Graphical Abstract

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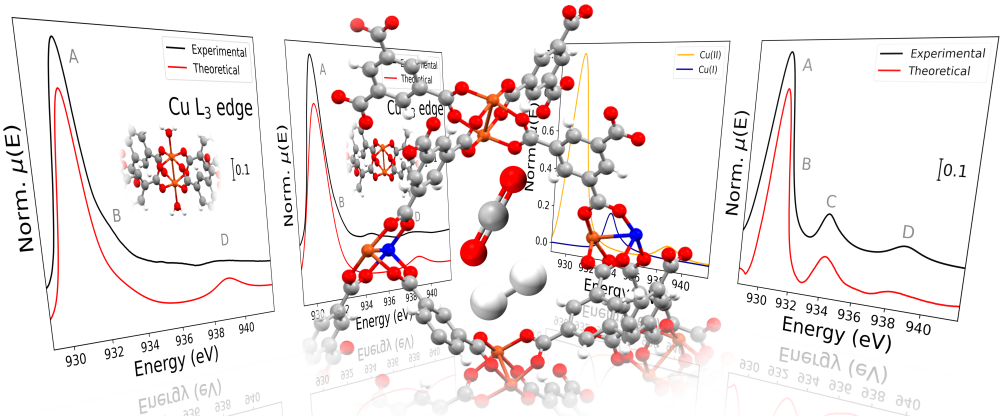

Insights into structure and reactivity of MOFs by ambient pressure soft X-ray absorption spectroscopy

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Abstract

Metal-Organic Frameworks (MOFs) are nanostructured porous materials made up by metal cations and organic linkers forming three-dimensional structures. Since their discovery, the local properties of metal centers in MOFs have often been studied with hard X-ray absortion spectroscopy, a powerful bulk-sensitive technique that can hardly provide accurate surface information on these systems. Here, we employ the ambient-pressure soft X-ray absorption spectroscopy, using a newly developed experimental setup, to unveil the formation mechanism of surface defective sites in the prototypical Cu(II)-based MOF HKUST-1, as well as the reactivity and selectivity of these sites towards CO_2 from the analysis of te Cu L_3-edge near edge X-ray absorption spectroscopy (NEXAFS) data. We observe that, upon thermal heating, Cu(I) defects are formed more abundantly on the surface of the material as compared to the bulk, a process that is almost fully reversed when the MOF is exposed to CO_2, even when mixed with H_2. Additionally, we propose a structure and a formation mechanism for such defective sites, supported by theoretical DFT-based calculations.

Keywords: MOF, AP-NEXAFS, operando, materials, gas sorption, carbon dioxide

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1. Introduction

A metal-organic framework (MOF) is a material formed by the coordination of polydentate ligands (mostly organic in nature, and often referred to as linkers) to metal ions or clusters (nodes) [1]. Since these materials present three-dimensional porous structures [2, 3] often featuring nanosized apertures and open metal sites [4, 5], they are extremely suitable for applications involving gas-solid interactions, such as heterogeneous catalysis [6, 7] and gas sorption (separation and storage) [8, 9, 10, 11, 12, 13]. In particular, some MOFs have been shown to perform extremely well in the selective capture of CO_2, due to their high porosity combined with the capability to form coordinatively unsaturated sites (CUSs) throughout the structure [14]. CUSs notably act as strong binding sites [4] for otherwise weakly binding molecules (e. g. CH_4, H_2 and C_2H_4), and they can manifest a preferential interaction with CO_2 in particular cases. Additionally, recent studies have shown that engineering defective sites in UiO-66, a Zr-based MOF, greatly enhances its CO_2 separation selectivity [15], pointing out the pivotal role of defects in this process. HKUST-1, a well-studied MOF made up by Cu^{2+} cations and the benzene-1,3,5-tricarboxilate (BTC) linker [16], is known to form defective Cu^{+} sites via both thermal [17] and mechanochemical [18] routes. Despite years of debate and thorough research, full consensus on the formation, structure and reactivity of these defective sites is yet to be reached. A clear and final assessment of such properties, especially about the interaction between carbon dioxide (universally regarded as an environmentally harmful species [19]) and the Cu^{+} sites would therefore provide crucial information to estimate their impact on CO_2 sorption.

