

# CHEMISTRY

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### Supporting Information

#### **Cooperative Catalysis for Selective Alcohol Oxidation with Molecular Oxygen**

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## Experimental details

### General

All chemicals were obtained from commercial sources and were used as is. The following precursor salts were used for impregnation:  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Reverse-osmosis water was used for all aqueous solutions.

### Procedure for catalyst preparation

Nitrogen-doped carbon (NC) has been prepared as described earlier (ref [8] in the manuscript). Carbon and alumina supports were impregnated with metal salt solutions (see below). Because of the large differences in particle size and mixing behaviour, separate impregnation procedures were used for both carbon and alumina. In both cases, the metal concentrations were calculated to provide an equal surface loading (1.32 mmol/g) for each material.

The impregnated catalysts (carbon or  $\text{Al}_2\text{O}_3$ ) were dried in an oven at 75 °C for 16 h followed by temperature-programmed heat-treatment (max 300 °C) under argon. First the sample was heated to 30 °C and kept at this temperature for 45 minutes, making sure the inert atmosphere was intact before heat-treatment. The heating was continued at a rate of 10°C/min to 300°C and kept at this temperature for 60 minutes. Finally, the catalyst was allowed to cool down naturally.

### Procedure for impregnation of nitrogen-doped carbon

Nitrogen-doped carbons (100 mg) were impregnated with aqueous metal solution (0.66M, 0.2 mL) inside a small vial (10 mL) with a screw cap and septum, stirred by a magnetic stirrer. Vacuum was applied through the septum using a 0.8 mm needle. Between the needle and the vacuum line a 0.45  $\mu\text{m}$  PTFE filter was installed to keep any small N:C carbon particles from entering the pump. After impregnation, the filter was weighed showing that in every case less than 0.1 mg catalyst escaped. Under vacuum, the carbon powder was stirred and the stirring rate was adjusted allowing the powder not to rise higher than approximately halfway the jar. A syringe charged with aqueous solution (0.4 mL) was introduced through the septum, automatically ejecting the solution from the syringe. Stirring was continued until a homogeneous appearance was obtained, which took no more than 2 minutes. Then the vacuum was removed by inserting a fresh needle through the septum. The catalyst was stirred for one additional minute after which the impregnated carbon was collected and dried in an oven at 75 °C for 24 hours, followed by the heat treatment described earlier.

### Procedure for impregnation of $\gamma\text{-Al}_2\text{O}_3$

Alumina ( $\gamma\text{-Al}_2\text{O}_3$ , Ketjen) was first ground and sieved (200-400 nm) to obtain a uniform, flowing powder. Batches of sieved alumina (1 gram) were impregnated with aqueous metal solutions (0.5M, 0.367 mL) using vacuum pore impregnation.

### Procedure for oxidation of cinnamyl alcohol

A 75 mL autoclave was loaded with cinnamyl alcohol (134 mg, 1 mmol), octane (0.5 mL, internal standard), ethanol (5 mL), catalyst (either 20 mg carbon or 147 mg alumina) and a stirring bar (30 mm). The autoclaves were sealed, flushed with oxygen twice before applying the final oxygen atmosphere (1 bar). The autoclaves were heated on an oil-bath to 80 °C for 16 h under

continuous magnetic stirring at 200 rpm. After reaction, the mixtures were filtered using 0.45  $\mu\text{m}$  PTFE syringe filters and analysed by GC.

### Characterization procedures

Gas chromatography (GC) analysis was performed on an Agilent 7820A instrument equipped with a flame ionization detector (FID), autosampler (G4513A) and a 30 m  $\times$  0.32 mm internal diameter VB-1 fused silica capillary column.

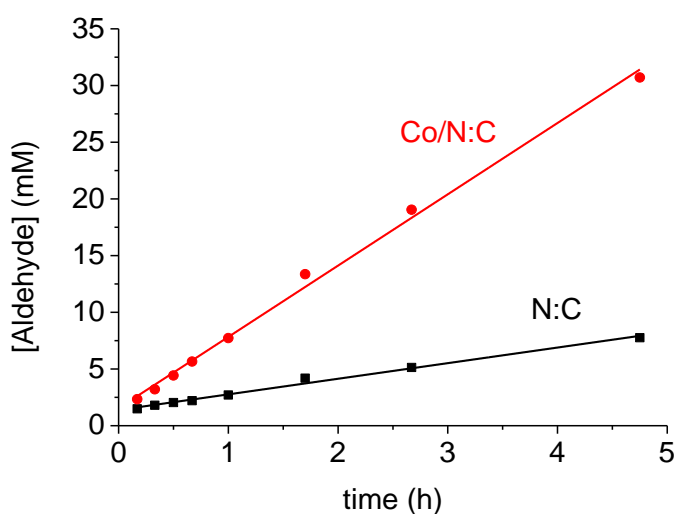
GC-MS analysis was performed using a Agilent 6890, Agilent 5973 Network Mass Elective Detector system, equipped with a 30 m  $\times$  0.25 mm i.d. Restex RTX® - 5 Amine fused silica capillary column, coated with Crossbond® 5 %/ diphenyl 95 % demethylpolysiloxane at 0.25  $\mu\text{m}$  film thickness.

X-Ray diffraction (XRD) patterns were obtained with a MiniFlex II diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. The X-ray tube was operated at 30 kV and 15 mA, with a  $0.01^\circ$  step and 1 s dwell time. The microstructure of the powders was examined by SEM/EDX on a Verios-460 microscope (FEI) using an accelerating voltage of either 5 or 10 kV. Working distance 2-5 mm.

