Supporting Information

for

Magnetic Properties of Reduced and Re-oxidized Mn-Na_2WO_4/SiO_2: A Catalyst for Oxidative Coupling of Methane (OCM)

Wiebke Riedel[1,2], Lukas Thum[3], Jannik Möser[2,4], Vinzenz Fleischer[3], Ulla Simon[5], Konrad Siemensmeyer[6], Alexander Schnegg[2,4], Reinhard Schomäcker[3], Thomas Risse[1,2], Klaus-Peter Dinse[7]*

[1]Institut für Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany.

[2]Joint EPR Lab, Berlin, Germany.

[3]Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany.

[4]Insititut Nanospektroskopie, Helmholtz-Zentrum Berlin, Kekuléstraße 5, 12489 Berlin, Germany.

[5]Fachgebiet Keramische Werkstoffe, Institut für Werkstoffwissenschaften und -technologien, Fakultät III, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin, Germany.

[6]Institut Quantenphänomene in neuen Materialien, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany.

[7]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.

The effect of temperature on the line width of this cw EPR signal in the reduced catalyst is shown in Figure S1. Upon cooling the line width ΔB_{pp} increases slightly from 50 mT at 300 K to about 65 mT at 50 K. A further reduction of temperature to 10 K broadens the line significantly (180 mT). The increase in line width at low temperature is found to be more pronounced at high mw frequency. It should be emphasized that the broad cw EPR signal

remains clearly detectable even at 10 K. This increase in cw EPR line width observed with decreasing temperatures is consistent with previous reports of nano-sized Mn(II) oxide clusters.[1-3]

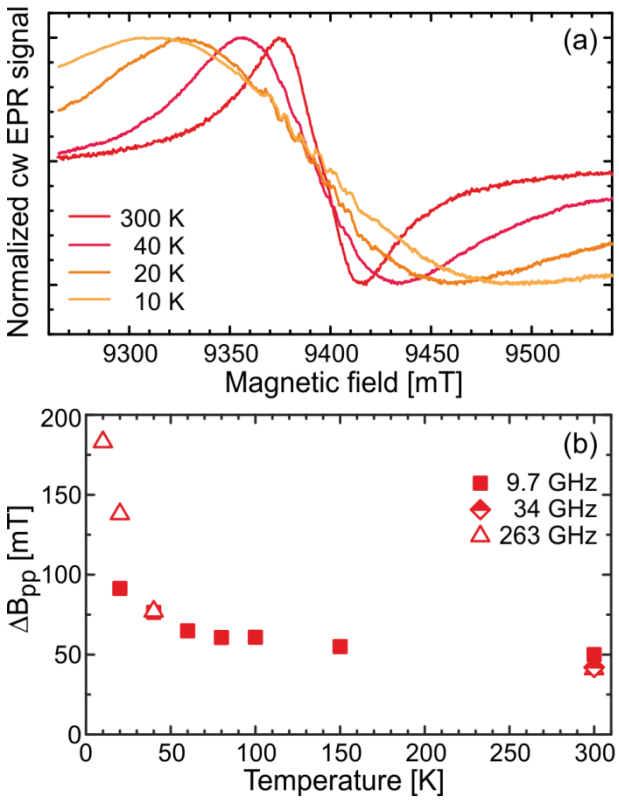

Figure S1. Temperature dependence of (a) the normalized 263 GHz cw EPR spectra (0.5 mT modulation amplitude, 10 kHz modulation frequency) and (b) the line width (ΔB_{pp}) of the reduced Mn-Na_2WO_4/SiO_2 catalyst.

From the temperature dependence of the (double) integrated cw EPR signal further information on the nature of the EPR active species is obtained. For simple paramagnetic species, the integrated intensity (EPR susceptibility) is expected to follow Curie's law and thus, increase with 1/T for decreasing temperatures. Figure S2a shows that the susceptibility measured at 9.7 GHz of the reduced Mn-Na_2WO_4/SiO_2 catalyst follows roughly the expected Curie behavior. In contrast, the re-oxidized catalyst exhibits clear deviations from Curie behavior: For this sample the susceptibility shows a strong decrease when lowering the temperature from 100 K to 80 K. The decrease in integrated signal intensity coincides with a

clear change in line shape (Figure S2b). These observations suggest that in the re-oxidized catalyst the EPR signal of at least one of the species decreases between 100 K and 80 K. A possible reason for the loss in EPR signal is an anti-ferromagnetic phase transition with a Néel temperature between 80 K and 100 K.

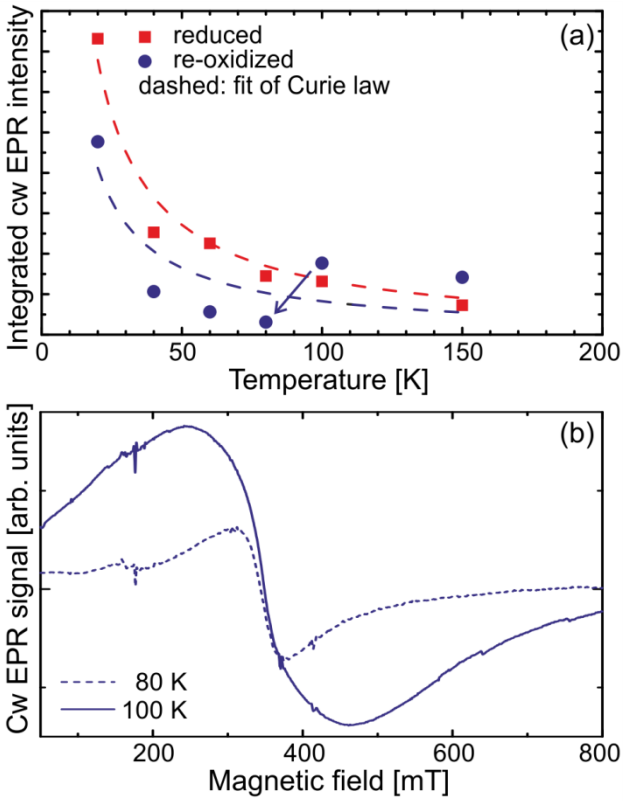

Figure S2. (a) Temperature dependence of the (double) integrated 9.7 GHz cw EPR spectra of the reduced and re-oxidized catalyst, and (b) 9.7 GHz cw EPR spectra of the re-oxidized catalyst at 100 K and 80 K (0.5 mT modulation amplitude, 5 kHz modulation frequency).

References

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3. Sako, S.; Ohshima, K., Antiferromagnetic Transition Temperatur of MnO Ultrafine Particle. *J. Phys. Soc. Jpn.* **1995**, *64*, 944-950.