Supporting Information: The Effect of Al-doping on nano-structured ZnO applied as catalyst support

Thermal analysis

Calcination of the co-precipitate was simulated in a TG-DSC experiment in a flow of synthetic air. The thermogram of the Al-containing ZnO sample is shown in Figure S1.

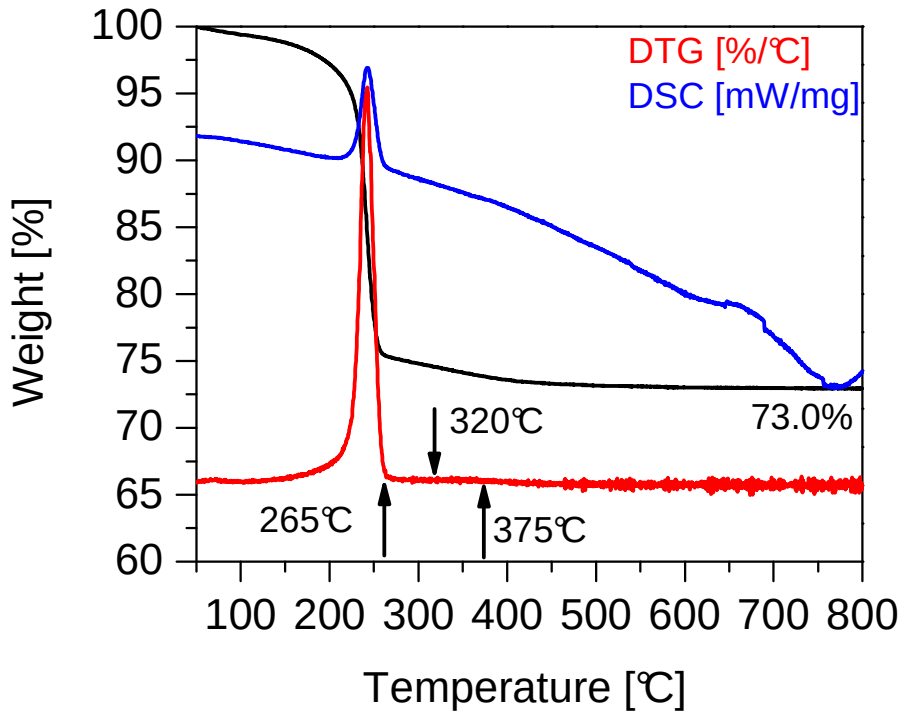

Figure S1: TG-DSC shows a single step endothermic decomposition of the co-precipitate around 250 °C. A further gradual mass loss is detected up to ca. 450 °C.

On basis of the TG curves three different calcination temperatures were chosen: 265 °C, 320 °C and 375 °C. The highest BET surface area of 104 m^2g^{-1} was found for the sample calcined at 320 °C. The decrease of BET surface area at lower calcination temperature (89 m^2g^{-1}) is ascribed to incomplete decomposition of the precursor phase, while the decrease at higher temperature (78 m^2g^{-1}) is due to beginning of particle sintering.

Variation of calcination temperature

Lattice parameters and Al-NMR spectra of the samples obtained from the Al-containing precursor at different calcination temperatures (T_{calc}) are shown in Figures S3 and S4.

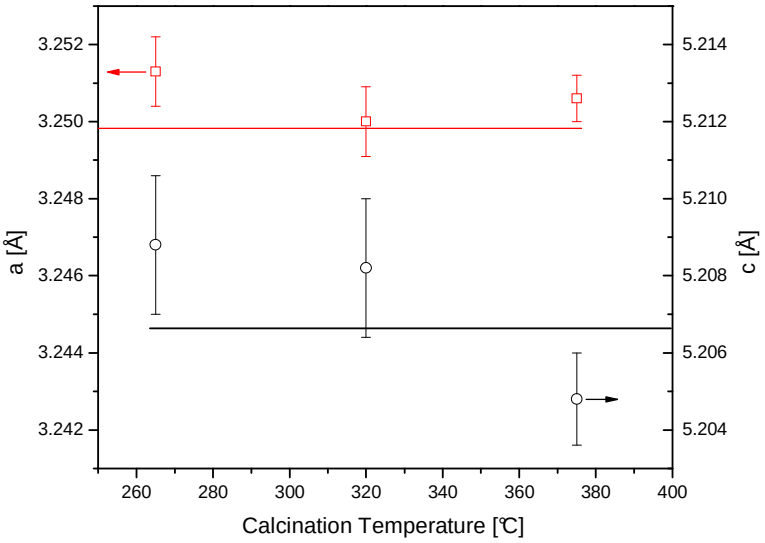

Figure S3: Evolution of the lattice parameters of ZnO (containing 3 % Al) as a function of T_{calc}. Literature values are given as lines (PDF 36-1415). The contraction of the c-axis at higher T_{calc} is ascribed to defect annealing.

