

Understanding the Excited State Dynamics of a Phase Transformable Photo-Active Metal-Organic Framework MIP 177 through Time-Resolved Infrared Spectroscopy

Authors : Aneek Kuila, Yaron Paz

Abstract : MIP 177 LT and HT are two-phase transformable metal organic frameworks consisting of a $\text{Ti}_{12}\text{O}_{15}$ oxocluster and a tetracarboxylate ligand that exhibits robust chemical stability and improved photoactivity. LT to HT only shows the changes in dimensionality from 0D to 1D without any change in the overall chemical structure. In terms of chemical and photoactivity MIP 177 LT is found to perform better than the MIP 177HT. Step-scan Fourier transform absorption difference time-resolved spectroscopy has been used to collect mid-IR time-resolved infrared spectra of the transient electronic excited states of a nanoporous metal-organic framework MIP 177-LT and HT with 2.5 ns time resolution. Analyzing the time-resolved vibrational data after 355nm LASER excitation reveals the presence of the temporal changes of ν (O-Ti-O) of Ti-O metal cluster and ν (-COO) of the ligand concluding the fact that these moieties are the ultimate acceptors of the excited charges which are localized over those regions on the nanosecond timescale. A direct negative correlation between the differential absorbance (Δ Absorbance) reveals the charge transfer relation among these two moieties. A longer-lived transient signal up to 180ns for MIP 177 LT compared to the 100 ns of MIP 177 HT shows the extended lifetime of the reactive charges over the surface that exerts in their effectivity. An ultrafast change of bidentate to monodentate bridging in the -COO-Ti-O ligand-metal coordination environment was observed after the photoexcitation of MIP 177 LT which remains and lives with for seconds after photoexcitation is halted. This phenomenon is very unique to MIP 177 LT but not observed with HT. This in-situ change in the coordination denticity during the photoexcitation was not observed previously which can rationalize the reason behind the ability of MIP 177 LT to accumulate electrons during continuous photoexcitation leading to a superior photocatalytic activity.

Keywords : time resolved FTIR, metal organic framework, denticity, photoacatalysis

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