Synthesis, characterisation and water-gas shift activity of nano-particulate mixed-metal (Al, Ti) cobalt oxides

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Supporting figures

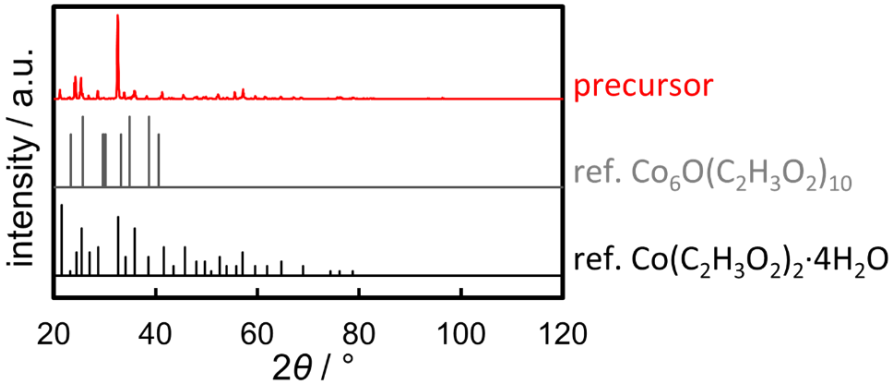

Figure S1 X-ray diffraction pattern of the cobalt precursor and reference patterns of the identified phases cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2{\cdot}4H_2O$) and cobalt oxide acetate ($Co_6O(C_2H_3O_2)_{10}$).

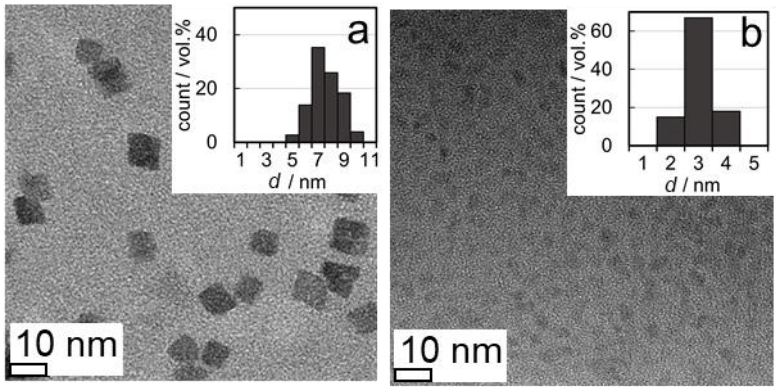

Figure S2 Transmission electron micrographs and volume-based size distributions of the (a) Co_3O_4 and (b) CoO nanoparticles synthesised *via* the benzyl alcohol route according to Wolf *et al.*[1]

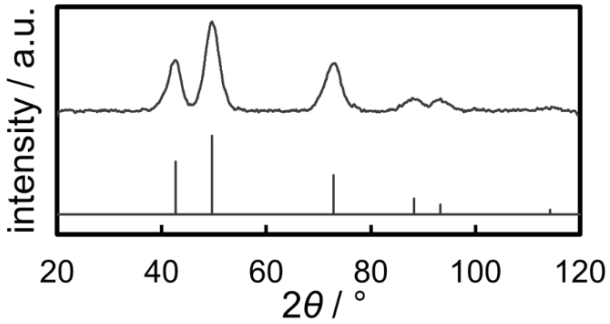

Figure S3 X-ray diffraction pattern of the CoO nanoparticles synthesised *via* the benzyl alcohol route according to Wolf *et al.*[1] with a reference pattern.

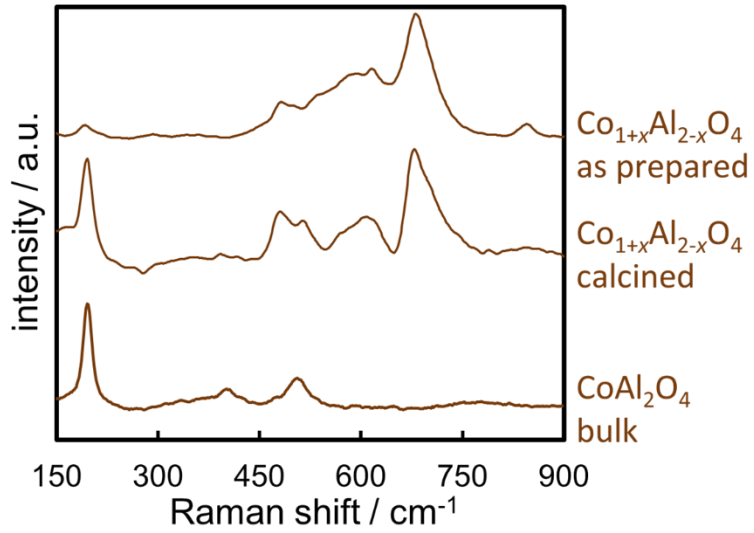

Figure S4 Raman spectra of the nanoparticles synthesised *via* the benzyl alcohol route targeting $CoAl_2O_4$ before and after calcination at 600 °C for 12 h, as well as of a bulk-sized $CoAl_2O_4$ sample with an ideal Co:Al composition of 1:2 synthesised *via* chemical precipitation.