Conventional hard X-ray absorption spectroscopy (XAS) has been widely applied to study the local structural and electronic properties of the metal centers present in MOFs, in general [20], and HKUST-1, in particular [21], but the high degree of penetration possessed by hard X-rays renders this otherwise powerful technique not well suited for determining the properties of surface metal sites. Understanding such properties is fundamental for the full comprehension of the interaction between solid materials and gaseous species, which most importantly happens at a surface level.

In this work, we present a thorough characterization of the defective sites formed in HKUST-1 by thermal heating. Following the considerations above, we employed soft X-ray absorption spectroscopy performed in total electron yield (TEY) mode. TEY mode, combined with the low penetration depth of

soft X-rays (few μm), renders this technique remarkably surface sensitive ($<$ 10 nm) [22] and suitable for this kind of application. Moreover, we have utilized a recently developed cell capable of performing *operando* AP-NEXAFS experiments in TEY mode. We have investigated the formation mechanism and reactivity with CO_2 and H_2 of defects in HKUST-1 via *operando* ambient-pressure X-ray absorption near edge structure (AP-NEXAFS) spectroscopy experiments and rationalized these findings by theoretical calculations. Such an approach has already proven succesful for the study of interfacial metal oxide properties [23, 24], and we believe that it is suited to become a widely adopted protocol for *operando* experiments on MOFs reactivity in the near future.

2. Materials and methods

2.1. Materials

HKUST-1 was purchased at analytical grade from Sigma-Aldrich and used without further purification. All gaseous reagents (He, H_2, CO_2) were instead supplied by Linde, with a purity of at least 99.999%.

2.2. Cu L_3-edge NEXAFS measurements

Operando Cu L_3-edge NEXAFS spectra were recorded using an innovative reaction cell (described in detail eslsewhere [25]) available at the APE-HE beamline [26] of the Elettra synchrotron radiation facility. This cell can operate at ambient pressure in a temperature range between room temperature (RT) and 350 °C. The experiments were performed collecting Cu L_3-edge NEXAFS spectra at different temperatures (room temperature and 160 °C) and under different gas fluxes (He, H_2 and CO_2) at 1 bar. 20 mg of the HKUST-1 MOF powder were pressed into a titanium sample holder which was then fixed into the reaction cell. The energy scale was calibrated by simultaneously collecting the Cu L_3-edge spectrum of a CuO reference during the sample measurements, assigning the first maximum of the L_3 edge to 931.9 eV.

2.3. Theoretical calculations

Cu L_3-edge spectra have been calculated using the FDMNES code [27], implementing the recently developed sparse solver method [28]. The spectra were calculated using multiple scattering theory including spin-orbit coupling, and the muffin-tin (MT) approximation was used for the potential. The

MT radii were chosen to minimize the difference between the potential inside the MT spheres and in the interstitial region. All atoms within a cutoff radius of 5 Å from the Cu centers have been included in the calculations. The structural model used in the calculations regarding the pristine HKUST-1 paddlewheel unit, along with those pertaining to the Cu^{2+}/Cu^{2+} and Cu^{+}/Cu^{2+} dimers resulting from dehydration and dehydration/decarboxylation of the pristine unit (see the following section), were built starting from the crystallographic structure of hydrated HKUST-1 [29]. In this structure, the Cu^{2+} ions are placed at a distance of 3.032 Å and coordinated by five oxygen atoms in a square pyramidal configuration. Four of the oxygen atoms belong to the BTC linkers and are at a Cu–O distance of 1.852 Å with the apical oxygen atom placed at 2.207 Å from the Cu^{2+} ion. A cluster containing the Cu^{2+}/Cu^{2+} dimer and the four bonded BTC ligands was cut from the crystal structure and used as a model for the pristine structure with no further manipulation, while the dehydrated and defective models were obtained removing the H_2O molecules and one of the BTC ligands entirely, respectively. In the dehydrated MOF model, the two Cu^{2+} atoms are coordinated in a square pyramidal (SP) geometry since all water molecules are removed. As far as the defective HKUST-1 model is concerned, one of the two copper atoms was reduced to Cu^{+} and the three remaining BTC ligands have been kept at the same geometry as the dehydrated model. The Cu^{2+} simulated spectra were aligned to the experimental data on the basis of the energy of the main L_3-edge peak. Conversely, the Cu^{+} theoretical spectra were aligned to the Cu^{+} peak present in the spectrum of the HKUST-1 sample measured in He (50ml/min, 1 bar) at 160 °C. In order to account for the experimental resolution, a Gaussian broadening of 0.7 eV was applied to all calculated spectra.

