791	5.77928	14.96892

Si	5.781448	9.012947	8.279991
Si	6.928761	3.711165	21.51852
Si	3.652502	6.878853	25.1184
Si	9.079133	5.737566	11.72639
Si	6.955501	9.047358	18.45742
Si	5.78112	3.662465	5.194314
Si	8.529287	2.529034	14.87431
Si	2.580392	4.225823	8.249176
Si	10.02655	8.478734	21.59073
Si	12.15373	10.0966	1.496821
Si	12.14616	6.87416	1.498219
Si	9.03914	10.06551	1.582597
Si	9.037788	6.892129	1.609794
Si	4.240569	10.03367	1.575056
Si	4.243543	6.828945	1.556362
Si	6.71558	10.90344	3.391057
Si	6.701979	6.018589	3.401033
Si	1.791413	10.92024	3.361322
O	10.59461	10.52283	1.621852
O	0.020025	10.58267	0.046956
O	0.316636	10.77032	2.701904
O	12.30081	8.48482	1.608724
O	10.59543	6.453823	1.698971
O	-0.00494	6.394419	0.044612
O	0.33564	6.149163	2.64193
O	8.188603	10.85624	2.712217
O	8.933609	8.481641	1.896932
O	8.404622	10.346	0.110284
O	8.173723	6.10951	2.72835
O	8.415362	6.562121	0.143949
O	5.597713	10.59514	2.250732
O	4.110452	8.429324	1.816729
O	2.947122	10.76468	2.22587
O	5.5853	6.222492	2.234333
O	2.944266	6.107826	2.193189
O	2.157672	2.179736	15.01556
O	2.186288	10.57544	8.189357
O	10.53199	2.126006	21.75893
O	2.137196	10.52652	25.09313
O	10.64161	2.155225	11.78007
O	10.52863	10.58493	18.52882
O	2.162377	2.131544	5.046963
O	0.077078	2.146468	13.37014
O	2.154369	0.048051	6.659358
O	10.60591	0.052766	20.08664
O	12.42695	1.813301	15.9562
O	1.828167	0.295242	9.276364
O	10.81326	12.37584	22.70421
O	12.42287	10.77108	24.00943
O	0.336171	1.819851	10.76587
O	10.89302	0.301347	17.44464
O	1.887286	12.38797	4.030561
O	0.410963	4.19602	15.01326
O	4.192976	12.34139	8.279793
O	8.506413	0.405413	21.67032
O	0.423928	8.487309	25.11056
O	12.37579	4.191472	11.78249
O	8.550082	12.36163	18.45352
O	4.201188	0.398689	5.036673
O	2.184188	6.189699	14.9229
O	6.202629	10.57783	8.358811
O	6.493771	2.155329	21.66931
O	2.098945	6.406971	25.01964
O	10.62256	6.193804	11.79703
O	6.560715	10.61605	18.36506
O	6.21874	2.10824	5.048485
O	0.057364	6.266725	13.36865
O	6.227841	12.62844	6.654664
O	6.474658	12.70493	20.05111
O	12.49011	6.542746	16.03223

O	6.560665	0.323397	9.279043
O	6.154584	12.43276	22.69588
O	12.34178	6.198882	24.07549
O	0.28808	6.53719	10.69471
O	6.216006	0.370946	17.44039
O	6.547843	12.38122	4.029706
O	4.573495	1.81266	16.0274
O	1.734991	8.189751	9.278009
O	10.88333	4.550263	22.67749
O	4.553026	10.84673	24.01193
O	8.209578	1.796234	10.68795
O	10.97963	8.189046	17.4408
O	1.824642	4.542992	4.041486
O	3.912809	4.17713	15.11009
O	4.200236	8.861068	8.6331
O	8.522989	3.843405	21.76302
O	3.758079	8.469657	24.82189
O	8.947017	4.145192	11.52147
O	8.537804	8.861062	18.16478
O	4.191721	3.822491	4.94232
O	4.268656	2.160334	13.41494
O	2.432585	8.395906	6.721327
O	10.52595	4.17944	20.05358
O	4.299871	10.34226	26.61057
O	8.489841	2.170558	13.28526
O	10.36383	8.398911	20.01215
O	2.247025	4.252154	6.661796
O	4.497853	6.532907	16.20903
O	6.636089	8.15852	9.368433
O	6.151984	4.617837	22.60897
O	4.525701	6.110366	23.99566
O	8.303161	6.472568	10.50461
O	6.146779	8.227969	17.31236
O	6.562317	4.566846	4.106364
O	4.519764	6.205893	13.55859
O	6.103372	8.424494	6.797499
O	6.568332	4.255842	20.03084
O	4.277727	6.558664	26.5857
O	8.315746	6.136752	13.14781
O	6.579074	8.449013	19.91581
O	6.134787	4.194186	6.683256
O	7.178641	1.893568	15.51562
O	1.994029	5.58698	8.878116
O	10.61404	7.158625	22.30278
O	7.178565	10.60804	24.40726
O	5.605886	1.8889	11.1984
O	10.72388	5.590464	17.84048
O	2.067048	7.159663	4.436796
O	8.600732	4.099484	15.12445
O	4.189064	4.089983	8.47324
O	8.419391	8.576808	21.82007
O	8.610846	8.431041	24.90279
O	4.186162	4.105217	11.60885
O	8.553686	4.098588	18.27036
O	4.29013	8.562482	4.844328
O	9.825831	1.797761	15.53091
O	1.897569	2.932754	8.943821
O	10.70511	9.802103	22.2228
O	9.828501	10.75675	24.55844
O	2.965002	1.812134	11.12508
O	10.80986	2.933698	17.73518
O	1.991205	9.803325	4.52237
O	6.999934	6.545382	15.3647
O	6.313892	5.590837	8.890491
O	6.146006	7.24153	22.2135
O	7.106546	6.287206	24.49279
O	5.830288	6.471388	11.3415
O	6.481283	5.665874	17.82524
O	6.549162	7.170776	4.535942
O	9.897074	6.641596	15.55968

O	6.555477	2.952997	8.96043
O	6.141184	9.883818	22.08593
O	9.741623	6.048186	24.55251
O	2.903638	6.643492	11.12731
O	6.217084	3.020457	17.72365
O	6.575115	9.814128	4.588714
O	6.388327	8.660975	13.23039
N	7.138098	10.78849	14.56904
N	6.897822	9.732701	14.26977

942

943 **Table S15.** CP2K α -O + N₂ product

atom	x	y	z
O	10.59573	10.52063	1.623249
Si	9.039267	10.06526	1.584722
O	8.409829	10.3512	0.112389
O	8.184185	10.85484	2.71336
Si	6.713628	10.91591	3.396768
O	6.56894	9.821953	4.593534
Si	5.874872	8.491543	5.205423
O	6.547999	7.175709	4.552258
Si	6.704667	6.03618	3.404607
O	6.560714	4.579548	4.105944
Si	5.784043	3.689561	5.210093
O	6.13218	4.268177	6.68716
Si	5.784491	4.207251	8.261886
O	6.555987	2.957832	8.934968
Si	6.715032	1.764155	10.032
O	5.606036	1.968668	11.18816
Si	4.227468	2.534682	11.82794
O	2.960482	1.798532	11.12363
Si	1.769817	1.7291	10.03033
O	1.895673	2.933	8.94591
Si	2.572995	4.225233	8.247686
O	4.18294	4.088441	8.470699
O	4.264546	2.158166	13.41468
Si	3.702309	2.557091	14.87847
O	3.846679	4.164271	15.1071
Si	3.707191	5.760372	14.97466
O	4.475146	6.204294	13.56557
Al	4.161533	5.799221	11.81465
O	2.872453	6.650682	11.12272
Si	1.728351	6.735033	10.0121
O	1.985614	5.586677	8.878142
Fe	6.410018	6.916123	13.3158
O	6.482116	8.525802	13.26469
N	7.460687	10.61594	15.23041
N	7.281491	11.47354	14.55024
Al	8.563017	5.788048	14.90743
O	9.863822	6.646864	15.56612
Si	10.99138	6.736828	16.69672
O	10.72348	5.590427	17.83134
Si	10.17705	4.228909	18.49171
O	10.81299	2.931558	17.76758
Si	10.96775	1.730698	16.68388
O	9.818954	1.807551	15.54713
Si	8.525246	2.524342	14.87704
O	8.598636	4.101312	15.11813
O	8.25805	6.124124	13.13099
Si	9.050536	5.73252	11.71667
O	8.27255	6.479227	10.50509
Si	6.734439	6.685491	10.028
O	5.812723	6.470287	11.4021
O	6.934564	6.52077	15.29368
Si	6.023119	6.72837	16.67376
O	6.557502	5.668343	17.76551
Si	6.969473	4.257697	18.45863
O	6.219053	3.032543	17.72046

