High-Frequency and -Field EPR of Catalytic Metal Complexes

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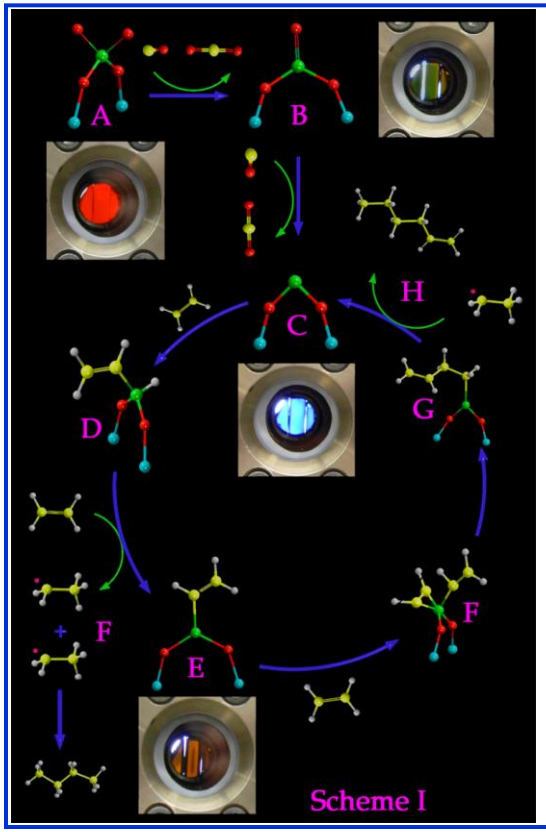
A catalyst is an agent that modifies the kinetics of a chemical reaction, making it occur faster, but is not itself consumed as part of the reaction. Catalysts are essential for commercial production of a number of economically important commodity and specialty chemicals.

For transition metals, oxidation states are related to spin states, and many of those states are paramagnetic and thus amenable to Electron Paramagnetic Resonance (EPR). The resolving power of high-frequency and -field EPR (HFEPR) as performed at the NHMFL makes it a very useful and attractive technique to study this area of applied research.

We have followed by HFEPR the oxidative dehydrogenation of propane (ODP) on supported vanadia catalyst, and the polymerization of ethylene using Phillips catalyst. In the case of the ODP project HFEPR with its excellent spectral resolution made possible identification of Ti^{3+} and V^{4+} ions proving involvement of "inert" support materials, as well as quantification of the number of spins. The Phillips catalyst project was able for the first time to determine unequivocally the active species as a Cr^{2+} complex.



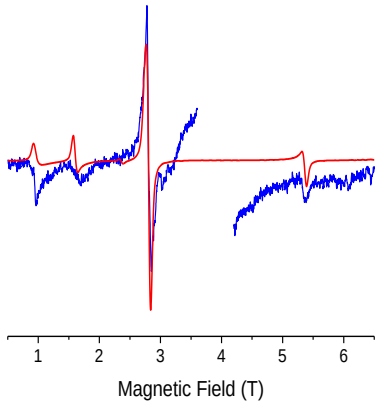


Figure 1. Left: The full cycle of ODP reactions using Phillips catalyst. Above: HFEPR spectrum of the catalytically active species (blue trace) at 106 GHz and 10 K, which was identified as a Cr^{2+} (S = 2) complex through simulation using known Cr^{2+} spin Hamiltonian parameters (red trace).

The obtained results have served better understanding the catalysis mechanisms and thus offer a potential for improving the efficiency of the catalysis, and developing new catalytic materials,

Facilities: The EMR facility including 12.5 and 15/17 T superconducting magnets was used in this research.
Acknowledgements : Dinse, K. P. (Deutsche Forschungsgemeinschaft SFB546); Stiegman A. E.
Citation: Dinse, A.; *et al.*, *J. Phys. Chem. C*, **2008,** *112,* 17664-17671; Brown, C.; *et. al.*, *J. Am. Chem. Soc*., to be submitted.