Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

A Non-Invasive approach for H_2S gas sensing under stimulated breathing conditions: kag-MOF based gas sensor as a case study

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Section S1: Materials and Methods

Powder X-ray diffraction (PXRD) measurements were carried out using a Bruker D8 ADVANCE X-ray diffractometer with Cu K_α radiation (λ = 1.54178 Å). TGA measurements were performed with a TA Instruments Q500 apparatus; the samples were heated under an air atmosphere (flow, 25 $cm^3.min^{-1}$; heating rate, 5 ^oC/min). Low-pressure gas adsorption measurements were performed at relative pressures of up to 1 atm with a fully automated 3Flex high-resolution gas adsorption analyzer (Micromeritics). The bath temperature for the CO_2 adsorption measurements was controlled with an ethylene glycol/H_2O recirculating bath. Field emission scanning electron microscope (FE-SEM) images were taken on a Quattro Dual Beam microscope at an acceleration voltage of 10 kV.

Section S2: Synthetic Procedures

The kag-MOF was prepared according to our previous report with a modified procedure to get a nano-sheet morphology structure. In general, tetrazole-5-ethylester (328 mg,2 mmol), and 20 mL of H_2O were heated in a Teflon-lined autoclave to 120°C for 24 hr. After cooling to room temperature, a solution of $Zn(NO_3)_3 \cdot 6H_2O$ (297 mg, 1 mmol) in 20 mL water is added to the previous solution. The mixture was shaken for several minutes and held for 24 hours to get a white milk-like solution. The particles were centrifuged and washed with water and methanol.

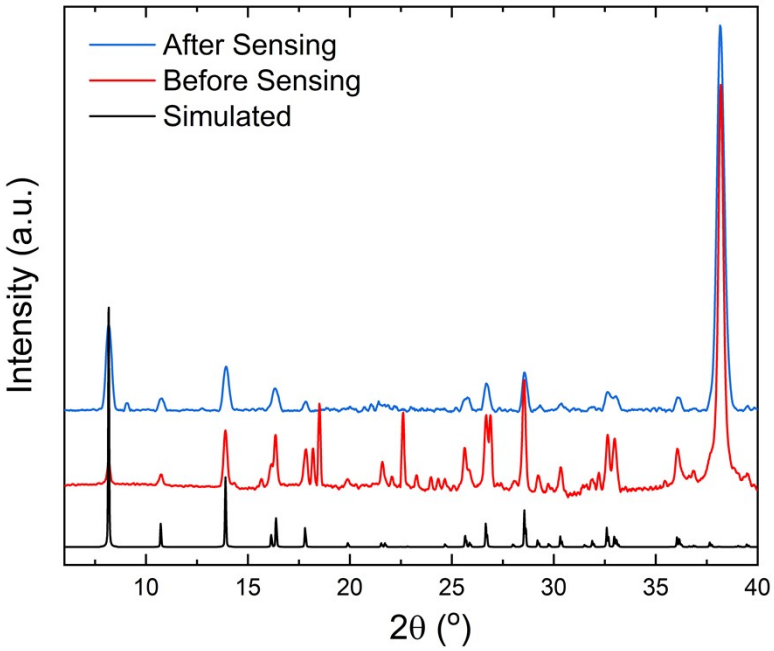

*Figure S 1. Figure S 1.PXRD analysis of the as synthesized **kag**-MOF before sensing (red), after sensing (blue) compared with the simulated (black).*

Section S3: Materials Characterization

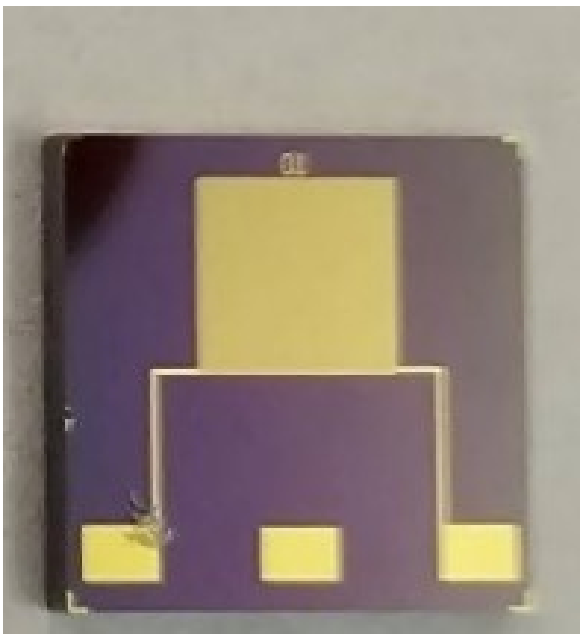

Figure S 2.An image for the IDE electrode used for the material deposition.