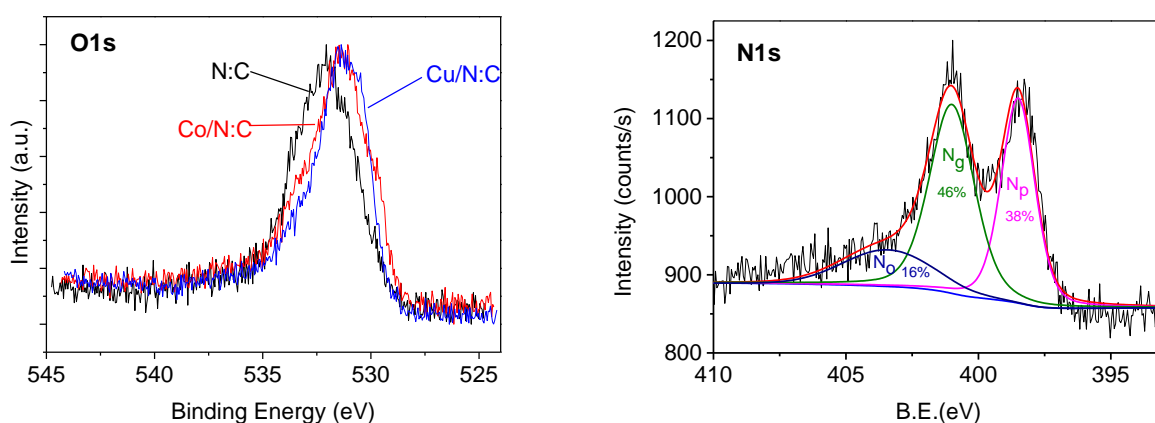
X-Ray Photoelectron Spectroscopy (XPS) measurements were carried out using a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany). Analysis was performed using a monochromatic Al  $\text{K}\alpha$  X-ray source of 24.8 W power with a beam size of 100  $\mu\text{m}$ . The spherical capacitor energy analyser was set at  $45^\circ$  take-off angle with respect to the sample surface. The pass energy was 46.95 eV yielding a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak. Peaks were calibrated with respect to the C-1s peak.

Procedure for Temperature programmed reduction (TPR) studies. Examples: Co/N:C catalysts: 25 mg of sample is placed on a quartz wool plug in a 4 mm i.d. quartz reactor. After purging with nitrogen, a flow of 5% hydrogen in nitrogen mixture was applied, the system is allowed to equilibrate after which the sample is heated with a  $5^\circ\text{C min}^{-1}$  heating rate to  $800^\circ\text{C}$  (no hold time).

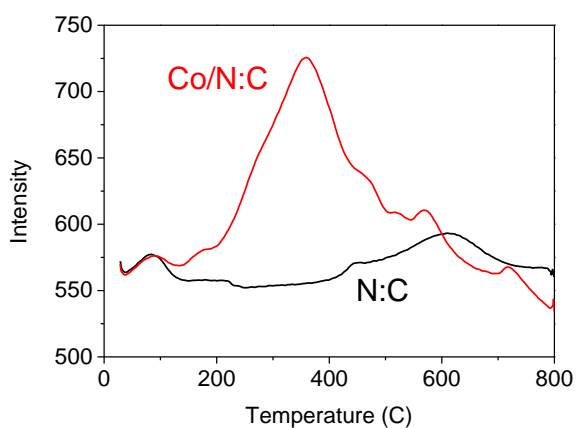
## Additional Tables and Figures



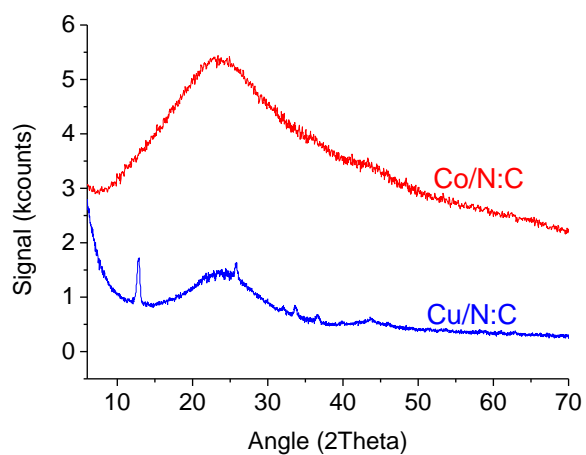
**Figure S1:** Initial rates for Co/N:C (red) and N:C (black)



**Figure S2:** X-ray photoelectron spectra for (a) O1s region in Co/N:C (red), Cu/N:C (blue) and N:C (black), and for (b) N1s region in N:C, fitted with typical pyridinic (N<sub>p</sub>), graphitic (N<sub>g</sub>) and oxidized (N<sub>o</sub>) nitrogen peaks.



**Figure S3:** Temperature programmed reduction (TPR) spectrum for Co/N:C (red) and N:C (black).



**Figure S4:** XRD data for Co/N:C (red) and Cu/N:C (blue)

**Table S1:** XPS-based atomic compositions of samples investigated in this work

Entry	Sample	C1s	N1s	O1s	Co2p	Cu2p
1	N:C	88.39	7.59	4.03	-	-
2	Co/N:C	85.31	7.31	5.99	1.38	-
3	Co/C <sub>undoped</sub>	87.82	1.80	8.06	2.31	-
4	Co/C <sub>comm</sub>	83.66	1.95	13.06	1.33	-
5	Cu/N:C	84.79	7.50	5.89	-	1.82
6	Cu/C <sub>undoped</sub>	89.75	1.14	6.97	-	2.14
7	Cu/C <sub>comm</sub>	83.82	3.51	11.79	-	0.88