

Illuminating the nature and behaviour of the active centre: the key for photocatalytic H₂ production in Co@NH₂-MIL-125(Ti)

Ana Iglesias-Juez^{a*}, Sonia Castellanos^{b*}, Manuel Monte^c, Giovanni Agostini^c, Dmitrii Osadchii^d, Alma Olivos^d, Sergey L. Veber^e, Matvey V. Fedin^e, Jorge Gascon^{d,f}

Advanced atomically resolved characterization methods unveil the behaviour of a promising photocatalytic Co@MOF(Ti) system for H₂ production. Combination of XAS and EPR experiments allows for the characterization of atomic and electronic rearrangements in photoinduced species. This information provides the basis for the optimization photocatalytic design.

The nanoporous nature of metal organic frameworks (MOFs) does not only endow these materials with high surface area but also with the possibility of confining active functionalities within their pores. This approach has been proven successful for the design of photocatalytic composites where the MOF acts as a photosensitizer and support.^{1,2,3,4,5}

The first example of ship-in-a-bottle protocol by Nasalevich et al. aimed at combining the advantages of homogeneous and heterogeneous catalysts by encapsulating a molecular Co-based hydrogen evolution catalyst in a Ti-based MOF (NH₂-MIL-125(Ti)).⁶ The Co@MOF system exhibited a 20-fold enhanced activity compared to the pristine NH₂-MIL-125(Ti). This protocol was later imitated with different Co complexes yielding an even larger increase in activity compared to the unloaded MOF by Li et al.²

It is generally assumed that the MOF scaffold absorbs the incident photons and then transfers electrons to the catalytic guests. Outside the field of MOFs, the few examples of photocatalysts for hydrogen evolution reaction (HER) based on TiO₂ materials doped with Co species assign to Co the role of co-catalyst that receives electrons from the photoexcited TiO₂ thus slowing down charge recombination.^{7,8} However, it is still challenging to experimentally probe the molecular and valence electronic structures of these complex systems due to the low loadings and heterogeneity of the sites.

Understanding the interaction between the two metallic components in Co@MOF(Ti) materials (the Ti-octamer cluster and the Co-based site) during the catalytic cycle is thus of major importance to unravel the mechanism of photon-induced hydrogen production and, ultimately, to optimize the photocatalytic performance. These investigations are particularly important for the development of solar light-driven sustainable energy sources, given the green character of a photocatalyst using visible light and based on cheap-earth-abundant and non-toxic elements such as Ti and Co.

Here an *in situ* X-ray absorption spectroscopy study sheds light on the structure of the encapsulated cobalt species and on mechanistic aspects of this multifunctional composite, providing an interpretation of the cooperative action of the photoactive matrix and the catalytically active encapsulated guest. The changes in the active sites were monitored during a

pre-catalysis incubation period and during photocatalytic H₂ production, thus yielding a detailed time resolved characterization of the electronic and structural behaviour of the system.

X-ray absorption near edge spectroscopy (XANES) spectra were registered for freshly suspended Co@MOF sample and during its *in situ* acetonitrile/triethylamine/water (AN/TEA/H₂O 5:1:0.1) incubation. The initial and final Co K-edge XANES spectra, displayed in Fig. 1., indicate the presence of Co(II) species in both cases as inferred from the edge position analysis.^{9,10} Comparison with appropriate references (see Fig. S2.) proves analogous surrounding local symmetry, likely an octahedral first coordination environment. The spectra clearly differ from those obtained for the isolated Co(III)-cobaloxime complex (Fig. S3.). This complex was expected to be formed in the pores by diffusing the linear oxime ligand in the MOF before letting Co²⁺ cations enter inside the pores followed by oxidation to Co³⁺ under O₂ flux.¹¹ The weak intensity of Co²⁺ Electron Paramagnetic Resonance (EPR) signals, which was found for the fresh catalyst in the dark⁶ seemed to support the assumption that most Co atoms resided in EPR-silent Co³⁺ state. However, the new XANES data reveal that the oxidation state is Co²⁺, thus requiring re-investigation of the catalyst structure.