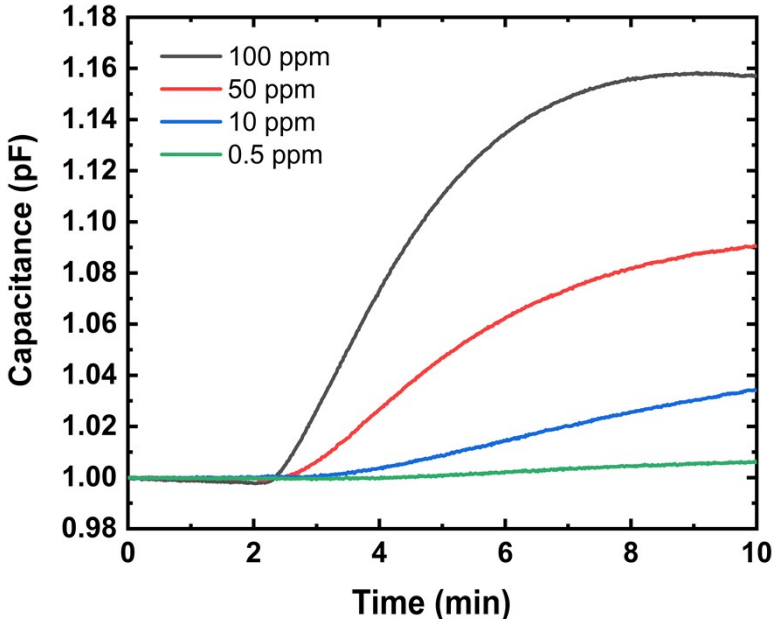

*Figure S 3. Normalized capacitance of the **kag**-MOF IDE in the presence of H_2S.*

Section S4: Sensing studies

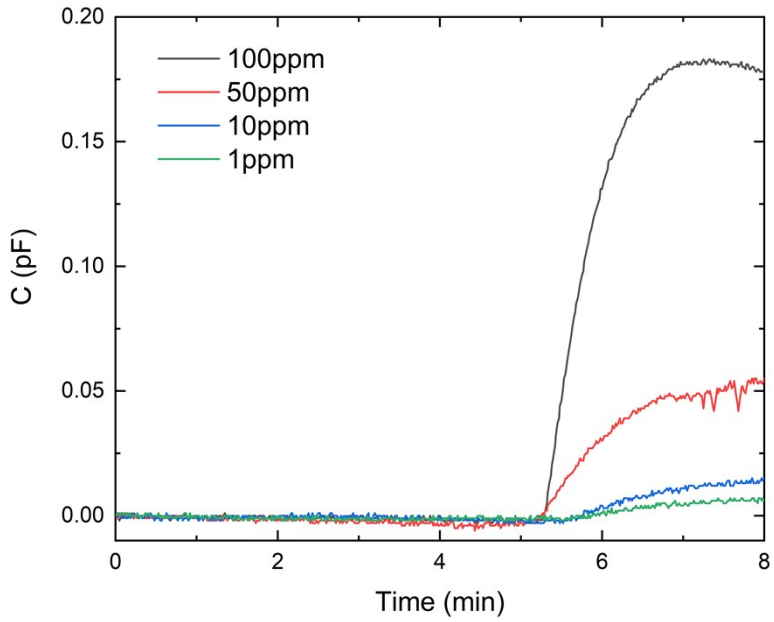

*Figure S 4. Normalized capacitance of the **kag**-MOF IDE in the presence of NH_3.*

