Characterization and Quantification of Reduced Sites on Supported Vanadium Oxide Catalysts Using High-Frequency EPR

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Introduction

Oxidative dehydrogenation of propane (ODP) has been studied extensively both with the goal to develop the reaction into a viable source of olefin and as a prototype process for understanding structure-function relationships in selective oxidation reactions. Because of the high frequencies applied in our study, superimposed signals caused by reduced active sites could be separated and interpreted in detail for the first time. By choosing a reliable spin standard for the HF-EPR, our previous study [1] was now extended by a quantitative determination of reduced V sites present on different support materials [2].

Experimental

Taking advantage of the high sensitivity of HF-EPR, sealed samples of ca. 100 mg, can be investigated in a cavity-free setup, thus allowing studying the influence of reaction conditions on the formation of paramagnetic centers [1, 2].

Results and Discussion

Quantification of EPR active sites can be performed by double integration of the field-derivative spectra and comparison with a Mn^{2+} standard. Spectral separation of different paramagnetic species due to g value differences is sufficiently large to result in separated steps in the doubly integrated curve, thus allowing for a determination of the relative amount of Mn^{2+} and V^{4+} spins. The step size is proportional to the spin susceptibilityχ, thus allowing us to obtain a direct measure of the relative spin concentrations that can be assigned to different spectral components (see **Figure 1**).

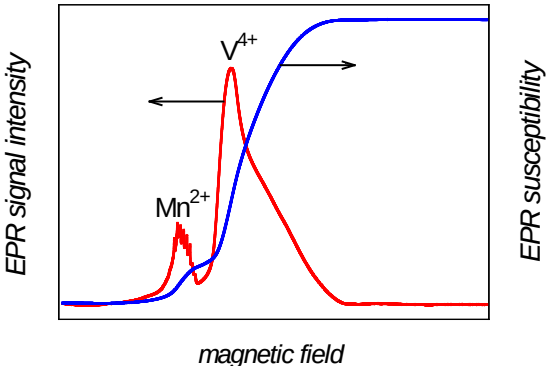

Figure 1. Quantification of the V^{4+} concentration by the EPR intensity measurements.

Conclusions

In our study it is demonstrated that the substantial gain in spectral resolution characteristic for HF-EPR can be used to perform quantification of paramagnetic centers of catalysts. The activity of catalysts for propane activation is proportional to the extent of reducibility of vanadia. We found that different supports loaded with the same amount of vanadia species do not exhibit identical reduced sites. Various supports have different ability to form heterodimer structures of diluted vanadia systems. One controlling factor for the activity is the ability of the support to accept electron density from the vanadia, requiring substantial covalence in the V-O-support bonds. The other factor is the hydrolytic stability of this bond.

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References

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[2] Dinse, A*., et al.*, ChemCatChem, **4**, 641-652 (2012).