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Formation of active phases of Fe/C, Cr/C and Fe–Cr/C catalysts in oxidative dehydrogenation of ethane

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The catalysts were synthesized *via* wet impregnation by moisture capacity with aqueous solutions of metal salts. Sibunite© was used as carbon support.[S1] Sibunite granules were previously dehydrated in the furnace at 500 °C for 2 h. Then, the moisture capacity of the material with distilled water was measured dropwise until saturation. The moisture capacity was 1.27 ml g^{-1}. Based on the data obtained, solutions of salts $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich, 99%), $Fe(NO_3)_3 \cdot 9H_2O$ (Acros Organics, 99%) of the required concentrations were prepared. Then Sibunite was impregnated with the relevant solutions to obtain 5% Cr/C, 5% Fe/C and 5% Cr–5% Fe/C oxide catalysts. The catalysts were dried in a furnace at 100 °C for 2 h. The final stage of catalyst synthesis was the thermal decomposition of the deposited salt to oxides at 600 °C in a reaction furnace in a CO_2 flow for 4 h.

Physico-chemical research of the catalysts

The crystallinity and phase composition of the initial and spent catalysts were determined by X-ray powder diffraction. XRD analysis was performed on a DRON-2 diffractometer using CuKα radiation. The goniometer rotation speed was 2° per min; 2θ range was from 5 to 40 degrees. Samples weighing 80 mg were examined.

The microstructure of the catalyst surface was studied by transmission electron microscopy (TEM) on a JEOL-2100F (Japan) electron microscope in light and dark field modes at an accelerating voltage of 200 k*V*. The crystallization regions were identified *via* comparison of the experimental interplane distances with those determined from the reference data (Crystallography Open Database).

The samples were examined by the Foner method *in situ* using a vibration magnetometer. Magnetometric analysis makes it possible to record the formation of ferromagnetic compounds such as iron, magnetite and carbides during the reaction. The method allows for detecting even low stable compounds.

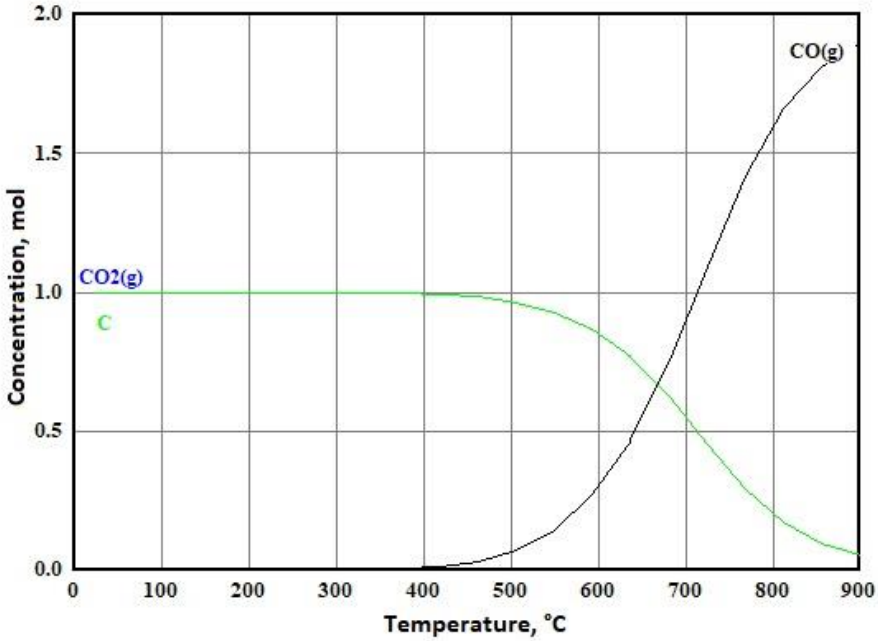

Figure S1 Thermodynamic calculation of the equilibrium concentrations of reagents and products in the Boudoir-Bell reaction: CO2 + C = 2 CO ($\Delta G^0 = 172.82 - 0.1776\,T$ kJ mol^{-1}).

