Simultaneously Coupled 4 in 1 Operando EPR/XANES/EXAFS/UV–vis/ATR–IR technique for Mechanistic Studies of Catalytic Gas-Liquid Phase Reactions

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For the first, we have simultaneously coupled 4 in 1 operando EPR, XANES/EXAFS, ATR-IR and UV-vis techniques for monitor for a catalytic gas-liquid phase reactions. As a model reaction, the selective aerobic benzyl alcohol (BnOH) oxidation to benzaldehyde (BA) over a $Cu^{I}OTf$ /TEMPO catalyst system [1] has been used to unravel Cu/TEMPO intermediates and active species which had been controversially discussed in literature. Detailed information on the time-dependent redox behavior of paramagnetic Cu^{II} (d^9, S = ½) and TEMPO (S = ½) species in the reaction solution has been gained from EPR. While XANES/EXAFS and UV-vis spectroscopy were able to reflect all valence and nucleation states of Cu, yet in less detail, due to their spectral superposition .Therefore, Multivariate Curve Resolution with Alternating Least Squares Fitting (MCR-ALS) has been used. The results indicate that an initially formed tetracoordinated (bpy)(NMI)Cu^{I} complex is converted to an EPR-active (bpy)(NMI)Cu^{II}OOH monomer and an EPR-silent dinuclear [(bpy)(NMI)Cu^{II} μ-OH]$_2$ which is irreversibly cleaved during the course of the reaction into EPR-silent (bpy)(NMI)(OOH)Cu^{II}-TEMPO. Both Cu monomer and dimer are catalytically active in the initial phase of the reaction. The gradual formation of non-reducible Cu^{II} leads to slight deactivation of the catalyst. Therefore, a new reaction mechanism has been proposed based on the above mentioned results.

These results highlight the advantages of the simultaneously coupled technique which is not only limited for monitoring gas-liquid phase reactions but also for heterogeneous catalytic processes under flowing gases at elevated temperature.

[1] Rabeah, J.; Bentrup, U.; Stößer, R.; Brückner, A., Angew. Chem. Int. Ed. 2015, 54, 11791.