

Electronic Supplementary Information

Oxygen-selective adsorption on high-silica LTA zeolite

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Experimental details

2.1. Materials. NaA, ZK-4 and NaUZM-9 samples were synthesized using the reported methods in the existing literature.¹⁻³ The LTA samples were dried at 100 °C before being calcined at 550 °C for 6h in air. The proton-type LTA samples referred to as NaA-H, ZK-4-H and NaUZM-9-H were obtained by NH₄⁺ cation exchange and calcination. Ion-exchange was carried out by repeatedly treating the calcined LTA powders at 100 °C with 0.1mol/L NH₄NO₃ solution (solid-to-liquid ratio 1:50) follow by filtration and washing with distilled water. The ion-exchanged samples were also calcined at 550 °C for 6h in air after drying at 100 °C.

2.2. Characterization. The powder X-ray diffraction (PXRD) patterns were collected on a PANalytical X'Pert PRO X-ray diffractometer. The λ of Cu-K α radiation is 1.54059 Å, which was operated at 40 kV and 40 mA. The step size was 0.02 °, and the scanning speed was 12 °/min. N₂ adsorption-desorption isotherms of the samples were measured on a Micromeritics ASAP2050 system at -196 °C, and the micropore region (P/P₀ < 0.02) of them were not measured. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface areas (S_{BET}), then Micropore surface areas (S_{micro}) and Micropore Volume (V_m) were obtained based on t-plot method. The TG-DSC curves were obtained by TAQ-600 analyzer from room temperature to 1200 °C. The heating rate was 10 °C/min, and the air flow was 100 ml/min. The Si/Al and Na/Al of these samples were calculated by the Philips Magix-601X-ray fluorescence (XRF) spectrometer.

2.3. O₂ and N₂ Adsorption Isotherm Measurements. Adsorption isotherms of N₂ and O₂ were acquired on a Micromeritics ASAP2050 system at 25 °C, pressure up to 103 kPa or 900kPa. The purity of N₂ and O₂ were 99.999% without any purification.

2.4. Molecular Simulation. Molecular simulation was carried out by Materials Studio, using the CASTEP module. The Perdew-Wang (PW91) exchange-correlation functional within the generalized gradient approach (GGA) was used to perform Density functional theory (DFT) calculations.⁴ To converge the total energy, a Self Consistent Field (SCF) tolerance of 0.002 meV/atom, a cutoff energy of 600 eV and a 2×2×2 k-point mesh were installed. All structure were optimized before introducing N₂ and O₂ molecules to Si-O-Al(Na) and Si-O-Si models. The single-point energy of optimized N₂, O₂ and Na⁺ were calculated by placing them in a cell which had the same cell dimensions as the cluster models respectively. Interaction energies (IE) between the fragments of zeolites and N₂/O₂ molecules were calculated as:

$$IE = E_{\text{complex}} - (E_{\text{cluster}} + E_{\text{Na}} + E_{\text{adsorbate}}) \quad (1)$$

$$IE = E_{\text{complex}} - (E_{\text{cluster}} + E_{\text{adsorbate}}) \quad (2)$$

E_{complex} is the total energy of the optimized adsorption fragment-adsorbate complex, E_{cluster} , E_{Na} and $E_{\text{adsorbate}}$ are the single-point energy of Si-O-Al(Na) or Si-O-Si fragment, Na⁺ and adsorbate molecule N₂/O₂, respectively.

2.5. Adsorption theories. In this work, we used Langmuir-Freundlich 1 site model to fit the adsorption isotherms of single component N₂ and O₂ at 25 °C and pressure up to 103 kPa or 900 kPa.⁵ The equation can be expressed as:

$$q = q_m b p^{1/n} / (1 + b p^{1/n}) \quad (3)$$

where q (mmol/g) are the amounts of N₂ or O₂ adsorbed in equilibrium, q_m is the amounts of N₂

or O₂ adsorbed at saturation (mmol/g), p is the bulk gas pressure in equilibrium (kPa), b is the adsorption equilibrium constant and n is a model constant.

The adsorption selectivity of O₂ over N₂ was obtained from the single component adsorption isotherms according to IAST (ideal adsorption solution theory).⁶ The final adsorption O₂/N₂ selectivity was calculated as:

$$S_{O_2/N_2} = (x_1/y_1)/(x_2/y_2) \quad (4)$$

The mole fractions of O₂ and N₂ in the adsorbed phase are x₁ and x₂ respectively, and the mole fractions of components O₂ and N₂ in the gas phase are y₁ and y₂, respectively.