3. Results and discussion

A comparison between the Cu L_3-edge NEXAFS spectrum of pristine HKUST-1 collected in He flux (1 bar, 50 mL/min) at room temperature and the spectrum collected at 160 °C after thermal treatment for 10 min is shown in Figure 1a. In the spectrum collected on the pristine sample, there is a main peak at 930.7 eV (peak A, Figure 1a) with a broad shoulder at 931.9 eV (peak B, 1a) that is completely absent in the spectrum collected at 160 °C. Likely, the disappearance of this feature is caused by a change in the local copper coordination environment, possibily due to the desorption

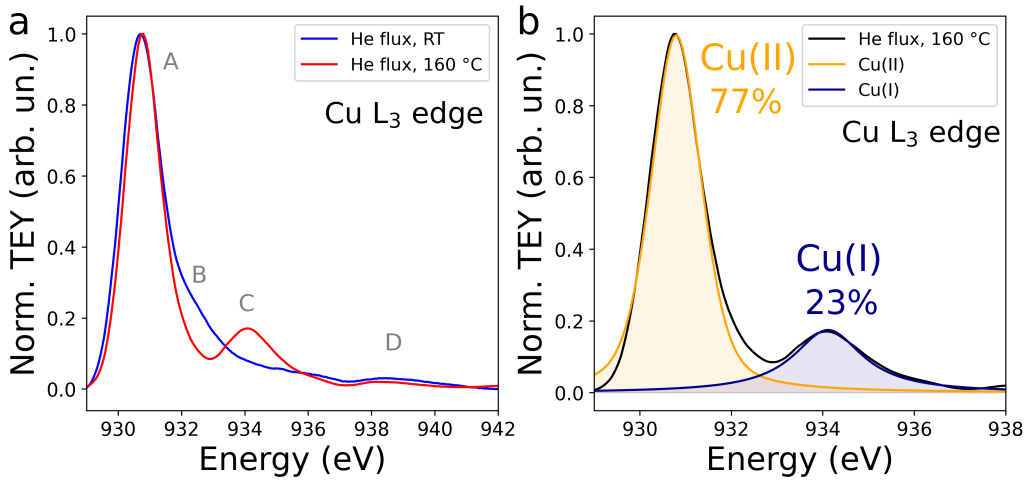

Figure 1: (a) Cu L_3-edge AP-NEXAFS spectra of HKUST-1 recorded in He (1 bar) at RT (blue line) and in He (1 bar) at 160 °C (red line). The main features are indicated by reference letters (A, B, C and D). (b) Fit of the Cu^{2+} (yellow line) and Cu^{+} (dark blue line) main peaks in the spectrum recorded in He at 160 °C (black line) using Voigt profiles. The determined relative percentages of Cu^{2+} and Cu^{+} are reported above the peaks.

of water molecules. The increase in temperature also leads to the formation of a very intense peak at 934.1 eV (peak C, 1a), a value compatible with the white line peak in the Cu L_3-edge spectrum of Cu_2O [30], even though the latter spectrum presents a far more asymmetric white line. Such transition is commonly ascribed to a 2p $\rightarrow$ 3d resonance which, in principle, should not be observed at all as formally the Cu^{+} ion is in the $3d^{10}$ electronic configuration. However, it is generally accepted that the Cu^{+} ion can show an unusually large partial 3d character in the empty density of states [31] thus allowing this transition to happen. Further, both spectra also present a very broad resonance at about 938.4 eV (peak D, Figure 1a) known to be due to a 2p $\rightarrow$ 4s electronic transition.