Si	6.05615	1.79436	16.67472
O	7.173955	1.899606	15.5161
O	4.103921	4.11138	11.61409
O	10.5342	4.252273	20.07407
Si	10.12379	3.692476	21.54178
O	8.522459	3.839963	21.76256
Si	6.929291	3.718112	21.50151
O	6.562433	4.286011	20.02309
O	8.56837	4.089795	18.33231
O	6.285192	5.587838	8.945758
O	6.110772	8.425391	6.809248
Si	5.758351	9.02137	8.282333
O	6.569746	8.16132	9.400967
O	4.281966	8.56469	4.879932
Si	2.675787	8.477597	5.135668
O	1.994015	9.806266	4.514474
Si	1.791142	10.92723	3.358357
O	1.891246	12.3947	4.029997
O	2.362948	8.401308	6.71939
Si	2.606473	9.016865	8.20648
O	4.17825	8.862624	8.629428
O	2.067463	7.159925	4.432401
Si	1.796089	5.99983	3.328915
O	1.825872	4.543088	4.040176
Si	2.599149	3.688163	5.178759
O	2.246586	4.253196	6.659477
O	6.212305	0.383182	17.44327
O	4.567085	1.816557	16.02753
O	0.254417	6.539928	10.69087
O	1.722633	8.19095	9.277646
O	6.555292	0.335964	9.285122
O	8.201261	1.796534	10.68648
Si	9.05953	2.553248	11.82698
O	8.492237	2.17247	13.28814
O	12.4715	6.542247	16.02911
O	10.97107	8.190428	17.43871
Si	10.10345	9.020504	18.52065
O	10.35374	8.401681	20.00106
Si	10.02518	8.485505	21.57725
O	10.70602	9.808812	22.2124
Si	10.93634	10.92464	23.36701
O	9.819437	10.76143	24.53662
Si	8.497464	10.05158	25.14874
O	8.606608	8.449489	24.90392
Si	8.475844	6.851086	25.16507
O	9.771684	6.11308	24.53163
Si	10.91135	6.014961	23.37709
O	10.62518	7.162234	22.27097
O	7.166554	10.61438	24.42459
Si	6.020175	10.9507	23.31832
O	6.143483	9.888224	22.09434
Si	6.821805	8.53845	21.50806
O	6.145373	7.245473	22.20323
Si	6.00787	6.068029	23.31549
O	7.122173	6.292426	24.47894
O	6.569018	8.474864	19.90954
Si	6.936883	9.058348	18.43959
O	6.138906	8.215385	17.29685
O	8.418445	8.576351	21.81363
O	12.3889	6.212773	24.00946
O	10.88269	4.551991	22.68309
O	6.167145	12.44284	22.69217
O	4.554351	10.86221	24.01131
Si	3.696411	10.06381	25.13129
O	4.299657	10.34914	26.61129
O	0.337753	6.14534	2.639113
O	2.948757	6.107952	2.190804
Si	4.240491	6.847447	1.55552
O	5.591977	6.284112	2.242793
O	4.484517	6.470766	16.213

O	6.159089	4.616633	22.60696
O	4.537256	6.108883	23.9947
Si	3.678056	6.894178	25.11673
O	4.285906	6.560311	26.58905
O	12.41207	1.816703	15.95821
O	10.88437	0.301673	17.44455
O	1.82573	0.296188	9.274416
O	0.328772	1.822709	10.76542
O	10.81192	12.39239	22.70204
O	12.41712	10.77167	24.00955
O	2.14078	2.158608	15.01473
Si	0.589327	2.585169	14.83824
O	0.410225	4.194397	15.01259
Si	0.578329	5.801389	14.83347
O	0.033562	6.266148	13.36662
O	0.064064	2.146727	13.37005
O	2.159694	6.20117	14.92194
O	2.184139	10.58226	8.190226
Si	2.591358	12.14679	8.108417
O	4.196894	12.34556	8.277144
Si	5.803236	12.13998	8.146169
O	6.281233	12.63128	6.671082
O	6.198447	10.57943	8.360146
O	10.54077	2.136483	21.68043
Si	10.11553	0.584093	21.52728
O	8.508639	0.412986	21.66964
Si	6.905603	0.595819	21.50195
O	6.487262	2.159793	21.59613
O	10.60573	0.043558	20.07857
O	2.139734	10.51498	25.09163
Si	0.577098	10.09958	25.21854
O	0.409767	8.491956	25.11027
Si	0.560336	6.881324	25.20561
O	2.116827	6.463252	25.01967
O	3.825771	8.480662	24.82155
O	10.62967	2.168891	11.77616
Si	12.18677	2.58348	11.91909
O	12.36876	4.193468	11.78231
Si	12.17631	5.799879	11.90492
O	10.59159	6.186624	11.79722
O	8.885312	4.146687	11.51985
O	10.52808	10.58383	18.52727
Si	10.14195	12.15183	18.62444
O	8.538621	12.35009	18.45506
Si	6.933239	12.16772	18.58091
O	6.475391	12.69039	20.04508
O	6.505414	10.61715	18.36203
O	8.522211	8.878071	18.16365
O	2.172335	2.132768	5.046375
Si	2.610396	0.582427	5.196767
O	4.216331	0.398263	5.04846
Si	5.822136	0.558475	5.224102
O	6.218937	2.129238	5.126048
O	2.154797	0.048079	6.655727
O	4.195448	3.828312	4.942667
O	8.932745	8.480557	1.896609
Si	9.040545	6.891842	1.603515
O	8.426579	6.562764	0.132452
O	10.59934	6.454336	1.697854
Si	12.15109	6.872039	1.490664
O	12.30573	8.48308	1.608707
Si	12.15533	10.09559	1.496558
O	8.17611	6.112009	2.728609
O	4.10164	8.446096	1.815195
Si	4.240007	10.04764	1.573718
O	2.943101	10.77104	2.22135
O	5.594726	10.60686	2.257058
O	6.552069	12.40141	4.031361
O	0.315867	10.773	2.70235
O	-0.00391	6.392884	0.032428

944 O 0.020823 10.58431 0.047352

945 **S5.2: Cluster models**

946 **Table S16.** Empty α -Fe(II) in BEA + gas-phase N₂O

atom	constrained?	x	y	z
Fe	no	1.9517	0.08535	-0.61297
O	no	1.00543	-1.11098	-1.88534
O	no	1.74637	1.23492	0.9947
O	no	1.43525	1.77645	-1.53241
O	no	2.14039	-1.62015	0.40097
H	yes	-4.24058	-3.0477	-5.38586
H	yes	-0.02667	-2.89053	-6.62082
O	yes	-3.59502	-2.02746	-3.22299
O	yes	-1.48668	1.81921	4.60368
H	yes	-3.42799	-4.4431	-3.7216
H	yes	-3.89986	-6.04147	0.74329
H	yes	-2.32254	5.93328	2.88125
H	yes	-4.1757	5.7065	1.50617
H	yes	-3.05737	-6.15416	-1.41403
O	yes	-1.81228	-2.98342	-4.90362
O	yes	0.83735	2.94897	5.09261
H	yes	6.56681	-3.27546	1.71136
O	no	0.58788	-1.8774	-4.41099
H	yes	4.33161	3.74356	-4.96775
O	no	2.68104	2.02147	3.37016
H	yes	0.29422	-4.28675	-4.80237
O	yes	-3.25862	-2.84072	3.9465
H	yes	2.08482	6.09651	1.59193
O	yes	-5.09834	2.49383	-1.61539
H	yes	1.35373	-5.94415	-2.68365
H	yes	3.25193	-5.78166	-1.36553
O	yes	-3.61928	0.41048	-2.22554
H	yes	2.99064	6.05269	-0.53987
O	yes	-1.85014	-0.63514	3.71875
H	yes	4.93872	-4.46321	0.5759
O	no	-1.34921	-0.5922	-3.07305
H	yes	3.47555	4.82615	-3.11144
O	no	0.43496	0.55876	3.24292
O	yes	-2.47098	-1.54883	-0.8901
O	yes	-1.75007	1.37701	2.02105
O	no	4.31405	-2.33937	1.7682
O	no	0.84403	0.64663	-3.85548
O	no	2.47854	2.63326	-3.83309
O	no	2.79682	-0.48617	2.70635
H	yes	5.01281	-4.52335	2.90248
H	yes	2.28992	4.83925	-5.11548
H	yes	0.94372	-4.7851	4.18624
H	yes	1.17016	-6.00904	-0.3768
O	yes	-2.92004	1.98553	-0.24351
H	yes	0.69247	6.09468	-0.25763
O	yes	-2.19805	-2.19531	1.63478
H	yes	0.2328	-4.63311	1.99087
O	no	-0.52823	2.90476	0.21716
H	yes	-1.25446	4.5967	-1.7883
O	no	-0.35964	-2.93762	-0.05122
H	yes	-1.61257	-6.20086	0.39885
O	yes	-2.55391	3.83818	1.58347
H	yes	-2.07901	6.05143	0.57846
O	yes	-2.72186	-4.05464	-0.14645
O	no	1.92121	-3.00654	2.72663
O	no	-0.09939	3.09116	-3.3496
O	yes	-0.65244	-2.98033	3.61183
O	no	2.11559	3.98446	0.29421
O	yes	-2.73694	2.84369	-2.7222
O	no	1.90603	-3.80719	-1.55869

