

## Superior CNT-supported bimetallic RuCu catalyst for the highly selective hydrogenolysis of glycerol to 1,2-propanediol

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## Supporting Information

### Carbon-Nano-Tubes (CNT)

The used CNT are commercially available MWCNT NC7000 by Nanocyl SA., Belgium. The CNTs were used without further treatment as received for all functionalization steps. The following properties have been determined for the catalyst support: The surface area according to BET characterization is 210 m<sup>2</sup>/g, the average diameter is 12 ±3 nm with a length of 0.1-10 µm having cylindrical shape. The overall composition determined by EDX is in wt% is C(92.15), O(5.96), Al(1.81), Si(0.08). The total amount of impurities determined by TGA was around 10 wt%. The TGA residues were analysed by SEM-EDX to show a composition of O (50 wt%), Al(40 wt%), Fe(2 wt%), C(8 wt%), Co(2 wt%).<sup>2</sup>

### Synthesis of Catalysts

The catalysts were synthesized using an improved version of the wet impregnation method described by Y. Yuan *et al.*<sup>1</sup> The CNTs (3.80 g) were suspended in water (500-750 mL) and aqueous solutions of the metal precursors (RuCl<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, or Cu(NO<sub>3</sub>)<sub>2</sub> respectively) were added. The overall metal loading was kept constant at 5 wt-%, the atomic ratio of the metals was varied accordingly. After mixing for 4 hours in a rotary evaporator with 100 rpm under a reduced pressure of 800 mbar, the solvent was removed under reduced pressure (200 mbar, 80 °C at 100 rpm). The material was then dried at 110 °C for 12 hours and calcined at 400 °C for 4 hours.

## Description of catalyst characterisation techniques

### **Determination of elemental composition via ICP-OES**

Inductive-coupled plasma (ICP-OES) analysis was carried out on a Perkin Elmer Optima 8300 DV at the central analytics department of TUHH (working group Dr. rer. nat. Elfers). 10 mg of the samples were dissolved in nitric acid and hydrochloric acid in a mixing ratio of 1 :3 (aqua regia) followed by threatening for 1.5 h at 260°C. For determining the concentration, the following wavelengths have been used: 238,204 nm (Fe), 327,393 nm (Cu), 240,272 (Ru).

### **Powder X-Ray Diffraction Measurements (PXRD)**

Powder X-Ray Diffraction Measurements (PXRD) were performed by the X-Ray Service Facility of the University Hamburg, using a X'Pert Pro MPD diffractometer from PANalytical with a theta-theta/Bragg-Brentano geometry and a Cu X-ray source.

### **Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) and elemental mapping via STEM-EDX characterization were performed using a FEI Talos F200X with acceleration voltage of 200 kV at BeEM, TUHH. Samples were prepared by pulsed ultrasonic dispersion for 30 s at 30 % amplitude in Hexane with a Bandelin Sonopuls (200 W, KE 76 cone tip). Drops of the dispersion were deposited on a Lacey carbon film gold grid.

### **Determination of the surface area according to the Brunauer-Emmett-Teller (BET) Method**

The determination of the specific surface area of all catalysts were carried out by N<sub>2</sub>-physisorption at 77.3 °K on a Quantachrome instrument, model Quadrasorb SI. Before the measurement, the samples were pre-treated and outgassed in a vacuum at 473 °K for 12 h.

### **CO-Chemisorption**

The metal dispersion of (Ru, Cu, Fe) and an average metal particle diameter of each catalyst were measured by CO-pulse-chemisorption on an Autochem II 2920 instrument from Micromeritics.

### **H<sub>2</sub>-Temperature Programmed Reduction (TPR)**

H<sub>2</sub>-TPR was measured with an Autosorb IQ instrument from Anton Parr. For a typical measurements 80-90 mg of the sample was pretreated in nitrogen (300°C for 30 min) and then cooled down to room temperature. A mixture von 10% H<sub>2</sub> in Nitrogen was employed at a flow rate of 60 ml/min and a heating rate of 10 K/min to 900°C. TCD monitored the H<sub>2</sub> consumption.