The Langmuir model and Freundlich model were also used to fit the adsorption isotherms of single component N₂ and O₂ at 25 °C and pressure up to 103 kPa.⁵ The Langmuir equation can be expressed as:

$$q = q_m b p / (1 + b p) \quad (5)$$

where q (mmol/g) are the amounts of N₂ or O₂ adsorbed in equilibrium, q_m is the amounts of N₂ or O₂ adsorbed at saturation (mmol/g), p is the bulk gas pressure in equilibrium (kPa), b is the adsorption equilibrium constant.

The Freundlich equation can be expressed as:

$$q = K p^{1/n} \quad (6)$$

where q (mmol/g) are the amounts of N₂ or O₂ adsorbed in equilibrium, p is the bulk gas pressure in equilibrium (kPa), K and n are the model constants.

It is worth noting that Langmuir-Freundlich, Langmuir and Freundlich equations can all fit the N₂ and O₂ adsorption behavior at the low-pressure region. In fact, two fit parameters are already sufficient for these isotherms, and the Langmuir equation whose parameters have a physical meaning is more applicable than Freundlich equation in this work. In addition, the Langmuir-Freundlich equation gives a slightly more accurate correlation than the Langmuir and Freundlich models because it has more adjustable parameters,⁵ which was used to calculate the O₂/N₂ selectivity.

Supporting Figures and Tables

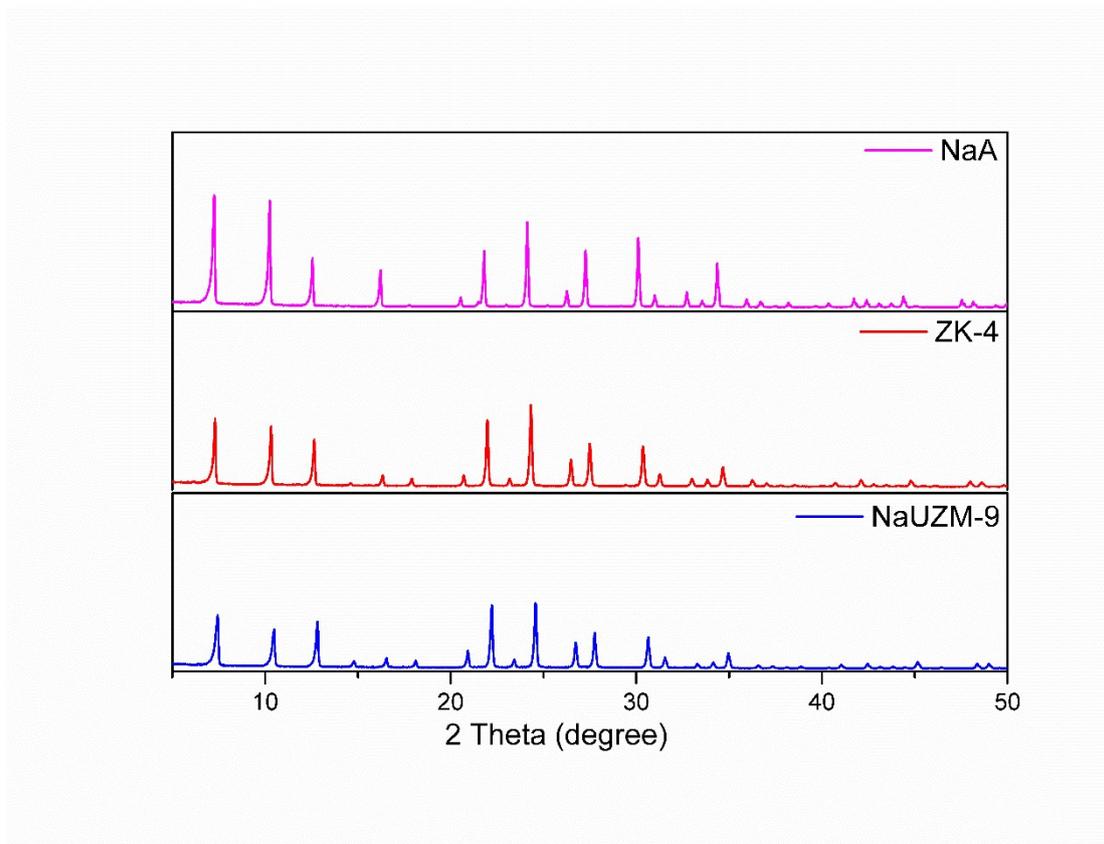


Fig. S1 XRD patterns of the as-synthesized samples NaA, ZK-4 and NaUZM-9.