Si	yes	-3.30236	-3.16448	-4.32637
Si	yes	-0.73935	3.00024	5.40529
Si	yes	-0.23645	-3.03905	-5.22417
Si	yes	2.33057	3.13449	4.52257
Si	yes	-2.77219	-0.95143	-2.3533
Si	yes	-1.17505	0.79118	3.40479
Si	yes	5.21778	-3.71727	1.75158
Si	no	0.24265	-0.75511	-3.31012
Si	yes	3.14033	4.07784	-4.27082
Si	no	1.88972	0.85162	2.59802
Si	yes	-1.9249	2.52109	0.90359
Si	yes	-1.93178	-2.67753	0.12166
Si	yes	0.59283	-3.88677	3.14399
Al	no	1.13609	2.64155	0.03831
Si	yes	-1.50954	3.85477	-2.97189
Al	no	1.11492	-2.54031	-0.78543
Si	yes	1.8782	-5.43571	-1.46595
Si	yes	-3.59229	1.9349	-1.70529
Si	yes	1.91514	5.60307	0.27126
Si	yes	-1.98661	-2.16422	3.23026
Si	no	2.77387	-1.9032	1.91415
Si	no	1.13806	2.07558	-3.14296
Si	yes	-2.82559	-5.65967	-0.10323
Si	yes	-2.78943	5.42884	1.63869
H	yes	-1.84121	4.75392	-4.01973
H	yes	-1.26793	4.25117	4.99035
H	yes	-0.95367	2.83468	6.79922
H	yes	2.45454	4.40991	3.91081
H	yes	3.26507	3.0344	5.58718
H	yes	-4.25731	-5.05539	3.45023
H	yes	-5.84629	4.63458	-0.6123
H	yes	-5.2099	-3.77995	5.13954
H	yes	-7.45137	3.2509	-1.55941
H	yes	-3.14789	-4.78282	5.47195
Si	yes	-3.99068	-4.15605	4.5163
Si	yes	-6.12148	3.73488	-1.67587
H	yes	-5.97173	4.40366	-2.91954
N	no	9.73078	0.17756	-1.62721
N	no	10.84307	0.34707	-1.67976
O	yes	12.01246	0.52523	-1.73507

947

948 **Table S17.** N₂O adsorbed on zeolite without α -Fe(II)

atom	constrained?	x	y	z
O	no	-1.33993	1.48326	-1.55098
O	no	1.34197	-1.49223	-1.5199
O	no	1.95743	0.97656	-2.09411
O	no	-1.95772	-0.98837	-2.09098
H	yes	-2.89777	6.34185	2.36083
H	yes	-2.91659	6.33775	-2.03305
O	yes	-1.89603	4.07705	2.31097
O	yes	1.89241	-4.05597	2.34257
H	yes	-4.31851	4.52684	2.10699
H	yes	-5.87892	0.38841	3.88218
H	yes	6.0302	-2.19953	2.49344
H	yes	5.87345	-0.35615	3.89126
H	yes	-6.03415	2.22158	2.47084
O	yes	-2.93023	5.19425	0.16646
O	yes	2.92879	-5.18888	0.20737
H	yes	-3.53629	-3.51183	-5.98896
O	no	-1.89714	4.0533	-2.02466
H	yes	3.54152	3.47225	-6.01048
O	no	1.89845	-4.06292	-1.99282
H	yes	-4.31761	4.5134	-1.77208
O	yes	-2.69433	-2.8902	4.04244
H	yes	6.00938	-2.20606	-2.1015
O	yes	2.6887	2.92352	4.02423
H	yes	-6.0083	2.19474	-2.12402

H	yes	-5.91786	0.39388	-3.57849
O	yes	0.54468	3.10815	2.51776
H	yes	5.92051	-0.41578	-3.5691
O	yes	-0.54866	-3.08568	2.53972
H	yes	-4.66146	-1.95449	-4.70078
O	no	-0.53175	3.32421	0.15953
H	yes	4.66522	1.92423	-4.70986
O	no	0.52762	-3.32581	0.18656
O	yes	-1.4544	1.51821	1.87207
O	yes	1.45115	-1.50056	1.88464
O	no	-2.52554	-2.93108	-3.82763
O	no	0.55827	3.22975	-2.23437
O	no	2.52908	2.90611	-3.84551
O	no	-0.55742	-3.24486	-2.20776
H	yes	-4.71535	-4.2071	-4.11357
H	yes	4.71858	4.18105	-4.13887
H	yes	-4.80668	-4.28978	0.15957
H	yes	-6.05672	0.03374	-1.29503
O	yes	2.09773	0.99723	2.34325
H	yes	6.05685	-0.0391	-1.28819
O	yes	-2.1019	-0.97618	2.34844
H	yes	-4.63454	-1.9842	0.21597
O	no	2.93288	-0.13961	0.11304
H	yes	4.63311	1.98977	0.20653
O	no	-2.93033	0.14898	0.10749
H	yes	-6.13237	0.07538	1.59887
O	yes	3.94115	-0.87306	2.43325
H	yes	6.12937	-0.05973	1.606
O	yes	-3.94506	0.89445	2.42268
O	no	-3.05693	-3.26355	-1.24436
O	no	3.05552	3.26038	-1.26385
O	yes	-2.94101	-3.30258	1.45548
O	no	3.85706	-0.90905	-2.2349
O	yes	2.9382	3.31712	1.43463
O	no	-3.85619	0.89669	-2.24632
Si	yes	-3.04846	5.06176	1.76486
Si	yes	3.04521	-5.04486	1.80488
Si	yes	-3.0511	5.05793	-1.43231
Si	yes	3.05123	-5.06415	-1.39224
Si	yes	-0.85115	3.00216	1.72423
Si	yes	0.84782	-2.98571	1.74698
Si	yes	-3.92255	-3.16667	-4.66662
Si	no	-0.81329	3.01423	-1.41356
Si	yes	3.92664	3.13678	-4.68542
Si	no	0.813	-3.02155	-1.3874
Si	yes	2.597	-0.38794	1.69125
Si	yes	-2.59971	0.40443	1.68538
Si	yes	-3.8992	-3.19787	0.16611
Si	yes	3.89752	3.20298	0.14711
Si	yes	-5.51684	0.87454	-2.30368
Si	yes	2.06869	2.58952	2.57759
Si	yes	5.51797	-0.88731	-2.29139
Si	yes	-2.07261	-2.56678	2.59389
Si	no	-2.03605	-2.60036	-2.32613
Si	no	2.03893	2.58619	-2.34181
Si	yes	-5.54437	0.89495	2.59834
Si	yes	5.54028	-0.87191	2.61086
H	yes	4.8053	4.29483	0.13356
H	yes	4.31495	-4.50737	2.14451
H	yes	2.89393	-6.32051	2.40998
H	yes	4.31827	-4.52213	-1.73455
H	yes	2.91755	-6.34832	-1.98378
H	yes	-4.86857	-2.11553	4.94855
H	yes	4.86195	2.15548	4.93831
H	yes	-3.54892	-3.4776	6.28692
H	yes	3.54086	3.52723	6.26531
H	yes	-4.63334	-4.37002	4.44416
Si	yes	-3.97663	-3.22042	4.95751
Si	yes	3.97001	3.26039	4.93827
H	yes	4.62728	4.40624	4.41728

Si	no	2.52993	-0.39826	-1.45128
Si	no	-2.52965	0.39085	-1.45903
N	no	-0.54607	0.98057	-4.41361
N	no	-0.01326	-0.00884	-4.36763
O	no	0.54659	-1.05072	-4.32939

949

950 **Table S18.** η^1 -O bound

atom	constrained?	x	y	z
Fe	no	-0.1813	-0.26297	2.42152
O	no	-1.42859	-1.50191	1.32636
O	no	1.18243	1.15196	1.9387
O	no	1.42685	-1.42659	2.08737
O	no	-1.72944	0.98267	2.07852
H	yes	-3.24938	-5.51204	-3.58104
H	yes	-3.70116	-6.09291	0.75084
O	yes	-2.01936	-3.41144	-3.12269
O	yes	2.60789	4.13669	-1.6688
H	yes	-4.48432	-3.58939	-3.18664
H	yes	-5.40692	0.9067	-4.46986
H	yes	6.51622	1.83213	-1.74302
H	yes	6.30046	0.22452	-3.39999
H	yes	-5.89727	-1.06646	-3.3551
O	yes	-3.37434	-4.67246	-1.25448
O	yes	3.54457	4.84079	0.68563
H	yes	-3.64324	3.14193	6.01977
O	no	-2.4647	-3.95197	1.17027
H	yes	2.604	-4.58371	5.61977
O	no	2.20873	3.53525	2.61789
H	yes	-4.86476	-4.09467	0.64054
O	yes	-1.88742	3.76958	-3.89222
H	yes	6.04293	1.227	2.78726
O	yes	2.80962	-2.6002	-4.26696
H	yes	-6.32226	-1.65718	1.18188
H	yes	-6.18225	-0.09094	2.88311
O	yes	0.52007	-2.72485	-2.98526
H	yes	5.61729	-0.71947	3.96919
O	yes	0.10799	3.50265	-2.20476
H	yes	-4.79692	1.91761	4.43211
O	no	-0.81504	-3.09531	-0.7632
H	yes	4.01076	-3.02252	4.65316
O	no	0.98515	3.24517	0.25445
O	yes	-1.35001	-1.00632	-2.28477
O	yes	1.85094	1.61487	-1.62195
O	no	-2.47598	2.74807	3.91873
O	no	0.05441	-3.65532	1.6729
O	no	1.85142	-3.64109	3.50415
O	no	-0.3668	3.21425	2.52107
H	yes	-4.54971	4.21847	4.1731
H	yes	3.87673	-5.17265	3.76936
H	yes	-4.20949	4.88187	-0.03627
H	yes	-6.05542	0.58517	0.67185
O	yes	2.26672	-0.85875	-2.38071
H	yes	5.93661	-0.80166	1.67698
O	yes	-1.67441	1.58894	-2.44832
H	yes	-4.28208	2.6008	-0.40984
O	no	2.97591	-0.15178	0.01784
H	yes	4.45709	-2.42613	-0.20706
O	no	-2.83205	0.30833	-0.50119
H	yes	-5.84923	0.94002	-2.19412
O	yes	4.30072	0.77086	-2.04756
H	yes	6.29619	-0.4033	-1.16805