## Experimental Details of Catalyst Testing

### Description of the experimental procedure

Hydrogenolysis of Glycerol for selective production of 1,2 propanediol was performed in a 10-fold parallel reaction system using 21 mL high-pressure stainless-steel (1.4571) vessels equipped with magnetic stirring. Immediately prior to the reaction, approx. 200 mg of the catalyst were reduced using a mixture of 5 vol% H<sub>2</sub> in N<sub>2</sub> (100 L/h) at 550 °C for 8 hours. For a typical run, each reactor was filled with 10 g of the substrate solution (20 wt% glycerol in water), the pre-reduced catalyst, and a PTFE-coated stirrer bar. The reactor was then closed and placed in a heating block above a magnetic stirrer, and connected to the gas supply.

The reactors were first purged three times with N<sub>2</sub> in order to remove residual air, then pressure tested at 70 bar N<sub>2</sub>, purged again two times with H<sub>2</sub> and eventually filled with approx. 35 bar of H<sub>2</sub> at room temperature. Then the reactors were heated to 200 °C, upon which the pressure reached approx. 50 bar. The stirrer speed was set to 330 rpm during the heating. After reaching the desired reaction temperature (200 °C) the reaction was then started by vigorous stirring at 770 rpm. After 20 hours the stirring was reduced (330 rpm) and the reactors were allowed to cool to room temperature.

### Description of Analytical Methods

Gas samples for analysis by gas chromatography (GC) were taken from the reactors using gas bags. Then the reactors were vented and purged with nitrogen gas (three times) before opening. Subsequently, the catalyst was filtered off and the liquid phase was analysed with high pressure liquid chromatography (HPLC). Additionally, <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured of the liquid phase to confirm the identity of the products.

The analysis of the gaseous by-products was performed using a Varian GC 450-TCD-FID equipped with a Shin Carbon ST column (2 m × 0.75 mm internal diameter) and both a thermal conductivity detector and a flame ionisation detector. The mobile phase used in the GC was Argon (pressure of 5 bar) and the temperature program used for the measurement was: holding at 40 °C for 1.5 min., heating with a rate of 18 °C min.<sup>-1</sup> up to 250 °C, holding at 250 °C for 12 min.

Liquid phase quantitative analysis was carried out using a HPLC system from SHIMADZU equipped with Aminex HPX-87H 300 mm × 7.8 mm BIORAD Column and a refractive index detector. The eluent for the measurements was 5 mmol of an aqueous sulfuric acid solution.

NMR Spectra were measured by the Division of NMR Spectroscopy in the Department of Chemistry of the University Hamburg using a Bruker Avance I 400 MHz spectrometer. Samples were prepared by combining 0.8 mL of the reaction solution with 0.1 mL D<sub>2</sub>O.

### Formulas for Calculations

$$\text{Conversion [\%]} = \frac{n(\text{Glycerin initial}) - n(\text{Glycerin after Reaction})}{n(\text{Glycerin initial})} \times 100$$

$$\text{Selectivity [\%]} = \frac{n(\text{Product}) \times \text{Number of C atoms in Product}}{(n(\text{Glycerin initial}) - n(\text{Glycerin after Reaction})) \times 3} \times 100$$

$$\text{Carbon Balance [\%]} = \frac{\sum (n(\text{Product}) \times \text{Number of C atoms in Product})}{n(\text{Glycerin initial}) \times 3} \times 100$$

