Interplay of Electronic and Steric Effects to Yield Low-Temperature CO Oxidation at Metal Single Sites in Defect-Engineered HKUST-1

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Abstract: In contrast to catalytically active metal single atoms deposited on oxide nanoparticles, the crystalline nature of metal-organic frameworks (MOFs) allows for a thorough characterization of reaction mechanisms. Using defect-free HKUST-1 MOF thin films, we demonstrate that Cu+/Cu2+ dimer defects, created in a controlled fashion by reducing the pristine Cu2+/Cu+ pairs of the intact framework, account for the high catalytic activity in low-temperature CO oxidation. Combining advanced IR spectroscopy and density functional theory we propose a new reaction mechanism where the key intermediate is an uncharged O2 species, weakly bound to Cu+. Our results reveal a complex interplay between electronic and steric effects at defect sites in MOFs and provide important guidelines for tailoring and exploiting the catalytic activity of single metal atom sites.

Atomically dispersed precious metals are presently receiving considerable attention in catalysis due to their unique chemical activities and large per-atom conversion yields. Conventional systems, that is, metal particles deposited on oxides by impregnation methods, typically yield broad size distributions, thus reducing the per-atom yield. Although the presence of single atom active sites has been demonstrated in a number of cases,[1] the typically rather amorphous nature of the metal/oxide interface with a high heterogeneity of metal clusters and particles have made the unambiguous identification of reaction mechanisms and the accurate validation of theoretical results very difficult. In this context, metal-organic frameworks (MOFs) offer a number of interesting features. First, many of these crystalline coordination polymers obtained by connecting metal or metal/oxo clusters via organic linkers feature coordinately unsaturated metal sites (CUS). In the MOF case, the metal atoms are prevented from sintering by strong ionic bonds to the molecular struts forming the framework. Furthermore, these metal single atom sites are located at well-defined positions of a crystalline, porous lattice and are thus homogeneously dispersed within the MOF. Consequently, MOF-based materials hold great promise as single-site catalysts.[2] However, in many cases it is unclear whether the observed catalytic activity is related to metal ions of the perfect framework, or whether the active sites are related to structural defects within the MOF. In fact, defect engineering of MOFs has been used in numerous cases to tune the structural, electronic and chemical properties of MOFs in a controlled fashion.[3]

MOF powders, the most common form of MOF materials, often exhibit large defect densities even before introducing them intentionally, and there is no case known where an unambiguous identification of active sites and the reaction mechanisms together with a fully satisfying theoretical analysis has been reported.

In order to achieve an atomic-level understanding of single active sites and the mechanism governing a prototype reaction, low-temperature CO oxidation, we have carried out an extensive experimental and theoretical study based on defect-free HKUST-1 thin films (surface-mounted MOFs, SURMOFs) fabricated using liquid-phase quasi-epitaxy.[4] The oxidation of carbon monoxide was then investigated by combining infrared reflection absorption spectroscopy (IRRAS) and quantum chemical calculations based on density functional theory (DFT) as well as complete active space (CAS) calculations to treat transition states with multi-reference character.[5]

After synthesis of the HKUST-1 SURMOF, the structure of the porous framework was characterized using X-ray diffraction (XRD, Supporting Information, Figure S1) and the defect density (i.e., the concentration of Cu+ species) was determined by IRRAS using CO as a probe molecule. As shown in Figure 1a, there is only one IR band at 2174 cm−1 characteristic for CO bound to the axial positions of pristine Cu2+/Cu+ paddle-wheel units (Figure 1b).[3c,6] This data as well as the deconvoluted Cu 2p XPS results (Supporting Information, Figure S2a) allow setting an upper limit of 2% to the concentration of the Cu+ species.

For the pristine HKUST-1 SURMOF, the activity for CO oxidation was found to be very low. In Figure S3 we show the in situ IRRAS data recorded during exposing the CO-
saturated SURMOF to O₂ at 105 K. The intensity of the CO-Cu²⁺ band remained nearly unchanged in oxygen atmosphere. This result is not consistent with conclusions reported in previous work,[8] the reasons will be discussed below.