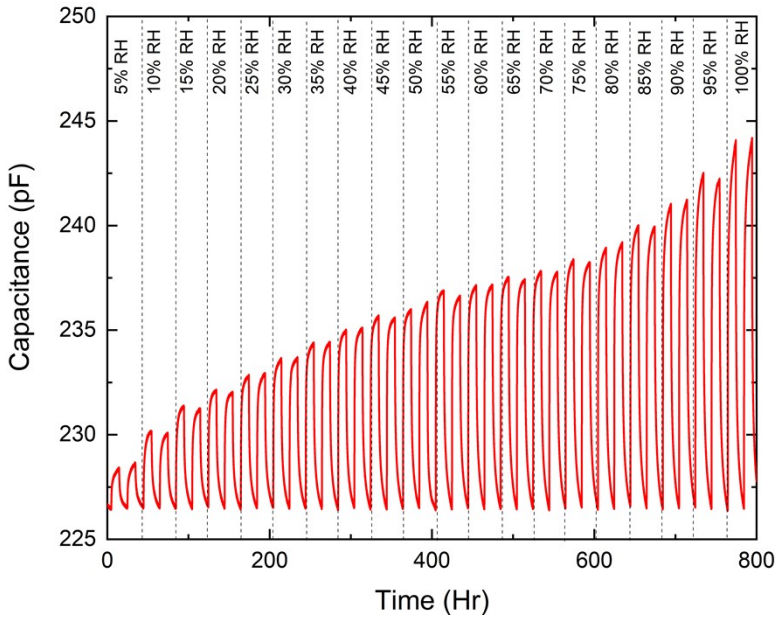

*Figure S 6. The Capacitance of the **kag**-MOF IDE in the presence of different percentage of relative humidity*

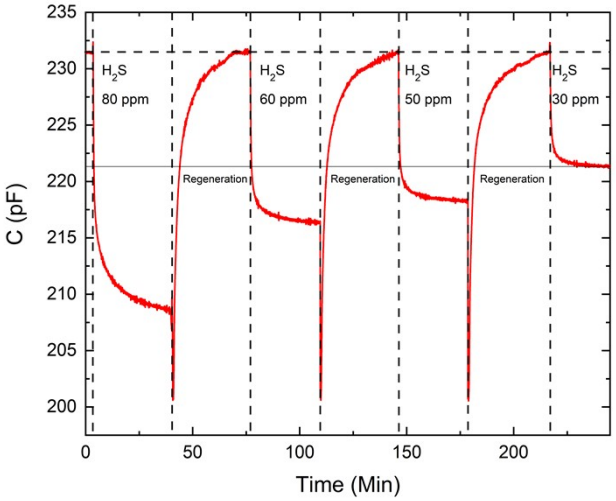

*Figure S 5. The capacitance of the **kag**-MOF IDE electrode in 40 %RH at different concentration of H_2S*

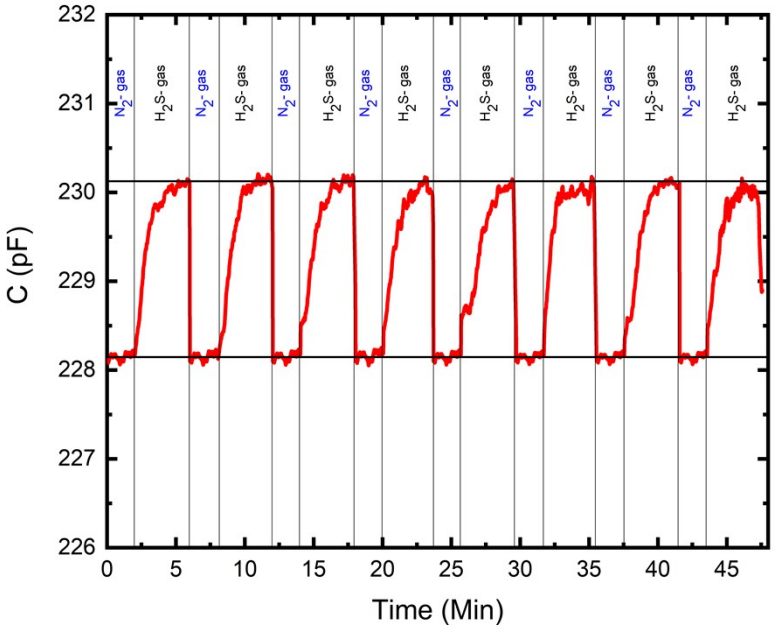

*Figure S 8. The recyclability of the **kag**-MOF IDE electrode in the presence of H_2S*