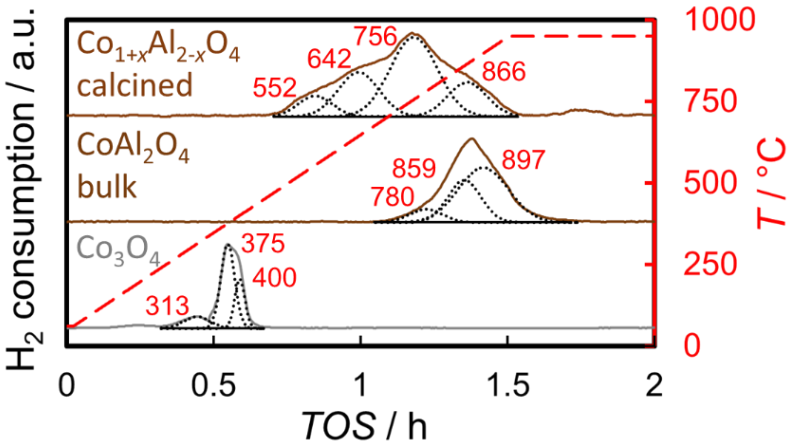

Figure S5 Temperature programmed reduction profiles with deconvoluted peaks of $Co_{1+x}Al_{2-x}O_4$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h, as well as of a bulk-sized $CoAl_2O_4$ sample and nano-sized Co_3O_4 synthesised *via* chemical precipitation and the benzyl alcohol route, respectively.

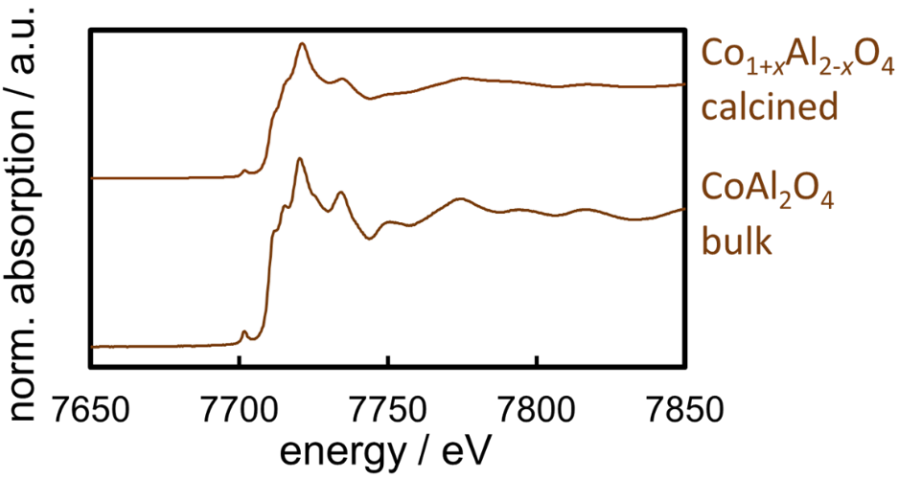

Figure S6 Normalised X-ray absorption near-edge structure spectra of $Co_{1+x}Al_{2-x}O_4$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h, as well as of a bulk-sized $CoAl_2O_4$ sample synthesised *via* chemical precipitation.

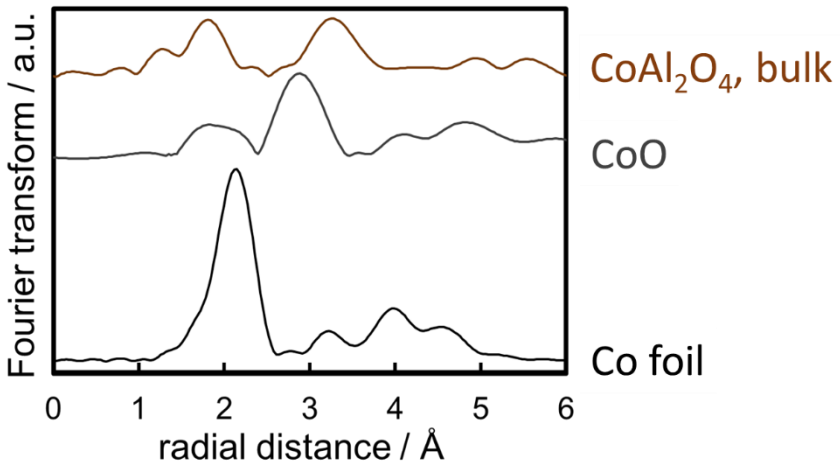

Figure S7 Radial distances as obtained after Fourier transform of extended X-ray absorption fine structure spectra of a bulk-sized $CoAl_2O_4$ sample synthesised *via* chemical precipitation, CoO nanoparticles, and cobalt foil.