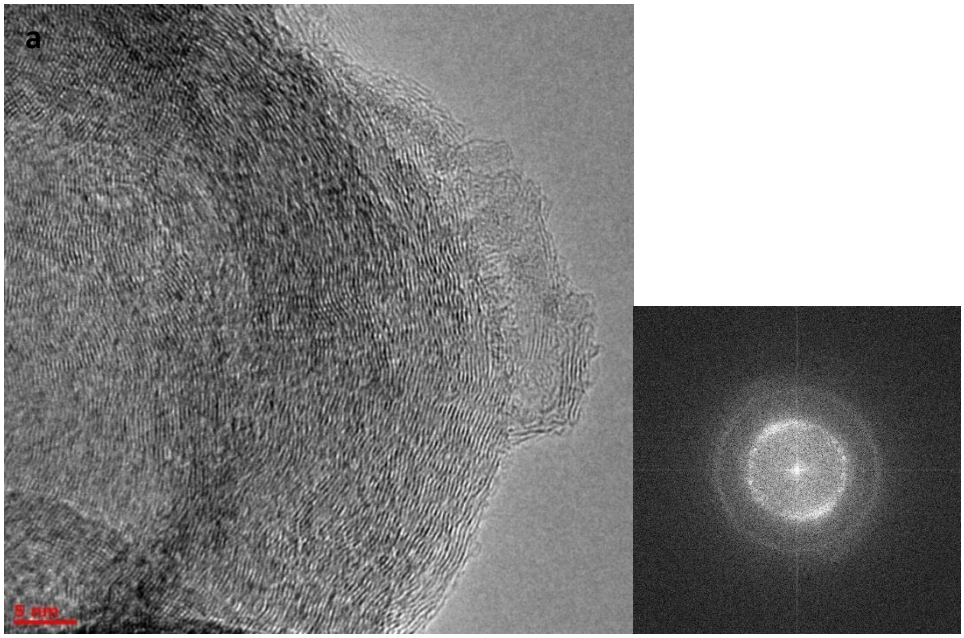

Figure S2 TEM image of Cr/C catalyst surface before the reaction and its Fourier image.

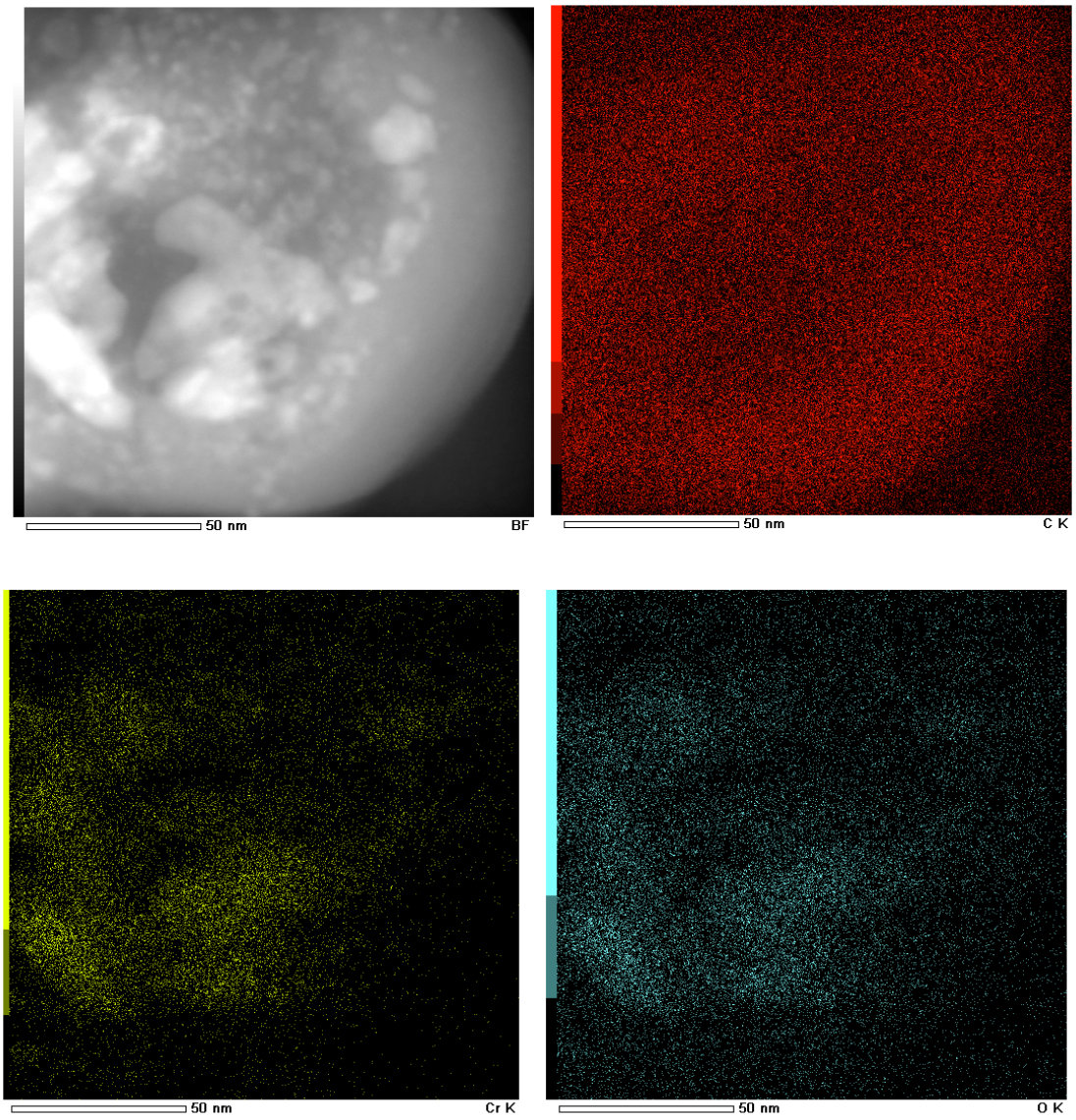

Figure S3 TEM image and EDS mapping for Cr/C catalyst surface after the reaction and its elemental composition.