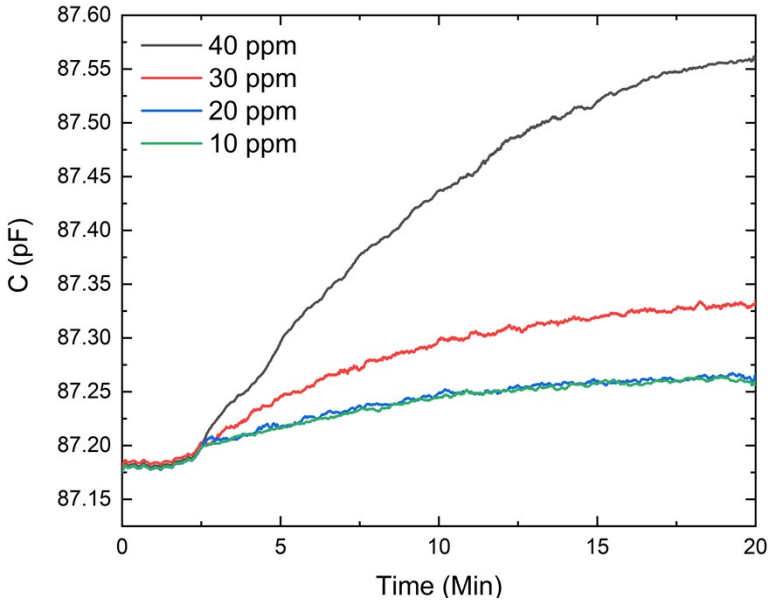

*Figure S 7. The capacitance of the **kag**-MOF IDE in the presence of Human breath mixture and different concentration of H_2S*

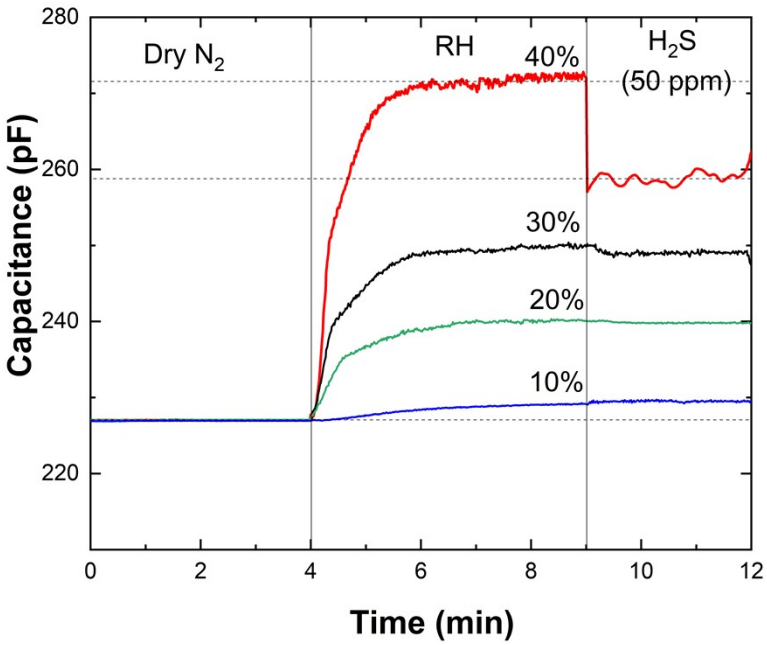

*Figure S 9. The capacitance of the **kag**-MOF IDE electrode for 50 ppm H_2S at different relative humidity*