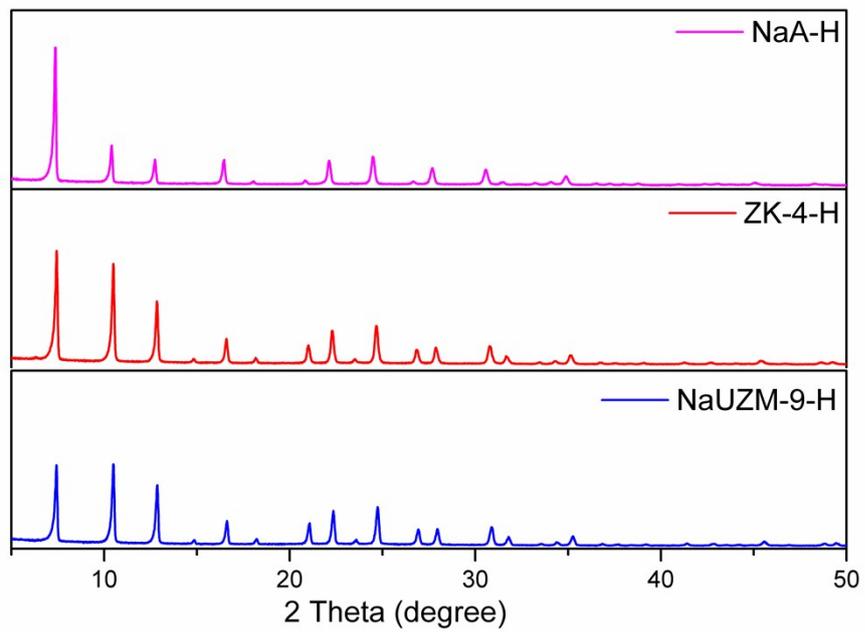


Fig. S2 XRD patterns of the as-synthesized samples NaA-H, ZK-4-H and NaUZM-9-H.

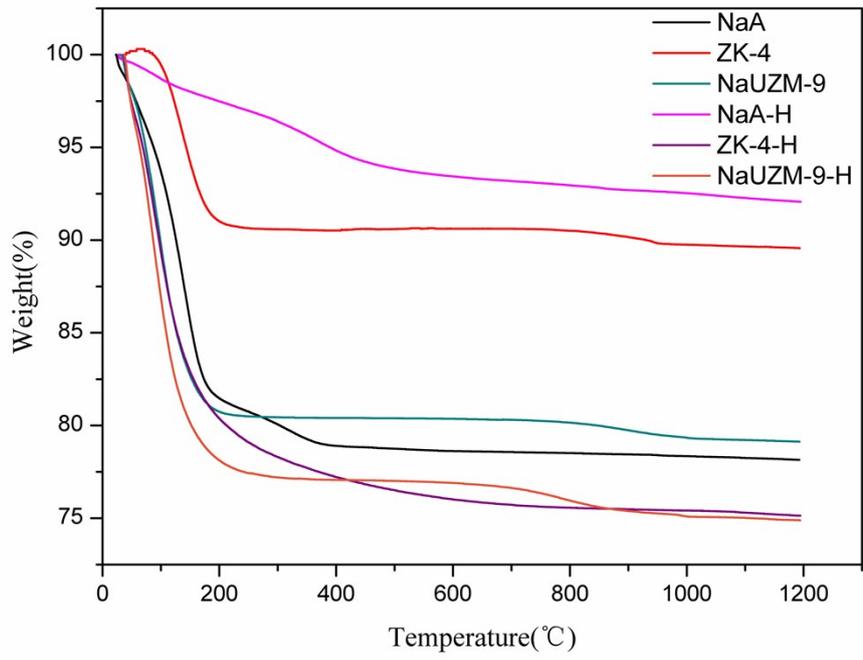


Fig. S3 TG curves of LTA and LTA-H.