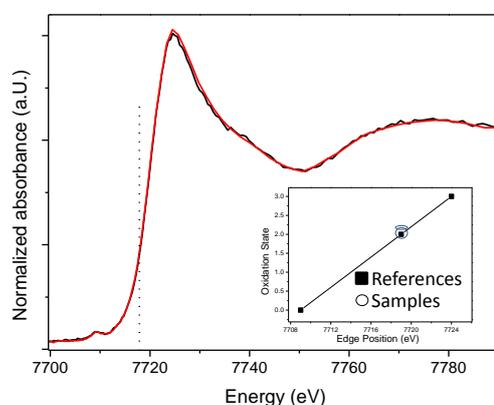


Fig. 1. XANES spectra of the freshly suspended Co@MOF (black) and after *in situ* AN-TEA-H₂O incubation (red).

To determine the nature of the Co species in the Co@MOF, the local structure around the Co atoms was studied by Extended X-ray absorption spectroscopy (EXAFS). The Fourier transforms of the Co k^2 -weighted spectra are shown in Fig. 2. left, and the structural parameters determined from the curve-fitting are summarized in Fig.2. right (complementary information in Fig. S4. and Table S1.).

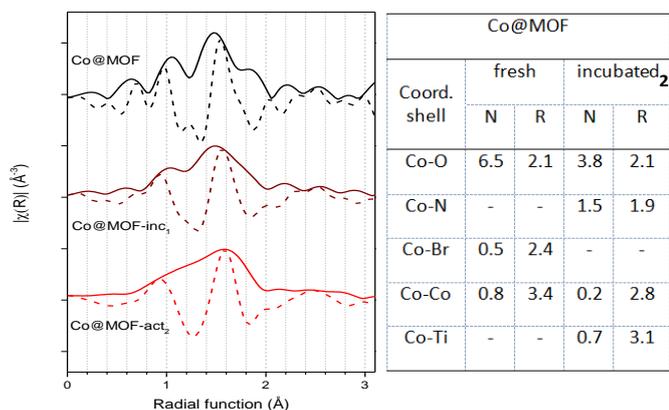
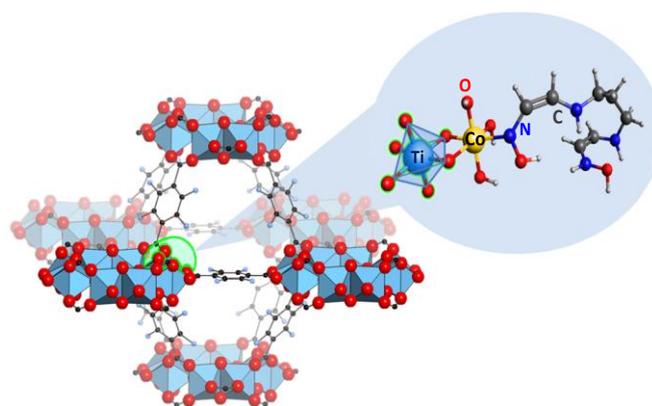


Fig. 2. Left: k^2 -weighted modulus and real part of the Fourier transform of Co K-edge EXAFS spectra corresponding to Co@MOF before (black) and after incubation period (red). Right: Structural parameters derived from EXAFS analysis.

The EXAFS data of the Co@MOF catalyst clearly differ from both CoBr_2 and Co-oxime references (Fig. S5.).^{12,13} The fitting suggests that the Co(II) species initially present an octahedral first coordination sphere formed by O and/or N atoms around 2 Å and also a small contribution of Br neighbors. O and N light scatters are difficult to distinguish in the EXAFS fitting (as can be derived from the evolution of scattering amplitude and phase shift functions with Z number)^{14,15} but participation of the N atom in the coordination of Co is supported by IR spectroscopy results, where the emergence of red shifted N-H stretching bands was detected for Co@MOF in comparison with the empty MOF.⁶ A Co-Co atomic distance of a second coordination shell is detected at 3.4 Å, suggesting the initial presence of Co dimers.¹⁶ The fitting shows that Co local environment evolves during the incubation period in AN/TEA/ H_2O . Specifically, after 12 h of incubation, an increase of the Co-N distance seems to occur together with a decrease on Co-Co coordination number and the appearance of more scatters in second-third coordination spheres. After 24 h, these differences are more obvious in the normalized Fourier transforms (Fig. 2.). On the one hand, near absence of the second coordination shell Co-Co (coordination number < 0.3) is observed; on the other hand, it can be seen that the shape of the module and real part of the 24 h incubated sample is significantly different from the fresh system, also from 12 h incubation, in the region between 2.0 and 3.2 Å. The comparison between normalized Fourier transforms could indicate the presence of metal-MOF wall interface contributions. Thus, it is required to introduce another coordination shell, Co-Ti, at longer distances ($R = 3.1$ Å) to obtain a good fit of the data (Fig.2.right). All these changes point out a reorganization of the Co species in the pores when treated with TEA and water. EXAFS fitting results on Co@MOF upon incubation with AN-TEA- H_2O suggest the presence of Co-monomers bonded to the Ti-cluster through oxygen atoms and to either $-\text{NH}_2$ residue in the organic linker or $-\text{N}$ atoms of the oxime ligand. The presence of the linear oxime ligands inside the pores could prevent oligomerization processes creating steric impediments and mediating the stabilization of the Co



