EPR spectroscopy in heterogeneous catalysis: combining in-situ and ex-situ approaches

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Electron Paramagnetic Resonance (EPR) is a spectroscopic technique which selectively detects paramagnetic (and more generally magnetic) species. It is therefore widely used for in-depth characterization of heterogeneous catalysts and provides valuable and detailed information about paramagnetic centres, which are frequently encountered in these systems and often represent the active sites for the catalytic reaction. These include transition metal ions, defects, magnetic nanoparticles and photoexcited states.

The present overview covers a series of applications of EPR in the field of heterogeneous catalysis which are being investigated in our group. Several of them focus on the characterization of single atom catalysts, consisting of metal centres atomically dispersed on a surface, which may consist in a metal oxide (alumina, ceria)[1] or a carbon-based support.[2] With continuous wave (CW) EPR we are able to track subtle changes in oxidation states and geometries of the paramagnetic sites, aggregation and redispersion processes and possibly identify and characterize the active sites. Advanced pulsed hyperfine techniques, such as Hyperfine Sublevel Correlation Spectroscopy (HYSCORE) and Electron Nuclear Double Resonance (ENDOR) provide further structural details about the local environment of the paramagnetic centres by detecting weak hyperfine couplings with nearby magnetic nuclei, which are typically not resolved by CW-EPR. A combined HYSCORE-DFT approach allowed us to characterize the changes in composition of heavy polyaromatic compounds (coke) inside the zeolites channels during the methyl coupling reaction.[3]

Moreover, what makes EPR particularly appealing for catalysis is the possibility to use it in situ or in *operando* mode, allowing to monitor the evolution of the catalyst in real time in the operational reaction conditions. With this approach we investigated In_2O_3 and Zn/ZrO_2 based catalyst for CO_2 reduction to methanol, in which the catalytic performance is determined by oxygen vacancies.[4,5]

This overview shows the potential of EPR to solve crucial and challenging problems in heterogeneous catalysis thanks to its high sensitivity and a unique ability to detect fine structural details of paramagnetic and magnetically coupled systems.

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