Previous investigations have suggested that mixed valence Cu^{+}/Cu^{2+} dimers in HKUST-1 can originate either by the reduction of defective clusters [32] or by the reduction of Cu^{2+} ions in perfectly coordinated paddle-wheel units [33]. In our mild experimental conditions, it is reasonable to assume that the temperature treatment can provoke the dehydration of pristine Cu^{2+}/Cu^{2+} paddle-wheel units in the HKUST-1 surface, as well as the formation of defective Cu^{+}/Cu^{2+} sites. We stress again that AP-NEXAFS

investigations performed in TEY mode only probe the first few atomic layers, therefore the effects we are observing are limited to the surface of the material. The relative surface abundance of the Cu^{2+} and Cu^{+} sites can be estimated by fitting peaks A and C in the spectrum of defective HKUST-1 (160 °C, He) via Voigt functions (Figure 1b), and by comparing the integral area of the two curves. The calculated ratio was adjusted by the respective cross sections of Cu^{2+} and Cu^{+} cations, following the procedure reported by Fracchia *et al.* [34]. The estimated surface concentration of Cu^{+} sites resulted to be 22.7%, which corresponds to a ratio of 45.4% of Cu^{+}/Cu^{2+} dimers.

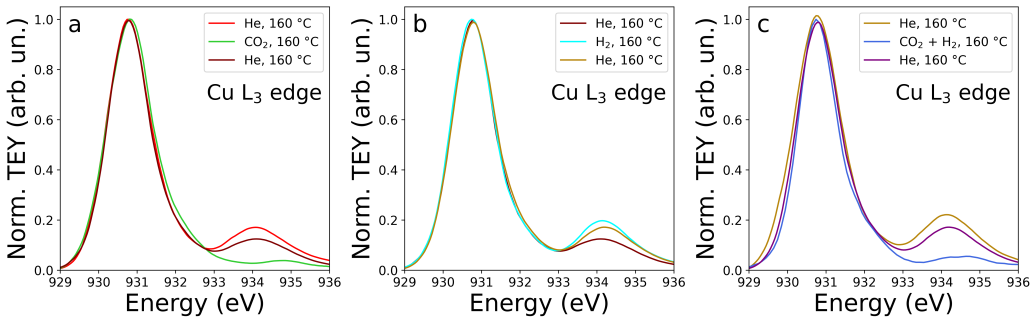

Figure 2: Series of Cu L_3-edge AP-NEXAFS spectra collected on the HKUST-1 sample: (a) in He flux before and after exposure to CO_2, and in He flux after purging CO_2 from the sample enviroment (red, bright green and maroon lines, respectively), (b) in He flux before and after exposure to H_2, and in pure He flux H_2 afterwards (brown, cyan and olive lines, respectively), (c) in He before, during and after exposure to a gas mixture containing CO_2 (2%) and H_2 (6%) (olive, blue and purple lines, respectively). All spectra were recorded at 160 °C and 1 bar of pressure.

After successfully observing the formation of defective sites in HKUST-1, we performed additional tests to assess their reactivity and selectivity towards two prototypical gas molecules, namely CO_2 and H_2. Carbon dioxide is known to be an oxidant gas but, notably, it has rarely been employed as a probe molecule to study metal sites in MOFs.

First, we collected the Cu L_3-edge spectra of defective HKUST-1 before and after exposure to a 2% flux of CO_2 at 160 °C, and compared them to the spectrum collected at 160 °C in He (Figure 2a). Upon exposure to CO_2, it can be observed that the intensity of peak C is drastically diminished, while peak B is not affected. This supports the hypothesis that no water molecules are left in the structure, confirming that peak B is the fingerprint of the api-

cal water ligands, and that almost all the Cu^{2+} sites are oxidized by carbon dioxide. As soon as the CO_2 flux is interrupted, however, the intensity of peak C is almost completely restored, proving the reversibility of this process. Conversely, the effect of a 6% flux of H_2 on the sample previously exposed to CO_2 at 160 °C is much more limited: the intensity of peak C increases only slightly, as hydrogen promotes the reduction of the Cu^{2+} sites, decreasing as soon as the H_2 flux is stopped (Figure 2b). Finally, we investigated the effect of exposing defective HKUST-1 to a mixture of CO_2 (2%) and H_2 (2%) to probe the degree of selectivity of the defective sites towards each gas. In this case, we obtained a spectrum surprisingly similar to that obtained while fluxing only CO_2 on the defective MOF: peak C is again almost completely absent from the spectrum (Figure 2c), proving that the Cu^+ sites interact preferentially with CO_2. This sequence of spectra further confirms the reversibility of CO_2 capture by defective HKUST-1 as we observed, once more, an almost complete recovery of peak C upon interruption of the flux.