complex with the Ti oxo-cluster of the MOF by coordination with N atoms from the ligand. In view of the XANES and EXAFS results, a structural model of the Co centers in the Co@MOF system is proposed (Fig. 3.).

Fig. 3. Proposed model, extracted from EXAF fitting data, for the active Co centers in the Co@MOF system.

The presence of Co(II) species in the form of O-bridged dimers which dissociate upon incubation can explain previous EPR results.⁶ In such dimers metal ions are typically coupled by a strong antiferromagnetic exchange in the order of 100-200 K,^{17,18} therefore at $T < 50$ K they become EPR silent. Indeed, freshly suspended sample, before illumination, shows only a weak signal at $g \sim 4$, which is assigned to residual Co(II) in high spin state. The photogeneration of a new signal at $g \sim 2$ region on the timescale of 10-20 hours is compatible with incubation and electron transfer reactions occurring in parallel. The photoinduced EPR signal shows several remarkable features. It has closely Gaussian lineshape at X/Q-bands with peak-to-peak width ~ 300 mT, but the apparent g -values differ at X- and Q-band, being ~ 2.65 and ~ 2.23 , respectively (Fig. 4, Fig. S8).

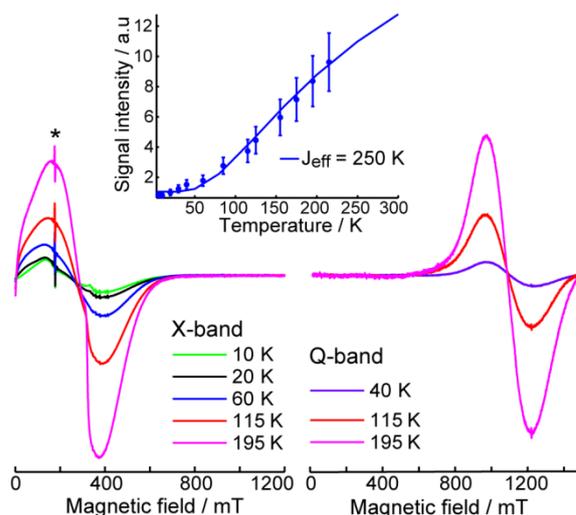


Fig. 4. Variable-temperature X/Q-band EPR spectra of Co@MOF in $\text{CH}_3\text{CN}/\text{TEA}/\text{H}_2\text{O}$, which was exposed to 380 nm light irradiation for 19 h prior to measurements. Asterisk marks the reference signal used for normalization of X-band spectra. Inset: signal intensity vs. temperature and the fit.

The intensity of this signal drastically grows with temperature, whereas the shape remains closely the same (Fig. 3, Fig. S8). These observations can be assigned to exchange-narrowed cluster/network of magnetically-coupled ions with noticeable distribution of structural parameters. The exchange coupling is clearly antiferromagnetic, and we can estimate its effective value J_{eff} by fitting the temperature dependence of signal intensity with a Boltzmann function $\exp(-J_{\text{eff}}/kT)$, giving $J_{\text{eff}} = 250 \pm 50$ K (Fig. 3). Such large values of exchange coupling assume rather short distances between paramagnetic centers in the cluster, allowing us to assume oxo-bridging.^{17,18} The clusters/networks can include both Co ions and photoinduced Ti(III) ions. Upon long illumination, the number of Ti(III) ions might exceed the number of Co(II) ions, therefore the properties of exchange clusters should be dominated by those of Ti(III). Indeed, we were able to detect the photoinduced EPR signal of Co@MOF up to nearly room temperatures, which is not common for fast-relaxing cobalt species, but is more plausible for slower-relaxing $3d^1$ Ti(III) species. Thus, X/Q-band variable-temperature EPR study supports the formation of antiferromagnetically-coupled exchange clusters/networks of Co and Ti(III) ions upon illumination of Co@MOF in reaction mixture, where the dominant exchange coupling occurs