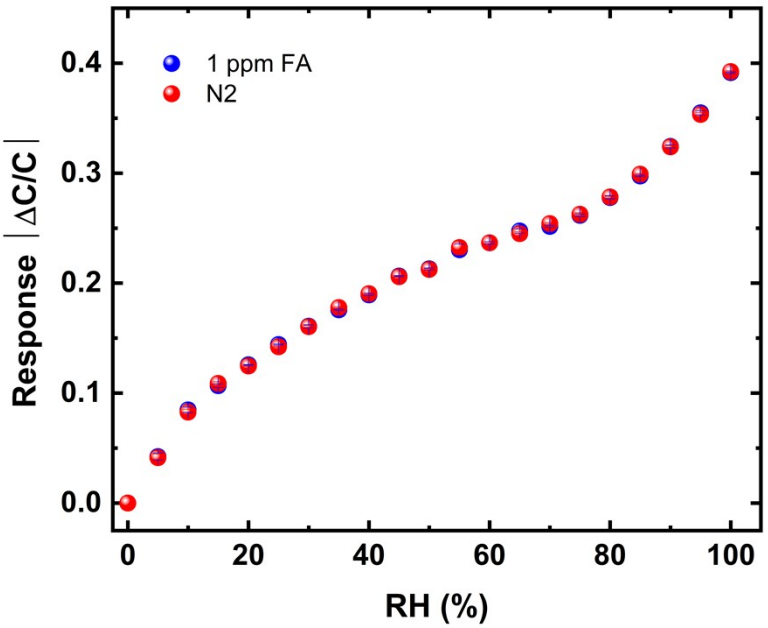

Figure S 10. the sensor response in different relative humidity condition in N_2 and 1 ppm FA

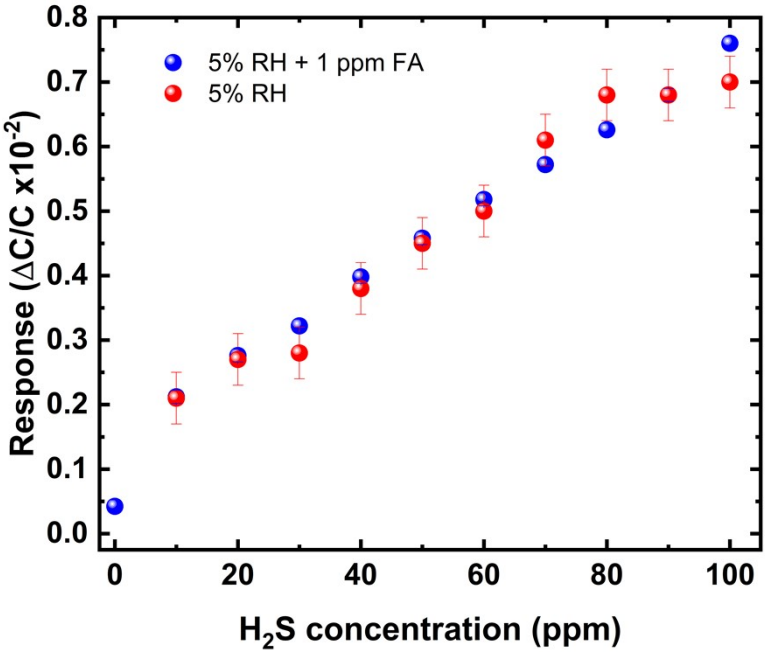

Figure S 11. the response of the sensor for different concentration of H_2S at 5% RH with and without the presence of 1 ppm FA

Section S5: Density Functional Theory Calculations

The structure of kag-MOF-1 was optimized using the Density Functional Theory method as implemented in Quantum Espresso (QS) code.[57] The measurement was performed using Quantum espresso 6.2.1 open source on Shaheen II (a Cray XC40 delivering over 7.2 Pflop/s of theoretical peak performance. With 5.536 Pflop/s of sustained LINPACK performance) with 32 task per node. We employed DFT with the generalized gradient approximation (GGA) functional in the parametrization of Perdew, Burke, and Ernzerhof (PBE) to account for exchange and correlation.[58] The projector-augmented wave method (PAW) was used for a basis set with a cutoff energy of 320 eV.[59, 60] The valence electronic configurations as given in the atomic potential files were $4s^2 3d^{10}$ for Zn, $2s^2 2p^4$ for O, $2s^2 2p^3$ for N, $2s^2 2p^2$ for C, and $1s^1$ for H. Brillouin zone integration was performed using Blöchl's tetrahedron method, with a k-mesh generated by the Monkhorst−Pack scheme. As we are using a very large supercell, optimizations were carried out at gamma point. kag-MOF-1was considered using a supercell of 992 atoms. Optimizations stopped when the maximum residual force of 0.01 eV per atom was reached. The electronic wave function criterion of convergence was 10^{-6} eV. While modelling the H_2S molecule, we have also used the implementation of the DFT-D_2 approach described by Grimme[45] to account for long-range dispersion forces. The isolated molecule was modelled in the center of the pores and near the metal sites.

The adsorption energy per molecule was calculated from the equation

$$E_{ads} = E_{complex} - (E_{MOF} + E_{mol})$$

where ($E_{complex}$) is the total energy of the adsorbate-substrate system, E_{MOF} is the energy of the naked MOF cluster, and E_{mol} is the energy of the isolated adsorbate molecules. Within this definition, negative adsorption energy indicates an exothermic process.