To rationalize our findings and shed light on the actual structure of the Cu sites in defective HKUST-1, we performed theoretical Cu L_3-edge calculations using the FDMNES program. The structural models used in these simulations, as well as the employed level of theory, are described in Section 2.3. First, we simulated the spectrum of the pristine MOF using the crystallographic structure of as-prepared HKUST-1. A comparison with the experimental spectrum collected at room temperature in He flux is shown in Figure 3a: the theoretical curve is in very good agreement with the experimental data, as the relative energy position and intensity of peaks A and D are correct and peak B is also nicely reproduced. Next, we calculated a theoretical spectrum using the dehydrated cluster model explained above, where all water ligands have been removed, and compared it to the experimental spectrum collected at 160 °C in CO_2 flux (Figure 3b) which should only probe non-defective, water-free Cu^{2+}/Cu^{2+} sites. Also in this case the theoretical spectrum is in good agreement with the experimental data: notably, the disappearance of peak B is correctly reproduced by the calculation, confirming that this peak is a fingerprint of the water ligands. In addition, this evidence also proves that the CO_2-promoted oxidation of the Cu^+ sites does in fact happen.

In order to reproduce the experimental spectrum of defective HKUST-1 collected at 160 °C in He flux, we calculated the spectrum of the Cu^+ centers present in the defective sites using a cluster model containing a Cu^+/Cu^{2+} dimer, shown in Figure 4b. Then, we combined this spectrum in a weighed