O	yes	-3.69235	-0.01929	-2.94365
O	no	-2.75855	3.38981	1.348
O	no	2.63115	-3.58798	0.95535
O	yes	-2.34219	3.85923	-1.30207
O	no	3.78164	0.20857	2.72328
O	yes	2.7583	-3.36351	-1.7493
O	no	-4.11329	-0.70024	1.83839
Si	yes	-3.31927	-4.31437	-2.82135
Si	yes	3.80192	4.89857	-0.90082
Si	yes	-3.63681	-4.73761	0.33181
Si	yes	3.49443	4.48967	2.25527
Si	yes	-0.92761	-2.55858	-2.3029
Si	yes	1.4007	3.1299	-1.32198
Si	yes	-3.93235	3.02583	4.6343
Si	no	-1.17781	-3.04369	0.8115
Si	yes	3.15188	-4.12305	4.39326
Si	no	1.02826	2.79305	1.80819
Si	yes	2.84551	0.35645	-1.4971
Si	yes	-2.38174	0.20269	-2.03523
Si	yes	-3.42845	3.69926	-0.12503
Al	no	2.50743	-0.03683	1.64448
Si	yes	3.5928	-3.53875	-0.38404
Al	no	-2.66688	-0.22155	1.09891
Si	yes	-5.71156	-0.44195	1.5901
Si	yes	2.08957	-2.39028	-2.84358
Si	yes	5.39602	-0.03637	2.744
Si	yes	-1.45033	3.18294	-2.45924
Si	no	-1.86647	2.59815	2.43625
Si	no	1.53387	-3.08278	2.0278
Si	yes	-5.2572	0.19662	-3.24923
Si	yes	5.90009	0.60092	-2.09057
H	yes	4.37183	-4.72406	-0.45299
H	yes	5.03361	4.26231	-1.2082
H	yes	3.84941	6.25253	-1.32619
H	yes	4.6557	3.75804	2.61937
H	yes	3.4422	5.68988	3.01247
H	yes	-4.03238	3.39057	-5.07709
H	yes	5.1325	-1.98435	-4.87802
H	yes	-2.44807	4.75029	-6.09151
H	yes	3.80873	-2.99722	-6.49344
H	yes	-3.60654	5.51252	-4.23542
Si	yes	-3.03008	4.37117	-4.85299
Si	yes	4.13108	-2.96378	-5.11092
H	yes	4.60643	-4.23973	-4.70794
O	no	-1.30348	-1.35708	4.17221
N	no	-3.11876	-2.79194	4.04833
N	no	-2.24301	-2.1004	4.10403

951

952 **Table S19.** η^1 -N bound

atom	constrained?	x	y	z
Fe	no	0.01914	-0.46754	-2.46805
O	no	1.1474	-1.72746	-1.24099
O	no	-1.12576	1.14373	-1.94397
O	no	-1.7209	-1.36911	-1.83193
O	no	1.73151	0.58454	-2.26791
H	yes	2.84207	-5.57658	3.8457
H	yes	2.89273	-6.54664	-0.43952
O	yes	1.85289	-3.37549	3.28681
O	yes	-1.89245	4.57565	1.48386
H	yes	4.27421	-3.86807	3.2076
H	yes	5.84375	0.55528	4.03419

H	yes	-6.04108	2.81365	2.00839
H	yes	-5.90426	1.32545	3.78124
H	yes	5.99943	-1.54569	3.06558
O	yes	2.89647	-4.94404	1.45189
O	yes	-2.90731	5.2107	-0.85775
H	yes	3.59338	2.17872	-6.47483
O	no	1.9086	-4.28898	-0.95972
H	yes	-3.52117	-4.611	-5.00616
O	no	-1.89627	3.58938	-2.74587
H	yes	4.30145	-4.71485	-0.57785
O	yes	2.67557	3.79923	3.43757
H	yes	-5.98699	1.80137	-2.47337
O	yes	-2.73804	-1.85455	4.66404
H	yes	6.00702	-2.53796	-1.42099
H	yes	5.93665	-1.10394	-3.23911
O	yes	-0.58418	-2.37614	3.25368
H	yes	-5.897	-0.27002	-3.5069
O	yes	0.54189	3.66444	1.91129
H	yes	4.7008	0.94155	-4.86435
O	no	0.51711	-3.09259	0.99185
H	yes	-4.64598	-2.80916	-4.09029
O	no	-0.54225	3.32084	-0.45501
O	yes	1.42795	-0.97613	2.28811
O	yes	-1.4615	1.98068	1.60733
O	no	2.54389	2.11256	-4.28063
O	no	-0.58747	-3.71131	-1.33719
O	no	-2.49195	-3.60186	-3.0436
O	no	0.61835	2.93742	-2.794
H	yes	4.76256	3.2681	-4.79046
H	yes	-4.71549	-4.88304	-3.03375
H	yes	4.8234	4.29567	-0.64138
H	yes	6.06086	-0.24715	-1.09123
O	yes	-2.12471	-0.3509	2.60291
H	yes	-6.05184	-0.13123	-1.20045
O	yes	2.08489	1.55939	2.20489
H	yes	4.63865	2.06067	-0.07678
O	no	-2.9291	0.26008	0.20421
H	yes	-4.64982	-1.78336	0.71852
O	no	2.92141	0.00213	0.30374
H	yes	6.11537	0.35345	1.74045
O	yes	-3.95874	1.49929	2.26096
H	yes	-6.1452	0.53073	1.6165
O	yes	3.91781	-0.25497	2.70725
O	no	3.0931	2.89363	-1.79102
O	no	-3.08624	-3.28453	-0.45714
O	yes	2.94295	3.62701	0.82551
O	no	-3.87235	0.50303	-2.46761
O	yes	-2.97068	-2.81155	2.22395
O	no	3.89467	-1.36688	-1.99382
Si	yes	3.0038	-4.46104	2.9821
Si	yes	-3.03609	5.42482	0.73094
Si	yes	3.02949	-5.16609	-0.13632
Si	yes	-3.01886	4.73507	-2.39097
Si	yes	0.81783	-2.45396	2.46804
Si	yes	-0.84944	3.39626	1.14894
Si	yes	3.96851	2.13392	-5.10593
Si	no	0.77085	-3.19515	-0.60453
Si	yes	-3.91407	-3.98877	-3.79164
Si	no	-0.75999	2.75707	-1.95753
Si	yes	-2.61186	0.85707	1.65607
Si	yes	2.58085	0.06464	1.86895
Si	yes	3.90983	3.23557	-0.40042
Al	no	-2.56358	0.17762	-1.44966
Si	yes	-3.92028	-2.9821	0.93548
Al	no	2.57235	-0.64183	-1.22706
Si	yes	5.52381	-1.28882	-1.89295
Si	yes	-2.1059	-1.85179	3.18453
Si	yes	-5.50126	0.47161	-2.36225
Si	yes	2.06287	3.16501	2.09188
Si	no	2.03501	2.14424	-2.75272

Si	no	-2.0139	-2.98336	-1.62561
Si	yes	5.5158	-0.22199	2.89188
Si	yes	-5.55909	1.54337	2.42114
H	yes	-4.8337	-4.0466	1.15681
H	yes	-4.31109	4.98055	1.17077
H	yes	-2.88242	6.80234	1.03946
H	yes	-4.28625	4.13506	-2.61499
H	yes	-2.87409	5.85555	-3.25123
H	yes	4.83904	3.23691	4.51072
H	yes	-4.91373	-0.89521	5.36723
H	yes	3.51701	4.8665	5.50299
H	yes	-3.60959	-1.94339	6.97609
H	yes	4.61947	5.32432	3.51728
Si	yes	3.95295	4.31948	4.26722
Si	yes	-4.0277	-1.97582	5.61942
H	yes	-4.68728	-3.20629	5.35996
N	no	0.21094	-2.03158	-4.01624
O	no	0.0712	-4.14917	-4.88603
N	no	0.13919	-3.07543	-4.43297

953

954 **Table S20.** η^1 -N' bound

atom	constrained?	x	y	z
Fe	no	-0.23361	-0.28345	2.46379
O	no	-1.44538	-1.47497	1.23983
O	no	1.15709	1.12481	1.96787
O	no	1.37087	-1.45218	2.12074
O	no	-1.74575	0.99375	2.04946
H	yes	-3.23807	-5.45878	-3.67044
H	yes	-3.77935	-6.05103	0.64962
O	yes	-1.99148	-3.37524	-3.18008
O	yes	2.69895	4.10977	-1.6072
H	yes	-4.45676	-3.52268	-3.2916
H	yes	-5.29985	0.9894	-4.57344
H	yes	6.57958	1.75772	-1.61672
H	yes	6.37584	0.15939	-3.28414
H	yes	-5.83537	-0.98196	-3.4764
O	yes	-3.39708	-4.62686	-1.34321
O	yes	3.59912	4.79309	0.7675
H	yes	-3.70919	3.16168	5.957
O	no	-2.531	-3.91478	1.10257
H	yes	2.44985	-4.63842	5.64371
O	no	2.21203	3.49306	2.66698
H	yes	-4.91618	-4.03825	0.52553
O	yes	-1.75734	3.80657	-3.91715
H	yes	6.01273	1.1407	2.90121
O	yes	2.86796	-2.61885	-4.22901
H	yes	-6.35389	-1.58519	1.04919
H	yes	-6.22722	-0.02747	2.75927
O	yes	0.55305	-2.72042	-2.99157
H	yes	5.54094	-0.80501	4.06674
O	yes	0.20216	3.50857	-2.1932
H	yes	-4.84726	1.95785	4.34264
O	no	-0.82715	-3.10288	-0.80508
H	yes	3.8937	-3.09084	4.71049
O	no	1.03062	3.22711	0.282
O	yes	-1.30893	-0.98182	-2.31962
O	yes	1.91054	1.59727	-1.58522
O	no	-2.50624	2.75975	3.87887
O	no	-0.01631	-3.6591	1.65118
O	no	1.74742	-3.68233	3.51816
O	no	-0.36701	3.21178	2.522
H	yes	-4.56712	4.25649	4.09792
H	yes	3.75033	-5.23568	3.81538
H	yes	-4.1387	4.93216	-0.10143
H	yes	-6.05006	0.6557	0.55363
O	yes	2.3105	-0.87828	-2.3462
H	yes	5.90284	-0.88214	1.78069

