Coupling of Vibrational and Electronic Spectroscopies: Effective Tools for Exploring Mechanisms of Catalytic Redox Processes

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Introduction and Objectives

The majority of catalytic reactions comprise redox steps in which electrons are transferred between substrate molecules and active sites in the catalyst. On the other hand, the molecular structure of reactands, intermediates, products, the local environment of active sites and sometimes even the phase structure of catalysts change during reaction. A comprehensive understanding of all of such processes is essential to derive structure-reactivity relationships as a basis for tailored catalyst optimization. This calls for the combination of spectroscopies monitoring both electronic and structural changes. In the last decade, the use of coupling techniques (e. g. *operando* EPR/UV-vis/Raman spectroscopy) was widely restricted to thermally activated heterogeneous catalytic gas-phase reactions [1,2]. Very recently, their application potential has been extended to heterogeneous and homogeneous liquid phase reactions as well as to photocatalytic processes. This will be illustrated in this talk by three examples from heterogeneous gas- and liquid-phase catalysis as well as from homogeneous catalysis. Besides the benefits, also limitations such as sensitivity differences of the methods will be discussed.

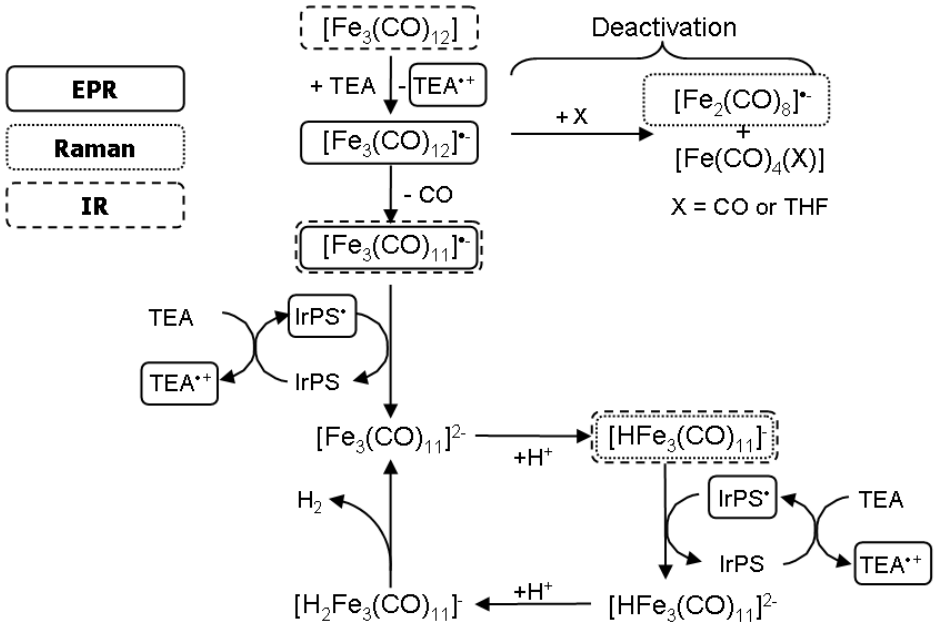
EPR/Raman combined with FTIR spectroscopy for photocatalytic water reduction

EPR spectroscopy monitors the transformation of the $Fe_3(CO)_{12}$ catalyst into different low-spin $[Fe_x(CO)_y]^{\bullet-}$ radical anions by electron transfer from the sacrificial agent triethylamine (TEA) *via* a $[Ir(ppy)_2(bpy)]PF_6$ photosensitizer in homogeneous solution. In contrast, the active $[HFe_3(CO)_{11}]^-$ species is diamagnetic and, thus, EPR-silent but visible by Raman and FTIR spectroscopy. For the first time, most of the intermediates in the reaction cycle (Scheme 1) have been visualized by the three in situ spectroscopies. Based on these results, a reliable reaction and deactivation mechanism could be established [3].

Coupled ATR-IR/UV-vis/Raman spectroscopy for imine hydrogenation

The heterogeneous liquid-phase hydrogenation of aromatic imines on a supported Pt/Al_2O_3 catalyst in the presence of a chiral phosphonic acid modifier has been monitored at a H_2 pressure of 20 bar in a special autoclave equipped with fibre optical probes for the three spectroscopies. While the interconversion of substrate and product could be properly seen in ATR and Raman spectra, UV-vis spectroscopy did not provide useful results

under the same conditions due to too high concentrations. Nevertheless, useful information on the interaction of substrate, modifyer and catalyst surface could be obtained by considering also the results of separate interaction studies using concentrations tailored for the detection range of the methods.



Scheme 1. Species detected by different methods during photocatalytic water reduction

EPR, Raman and UV-vis spectroscopy (coupled or separate) for heterogeneous gas-phase reactions

Several binary and ternary vanadium containing VMON (M = Al, Zr, Mo) oxynitrides have been studied during nitridation of the oxide precursors in NH_3 flow as well as during ammoxidation of 3-picoline to 3-cyanopyridine. Using the three *in situ* techniques supported by other methods such as XRD and XPS essential features of high catalytic performance as well as the reason for the unexpected detrimental effect of phosphorus could be identified. By combined EPR and UV-vis spectroscopy coupled to mass spectrometry, special Fe^{3+} sites being responsible for the strong acceleration of the selective catalytic reduction of $NO/NO_2/O_2$ mixtures by NH_3 (fast SCR) in comparison to NO/O_2 (standard SCR) could be discriminated among a variety of Fe^{3+} sites present in Fe-ZSM-5.

References

[1] A. Brückner, *Chem. Commun.* 13 (2005) 1761.
[2] U. Bentrup, *Chem. Soc. Rev.* 39 (2010) 4718.
[3] D. Hollmann, F. Gärtner, R. Ludwig, E. Barsch, H. Junge, M. Blug, S. Hoch, M. Beller, A. Brückner, *Angew. Chem. Int. Ed.* 50 (2011) 10246.