Synthesis of Nitriles from Amines using Nanoscale Co₃O₄-based Catalysts *via* Sustainable Aerobic Oxidation

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<u>1. Procedure for the preparation of the Co₃O₄/NGr@C -catalyst</u>

Unless specified, all amines and chemicals used for the preparation of catalysts are commercially available. $Co(OAc)_2.4H_2O$, 1,10-phenanthroline were purchased from SIGMA-ALDRICH. The vulcan XC72R was purchased form Cabot Limited. The pyrolsis experiments were carried out in CenturionTM Neytech Qex Vacuum Furnace. The tyipcal procedure for the preparation of the active catalyst is described as follows: A mixture of $Co(OAc)_2.4H_2O$ (corresponds to 3 wt% Co) and 1,10-phenanthroline (Co:phenanthroline = 1:2 mole ratio) in ethanol was stirred for 20-30 minutes at room temperature. Then, vulcan XC72R carbon powder was added and the whole reaction mixture was stirred at 60 °C for 5-6 hours. The reaction mixture was cooled to room temperature and ethanol was removed slowely under vacuum. The remaining solid sample obtained was dried at 60 °C for 12 hours. The dried sample was grinded to a powder. Then, the grinded powder was pyrolyzed at 800 °C for 2 hours in argon atmosphere and cooled to room temperature.

Elemental analysis of Co-Phenanthroline/C (Wt%): C = 89.68, H = 0.199, N = 2.70, Co = 3.05.

XPS data of Co-Phenanthroline/C (Atom%): C = 92.38, N = 2.80, Co = 0.61, O = 4.02

2. Characterization of the Co₃O₄/NGr@C-catalyst

2.1. XRD measurements of the Co₃O₄/NGr@C-catalyst: The XRD powder pattern was recorded on a Stoe STADI P diffractometer, equipped with a linear Position Sensitive Detector (PSD) using Cu K α radiation ($\lambda = 1.5406$ Å). Processing and assignment of the powder patterns was done using the software WinXpow (Stoe) and the Powder Diffraction File (PDF) database of the International Centre of Diffraction Data (ICDD). The powder pattern of the catalyst shows two sharp peaks characteristic for metallic Co (Fig. S1) at 2 Θ = 44.16° and 51.42° besides weak reflections at 2 Θ = 36.35°, 36.89°, 42.47 and 61.52°. The peaks at 36.35°, 42.47° and 61.52° confirm the existence of CoO, whereas the peak at 36.89° and the features around 59° 65.5° point to small Co₃O₄ particles just above the detection limit of XRD, which were confirmed by TEM (see below).



Figure S1. XRD powder pattern of the active cobalt catalyst. The PDF (Powder Diffraction Files) numbers are in brackets.

2.2. TEM mesurements and images of the Co₃O₄/NGr@C-catalyst: The TEM measurements were performed at 200kV on a JEM-ARM200F (JEOL) which is aberration corrected by a CESCOR (CEOS) for the STEM applications. The microscope is equipped with a JED-2300 (JEOL) EDXS spectrometer for chemical analysis. The HAADF imaging was performed with spotsize 6c and a 40um condenser aperture. The sample was deposited on a holey carbon supported grid mesh 300 and transferred to the microscope. To image the full size spectra of Co₃O₄ particles, High Angle Annular Dark Field (HAADF) at a Cs corrected microscope was used. With a conventional TEM it was not possible to image the smallest particles due to the weak contrast. As shown in Figures S2, in the catalyst contains mainly small particles of 2-10 nm in size. By EDXS analysis, cobalt along with oxygen was detected in such particles (Fig. S2), suggesting that they consist of CoO and/or Co₃O₄. This agrees very well with the XRD pattern showing only very weak signals of CoO and Co_3O_4 (Fig. S1). Due to their small size, such particles are hardly visible by XRD. Besides the small particles shown in Fig. S2 and S3, there are also a few larger particles and agglomerates in a range of 20-80 nm and occasionally even larger structures up to 800 nm. As an example, one of these structures is shown in Fig. S4. EDXS mapping shows clearly that Co is concentrated in the core of such particles, while oxygen is enriched in the shell. Thus, those larger particles might consist of a Co core and a CoO and/or Co_3O_4 shell. In the XRD pattern (Fig. S1) these particles, though much less abundant than the small particles shown in Fig. S2, give rise to the sharp reflections for metallic Co. This is due to their much larger size and higher crystallinity.



Figure S2-STEM-HAADF of Co₃O₄-NGr@C-catalyst



Figure. S3. EDX analysis (right) of the particle indicated in the left plot. 7.00 8.00 9.00 10.00

JuKa

oKa

keV

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Figure S4. Micrograph and elemental mapping (green: Co; red: oxygen; blue: carbon (from the grid)