O	yes	-1.59848	1.61785	-2.47852
H	yes	-4.23198	2.65363	-0.48578
O	no	2.97322	-0.18939	0.06978
H	yes	4.43979	-2.48093	-0.13785
O	no	-2.81881	0.35804	-0.56318
H	yes	-5.78499	1.01922	-2.30639
O	yes	4.35751	0.72492	-1.9677
H	yes	6.32139	-0.47707	-1.05531
O	yes	-3.62608	0.03645	-3.01878
O	no	-2.73419	3.41577	1.30498
O	no	2.57634	-3.61642	0.98474
O	yes	-2.26023	3.89165	-1.33576
O	no	3.73983	0.14771	2.786
O	yes	2.75938	-3.39134	-1.71597
O	no	-4.14208	-0.65193	1.75223
Si	yes	-3.30781	-4.26333	-2.90725
Si	yes	3.88733	4.85392	-0.81352
Si	yes	-3.69051	-4.695	0.23752
Si	yes	3.51481	4.43647	2.33443
Si	yes	-0.90523	-2.53907	-2.33617
Si	yes	1.47317	3.11652	-1.28757
Si	yes	-3.97325	3.05456	4.56582
Si	no	-1.22083	-3.02888	0.76195
Si	yes	3.02657	-4.17972	4.42975
Si	no	1.03502	2.76835	1.8347
Si	yes	2.88713	0.32625	-1.44672
Si	yes	-2.3304	0.23877	-2.08471
Si	yes	-3.3706	3.74041	-0.18025
Al	no	2.47488	-0.0753	1.68888
Si	yes	3.56552	-3.58215	-0.33584
Al	no	-2.67588	-0.18987	1.03303
Si	yes	-5.7363	-0.37915	1.47399
Si	yes	2.12354	-2.4057	-2.81871
Si	yes	5.3514	-0.11446	2.84041
Si	yes	-1.35481	3.20901	-2.47857
Si	no	-1.87066	2.61038	2.40582
Si	no	1.46267	-3.10961	2.03956
Si	yes	-5.18208	0.27275	-3.35314
Si	yes	5.95522	0.53554	-1.98102
H	yes	4.33121	-4.77665	-0.3949
H	yes	5.1168	4.2038	-1.10008
H	yes	3.95943	6.20885	-1.23229
H	yes	4.65992	3.68922	2.71749
H	yes	3.4628	5.63424	3.09548
H	yes	-3.8838	3.45856	-5.14413
H	yes	5.2094	-2.02917	-4.79326
H	yes	-2.26398	4.8027	-6.12261
H	yes	3.90439	-3.01938	-6.43774
H	yes	-3.44821	5.57181	-4.28571
Si	yes	-2.87406	4.4259	-4.89696
Si	yes	4.20072	-2.99531	-5.04921
H	yes	4.65271	-4.27857	-4.64257
N	no	-2.49762	-1.96673	4.17202
N	no	-1.54738	-1.37598	4.03164
O	no	-3.47574	-2.58214	4.33974

955

956 **Table S21.** S=2 Transition state

atom	constrained?	x	y	z
Fe	no	0.16065	-0.07972	2.50149
O	no	1.14666	1.42811	1.59534
O	no	-0.95515	-1.53352	1.66854
O	no	-1.58869	0.89442	2.2178
O	no	1.85855	-1.0365	1.86035
H	yes	2.4436	6.53026	-2.47942
H	yes	2.80707	6.37984	1.89688
O	yes	1.52636	4.22978	-2.4344
O	yes	-1.97484	-4.03097	-2.46798

H	yes	3.94059	4.76102	-2.40187
H	yes	5.4965	0.74426	-4.44088
H	yes	-6.1724	-2.32328	-2.23172
H	yes	-6.18836	-0.42967	-3.56981
H	yes	5.69964	2.53365	-2.98028
O	yes	2.68692	5.3118	-0.3371
O	yes	-2.80163	-5.27177	-0.30158
H	yes	4.06878	-3.56726	5.43392
O	no	1.91976	3.999	1.87769
H	yes	-3.21842	3.14817	6.25453
O	no	-1.68989	-4.12389	1.85869
H	yes	4.24433	4.61778	1.46266
O	yes	2.42221	-2.64163	-4.47347
H	yes	-5.79115	-2.48276	2.34462
O	yes	-3.13693	2.9671	-3.82936
H	yes	6.03515	2.35214	1.59883
H	yes	6.12016	0.50149	2.98979
O	yes	-0.88889	3.17966	-2.48715
H	yes	-5.64824	-0.74055	3.86486
O	yes	0.40887	-2.96586	-2.81764
H	yes	5.03587	-1.92745	4.12002
O	no	0.38685	3.30063	-0.19522
H	yes	-4.38746	1.60441	4.98932
O	no	-0.50035	-3.25509	-0.36702
O	yes	1.2075	1.64334	-2.05574
O	yes	-1.58608	-1.4778	-1.95328
O	no	2.85749	-2.96508	3.40445
O	no	-0.56496	3.33262	2.26728
O	no	-2.34234	2.71213	4.02082
O	no	0.83019	-3.47345	1.90522
H	yes	5.12008	-4.15567	3.44914
H	yes	-4.56197	3.87561	4.50627
H	yes	4.87882	-4.09196	-0.81846
H	yes	6.09161	0.22329	0.69094
O	yes	-2.351	1.00856	-2.26993
H	yes	-5.97568	-0.29297	1.61644
O	yes	1.8995	-0.80834	-2.67035
H	yes	4.62471	-1.79372	-0.77788
O	no	-2.94845	-0.22034	-0.05414
H	yes	-4.74324	1.83556	0.09068
O	no	2.85269	0.25982	-0.49301
H	yes	5.93868	0.36451	-2.19677
O	yes	-4.13127	-0.92384	-2.28501
H	yes	-6.2742	-0.21944	-1.26239
O	yes	3.66695	1.13018	-2.81904
O	no	3.22486	-3.10839	0.76933
O	no	-3.10542	3.02366	1.4892
O	yes	2.88472	-3.13104	-1.9298
O	no	-3.69532	-1.15313	2.51928
O	yes	-3.19562	3.26445	-1.21554
O	no	3.98403	0.99681	2.00454
Si	yes	2.68384	5.23736	-1.94358
Si	yes	-3.04783	-5.07874	-1.87909
Si	yes	2.93715	5.12669	1.24169
Si	yes	-2.80243	-5.20531	1.30626
Si	yes	0.56759	3.09849	-1.8081
Si	yes	-0.92397	-2.9435	-1.91632
Si	yes	4.33854	-3.16429	4.09921
Si	no	0.74177	3.02697	1.35949
Si	yes	-3.69464	2.84335	4.95184
Si	no	-0.60216	-3.10602	1.24095
Si	yes	-2.75031	-0.41488	-1.6321
Si	yes	2.40138	0.56639	-1.99887
Si	yes	3.93679	-3.0344	-0.71539
Al	no	-2.46824	-0.53533	1.54005
Si	yes	-4.0468	3.07211	0.13706
Al	no	2.61781	0.44967	1.17444
Si	yes	5.60434	1.00971	1.76821
Si	yes	-2.39449	2.60783	-2.44796
Si	yes	-5.33143	-1.15405	2.54375

Si	yes	1.90554	-2.38977	-2.97073
Si	no	2.23027	-2.64883	1.95507
Si	no	-1.94333	2.49878	2.47975
Si	yes	5.24665	1.19491	-3.1176
Si	yes	-5.73851	-0.97546	-2.33843
H	yes	-4.98723	4.12901	0.26014
H	yes	-4.35777	-4.57711	-2.10001
H	yes	-2.90127	-6.32707	-2.53984
H	yes	-4.0564	-4.72175	1.76465
H	yes	-2.57931	-6.50272	1.83874
H	yes	4.49116	-1.75793	-5.51604
H	yes	-5.34786	2.15096	-4.60018
H	yes	3.1176	-3.1219	-6.797
H	yes	-4.18218	3.61382	-5.97464
H	yes	4.37282	-4.03514	-5.07697
Si	yes	3.63926	-2.89384	-5.49614
Si	yes	-4.49666	3.28719	-4.62897
H	yes	-5.14955	4.39011	-4.01767
O	no	0.52298	-0.15409	4.29195
N	no	2.10043	-0.65087	6.04729
N	no	1.72597	-0.57907	4.99173