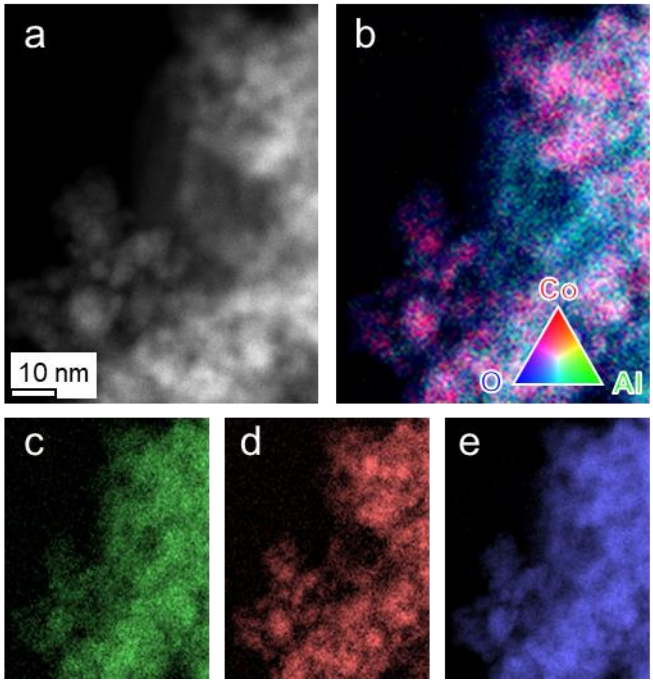

Figure S8 (a) High-resolution high angular annual dark-field scanning transmission electron micrograph of $Co_{1+x}Al_{2-x}O_4$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h with (b) an elemental mapping as obtained *via* electron energy loss spectroscopy and the particular contributions of (c) aluminium, (d) cobalt, and (e) oxygen.

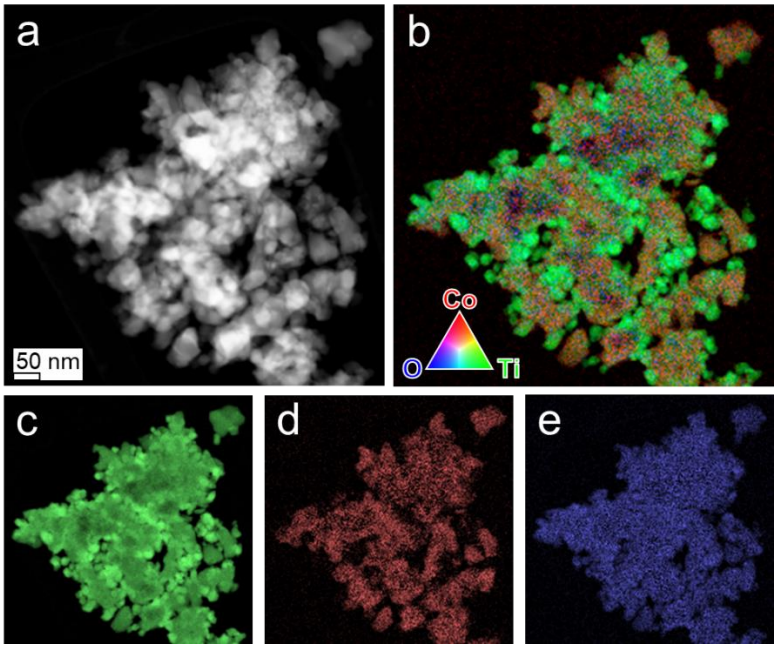

Figure S9 (a) High-resolution high angular annual dark-field scanning transmission electron micrograph of $CoTiO_3$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h with (b) an elemental mapping as obtained *via* electron energy loss spectroscopy and the particular contributions of (c) titanium, (d) cobalt, and (e) oxygen.