2.3. XPS data of the Co₃O₄/NGr@C-catalyst: To obtain further insight into the structure of the catalyst surface and especially into the role of nitrogen coming from the organic ligand, XPS investigations of N and Co species were carried out. Interestingly, three distinct peaks are observed in the N1s spectra of the Co₃O₄/NGr@C-catalyst with an electron binding energy of 399.0 eV, 400.8 eV and 402.3 eV (Figure S5). The lowest binding energy peak can be attributed to pyridine-type nitrogen, which is bound to a metal ion.^{S1} The electron binding energy of 400.8 eV is characteristic for pyrrole-type nitrogen contributing two electrons to the carbon matrix. It is bound to a hydrogen atom. Such types of nitrogen are found after the carbonization of nitrogen-containing organic materials.^{S2} Finally, the small peak at 402.3 eV is typical for ammonium species like NH₄⁺ or R-NH₃⁺.^{S3} The ratio between all Co atoms and all N atoms in the near surface region is 1:4.7. Deconvolution reveals that around 64% of all N atoms are bound to the metal ions. In the cobalt region, only peaks characteristic for oxidic Co are found (Fig. S6) with the typical binding energy of 780.4 eV of the Co $2p_{3/2}$ and 795.3 eV of the Co $2p_{1/2}$ electrons are found. Additionally, the satellite peaks at 786.7 eV and 802.8 eV are charecteristic for oxidic Co. This agrees very well with TEM results, which suggest that the very small particles of 2-10 nm are oxidic (in line with XRD) and the bigger particles contain a Co core and a cobalt oxide shell. In the literature^{S4} it is discussed, that CoO on the surface is not stable and therefore oxidized to Co₃O₄. Thus, it can be concluded that the surface of all Co-containing particles in the catalyst consists of Co₃O₄ while CoO and Co (reflected by XRD) might be enriched in the bulk.



Figure S5. N1s spectrum of the catalyst. The different N1s state are labelled: N_{CoN} N bound to Co; N_{pyrrol} : pyrrolic N; N_{amm} : N of ammonium species



Figure S6. Co2p spectrum of the catalyst with the typical

features of Co₃O₄.

2.4. EPR measurements of the catalyst: Besides XRD and TEM, EPR spectroscopy is another suitable method to gain information on the nature of Co containing particles. EPR spectra were recorded in X-band at 80 K and 290 K on a Bruker EMX CW-micro spectrometer equipped with an ER 4119HS-WI high-sensitivity cavity and a variable temperature control unit (microwave power: 6.64 mW, modulation frequency: 100 kHz, modulation amplitude: 1 G). The EPR spectrum of the active catalyst contains a broad signal at g = 2.12 (Fig. S7). The intensity of this signal increases slightly with rising temperature, which is characteristic for antiferromagnetic Co₃O₄ particles. The Neel temperature T_N above which bulk Co₃O₄ becomes paramagnetic is below 40 K.^{S5,S6} Previously it was found that the temperature dependence of the EPR signal intensity reflects very sensitively the onset of anti-ferromagnetic ordering in Co₃O₄ and also in

other antiferromagnetic oxide materials already well above T_N .^{S7} In bulk Co_3O_4 the EPR intensity increased gradually up to 150 K and then remained constant up to 250 K before it started decreasing.^{S6} The observed intensity behaviour in Figure S7 is exactly in line with these previous results.



Figure S7. EPR spectra of the active cobalt catalyst recorded at 88 and 290 K.

The EPR signal at g = 2.12 is superimposed on a second very broad anisotropic signal, the positive lobe of which is cut off at B = 0. This suggests that the magnetic properties are not exactly the same for each particle. The reason may be different particle sizes (see below) and/or replacement of O by N in the coordination of Co (as observed by XPS see below). In contrast to Co_3O_4 , CoO is not expected to contribute to the EPR spectrum since CoO is antiferromagnetic below $T_N \approx 293K^{S8}$ and thus EPR silent. Metallic Co is ferromagnetic up to a Curie temperature of 1120 °C^{S9} and could in principle cause a ferromagnetic resonance signal, the intensity of which does not depend on temperature between 88 and 290 K. Such signal is not seen in Fig. 7 (possibly due to the very low amount of metallic particles in the catalyst as suggested by TEM), however, it cannot be excluded that it contributes to some extend to the background of the EPR spectrum.

3. General procedure for the synthesis of nitriles:

A magnetic stirring bar and the corresponding amine were transferred to a glass vial (7 mL) and then the solvent was added. Next, the catalyst was added followed by addition of aqueous NH₃. Then, the vial was fitted with septum, cap and needle. The reaction vials (8 vials) were placed into a 300 mL autoclave and the autoclave was pressurized with 2-3 bar of oxygen. The autoclave was placed into an aluminium block (placed 30 minutes before counting the reaction time in order to attain reaction temperature) preheated at 120 °C and the reactions were stirred for the required time. During the reaction, the inside temperature of the autoclave was measured to be 110 °C and this temperature was taken as the reaction temperature. After completion of the reaction, the autoclave was cooled to room temperature. The remaining oxygen was discharged and the samples were removed from the autoclave. To the individual vials, 100 μ L n-hexadecane as standard was added and the reaction product was filtered through a

plug of silica and then analyzed by GC and GC-MS. Qualitative and quantitative analysis of all products were made using GC and GC-MS analysis.

Procedure for product isolation. Under similar experimental conditions vide supra, after completion of the reaction, the autoclave was cooled to room temperature and remaining oxygen was discharged. The catalyst from the reaction mixture was filtered off and washed with ethyl acetate. The solvent from the filtrate containing the reaction product was removed in vacuo. The corresponding nitrile was purified by column chromatography (silica; n-hexane-ethyl acetate mixture). All products were analyzed by GC and GC-MS analysis.

4. Procedure for catalyst recycling

The recycling of the catalyst system was carried out for the synthesis of benzonitrile under the same procedure vide supra: 1 mmol benzylamine, 80 mg $Co_3O_4/NGr@C$ (4% Co), 400 µL aq. NH₃, 2-3 bar O₂, 4mL t-amyl alcohol, 110 °C, 15-20h, yields were determined by GC using 100 µL n-hexadecane standard. In each run, after the reaction the catalyst was separated by centrifugation, washed thoroughly with ethyl acetate and dried. Then, the dried catalyst was used further, without any purification or re-activation.

5. References

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