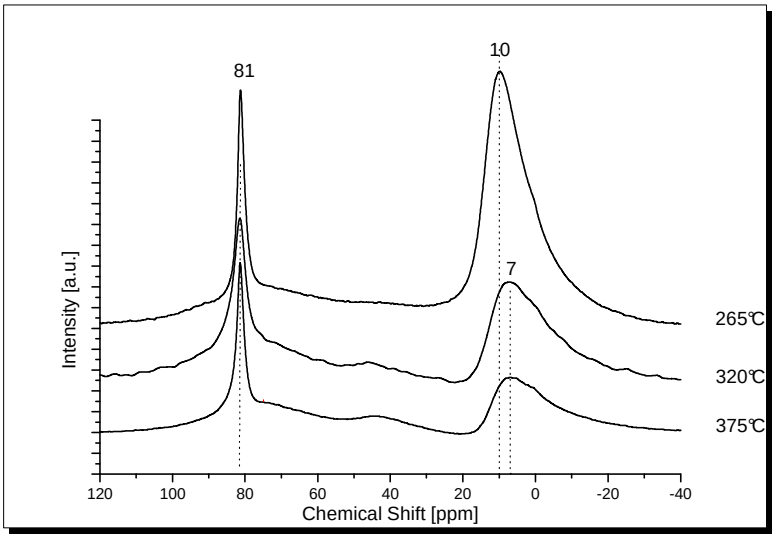

Figure S4: ^{27}Al-MAS-NMR of the ZnO materials (containing 3 % Al) as a function of T_{calc}, see main text for assignment. The decrease of the signal at 10 ppm with T_{calc} supports the idea that it is due to an octahedrally coordinated Al precursor species in the precipitate, which is hard to decompose (cf. gradual mass loss at 265 °C < T < 375 °C in Fig. S1).

Rietveld refinements

The graphical representations of the Rietveld refinements of the pure ZnO and the Al-comtaining material after calcination at 320 °C are shown in Figure S5. Lattice parameters are given in Tab. 1 of the main text. Structural model was taken from literature [PDF 36-1415]. Size/strain analysis resulted in LVol-IB = 14.7(4) nm, e_0 = 0.227(7) and LVol-IB = 9.4(2) nm, e_0 = 0.301(10) for the Zn:Al = 100:0 and Zn:Al = 97:3 sample, respectively.

