Exploring the Structure of Paramagnetic Centers in SBA-15 Supported Vanadia Catalysts With Pulsed One- and Two-dimensional Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR)

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Supporting information

Simulation frequencies were chosen according to the observed positions of vanadium signals in the 2D plot. Experimental intensities were determined by projecting the 2D plot onto the T_1 related axis. Experimental data shown were obtained using the H_2 reduced sample with 1.8 wt. % V (2V/SBA-15).

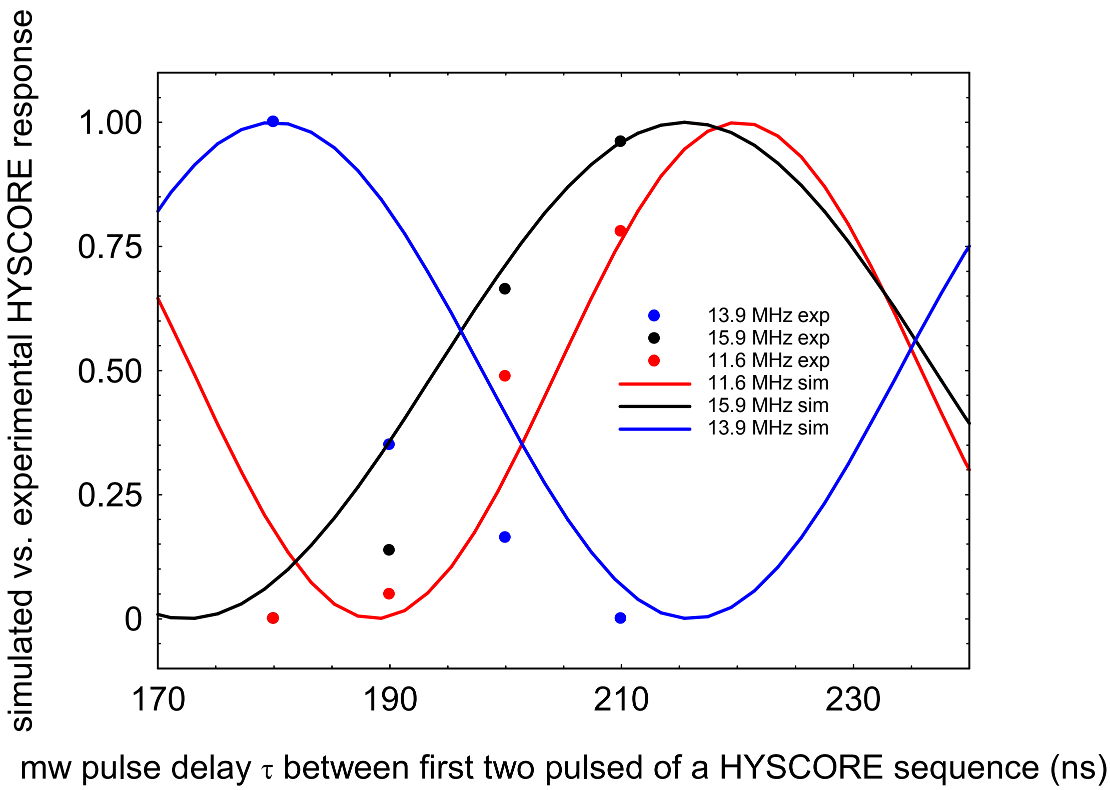

Fig. S1: Simulated and experimental HYSCORE response as function of the delay time τ of the first pulses of a HYSCORE sequence.

For comparing the relative signal intensities of "free" and "coupled" peaks in samples of different vanadia loading as shown in Fig. 10, a pulse delay $\tau = 200$ ns was chosen. Although the center peak is depressed significantly under this condition, the difference in relative intensities can be observed for all three samples.

In order to obtain a qualitative measure of the relative contribution of "local" and "distant" vanadium atoms, the intensity of projected 2D peaks is summed for the 4 delay values shown in Fig. S2. Because the range of τ values covers the conditions from "full" sensitivity to total suppression, a rough guess of the undistorted relative intensities can be obtained. For the H_2 reduced sample with 1.8 wt. % vanadium loading the intensity values are 8.1/13/7.7 (with increasing frequency), thus indicating that oligomeric and monomeric sites are visible in similar amounts.