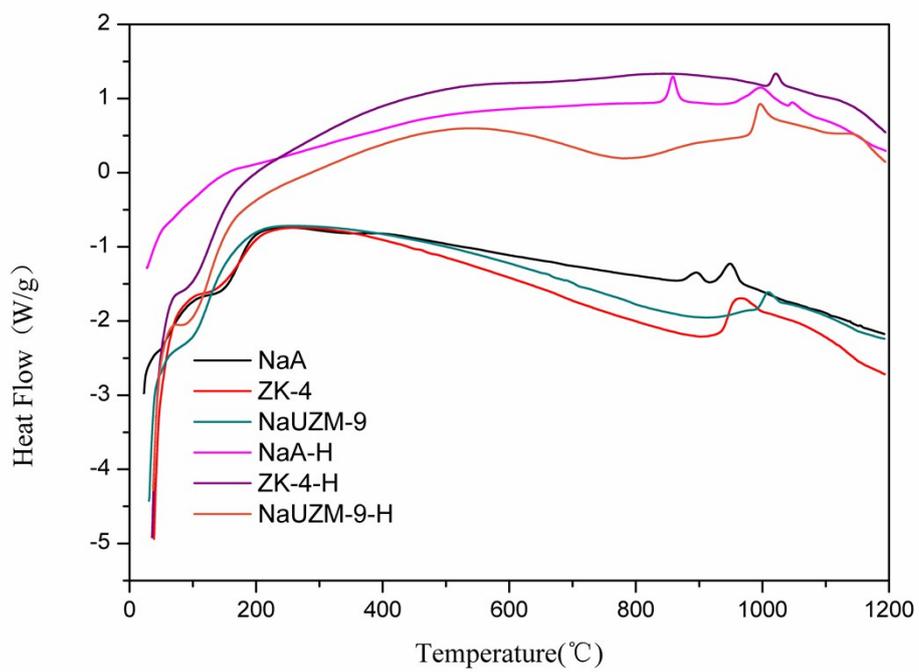


Fig. S4 DSC curves of LTA and LTA-H.

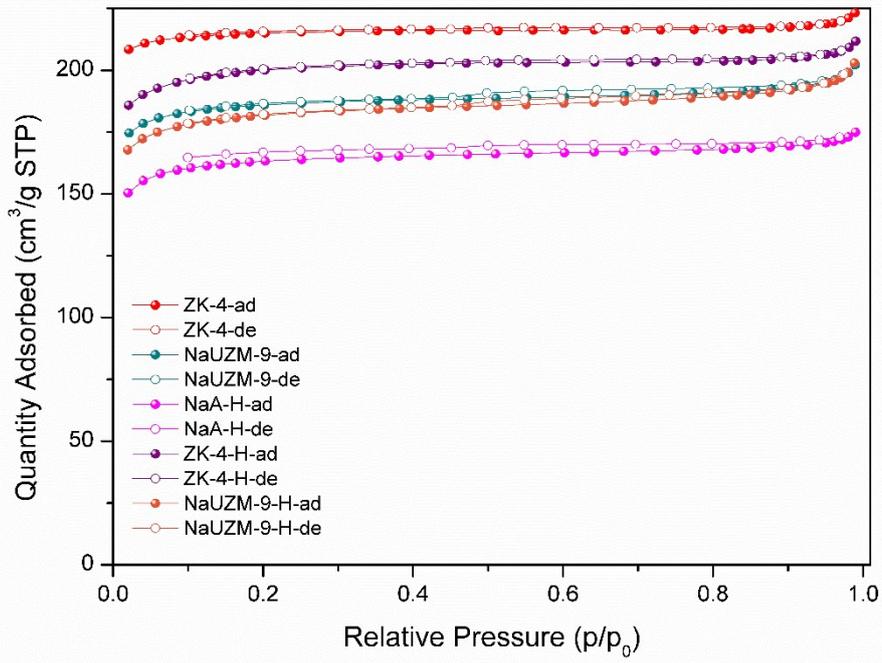


Fig. S5 N₂ adsorption-desorption isotherms of LTA and H-form LTA samples at -196 °C (adsorption: filled circle, desorption: hollow circle).