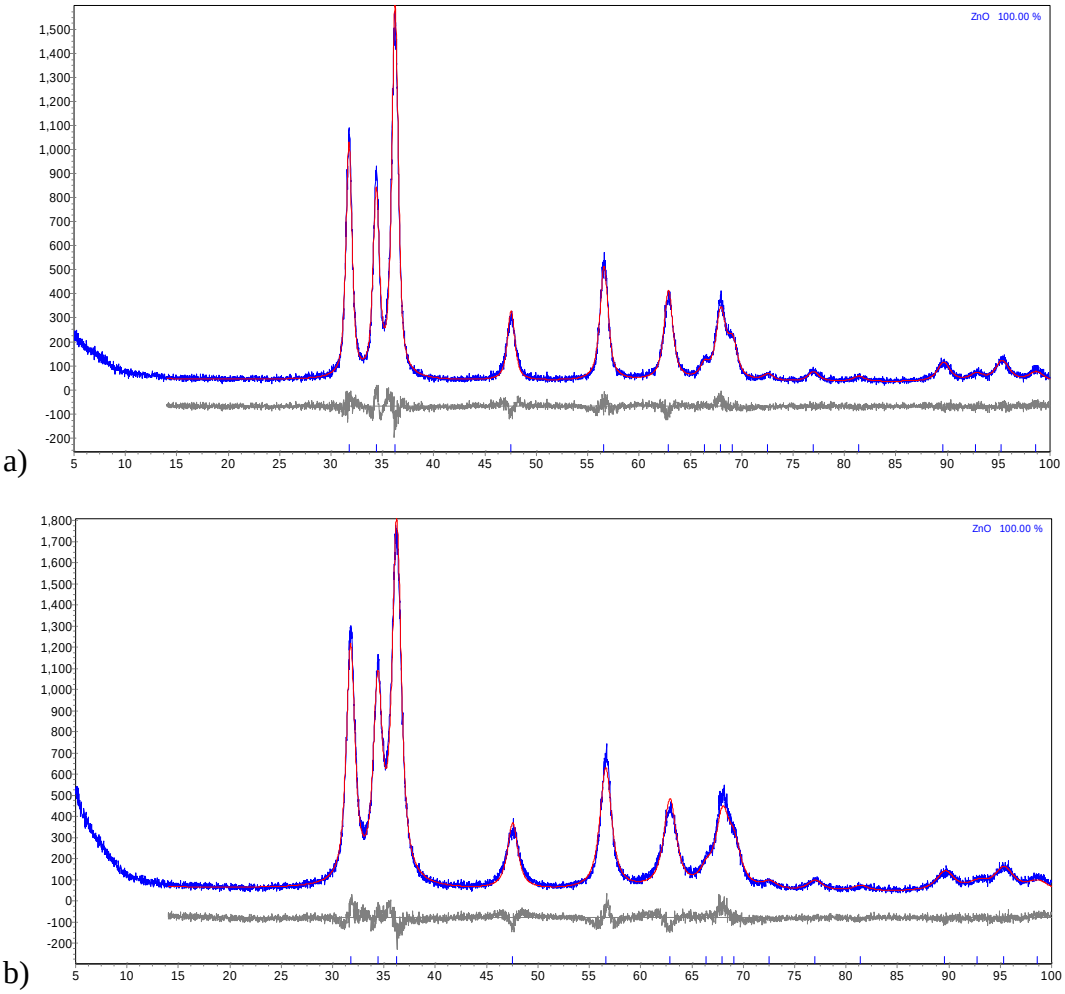

Figure S5: Rietveld plots for the Al-free (a) and 3 % Al-sample (b) – blue line: experimental pattern, red line: calculated pattern, tick marks: positions of Bragg reflections, bottom curve: difference plot

^{27}Al-MAS-NMR after hydrogen treatment

The Al-containing sample was treated in a flow of 2 % H_2 / Ar for 3 and 10 hours. Al-NMR spectra were taken (after contact to air) and are shown in Figure S6.

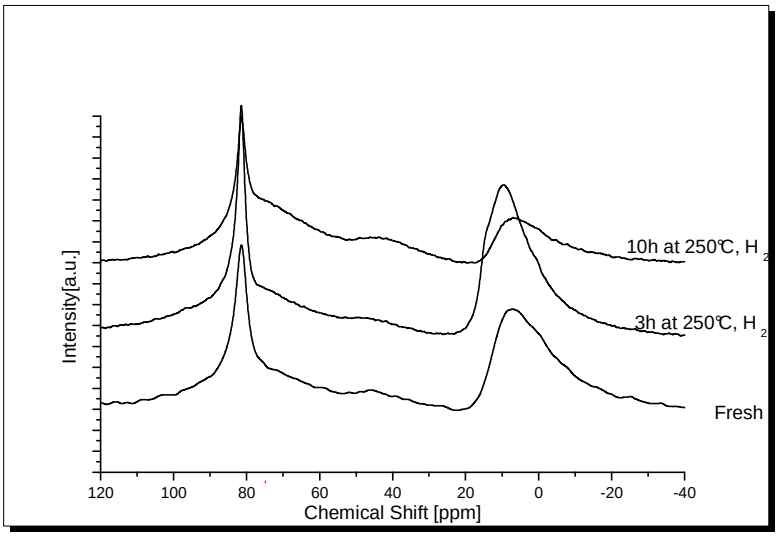

Figure S6: ^{27}Al-MAS-NMR of the ZnO materials (containing 3 % Al) as a function of time on stream in hydrogen, see main text for assignment. The relative increase of the intensity between the two main signal suggest the formation of unsaturated penta-coodinated Al species at the surface in agreement with the surface migration of Al detected by other methods (see main text).