Operando XAFS Studies of Homogeneous and Heterogeneous Catalysts in Liquid-Phase Hydrogenation Reactions up to 200°C and 50 bar.

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The method of operando XAFS provides transformational information about the details of the catalyst structure, and thereby the reaction pathways and kinetics. Different types of liquid-phase reactions involving metal ions (Mn^{2+}), metal clusters (homogeneous $Rh(0)_4$) and supported nanoparticles (heterogeneous Pd nanoparticles) are reported at conditions up to 200°C and 50 bar. The reactions include benzene and phenol hydrogenations, and amine borane dehydrocoupling in a variety of different liquid phase solvents including water, toluene, and iso-propanol. We find in many instances that the chemical state of the catalyst under operating conditions is often dramatically different than the ex situ state. XAFS can provide critical information about the true, kinetically dominant catalytically active species. Further when XAFS results are combined with other methods such as analysis of reaction kinetics, NMR, or mass spectrometry, then a much clearer picture of the catalyst mechanism emerges. The described reactions are relevant to hydrogen storage, synthesis of transportation fuels and arene hydrogenation.

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