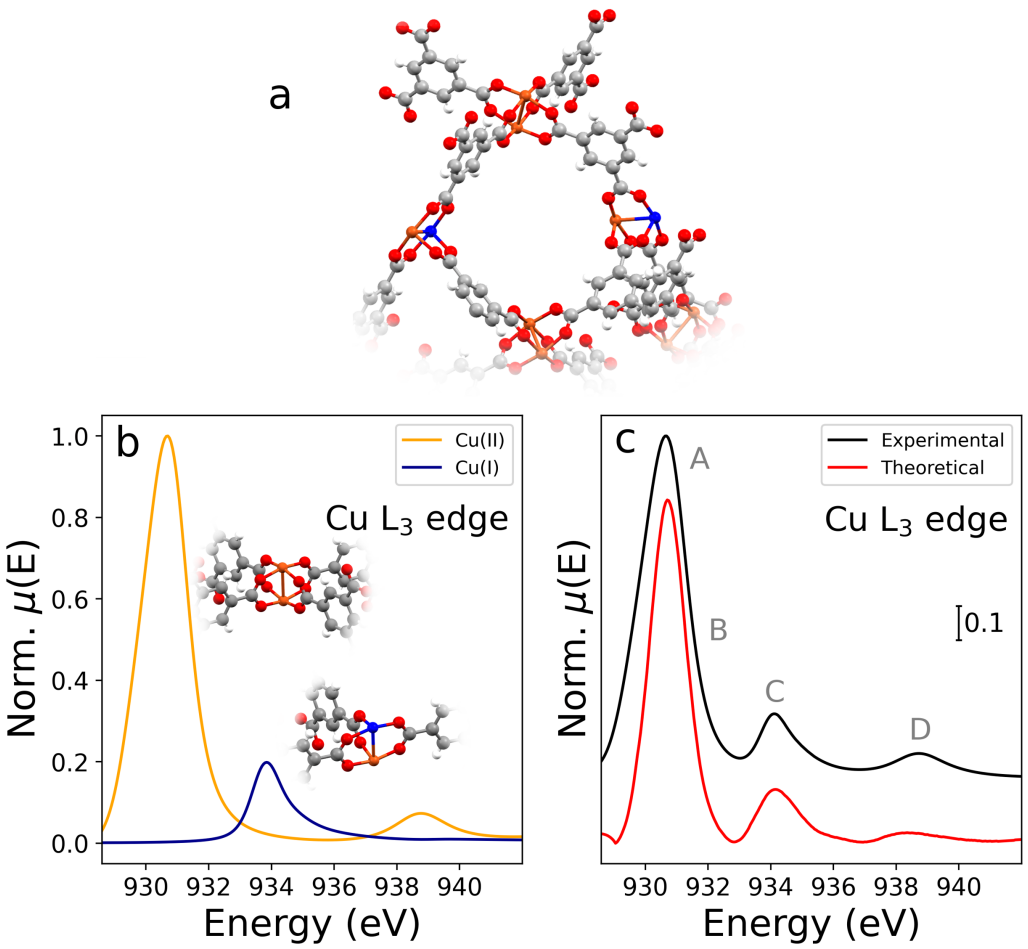

Figure 3: (a) Comparison between the Cu L_3-edge AP-NEXAFS experimental spectrum relative to the pristine HKUST-1 MOF collected at RT in He flux (black) and the corresponding theoretical calculation (red). (b) Comparison between the Cu L_3-edge experimental spectrum relative to the pristine HKUST-1 MOF collected at 160 °C while exposing the MOF to CO_2 (black) and the corresponding theoretical calculation (red). The associated molecular clusters are also shown, where the Cu^{2+} cation and the oxygen, carbon and hydrogen atoms are depicted in orange, red, grey and white, respectively.

sum together with the calculation relative to the Cu^{2+} ions within the dehydrated cluster, using the relative surface abundance that we had previously determined for each as weigh. The comparison with the experimental spectrum collected on HKUST-1 at 160 °C is shown in Figure 4c, and the agreement between the experimental and theoretical curves is once again very

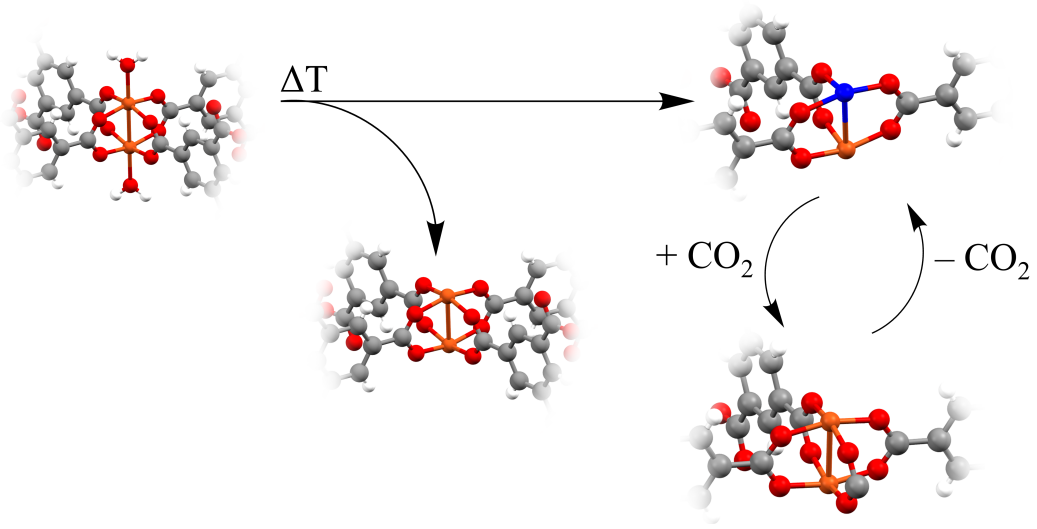

Figure 4: (a) Depiction of the surface copper sites formed upon heating HKUST-1 at 160 °C in He flux. Color code: orange, Cu^{2+}; blue, Cu^{+}; red, oxygen; grey, carbon; white, hydrogen. (b) Theoretical Cu L_3-edge spectra calculated for the Cu^{2+} (yellow) and Cu^{+} (blue) cations present in the Cu^{2+}/Cu^{2+} and Cu^{+}/Cu^{2+} dimers, respectively, and weighted by the estimated relative surface abundance. (c) Comparison between the experimental Cu L_3-edge spectrum collected on HKUST-1 at 160 °C in He flux (black) and the weighted sum of the theoretical spectra belonging to the Cu^{2+} and Cu^{+} surface species (red).

good, confirming our hypothesis for the structure of the defective sites and our picture for the overall structure of the thermally heated MOF (shown schematically in Figure 4a) where defective sites coexist with coordinatively unsaturated paddle-wheels.