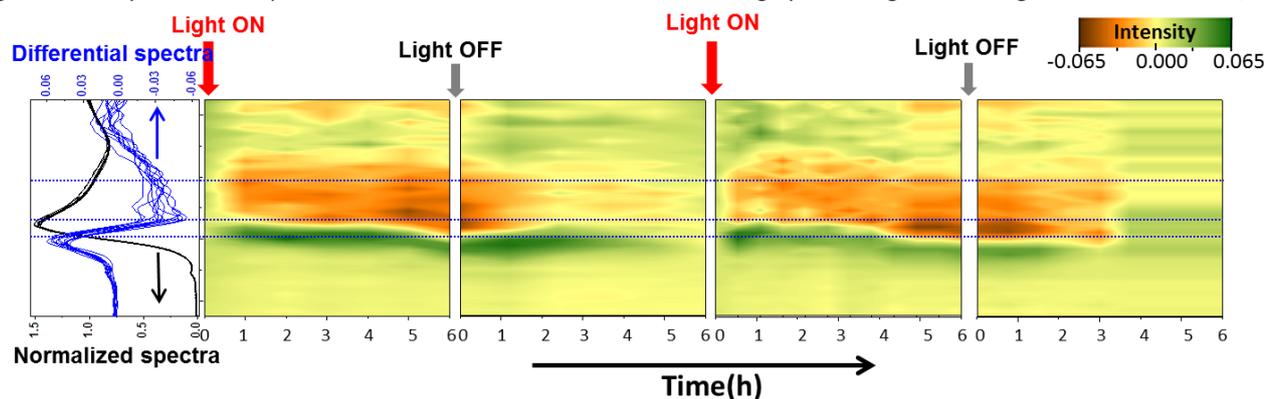
between closely located pairs of ions, possibly connected via the oxo-bridge.

Operando XANES experiments were performed to investigate how light induced catalytic activity. Differential mode analysis of Co K edge (see SI for more details) provides information about the metal properties together with the charge localization process upon photoexcitation (Fig. 5.).

The illumination of the suspension with visible light in the reaction media induced a shift of the XANES edge toward lower energies (green features). The shift was accompanied by a concomitant decrease in the white line intensity and the shoulder around 7737 eV, attributed to an electron density increase of the p and d states, respectively, involved in the $1s-4sp$ and $1s-3d$ resonance transitions (orange features). Therefore, the results point to a partial reduction of the Co centres¹⁹ by charge transfer directly into p and d_{eg} states.

These changes became more evident after 5 h, in line with the activation period induced by illumination previously reported for this system⁶ and proved to be reversible after the light was switched off, as well as reproducible upon a second light exposure cycle (Fig. 5).

Fig. 5. Intensity contour map of normalized differential absorbance during cycles of light switching for Co@MOF in AN/TEA/H₂O



solution.

Therefore, photoinduced charge transfer reaches a photostationary state and reverts to the original situation in the absence of light, which indicates that the electrons accumulated in the Co-sites electronically coupled to the Ti atoms of the MOF platform are used for photocatalytic water reduction in a reversible manner. Several reported studies in the literature claim that Co-based hydrogen evolution catalysts require the formation of Co(I) intermediates for water reduction. This work shows that a partial reduction of Co centers takes place by charge transfer and these reduced species are the active center for H₂ formation, but no total reduction to Co(I) occurs.

In summary, XANES and EXAFS analyses unveil the structure and properties of this promising composites together with the charge localization process after photo-excitation. The results indicate that during the incubation period Co-dimers in

Co@NH₂-MIL-125(Ti) partially dissociate and bring Co²⁺ species closer to the Ti-clusters. In this configuration, visible light promotes the partial reduction of the Co(II)-sites, which are the active catalytic centres responsible for hydrogen evolution. This configuration is in line with the observed evolution of the EPR spectra upon illumination of Co@MOF, where the registered broad signal in the photostationary state is indicative of the electronic coupling between Co and Ti. Thus, while the linear oxime ligand does not seem to promote the formation of molecular complexes in the pore, its function might favour the dispersion of the Co(II) cations and enable the formation of Co-sites with monomeric configuration that can connect to the Ti-oxoclusters of the MOF in the active state.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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