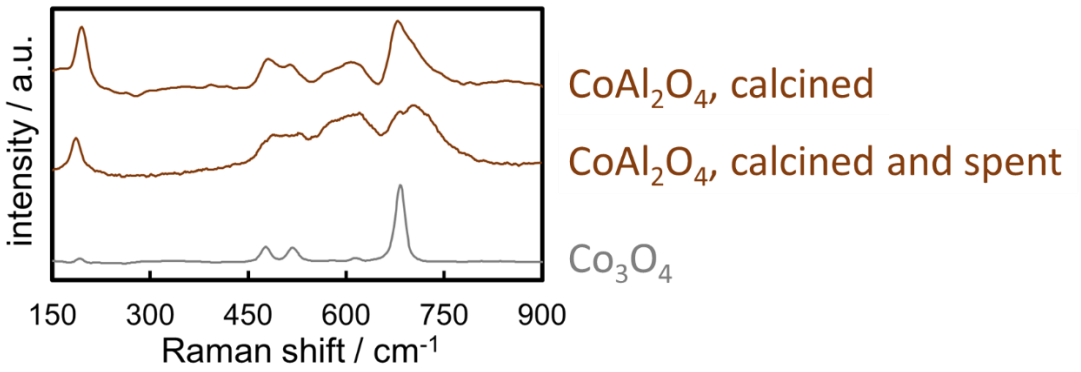

Figure S10 Post-run Raman spectra of the $Co_{1+x}Al_{2-x}O_4$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h after water-gas shift activity measurements with spectra of the calcined sample and nano-sized Co_3O_4 for comparison.

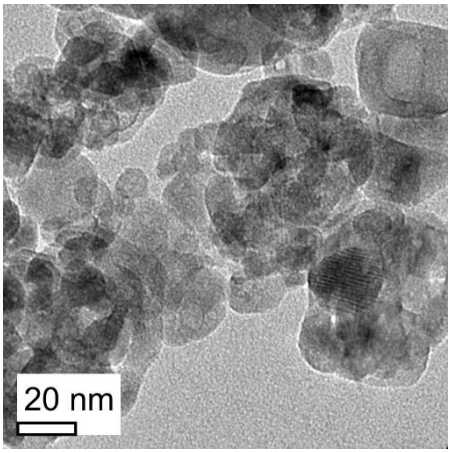

Figure S11 Transmission electron micrograph of commercial anatase-TiO_2.

Supporting tables

Table S1 Analysis of overall consumption of H_2 during TPR of $Co_{1+x}Al_{2-x}O_4$ and $CoTiO_3$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h.

Sample	Expected / mol_{H2} g^{-1}	Measured / mol_{H2} g^{-1}
$Co_{1+x}Al_{2-x}O_4$	0.113	0.145
$CoAl_2O_3$	0.113	0.107
$CoTiO_3$	0.129	0.124

Table S2 Results of peak deconvolution of the H_2 consumption profiles during TPR of $CoTiO_3$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h.

Peak	Temperature / °C	Peak area / %
1	587.1	31.3
2	679.7	68.7

Table S3 Results of peak deconvolution of the H_2 consumption profiles during TPR of $Co_{1+x}Al_{2-x}O_4$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h.

Peak	Temperature / °C	Peak area / %
1	552.3	8.9
2	642.3	23.0
3	755.6	51.3
4	866.1	16.9

Table S4 Results of peak deconvolution of the H_2 consumption profiles during TPR of $Co_{1+x}Al_{2-x}O_4$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h.

Peak	Temperature / °C	Peak area / %
1	780.4	9.6
2	858.6	30.5
3	897.2	59.9

Table S5 Characteristics of the X-ray absorption near edge structure spectra of $Co_{1+x}Al_{2-x}O_4$ and $CoTiO_3$ nanoparticles synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h and a bulk-sized $CoAl_2O_4$ sample.

Sample	Normalised pre-edge intensity	Edge shift / eV	Normalised white line intensity
$Co_{1+x}Al_{2-x}O_4$	0.09	1.0	1.43
$CoAl_2O_4$	0.12	1.1	1.40
$CoTiO_3$	0.06	3.2	1.47

Table S6 Radial distances of metal-metal and metal-oxygen bonds as obtained after phase corrected Fourier transform of extended X-ray absorption fine structure spectra of $Co_{1+x}Al_{2-x}O_4$ and $CoTiO_3$ synthesised *via* the benzyl alcohol route after calcination at 600 °C for 12 h, as well as Co_3O_4 and CoO nanoparticles, Co foil and a bulk-sized $CoAl_2O_4$ sample.

Sample	Co-O	Co-Co	Co-Al/Co	Co-Co/Ti
$Co_{1+x}Al_{2-x}O_4$	1.79	-	3.18	-
$CoAl_2O_4$	1.81	-	3.27	-
$CoTiO_3$	1.91	-	-	2.86
Co_3O_4	1.78	2.77	-	-
CoO	1.84	2.89	-	-
Co foil	-	2.14	-	-

References

1 M. Wolf, N. Fischer and M. Claeys, *Mater. Chem. Phys.*, 2018, **213**, 305–312.