957

958 **Table S22.** α -O product

atom	constrained?	x	y	z
Fe	no	0.00014	0.00014	-2.59121
O	no	-1.08935	1.45813	-1.72678
O	no	1.08952	-1.45788	-1.72675
O	no	1.66022	0.99643	-2.15172
O	no	-1.65991	-0.99607	-2.1516
H	yes	-2.835	6.35866	2.40362
H	yes	-2.85598	6.37087	-1.99027
O	yes	-1.85522	4.0844	2.34491
O	yes	1.85488	-4.08471	2.3448
H	yes	-4.2732	4.5583	2.14385
H	yes	-5.87252	0.4286	3.90465
H	yes	6.0105	-2.26863	2.50038
H	yes	5.87214	-0.42897	3.90503
H	yes	-6.01078	2.26836	2.50011
O	yes	-2.8795	5.21943	0.20508
O	yes	2.87937	-5.21958	0.20494
H	yes	-3.57237	-3.45783	-5.98196
O	no	-1.90844	4.01525	-1.99083
H	yes	3.57251	3.458	-5.98146
O	no	1.90867	-4.01503	-1.99117
H	yes	-4.27428	4.5591	-1.73523
O	yes	-2.71955	-2.88104	4.05127
H	yes	5.98745	-2.25809	-2.09451
O	yes	2.71915	2.88067	4.05164
H	yes	-5.98746	2.2581	-2.09477
H	yes	-5.91501	0.46173	-3.55589
O	yes	0.57629	3.0914	2.54695
H	yes	5.91513	-0.46167	-3.55552
O	yes	-0.57659	-3.09175	2.54669
H	yes	-4.68222	-1.89471	-4.68792
O	no	-0.51813	3.27837	0.17045
H	yes	4.68188	1.89449	-4.68708
O	no	0.51848	-3.2785	0.17015
O	yes	-1.43834	1.5232	1.89646
O	yes	1.43811	-1.52344	1.89652
O	no	-2.54231	-2.89123	-3.83715
O	no	0.61536	3.4266	-2.20985
O	no	2.54284	2.8923	-3.83663
O	no	-0.61521	-3.42632	-2.21003
H	yes	-4.75695	-4.14838	-4.10825
H	yes	4.75719	4.14858	-4.10785
H	yes	-4.84712	-4.24597	0.16439
H	yes	-6.05612	0.09459	-1.27378

O	yes	2.10893	0.96632	2.36398
H	yes	6.05612	-0.09466	-1.27332
O	yes	-2.10916	-0.96658	2.36377
H	yes	-4.65287	-1.94245	0.22917
O	no	2.91598	-0.1549	0.1594
H	yes	4.65273	1.94229	0.22961
O	no	-2.91647	0.15507	0.15906
H	yes	-6.13005	0.12641	1.62032
O	yes	3.93429	-0.92184	2.44616
H	yes	6.12983	-0.12663	1.62075
O	yes	-3.93454	0.92154	2.44599
O	no	-3.08861	-3.1154	-1.24511
O	no	3.08859	3.11567	-1.24446
O	yes	-2.97124	-3.28159	1.46281
O	no	3.87541	-0.96457	-2.3852
O	yes	2.97103	3.28135	1.46325
O	no	-3.87519	0.96481	-2.38566
Si	yes	-2.99819	5.08233	1.80302
Si	yes	2.99799	-5.08253	1.80292
Si	yes	-3.00218	5.09036	-1.39419
Si	yes	3.00227	-5.09023	-1.39437
Si	yes	-0.82076	3.00197	1.75383
Si	yes	0.82067	-3.00206	1.75357
Si	yes	-3.95437	-3.11354	-4.65822
Si	no	-0.74736	3.05927	-1.41536
Si	yes	3.95503	3.11402	-4.65777
Si	no	0.74759	-3.05906	-1.41563
Si	yes	2.59449	-0.42119	1.70696
Si	yes	-2.59478	0.42087	1.70662
Si	yes	-3.92885	-3.16272	0.17439
Al	no	2.56211	-0.43329	-1.4735
Si	yes	3.92883	3.16268	0.17502
Al	no	-2.56202	0.43359	-1.4737
Si	yes	-5.50862	0.93429	-2.27976
Si	yes	2.09532	2.55798	2.6041
Si	yes	5.50882	-0.93398	-2.27941
Si	yes	-2.09564	-2.55823	2.60385
Si	no	-2.01761	-2.62126	-2.3471
Si	no	2.01788	2.6217	-2.3468
Si	yes	-5.53372	0.93658	2.62254
Si	yes	5.53343	-0.93683	2.62288
H	yes	4.84703	4.24585	0.165
H	yes	4.27297	-4.55857	2.14387
H	yes	2.83471	-6.35892	2.40342
H	yes	4.27435	-4.55916	-1.73521
H	yes	2.85601	-6.37087	-1.99042
H	yes	-4.8858	-2.08883	4.96131
H	yes	4.88535	2.08842	4.9618
H	yes	-3.57868	-3.46843	6.29401
H	yes	3.57814	3.46793	6.29449
H	yes	-4.67251	-4.34361	4.44855
Si	yes	-4.00452	-3.20227	4.96577
Si	yes	4.00407	3.20185	4.96625
H	yes	4.6721	4.34323	4.44914
O	no	0.00071	-0.0011	-4.17989

959

960 **Table S23.** α -Fe(II) Toy model for figure 5

atom	constrained?	x	y	z
Fe	no	0.00013	-0.00004	-0.00001
O	no	-1.28051	1.54571	-0.1282
O	no	1.28038	-1.54601	-0.12908
O	no	-1.28043	-1.54579	0.12879
O	no	1.28047	1.54591	0.12846
O	no	-3.46568	-0.00021	-0.00065
O	no	3.46541	-0.00023	0.00074
H	no	-0.12923	-3.6699	-1.38789
H	no	0.12775	3.67226	-1.38421

H	no	0.12844	-3.67235	1.38415
H	no	-0.12852	3.66977	1.38796
Si	no	-2.93616	1.52127	-0.35985
Si	no	2.93621	-1.52159	-0.35933
Al	no	-0.00027	-2.90681	-0.0012
Al	no	-0.00026	2.90671	0.0012
Si	no	2.93637	1.52178	0.35833
Si	no	-2.936	-1.52108	0.36086
H	no	3.24111	1.81582	1.77544
H	no	3.57169	2.49394	-0.5566
H	no	3.24047	-1.81336	-1.77704
H	no	3.57179	-2.49521	0.55383
H	no	-3.23864	-1.81089	1.77931
H	no	-3.57258	-2.496	-0.55024
H	no	-3.23929	1.81323	-1.77775
H	no	-3.57245	2.49482	0.55293

961

962 **Table S24.** Empty α -Fe(II) in BEA + gas-phase N₂O (method figure 6)

atom	constrained?	x	y	z
Fe	no	1.96388	-0.46228	-0.40506
O	no	0.86884	-1.33593	-1.8185
O	no	1.89073	0.67358	1.22825
O	no	1.99757	1.32547	-1.29014
O	no	1.56549	-2.17079	0.54666
H	yes	-4.32932	-1.72135	-5.8931
H	yes	-0.11821	-2.68004	-6.70197
O	yes	-3.67016	-0.95155	-3.6329
O	yes	-1.46199	2.04437	4.53088
H	yes	-4.09814	-3.31375	-4.22336
H	yes	-5.44973	-4.80723	0.09583
H	yes	-0.98776	6.26227	2.92606
H	yes	-2.67737	6.56684	1.36756
H	yes	-4.44271	-5.10303	-1.97176
O	yes	-2.03668	-2.32078	-5.17351
O	yes	1.0128	2.49895	5.29593
H	yes	5.21097	-4.97383	2.20789
O	no	0.51028	-1.90733	-4.40663
H	yes	5.64282	2.50764	-4.32773
O	no	2.72333	1.13658	3.72658
H	yes	-0.37481	-4.14389	-4.92701
O	yes	-4.32672	-1.95522	3.49015
H	yes	3.41613	5.25842	2.08232
O	yes	-4.08187	3.77749	-1.97363
H	yes	-0.02492	-6.0632	-2.79339
H	yes	1.69685	-6.44075	-1.29008
O	yes	-3.15255	1.38471	-2.53153
H	yes	4.4994	5.01147	0.04946
O	yes	-2.36746	-0.20553	3.50275
H	yes	3.45649	-5.65955	0.86541
O	no	-1.14855	-0.18889	-3.19155
H	yes	4.91224	3.74659	-2.51612
O	no	0.19642	0.34868	3.30063
O	yes	-2.71433	-0.835	-1.18183
O	yes	-1.55685	1.73615	1.91728
O	no	3.30292	-3.46598	2.09656
O	no	1.36434	0.44158	-3.70911
O	no	3.45435	1.9118	-3.44296
O	no	2.23711	-1.29306	2.95726
H	yes	3.26389	-5.77958	3.18286
H	yes	3.99289	4.11419	-4.62366
H	yes	-0.8414	-4.96142	4.04958
H	yes	-0.46358	-6.1182	-0.52095
O	yes	-2.27545	2.67768	-0.42035
H	yes	2.27829	5.6644	0.10748
O	yes	-2.8931	-1.57674	1.32522
H	yes	-1.24863	-4.58417	1.80458
O	no	0.21615	2.90024	0.32376