In order to unravel the role of defects in this system, we introduced Cu⁺-containing defects in a controlled fashion by using a thermal defect-engineering (DE) strategy.[9] Briefly, subjecting the pristine, virtually perfect HKUST-1 SURMOF to annealing in UHV at elevated temperatures leads to an oxidative decarboxylation, causing a reduction of the Cu²⁺/Cu⁺ paddle-wheel units, thus yielding Cu⁺/Cu²⁺ defect pairs. A thorough XPS analysis yields a Cu⁺ concentration of 30% created by heating the pristine MOFs at 430 K for 30 min (Supporting Information, Figure S2b).

The IRRAS data, obtained after exposure of these DE-HKUST-1 SURMOFs to CO, clearly reveal a vibrational band at 2118 cm⁻¹ (Figure 1a). This band, red-shifted by 56 cm⁻¹ relative to CO bound to Cu²⁺ species within a perfect paddle wheel, is characteristic for CO ligated to Cu⁺ species.[3c,6] Figure 1c shows the DFT-optimized atomic structure of CO species bound to Cu⁺/Cu²⁺ dimer defects. The computed red shift of CO-Cu⁺ vs. CO-Cu²⁺ (50 cm⁻¹) is in excellent agreement with the experimental results.

Importantly, the loss of the carboxylate group reducing one of the Cu ions to yield Cu⁺/Cu²⁺ creates additional open space. Based on the DFT calculations, a second CO can bind to the Cu⁺ ion, see Figure 1d. Accordingly, the band at 2153 cm⁻¹ (Figure 1a) is assigned to the asymmetric stretching mode of geminal (CO₂) dimers at the Cu⁺ CUS sites. As shown in Figure 2a and 2b, the DE-HKUST-1 SURMOF exhibits pronounced catalytic activity for the CO oxidation reaction. Even at low temperatures of 105 K, exposure to O₂ leads to a substantial reduction of the CO-Cu²⁺ vibrational band at 2180 cm⁻¹. While the CO₂ product was observed inside HKUST-1 powders,[7] for the very thin (100 nm) SURMOFs the amount was too small to be detected.

On the basis of these observations, we propose that the catalytic activity of HKUST-1 for CO oxidation results from the presence of reduced Cu⁺/Cu²⁺ dimer defects, thus challenging the interpretation put forward in previous work.[7] In order to further corroborate this hypothesis and to unravel the detailed reaction mechanism, a comprehensive set of DFT and ab initio calculations using the Turbomole[9] and ORCA[10] program packages was carried out.

We started with calculations at the M06 level of theory[11] employing an intact paddle wheel unit and found that CO and O₂ are not able to adsorb simultaneously on the same Cu²⁺ metal site, but could exchange with one another with a relatively low barrier (less than 0.2 eV). We performed an extensive search for a transition state of CO oxidation with molecular O₂ (and vice versa) on the pristine paddle wheel. Based on relaxed scans (see Supporting Information for more details) the smallest barrier is estimated to be higher than 2 eV, no barriers with lower energies were found. On the basis of this rather extensive set of calculations we conclude that low-temperature CO oxidation at the intact Cu²⁺/Cu⁺ pairs is not possible.