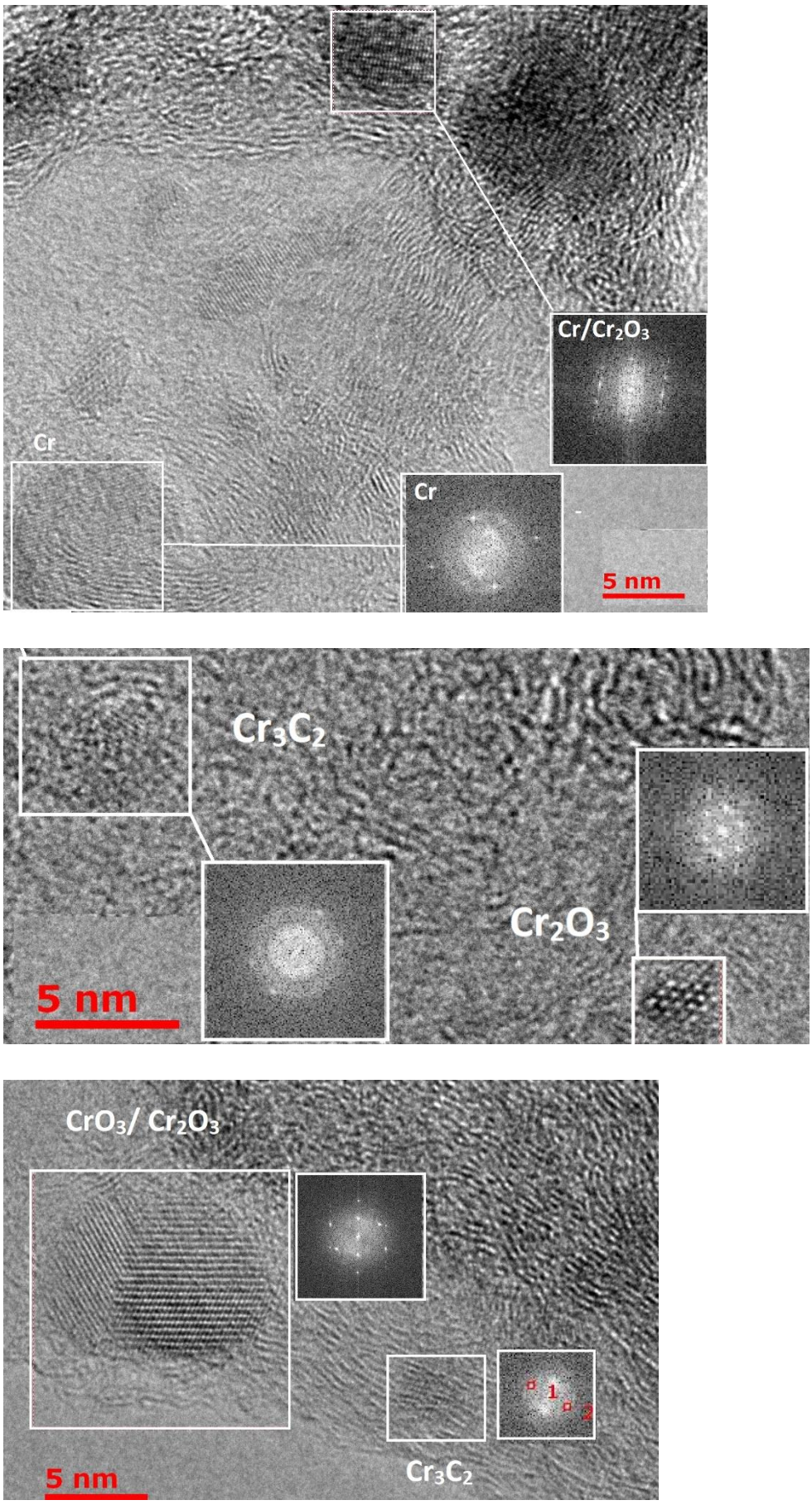

Figure S4 TEM image of Cr/C catalyst surface after the reaction. Fourier images of the highlighted areas, which were used to determine the phase composition, are shown.

References

S1 N. Lebedeva, A. Booij, I. Voropaev, P. Simonov, A. Romanenko and V. Bukhtiyarov, *ECS Transactions,* 2009, **25**, 1909. https://doi.org/10.1149/1.3210746