H	yes	0.178	4.77277	-1.67333
O	no	-1.14341	-2.74479	-0.22001
H	yes	-3.26358	-5.56918	-0.03049
O	yes	-1.62738	4.33033	1.51691
H	yes	-0.47794	6.35239	0.66595
O	yes	-3.69891	-3.19427	-0.58227
O	no	0.72503	-3.48439	2.77628
O	no	1.05179	3.03786	-3.18043
O	yes	-1.8308	-2.78398	3.4056
O	no	3.03231	3.23903	0.69395
O	yes	-1.60842	3.49989	-2.8272
O	no	0.96004	-4.17704	-1.52405
Si	yes	-3.57404	-2.10518	-4.75353
Si	yes	-0.51773	2.96638	5.45512
Si	yes	-0.5073	-2.79203	-5.3408
Si	yes	2.55358	2.28667	4.88362
Si	yes	-2.68868	-0.15219	-2.63842
Si	yes	-1.3086	0.99234	3.32216
Si	yes	3.79674	-5.0375	2.09578
Si	no	0.3643	-0.76054	-3.28616
Si	yes	4.51582	3.13706	-3.73588
Si	no	1.73955	0.24226	2.8188
Si	yes	-1.30182	2.90521	0.84188
Si	yes	-2.60487	-2.08525	-0.17522
Si	yes	-0.82829	-3.98308	3.02046
Al	no	1.76635	2.2101	0.28203
Si	yes	-0.13736	4.14828	-2.90903
Al	no	0.46104	-2.7559	-0.77429
Si	yes	0.48298	-5.73658	-1.5082
Si	yes	-2.77748	2.83611	-1.94158
Si	yes	3.26314	4.85278	0.7301
Si	yes	-2.85206	-1.63256	2.93347
Si	no	1.92569	-2.63768	2.10383
Si	no	1.9513	1.72401	-2.9062
Si	yes	-4.22889	-4.71289	-0.62325
Si	yes	-1.43678	5.92449	1.62195
H	yes	-0.10501	5.12234	-3.94179
H	yes	-0.64809	4.32066	5.0485
H	yes	-0.91541	2.83925	6.81234
H	yes	3.07598	3.49274	4.3462
H	yes	3.30918	1.91983	6.02869
H	yes	-5.81867	-3.81064	2.79737
H	yes	-4.33721	6.02193	-0.95102
H	yes	-6.57279	-2.35699	4.44241
H	yes	-6.1417	5.13791	-2.11302
H	yes	-4.89841	-3.88297	4.92818
Si	yes	-5.43795	-3.03553	3.92462
Si	yes	-4.72649	5.24873	-2.07663
H	yes	-4.27313	5.8751	-3.26764
N	no	11.27855	-0.77582	-1.65226
N	no	11.53508	-1.72096	-1.09617
O	yes	11.80476	-2.71455	-0.51164

963

964 **Table S25.** η^1 -O (method fig 6)

atom	constrained?	x	y	z
Fe	no	0.15406	0.33906	2.49893
O	no	1.40112	1.56108	1.32209
O	no	-1.18744	-1.10808	1.98032
O	no	-1.45086	1.47024	2.0192
O	no	1.69959	-0.9003	2.16186
H	yes	3.26654	5.40442	-3.72439
H	yes	3.62407	6.1497	0.59104
O	yes	2.05316	3.30634	-3.21304
O	yes	-2.51021	-4.24241	-1.57251
H	yes	4.51656	3.51363	-3.235
H	yes	5.5195	-1.01425	-4.33278
H	yes	-6.44402	-1.99276	-1.8087

H	yes	-6.21453	-0.44442	-3.51937
H	yes	5.96325	1.00466	-3.28228
O	yes	3.35481	4.65248	-1.36638
O	yes	-3.48544	-4.87165	0.78747
H	yes	3.57227	-2.88528	6.19559
O	no	2.399	4.02687	1.07951
H	yes	-2.7593	4.73895	5.38757
O	no	-2.20434	-3.48191	2.70182
H	yes	4.81365	4.16385	0.57766
O	yes	2.02418	-3.89917	-3.71909
H	yes	-6.06957	-1.21563	2.7047
O	yes	-2.74157	2.3914	-4.4213
H	yes	6.28971	1.76693	1.23738
H	yes	6.1344	0.26244	2.99213
O	yes	-0.47997	2.59252	-3.10029
H	yes	-5.69139	0.77829	3.82183
O	yes	-0.00791	-3.59624	-2.08226
H	yes	4.74256	-1.70538	4.58677
O	no	0.82044	3.05665	-0.86149
H	yes	-4.12708	3.12529	4.45177
O	no	-0.94373	-3.25406	0.35219
O	yes	1.3964	0.92517	-2.30008
O	yes	-1.78515	-1.71105	-1.60403
O	no	2.43714	-2.62468	4.06388
O	no	-0.12498	3.70014	1.52295
O	no	-1.9443	3.74082	3.32817
O	no	0.36766	-3.13591	2.64269
H	yes	4.52894	-4.01731	4.40834
H	yes	-4.0016	5.24312	3.49202
H	yes	4.28166	-4.8391	0.22008
H	yes	6.0604	-0.49583	0.80529
O	yes	-2.21563	0.72749	-2.46171
H	yes	-5.96552	0.77197	1.52231
O	yes	1.75561	-1.66994	-2.36123
H	yes	4.33371	-2.57245	-0.23569
O	no	-2.93851	0.09442	-0.04874
H	yes	-4.46806	2.34515	-0.39085
O	no	2.84228	-0.29157	-0.43801
H	yes	5.91627	-0.95831	-2.04908
O	yes	-4.2359	-0.91489	-2.10858
H	yes	-6.26283	0.26492	-1.31252
O	yes	3.76338	-0.05506	-2.87586
O	no	2.7767	-3.32454	1.51843
O	no	-2.67927	3.5734	0.76725
O	yes	2.42787	-3.88782	-1.11904
O	no	-3.81852	-0.16643	2.65184
O	yes	-2.75026	3.2472	-1.93306
O	no	4.07914	0.79198	1.88791
Si	yes	3.33566	4.23644	-2.91973
Si	yes	-3.71007	-4.99094	-0.80051
Si	yes	3.58449	4.77936	0.22125
Si	yes	-3.47124	-4.46274	2.34379
Si	yes	0.95557	2.47026	-2.38383
Si	yes	-1.32254	-3.2082	-1.23936
Si	yes	3.88774	-2.81669	4.81268
Si	no	1.14014	3.07088	0.72596
Si	yes	-3.27663	4.22658	4.16835
Si	no	-1.0138	-2.75203	1.89106
Si	yes	-2.79712	-0.46203	-1.54541
Si	yes	2.43748	-0.2603	-1.98583
Si	yes	3.48812	-3.67085	0.07245
Al	no	-2.51513	0.04473	1.59794
Si	yes	-3.61409	3.46168	-0.59175
Al	no	2.64518	0.27711	1.14545
Si	yes	5.68559	0.5597	1.67804
Si	yes	-2.04779	2.24321	-2.9772
Si	yes	-5.43724	0.05376	2.62734
Si	yes	1.55115	-3.26602	-2.31759
Si	no	1.86175	-2.50369	2.56831
Si	no	-1.59917	3.11974	1.88279

Si	yes	5.33658	-0.26182	-3.14241
Si	yes	-5.83604	-0.76729	-2.18931
H	yes	-4.40617	4.6334	-0.72005
H	yes	-4.94299	-4.38234	-1.15539
H	yes	-3.73252	-6.36013	-1.17643
H	yes	-4.64836	-3.73306	2.6576
H	yes	-3.41981	-5.63348	3.14563
H	yes	4.1878	-3.53626	-4.87475
H	yes	-5.04402	1.72362	-5.05477
H	yes	2.64089	-4.95264	-5.86919
H	yes	-3.7004	2.69352	-6.68017
H	yes	3.77095	-5.63122	-3.96377
Si	yes	3.19318	-4.52082	-4.63431
Si	yes	-4.05009	2.70668	-5.30394
H	yes	-4.54896	3.99033	-4.95784
O	no	1.3497	1.6095	4.13588
N	no	1.93489	3.85057	4.03696
N	no	1.64955	2.77116	4.07209

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966 **Table S26.** Transition state (method fig 6)

atom	constrained?	x	y	z
Fe	no	0.1232	-0.09305	2.53229
O	no	1.13424	1.41632	1.64792
O	no	-0.98274	-1.53747	1.65773
O	no	-1.6151	0.89637	2.18984
O	no	1.82577	-1.05395	1.90482
H	yes	2.53209	6.52905	-2.41374
H	yes	2.81186	6.35749	1.96792
O	yes	1.6028	4.23304	-2.39647
O	yes	-1.9379	-4.00978	-2.53352
H	yes	4.01859	4.75198	-2.31587
H	yes	5.59297	0.7365	-4.34317
H	yes	-6.13069	-2.28209	-2.36901
H	yes	-6.11195	-0.38253	-3.69861
H	yes	5.77725	2.51838	-2.87094
O	yes	2.72877	5.29994	-0.27272
O	yes	-2.81169	-5.25597	-0.38877
H	yes	3.95719	-3.61134	5.48331
O	no	1.90952	3.98868	1.92767
H	yes	-3.31097	3.13694	6.19619
O	no	-1.73141	-4.13009	1.80224
H	yes	4.24836	4.59017	1.55303
O	yes	2.50315	-2.63372	-4.44918
H	yes	-5.83698	-2.46368	2.21296
O	yes	-3.03941	2.99998	-3.88507
H	yes	6.02507	2.31498	1.71284
H	yes	6.07458	0.4578	3.09679
O	yes	-0.81617	3.19531	-2.49963
H	yes	-5.71429	-0.72894	3.74347
O	yes	0.45724	-2.95513	-2.83321
H	yes	4.95709	-1.97063	4.19535
O	no	0.42554	3.28865	-0.17852
H	yes	-4.46345	1.60467	4.90214
O	no	-0.50671	-3.24375	-0.39621
O	yes	1.26405	1.64659	-2.03557
O	yes	-1.54635	-1.4609	-2.00004
O	no	2.78326	-3.00648	3.44066
O	no	-0.584	3.33245	2.26294
O	no	-2.39189	2.71633	3.98186
O	no	0.78782	-3.48934	1.89553
H	yes	5.04298	-4.19626	3.51614
H	yes	-4.61757	3.87883	4.42612
H	yes	4.8829	-4.1125	-0.75492
H	yes	6.08819	0.1899	0.79658
O	yes	-2.29284	1.03065	-2.3199
H	yes	-5.99687	-0.26979	1.4913
O	yes	1.95546	-0.80581	-2.64803