We thus turned our attention to the reduced Cu⁺/Cu²⁺ dimers. First, the extra electron available at the Cu⁺ ion increases the CO binding energy to almost twice the value for the fully oxidized case, ΔG = 0.38 vs. 0.16 eV (at 100 K). Second, as a result of the additional space (see above), now O₂ and CO can bind simultaneously on the metal site (see Figure 3). Starting from a O₂-Cu²⁺-Cu⁺-CO complex (III), the

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reaction path for the overall oxidation of CO contains two transition states, (TS-I) where the first C–O bond forms and (TS-II) that leads to the formation of the second C–O bond with simultaneous cleavage of the O–O bond. We note that TS-I has significant multi-configurational and multi-reference character. The calculated value for M06 is over 1.2 eV, while CASSCF[22] and NEVPT2[23] that explicitly account for the multi-reference character calculate TS-I to 0.56 eV (see Supporting Information for more details). This value is in fair agreement with the experimental observation of CO oxidation at temperatures as low as 105 K. TS-II on the other hand, can be successfully treated with single-reference methods and has a barrier of 0.43 eV (see Supporting Information for more details).

While the activation energies related to this reaction path are fully consistent with the experimental findings, the presence of an uncharged O2 species is somewhat surprising (see Figure 4a,b). In previous reaction schemes for CO oxidation, typically activated oxygen species such as superoxo or peroxy as well as surface lattice oxygen species were considered.[14] It has been reported that the adsorption of these activated oxygen species with CO can lead to a frequency shift of the CO stretching vibration due to electronic modifications (see for example, Au/TiO2[15] or Au/ZnO[16]). This was not observed in the present IRRAS data.

A crucial test for the proposed reaction mechanism in Figure 3 is to demonstrate the presence of the activated O2 species adsorbed on Cu CUS. While the O2 stretching vibration is IR-inactive in the gas phase, the weak binding to metal cations results in a small transition dipole moment, so that an observation by IR should, in principle, be possible.[15] Indeed, after exposing the pristine HKUST-1 O2 species at 1546 and 1550 cm⁻¹. The spectra recorded after slight annealing revealed that the binding energies of both O2 species are extremely low: the pristine Cu²⁺-related O2 band at 1550 cm⁻¹ disappears at about 60 K, while the signal at 1546 cm⁻¹ disappears only after heating to 67 K (Figure 4e). Based on DFT calculations, the latter one is assigned to activated, uncharged dioxygen species adsorbed to Cu²⁺ CUS of the reduced Cu/Cu²⁺ dimers (Figure 4b). Again, the computed frequency (10 cm⁻¹ red-shift in comparison to O2 on pristine paddle wheel) and binding energy (0.1 eV) are in good agreement with the experimental results that show the binding only occurs at low temperatures.

After providing strong support for the reaction pathway described in Figure 3 by demonstrating the presence of the uncharged O2 as an important intermediate, we come to the experimental observation that upon exposure to O2, for the DE-HKUST-1 only the CO-Cu²⁺ band decreases in intensity, while the intensity of the band assigned to the CO-Cu⁺, which should be consumed during the reaction, stays virtually constant (Figure 2b). Considering that the binding energy is larger (by 0.2 eV, according to our DFT calculations) in the latter case, this observation can be explained by a quick replenishing of the consumed CO-Cu⁺ species by direct transfer from adjacent Cu²⁺ sites, where CO is more weakly bound. Indeed, a careful analysis of the coverage-dependent IRRAS data (Supporting Information, Figure S5) revealed that the activation energy to transfer CO from Cu²⁺ to Cu⁺ sites must be lower than 0.20 eV, assuming a diffusion prefactor of 2.5·10⁻¹⁸ cm² s⁻¹.[19] Similarly, our DFT calculations result in a binding energy of CO to the ideal pristine paddle wheel of about 0.4 eV that, taking entropy corrections at 100 K into account, leads to a desorption barrier of 0.16 eV.
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Interplay of Electronic and Steric Effects to Yield Low-Temperature CO Oxidation at Metal Single Sites in Defect-Engineered HKUST-1

A complex interplay: A thorough study combining advanced spectroscopy and theory reveals that electronic and steric effects occur at reduced Cu$^+$/Cu$^{2+}$ single dimers in defect-engineered HKUST-1 SURMOF to yield high catalytic activity for low-temperature CO oxidation. We present a new reaction mechanism involving an uncharged O$_2$ species as the key intermediate.