Supporting Information: “Comparison of Surface-Bound and Free-Standing Variations of HKUST-1 MOFs: Effect of Activation and Ammonia Exposure on Morphology, Crystallinity, and Composition”

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**Energy Dispersive X-ray Spectroscopy Characterization**

Energy dispersive x-ray spectroscopy (EDS) was utilized alongside scanning electron microscopy (SEM) to characterize bulk powder and drop-cast film samples of HKUST-1. While SEM elucidated the morphological properties of the material, EDS yielded qualitative and quantitative elemental composition information. The coordination of the DMSO solvent within the HKUST-1 framework in a 1:1 ratio with the copper ions was a significant EDS finding for the as-synthesized powder and drop-cast film. Upon exposure to ammonia gas, the reduction of S (relative to the Cu) within the framework is quantitatively measured. The uptake of ammonia can be observed by the appearance/increase of a N peak within the EDS spectra. Due to the overlap of the N peak with that of C and O (also found within the framework), the amount of nitrogen within the framework could not be quantitatively determined. The Kα1 energy levels for C, N, O, Si, S, and Cu are all given in SI Table 1. The Kα1 was what was used to quantitatively determine elemental compositions (i.e. % Cu and %S).

**SI Table 1. X-Ray Wavelengths in keV**

| Element | Energy (keV) |
|---------|-------------|
| C       | 0.277       |
| N       | 0.392       |
| O       | 0.525       |
| Si      | 1.740       |
| S       | 2.309       |
| Cu      | 8.046       |

**As-synthesized HKUST-1 Powder**

Shown in SI Figure 1a is the full spectrum collected for the as-synthesized HKUST-1 powder with the Cu and S peaks identified. SI Figure 2a and SI Figure 3 provide spectra for powder after exposure to ammonia without and with prior activation, respectively. Noteworthy is that the size of the S peak relative to Cu decreases significantly. Quantitatively, the decrease in the amount of S is ~90%.

SI Figure 1b and 2b highlight the 0-3 keV region of the spectra and identify the C, N, O, S, and Cu x-ray lines. The increase in the N peak can be readily observed at this resolution. Note that the increase in peak intensity in this region (~0.4 keV) can also be observed in SI Figure 2a
and 3 in comparison to SI Figure 1a. This qualitative increase in the N peak is indicative of the ammonia uptake that was confirmed by IR analysis (Figure 3).

**As-synthesized HKUST-1 Drop-Cast Thin Film**

SI Figure 4 provides the full spectrum collected for the as-synthesized HKUST-1 drop-cast film, and SI Figure 5 and 6 display spectra for the drop-cast film after ammonia exposures without and with prior activation, respectively. Note that the Cu and S percentages are quantitatively determined and given within the caption, while the nitrogen peak at ~0.4 eV can be observed for qualitative comparison. The decrease in S and increase in N are confirmation that the paddlewheel adsorbates are being displaced by the uptake of ammonia. This is also confirmed by IR analysis (Figure 3).

**Standard HKUST-1 Powder to Examine Solvent Effects**

SI Figure 7a displays the full spectrum collected for the HKUST-1 standard powder (Basolite C), and SI Figure 7b highlights the 0-3 keV region and permits the identification of C, N, O, Si, S, and Cu. Very minor amounts of N, Si, and S are observed. SI Figure 8 and 9 exhibit spectra for this standard powder after ammonia gas exposure with and without activation, respectively. Note the 0-3 keV region is shown so that the qualitative increase in N is clearly apparent. No quantitative analysis is undertaken for these spectra.

SI Figure 10 corresponds to the HKUST-1 standard powder that had undergone the introduction of water vapor prior to ammonia activation. This spectrum is also shown highlighting the 0-3 keV region for ease of identifying the uptake of ammonia via the increase in the N peak. No quantitative analysis is undertaken for this spectrum.

SI Figure 11 provides the full spectrum for the HKUST-1 standard powder that had undergone the introduction of DMSO solvent. The amount of Cu and S are quantitatively determined, and this spectrum should be compared to SI Figure 1, as the amount of S relative to Cu for the as-synthesized HKUST-1 powder is similar. SI Figure 12 represents this sample after ammonia exposure. The decrease in S is quantitatively determined, and the increase in N can be qualitatively observed by comparing the spectral peaks at ~0.4 keV.
**SI Figure 1.** As-synthesized HKUST-1 powder. Quantification yielded 54% Cu and 46% S at 8.0 keV and 2.3 keV, respectively.

**SI Figure 2.** As-synthesized HKUST-1 powder after exposure to ammonia. Note that in comparison to SI Figure 1, the S peak at 2.3 keV is significantly reduced and N peak at ~0.4 keV becomes apparent. (94% Cu, 6% S)
SI Figure 3. As-synthesized HKUST-1 powder after activation and subsequent exposure to ammonia. Note that in comparison to SI Figure 1, the S peak at 2.3 keV is significantly reduced, and N peak at ~0.4 keV becomes apparent. (95% Cu, 5% S)

SI Figure 4. As-synthesized HKUST-1 drop-cast thin film. Quantification yielded 48% Cu and 52% S.

SI Figure 5. As-synthesized HKUST-1 drop-cast thin film after exposure to ammonia. Note that in comparison to SI Figure 4, the S peak at 2.3 keV is significantly reduced and N peak at ~0.4 keV becomes apparent. (98% Cu, 2% S)
SI Figure 6. As-synthesized HKUST-1 drop-cast thin film after activation and subsequent exposure to ammonia. Note that in comparison to SI Figure 4, the S peak at 2.3 keV is significantly reduced and N peak at ~0.4 keV becomes apparent. (95% Cu, 5% S)

SI Figure 7. Standard HKUST-1 powder as-received. Quantification yielded 92% Cu and 3% S. (Note 5% Si was observed due to the presence of diatomaceous earth.)
SI Figure 8. Standard HKUST-1 powder after activation and subsequent exposure to ammonia. Note the increase in the N peak at ~0.4 keV relative to SI Figure 7b.

SI Figure 9. Standard HKUST-1 powder after exposure to ammonia. Note the increase in the N peak at ~0.4 keV relative to SI Figure 7b.

SI Figure 10. Standard HKUST-1 powder after prior exposure to H\textsubscript{2}O and subsequent exposure to ammonia. Note the increase in the N peak at ~0.4 keV relative to SI Figure 7b.
SI Figure 11. Standard HKUST-1 powder after exposure to DMSO. Quantification yielded 45% Cu and 55% S. Note that in comparison to as-received sample data in SI Figure 7a, the S peak at 2.3 keV increased significantly and is similar to as-synthesized sample data in SI Figure 1a.

SI Figure 12. Standard HKUST-1 powder after prior exposure to DMSO and subsequent exposure to ammonia. Note that in comparison to SI Figure 11, the S peak at 2.3 keV is significantly reduced and N peak at ~0.4 keV becomes apparent. (90% Cu, 10% S)