H	yes	4.63942	-1.81321	-0.7088
O	no	-2.9304	-0.21644	-0.11813
H	yes	-4.72524	1.85922	-0.00126
O	no	2.85867	0.25669	-0.4413
H	yes	5.99069	0.34464	-2.09283
O	yes	-4.08203	-0.8927	-2.37737
H	yes	-6.24044	-0.18206	-1.3923
O	yes	3.73496	1.12445	-2.75451
O	no	3.20408	-3.12219	0.80854
O	no	-3.11053	3.03582	1.43682
O	yes	2.91498	-3.13668	-1.89945
O	no	-3.73901	-1.14457	2.44034
O	yes	-3.14612	3.28608	-1.27151
O	no	3.96176	0.96957	2.07764
Si	yes	2.75574	5.23261	-1.8793
Si	yes	-3.02702	-5.05474	-1.96976
Si	yes	2.94813	5.10661	1.30967
Si	yes	-2.84261	-5.19661	1.21906
Si	yes	0.62677	3.10383	-1.79352
Si	yes	-0.89231	-2.93006	-1.95718
Si	yes	4.25417	-3.20384	4.15578
Si	no	0.74168	3.01637	1.38711
Si	yes	-3.76394	2.84027	4.88336
Si	no	-0.63199	-3.10713	1.2134
Si	yes	-2.71119	-0.39357	-1.69616
Si	yes	2.45131	0.56341	-1.96097
Si	yes	3.94433	-3.05068	-0.66493
Al	no	-2.48733	-0.52833	1.49045
Si	yes	-4.02371	3.09205	0.06386
Al	no	2.60421	0.42981	1.22827
Si	yes	5.5845	0.974	1.86798
Si	yes	-2.32505	2.63088	-2.4915
Si	yes	-5.37456	-1.13819	2.42674
Si	yes	1.95937	-2.3859	-2.95536
Si	no	2.18914	-2.67079	1.98261
Si	no	-1.96815	2.50204	2.44792
Si	yes	5.32033	1.18256	-3.02284
Si	yes	-5.6882	-0.936	-2.46141
H	yes	-4.96107	4.15311	0.17389
H	yes	-4.33004	-4.54556	-2.21316
H	yes	-2.87413	-6.30087	-2.63324
H	yes	-4.10264	-4.70878	1.65582
H	yes	-2.63604	-6.49745	1.74981
H	yes	4.59582	-1.75584	-5.44843
H	yes	-5.23935	2.19837	-4.70125
H	yes	3.24004	-3.10722	-6.76128
H	yes	-4.04064	3.66141	-6.04681
H	yes	4.45794	-4.03433	-5.02195
Si	yes	3.73809	-2.88753	-5.44977
Si	yes	-4.38215	3.33042	-4.70881
H	yes	-5.04105	4.4339	-4.105
O	no	0.30799	-0.17814	4.34888
N	no	1.47849	-0.68353	6.38445
N	no	1.32067	-0.64283	5.27241

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968 **Table S27.** α -O + N₂ product (method fig 6)

atom	constrained?	x	y	z
Fe	no	-0.25652	-0.18052	2.4887
O	no	-1.3295	-1.4786	1.37601
O	no	1.0289	1.25065	1.88584
O	no	1.37319	-1.27007	2.14915
O	no	-1.77636	0.97487	1.93417
H	yes	-2.87833	-5.87073	-3.3885
H	yes	-3.44557	-6.23571	0.95337
O	yes	-1.75896	-3.69355	-3.01097
O	yes	2.47682	4.12874	-1.84085
H	yes	-4.21007	-3.98879	-3.13952

H	yes	-5.28976	0.38333	-4.69882
H	yes	6.48439	2.00718	-1.66804
H	yes	6.39501	0.30364	-3.23855
H	yes	-5.72788	-1.54697	-3.49112
O	yes	-3.11684	-4.91268	-1.11724
O	yes	3.30346	5.00239	0.49794
H	yes	-3.97262	3.26463	5.69845
O	no	-2.34132	-3.98204	1.28417
H	yes	2.62299	-4.17359	5.91927
O	no	1.98131	3.71504	2.45613
H	yes	-4.69288	-4.30248	0.6966
O	yes	-1.92232	3.4334	-4.17543
H	yes	5.89028	1.62781	2.87253
O	yes	3.06397	-2.72276	-4.05195
H	yes	-6.27468	-1.90935	1.05677
H	yes	-6.26052	-0.24816	2.67148
O	yes	0.74146	-2.88354	-2.83522
H	yes	5.51339	-0.26922	4.14774
O	yes	0.0266	3.35135	-2.41606
H	yes	-5.01831	1.90402	4.14768
O	no	-0.66289	-3.16278	-0.62496
H	yes	3.98966	-2.6037	4.91013
O	no	0.8404	3.24985	0.08643
O	yes	-1.22538	-1.21806	-2.28857
O	yes	1.832	1.58082	-1.6764
O	no	-2.72113	2.80486	3.65499
O	no	0.16886	-3.60983	1.84451
O	no	1.90295	-3.37077	3.73175
O	no	-0.58172	3.30826	2.31391
H	yes	-4.8649	4.1959	3.76779
H	yes	3.9807	-4.80255	4.14393
H	yes	-4.41687	4.64475	-0.45961
H	yes	-6.09151	0.31195	0.43085
O	yes	2.38238	-0.90846	-2.28305
H	yes	5.91104	-0.46092	1.87438
O	yes	-1.65969	1.34666	-2.60638
H	yes	-4.37538	2.34584	-0.70746
O	no	2.97077	-0.026	0.09763
H	yes	4.56804	-2.25218	0.03993
O	no	-2.79829	0.10397	-0.6154
H	yes	-5.8075	0.5197	-2.44291
O	yes	4.32964	0.82938	-1.97987
H	yes	6.34558	-0.2015	-0.97623
O	yes	-3.58655	-0.37788	-3.07215
O	no	-2.93029	3.2661	1.04183
O	no	2.75649	-3.40972	1.21043
O	yes	-2.46527	3.6425	-1.60922
O	no	3.67498	0.48779	2.80241
O	yes	2.96425	-3.34969	-1.49837
O	no	-4.13326	-0.81334	1.72019
Si	yes	-3.02644	-4.63811	-2.69924
Si	yes	3.60985	4.98574	-1.08074
Si	yes	-3.42796	-4.90373	0.46153
Si	yes	3.2176	4.73508	2.08249
Si	yes	-0.73374	-2.74784	-2.20741
Si	yes	1.30502	3.08739	-1.47511
Si	yes	-4.21011	3.05966	4.31341
Si	no	-1.06116	-3.06721	0.94186
Si	yes	3.18972	-3.75536	4.6861
Si	no	0.8433	2.89354	1.66608
Si	yes	2.8771	0.37861	-1.45158
Si	yes	-2.31766	-0.04637	-2.13817
Si	yes	-3.58136	3.49641	-0.4585
Al	no	2.44716	0.13537	1.70342
Si	yes	3.76056	-3.41171	-0.10086
Al	no	-2.68012	-0.32053	1.02279
Si	yes	-5.73237	-0.64696	1.4149
Si	yes	2.28897	-2.46945	-2.66492
Si	yes	5.30224	0.33526	2.8802
Si	yes	-1.50674	2.94638	-2.69942

Si	no	-2.04109	2.60631	2.21847
Si	no	1.59261	-2.93013	2.22289
Si	yes	-5.14863	-0.2517	-3.43651
Si	yes	5.93554	0.73167	-1.96489
H	yes	4.59352	-4.56158	-0.07995
H	yes	4.87811	4.3915	-1.31473
H	yes	3.61081	6.31534	-1.57934
H	yes	4.39783	4.079	2.5218
H	yes	3.08711	5.97102	2.76963
H	yes	-4.00824	2.89156	-5.40173
H	yes	5.37586	-2.03402	-4.62578
H	yes	-2.45375	4.26614	-6.44196
H	yes	4.15227	-3.19344	-6.22156
H	yes	-3.7053	5.07357	-4.6672
Si	yes	-3.05856	3.92829	-5.20242
Si	yes	4.4273	-3.07002	-4.83391
H	yes	4.94563	-4.29879	-4.3462
O	no	-0.42001	-0.25163	4.06917
N	no	-3.18618	-1.88753	4.9066
N	no	-3.63023	-0.99325	5.35678

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