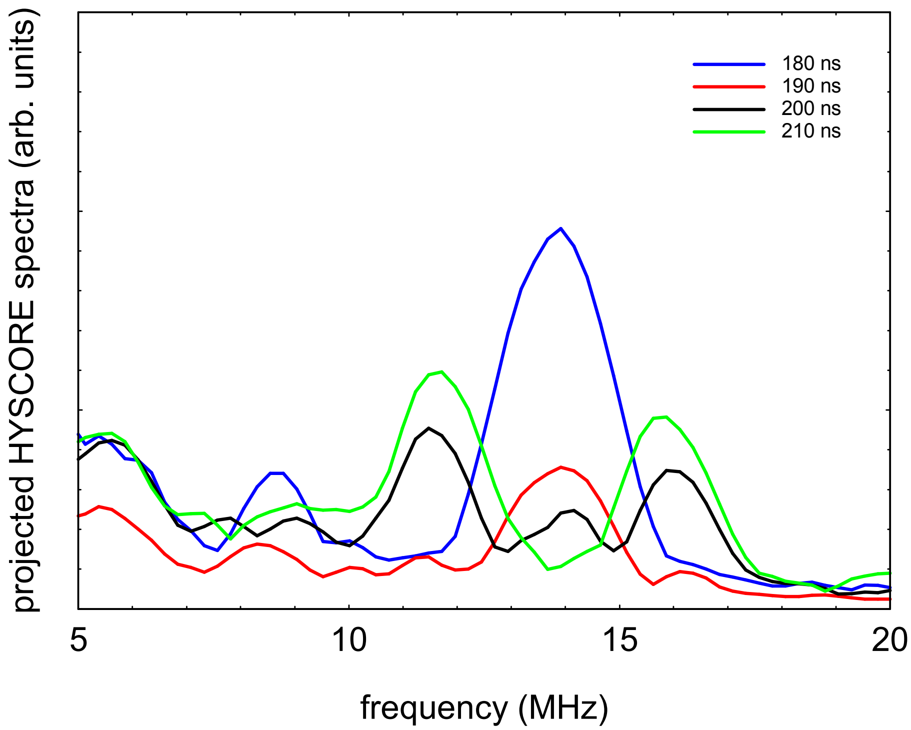

Fig. S2: 34 GHz projected HYSCORE data of SBA-15 supported VO_x catalysts with 1.8 wt. % vanadium loading (2V/SBA-15, H_2 reduced, sealed), T = 10 K, showing the effect of variation of time delay of the first two mw pulses in a 4-pulse HYSCORE sequence.

Sample properties are compiled in Table S1.

sample name	FHI serial number	V [wt%] XRF	V [mmol/g]	S(BET) [m^2/g]	V surface density [nm^{-2}]	V surface density [nm^{-2}]
SBA-15	7724	0	0	987	0	0
1V/SBA-15	7779	0.99	0.19	939	0.125	0.119
2V/SBA-15	7802	1.77	0.35	926	0.226	0.212
3.5V/SBA-15	7815	3.45	0.68	807	0.505	0.413
6.5V/SBA-15	7817	6.34	1.24	679	1.103	0.759
9V/SBA-15	7827	9.15	1.80	529	2.045	1.096

Table S1: Vanadium surface densities are calculated using either specific surface area of the parent SBA-15 support (outmost column) or using the surface area of samples (5^{th} column) after grafting, respectively.

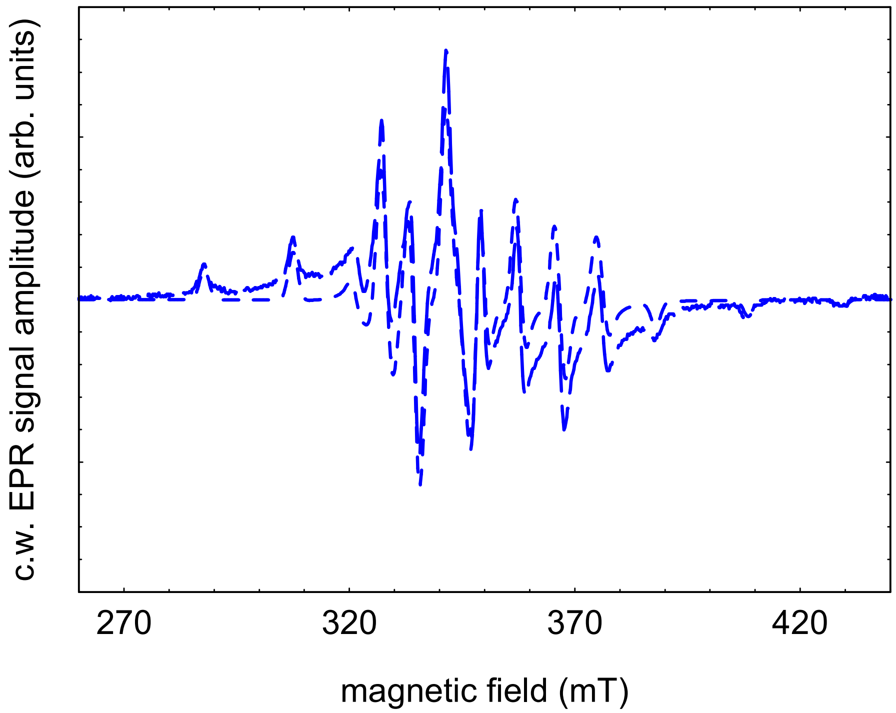

Fig. S3: C. w. EPR spectrum of sample with 6.3 wt % V (6.5V/SBA-15, as prepared) measured at 80 K. Dashed line is a best fit using the following parameters: g = (1.9859 1.9895 1.0415), A = (197.0 217.6 548.7) MHz, line width 2.4 mT.