## Detailed catalyst characterisation

### Powder-XRD diffractograms of synthesized catalysts

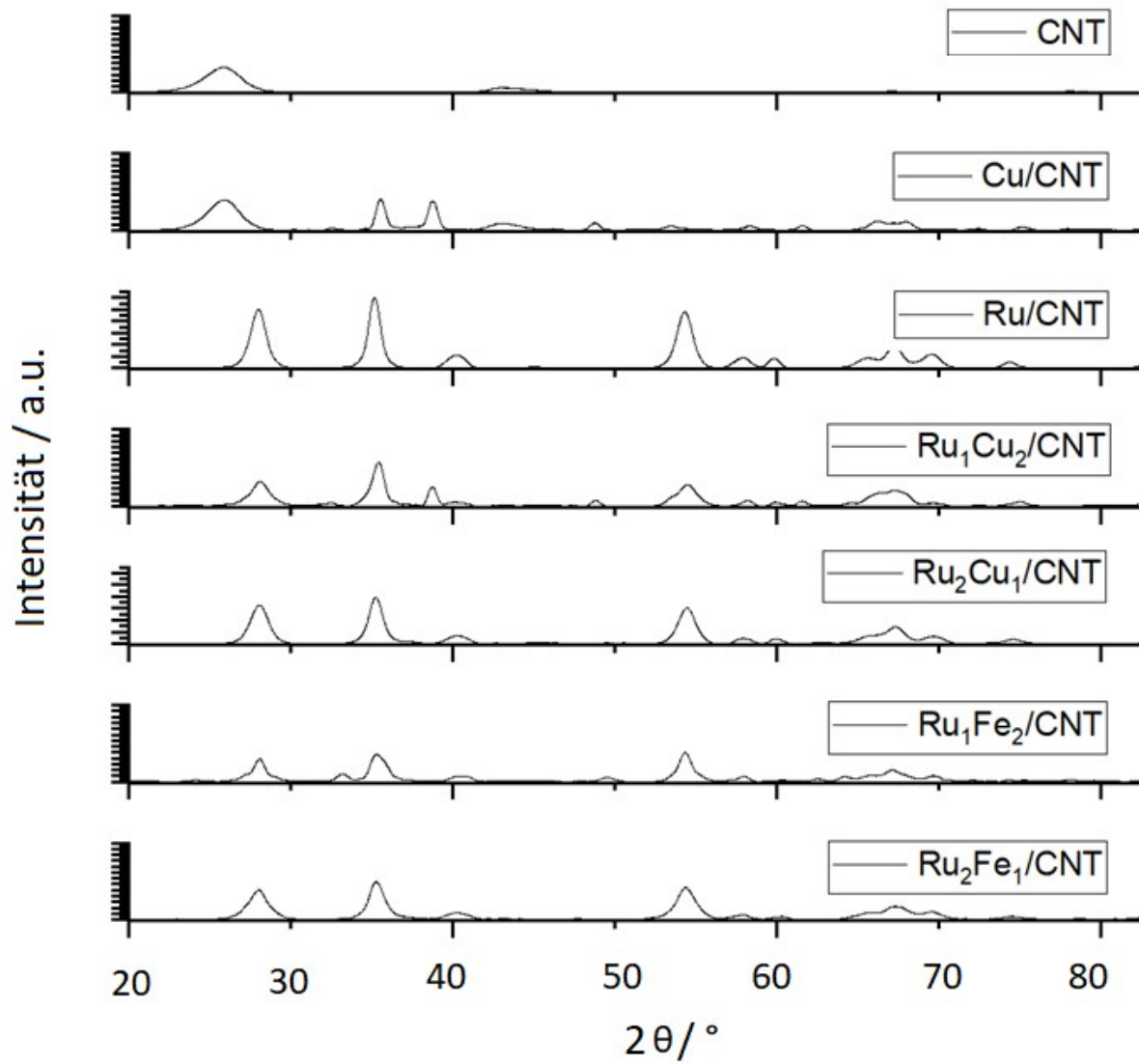


Figure S1: PXRD-diffractograms of all catalysts, measured with Cu-K $\alpha$  radiation, the blue triangle indicates reflexes for graphitic carbon, the yellow square for RuO<sub>2</sub>, the red triangle for CuO and the black square for Fe<sub>2</sub>O<sub>3</sub>

## TEM images and EDX-elemental mapping of various catalysts

CNT:

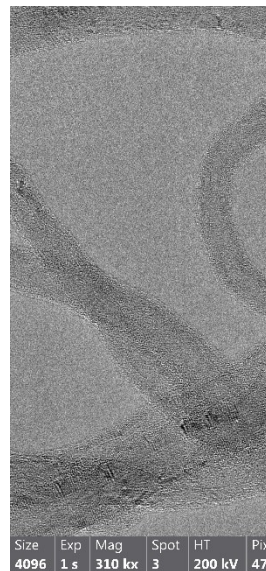
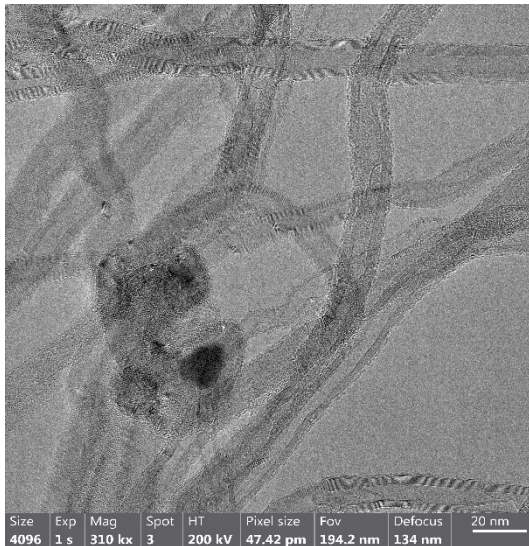
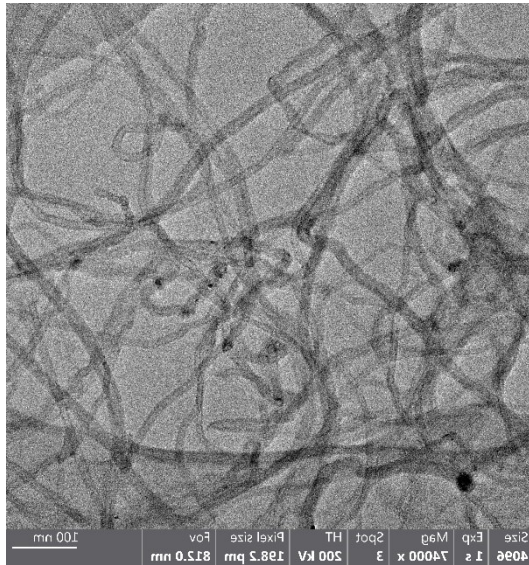


Figure S2: BF-TEM of pure CNT.

Cu/CNT:

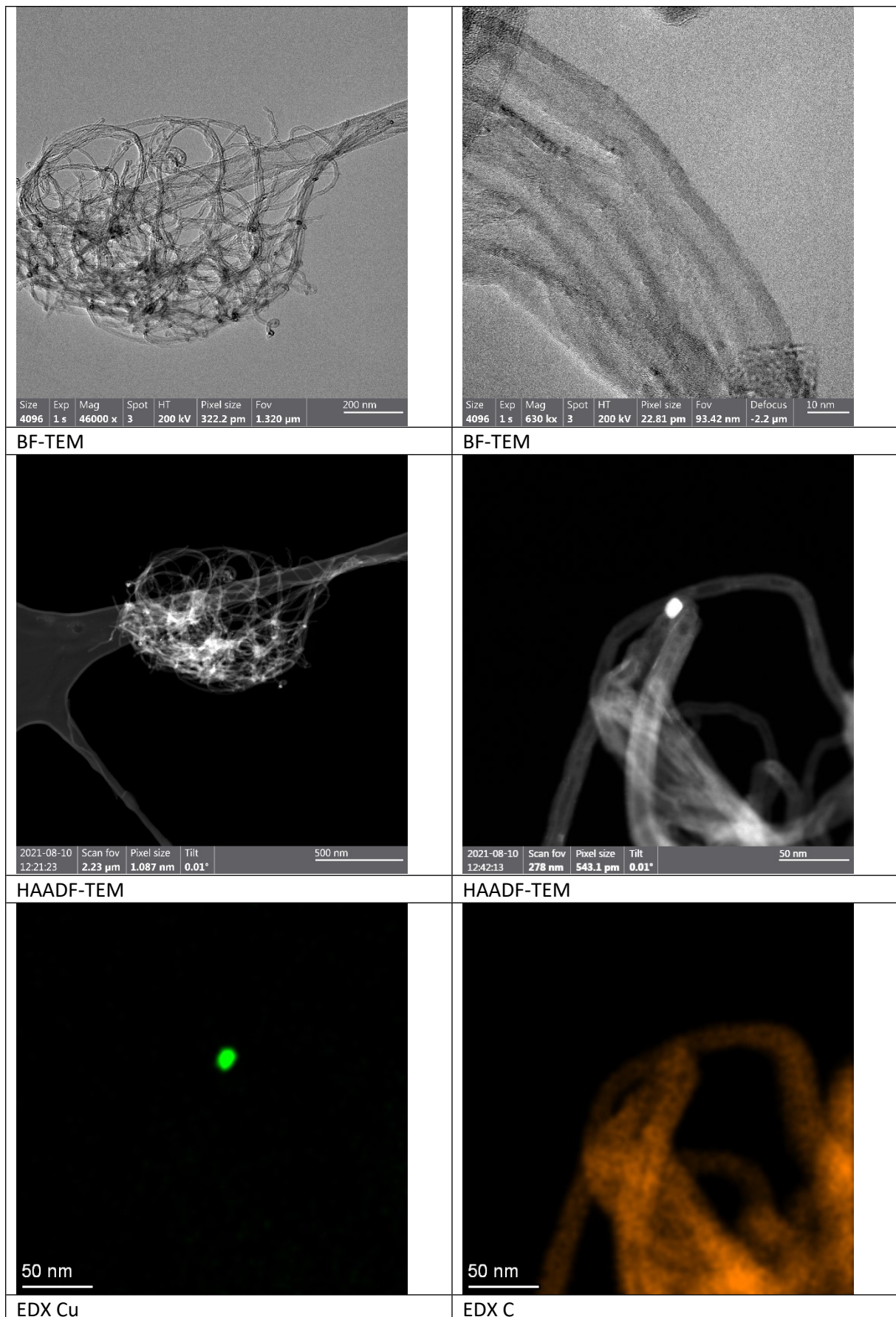


Figure S3: BF-TEM, HAADF-TEM and EDX of Cu/CNT.

Ru/CNT:

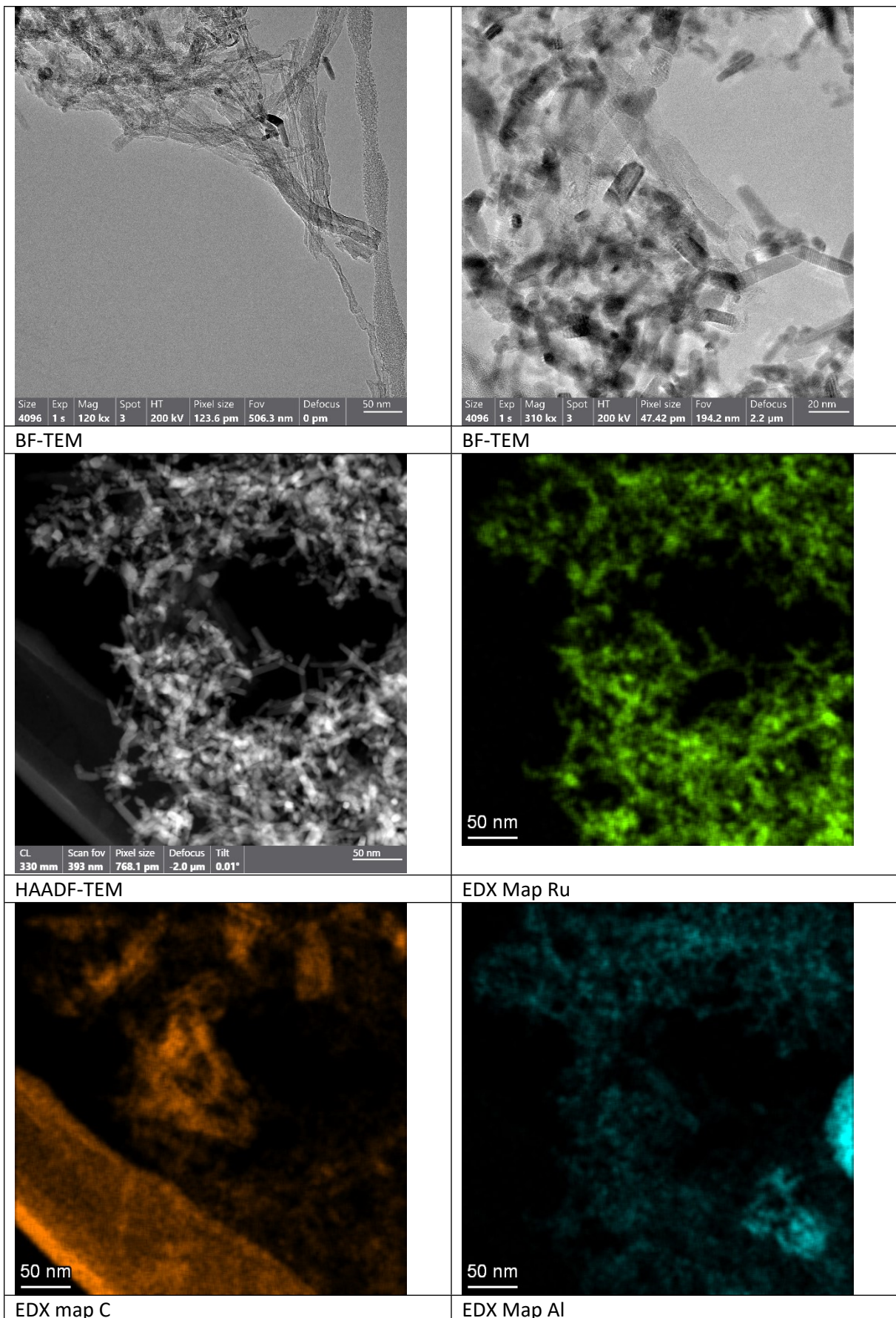


Figure S4: BF-TEM, HAADF-TEM and EDX of Ru/CNT.

Ru<sub>1</sub>Fe<sub>2</sub>/CNT:

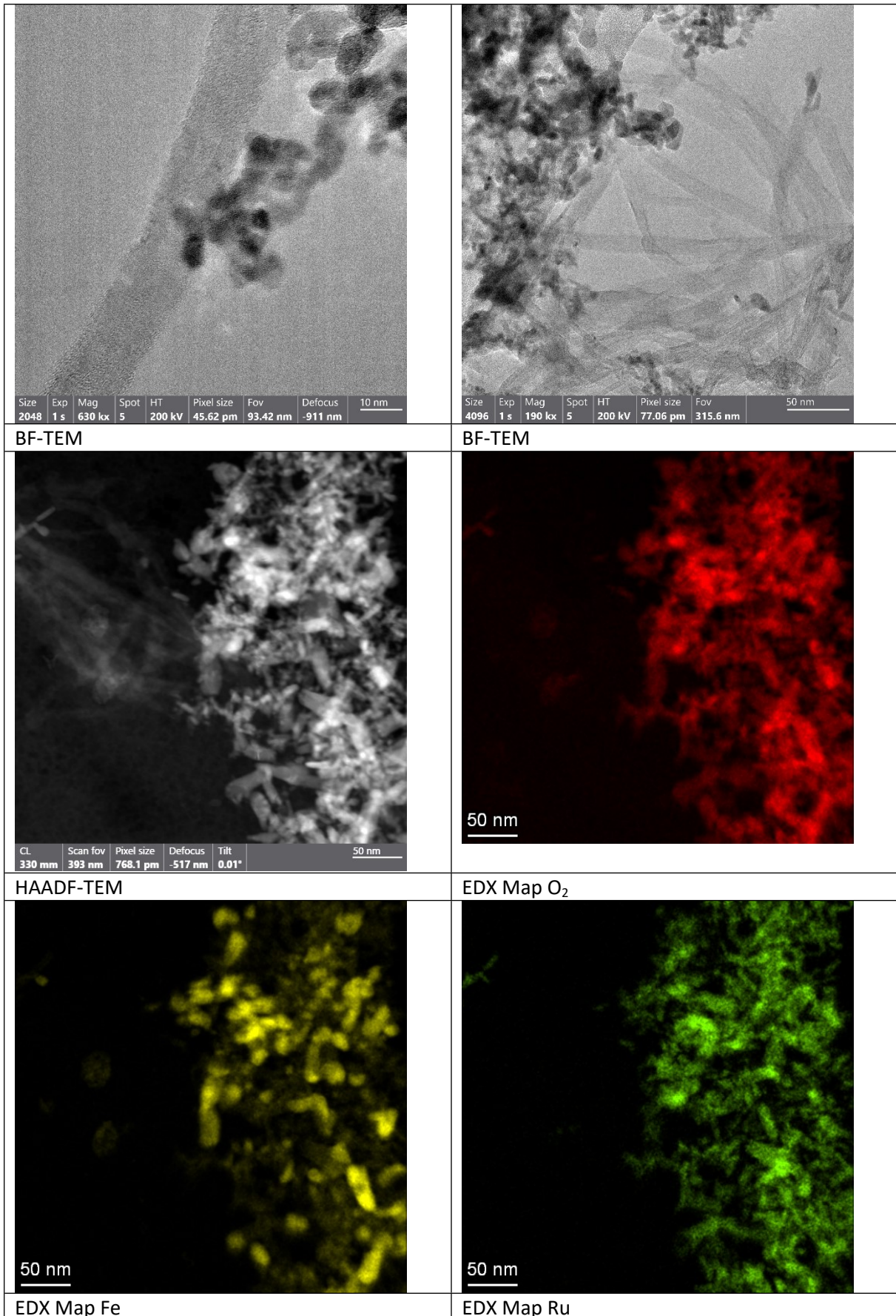


Figure S5: BF-TEM, HAADF-TEM and EDX of Ru<sub>1</sub>Fe<sub>2</sub>/CNT.



## H<sub>2</sub>-TPR profiles of several CNT supported catalysts

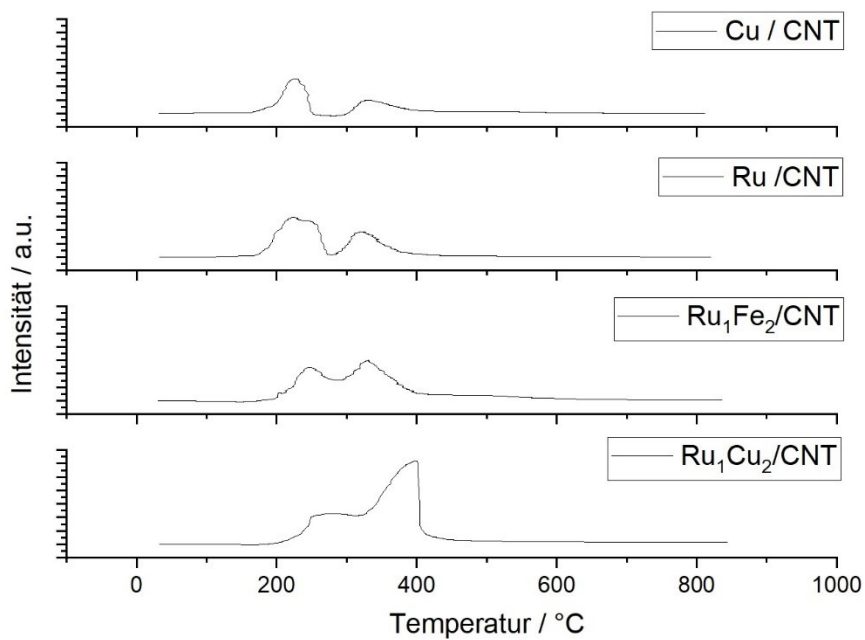


Figure S6: H<sub>2</sub>-TPR profiles of several metal/CNT catalysts.

## Details of ICP-OES elemental analysis

Table S1: Results of ICP-OES elemental analysis.

Analysenmethode	M 02.015	M 02.015	M 02.015	M 02.015	M 02.015
	Fe	Al	Si	Cu	Ru
Probe	g/Kg	g/Kg	g/Kg	g/Kg	g/Kg
CNT rein	3.99	53.4	--	< 1,20	< 1,20
Cu / CNT	13.2	173	--	162	< 1,20
Ru / CNT	13.2	230	--	< 1,20	13.6
Ru1Fe1 / CNT	96.4	246	--	< 1,20	56.2
Ru1Fe2 / CNT	131	245	--	< 1,20	53.3
Ru2Fe1 / CNT	58.6	233	--	< 1,20	44.0
Ru1Cu2 / CNT	18.0	248	--	133	20.4
Ru2Cu1 / CNT	15.8	251	--	44.4	14.8

## References

- 1 B. Li, J. Wang, Y. Yuan, H. Ariga, S. Takakusagi and K. Asakura, *ACS Catal.*, 2011, **1**, 1521–1528.
- 2 H. Meeuw, J. Körbelin, V. Wisniewski, A. Nia, A. Vázquez, M. Lohe, X. Feng, B. Fiedler, *Polymers*, 2019, **11** (2), 231.