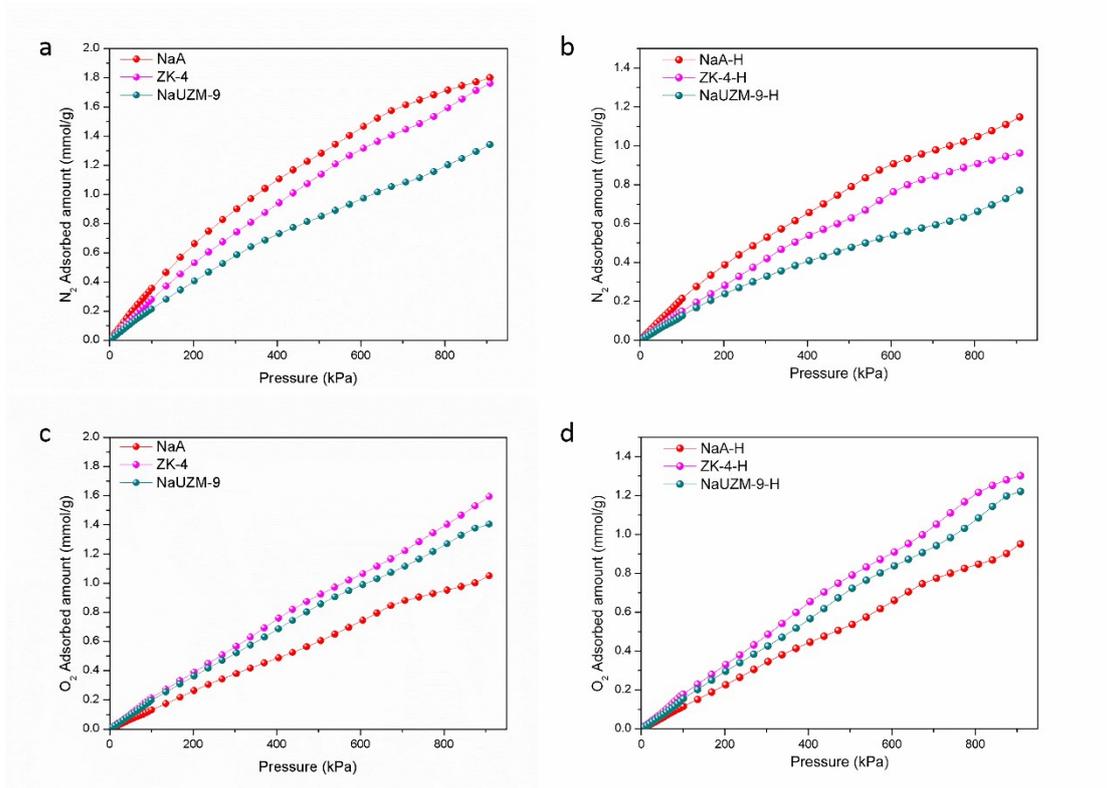


Fig. S6 N_2 adsorption isotherms of the LTA (a) and LTA-H (b) samples at 25 °C and the pressures up to 900 kPa; O_2 adsorption isotherms of the LTA (c) and LTA-H (d) samples at 25 °C and the pressures up to 900 kPa.