Finally, the findings we presented thus far allowed us to derive a mechanistic picture which encompasses the formation mechanism of surface defective sites in HKUST-1 and their interaction with CO_2. A schematic representation of this picture is reported in Figure 5: we propose that in the first step upon thermal heating the desorption of water molecules from the paddle-wheel units occurs, leaving behind coordinatively unsaturated Cu^{2+}/Cu^{2+} dimers. Afterwards, when higher temperatures are reached, a fraction of the BTC ligands undergoes a decarboxylation process which in turn causes a partial reduction of the dimer to form defective Cu^{+}/Cu^{2+} sites. These sites can then readily interact with CO_2, which reoxidizes the unit to Cu^{2+}/Cu^{2+} in a process that is completely reversed when the MOF is not exposed to

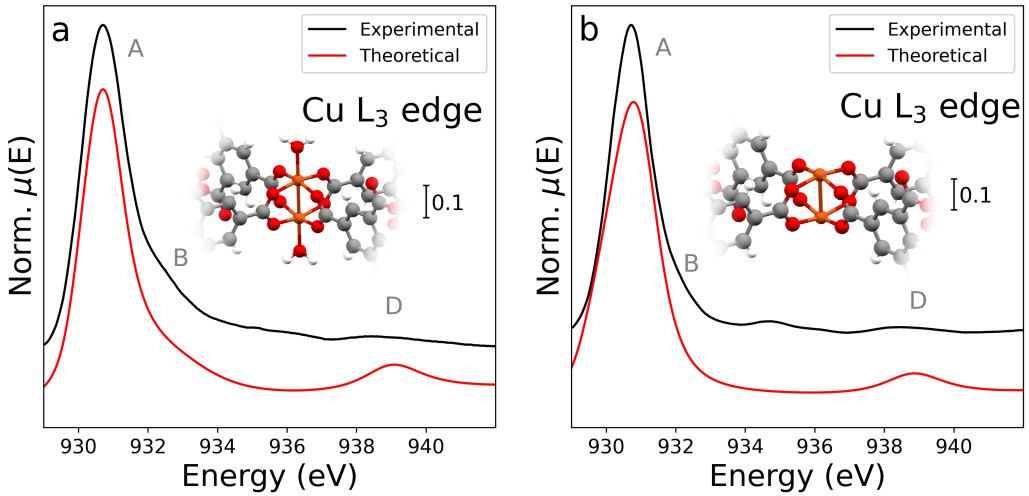

Figure 5: Proposed mechanism for the formation and reactivity of surface defective sites in HKUST-1. Upon heating at 160 °C, water molecules are released from the paddle-wheel units of the pristine MOF. These are converted into coordinatively unsaturated Cu^{2+}/Cu^{2+} dimers which then partially undergo an oxidative decarboxylation of the BTC ligand and yield Cu^{+}/Cu^{2+} complexes. The Cu^{2+}/Cu^{2+} dimer can then be reversibly replenished upon exposure of the Cu^{+}/Cu^{2+} sites to CO_2. Color code: orange, Cu^{2+}; blue, Cu^{+}; red, oxygen; grey, carbon; white, hydrogen.

carbon dioxide anymore.

4. Conclusions

In this work we highlighted how AP-NEXAFS can provide valuable information on the structure and reactivity of MOFs, presenting a thorough characterization of the thermally induced properties of surface Cu centers in HKUST-1. We also demonstrated how this newly developed technique can be combined effectively with theoretical calculations. Cu L_3-edge spectra of HKUST-1 have been collected at ambient pressure and at room temperature and 160 °C, while also varying the gaseous environment (He, CO_2, H_2, CO_2/H_2). The structural properties of copper sites present in the first atomic layers of HKUST-1 were unveiled, proving also that defective Cu^{+}/Cu^{2+} dimeric sites are largely present on the surface of this material. We provided evidence of the formation of Cu^{+} surface species upon thermal treatment of pristine HKUST-1 at 160 °C, and we estimated that these species account for about 45.4% of the total surface Cu content. Further, we have proved that

Cu^+/Cu^{2+} dimeric units arise from the decarboylation of the BTC ligands in the dehydrated Cu^{2+}/Cu^{2+} dimers, ruling out the formation of Cu^+ defective sites due to the presence of Cu_2O impurities in the MOF, which had been previously proposed [35]. Further, we showed that these defective sites can be readily and reversibly oxidized by CO_2, a molecule which has rarely been used as a probe to investigate the surface properties of HKUST-1. We believe that the combined experimental and theoretical methodology employed in this work can pave the way for the establishment of AP-NEXAFS as a routine technique to be employed in the operando characterization of MOFs.

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