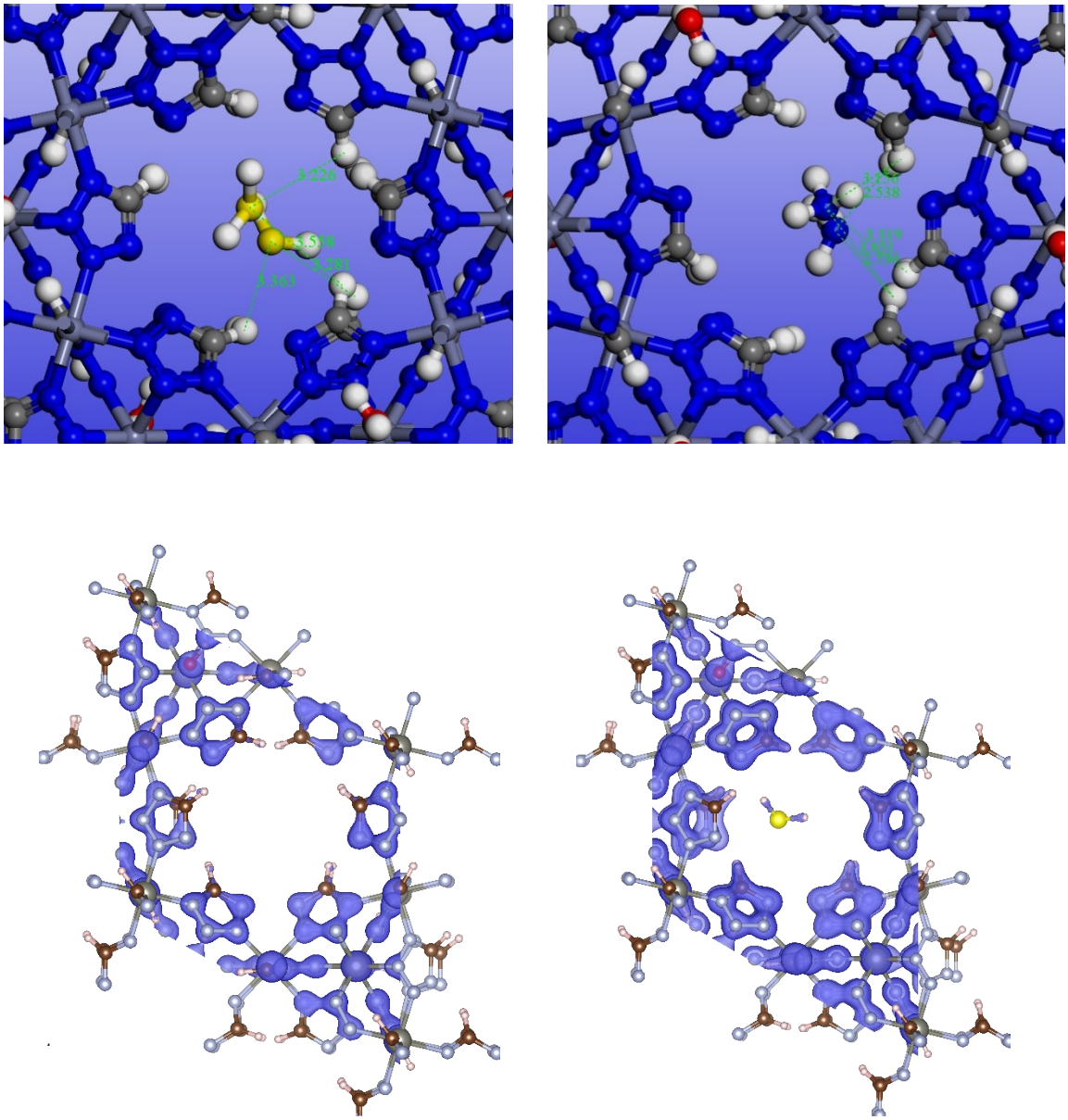

Figure S6. Positive Charge density difference before and after adding the H_2S. Isosurfaces drawn at resolution of 0.05 electron/bhor3. Color code is as following; brown (C) light-blue (N), white (H), gray (Zn), and red (O).