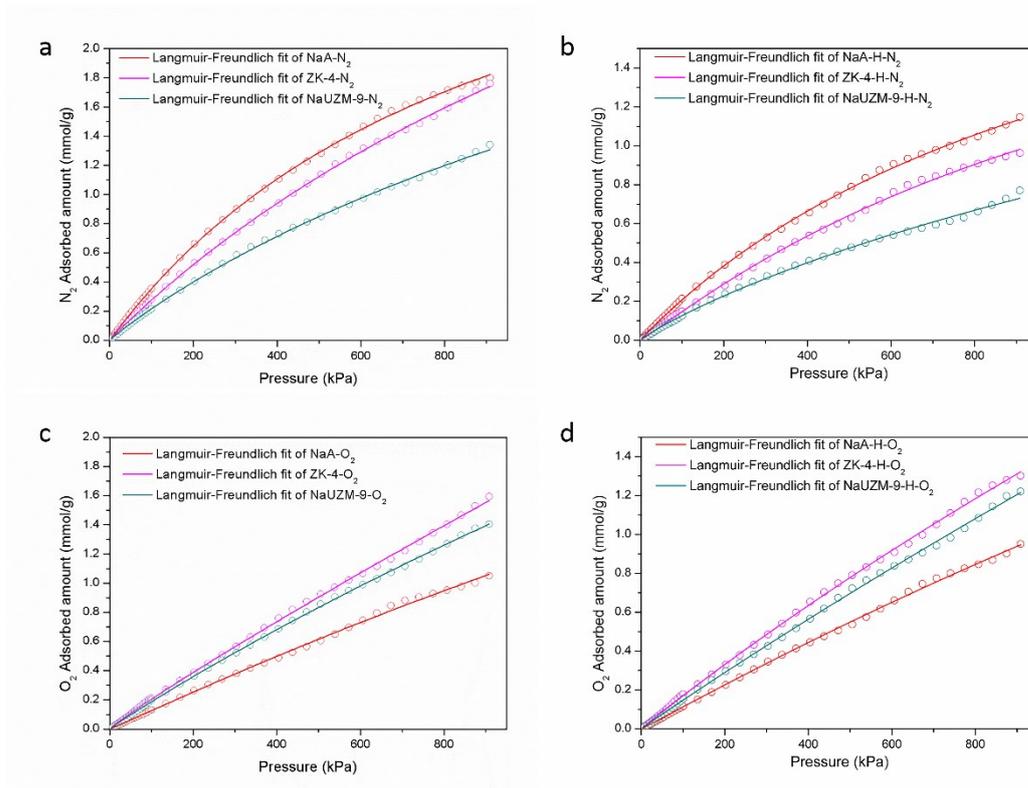


Fig. S7 N_2 fitting curves of the LTA (a) and LTA-H (b) samples at 25 °C and the pressures up to 900 kPa by Langmuir-Freundlich model; O_2 fitting curves of the LTA (c) and LTA-H (d) samples at 25 °C and the pressures up to 900 kPa by Langmuir-Freundlich model.

Table S1. Fitting parameters of the Langmuir-Freundlich 1 site model at 25 °C and pressure up to 103 kPa.

Parameters		q_m	b	$1/n$	R^2
NaA	N ₂	3.339	0.00120	1.006	0.999841
	O ₂	1.542	0.000786	1.035	0.999992
ZK-4	N ₂	4.214	0.000723	1.002	0.999867
	O ₂	14.333	0.000146	1.004	0.999896
NaUZM-9	N ₂	3.084	0.000824	1.001	0.999904
	O ₂	9.552	0.000227	0.993	0.999846
NaA-H	N ₂	1.710	0.00144	1.045	0.999752
	O ₂	3.132	0.000411	1.020	0.999927
ZK-4-H	N ₂	3.382	0.000545	0.996	0.999931
	O ₂	8.298	0.000283	0.965	0.999646
NaUZM-9-H	N ₂	4.141	0.000380	1.002	0.999927
	O ₂	8.545	0.000281	0.956	0.999321

Table S2. Fitting parameters of the Langmuir model at 25 °C and pressure up to 103 kPa.

Parameters		q_m	b	R^2
NaA	N ₂	3.565	0.00115	0.999786
	O ₂	4.454	0.000302	0.999979
ZK-4	N ₂	4.430	0.000692	0.999887
	O ₂	13.987	0.000153	0.999879
NaUZM-9	N ₂	3.117	0.000816	0.999895
	O ₂	7.205	0.000293	0.999853
NaA-H	N ₂	3.488	0.000802	0.999853
	O ₂	3.522	0.000396	0.999856
ZK-4-H	N ₂	3.168	0.000573	0.999981
	O ₂	3.707	0.000302	0.999835
NaUZM-9-H	N ₂	4.541	0.000349	0.999990
	O ₂	6.798	0.000294	0.999661

Table S3. Fitting parameters of the Freundlich model at 25 °C and pressure up to 103 kPa.

Parameters		K	1/n	R ²
NaA	N ₂	0.00473	0.946	0.999718
	O ₂	0.00139	0.987	0.999959
ZK-4	N ₂	0.00339	0.964	0.999617
	O ₂	0.00188	1.027	0.999967
NaUZM-9	N ₂	0.00286	0.958	0.999640
	O ₂	0.00193	1.016	0.999951
NaA-H	N ₂	0.00311	0.961	0.999419
	O ₂	0.00123	1.023	0.999986
ZK-4-H	N ₂	0.00187	0.983	0.999934
	O ₂	0.00195	1.004	0.999930
NaUZM-9-H	N ₂	0.00167	0.982	0.999896
	O ₂	0.00185	1.012	0.999841

References

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