Journal Name

ARTICLE

Supplementary information

Carbon supported Ru clusters prepared by pyrolysis of Ru precursor-impregnated biopolymer fibers

Andreas Kalytta-Mewes,[a] Sebastian Spirkl,[a] Sebastian Tränkle,[a] Manuel Hambach [a] and Dirk Volkmer*[a]

[a] *A. Kalytta-Mewes, S. Spirkl, S. Tränkle, M. Hambach, Prof. Dr. D. Volkmer*
Chair of Solid State Chemistry
University of Augsburg, Institute of Physics
Universitätstrasse 1, 86159 Augsburg, Germany
E-mail: dirk.volkmer@physik.uni-augsburg.de

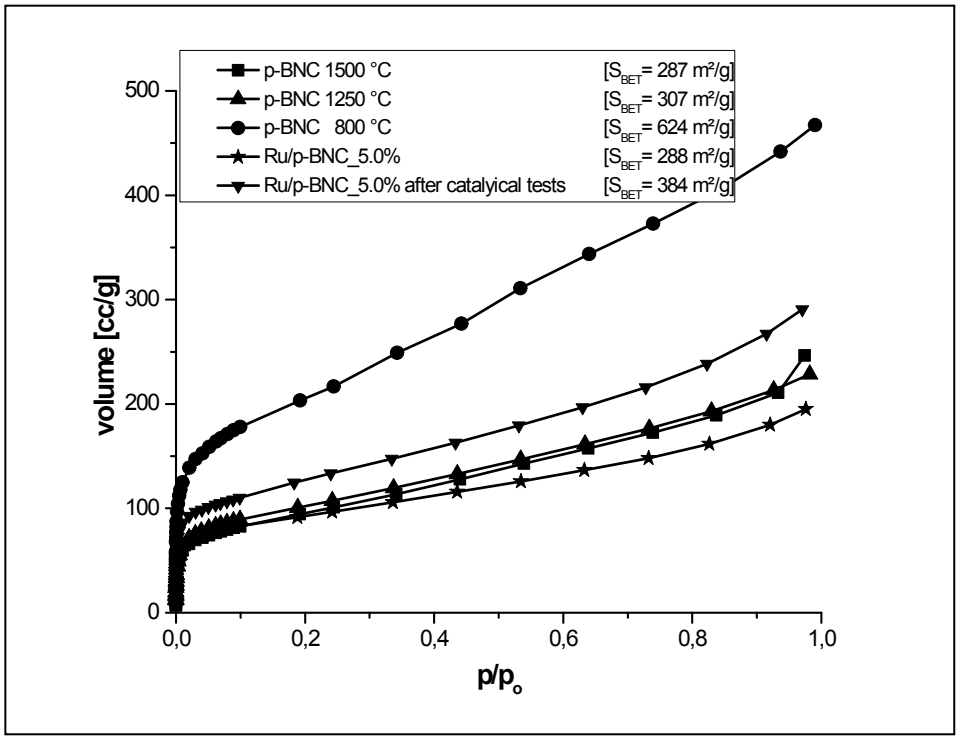

Figure A Adsorption isotherms (Ar, 77K) of BNC pyrolized at 800 °C and 1500 °C under N_2 atmosphere and BNC pyrolized at 1250 °C under Ar atmosphere, in comparison to a sample of Ru/p-BNC_5.0% before and after catalytic tests.

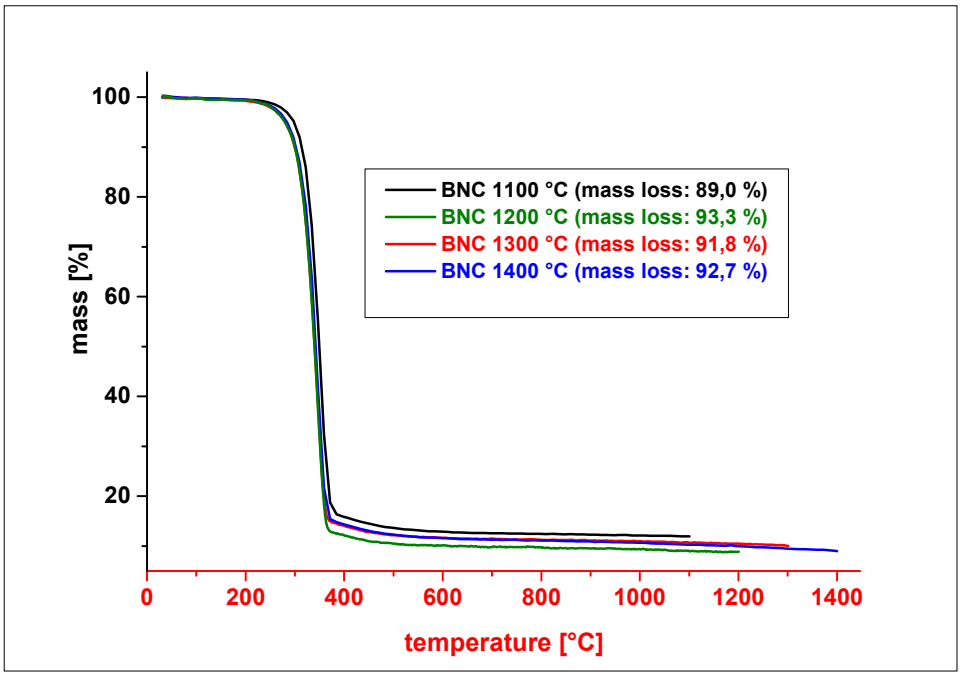

Figure B Thermogravimetric measurements of BNC samples up to different temperatures in Ar atmosphere. The end temperatures are stepwisely increased at 100 °C steps from 1100 °C to 1400 °C.

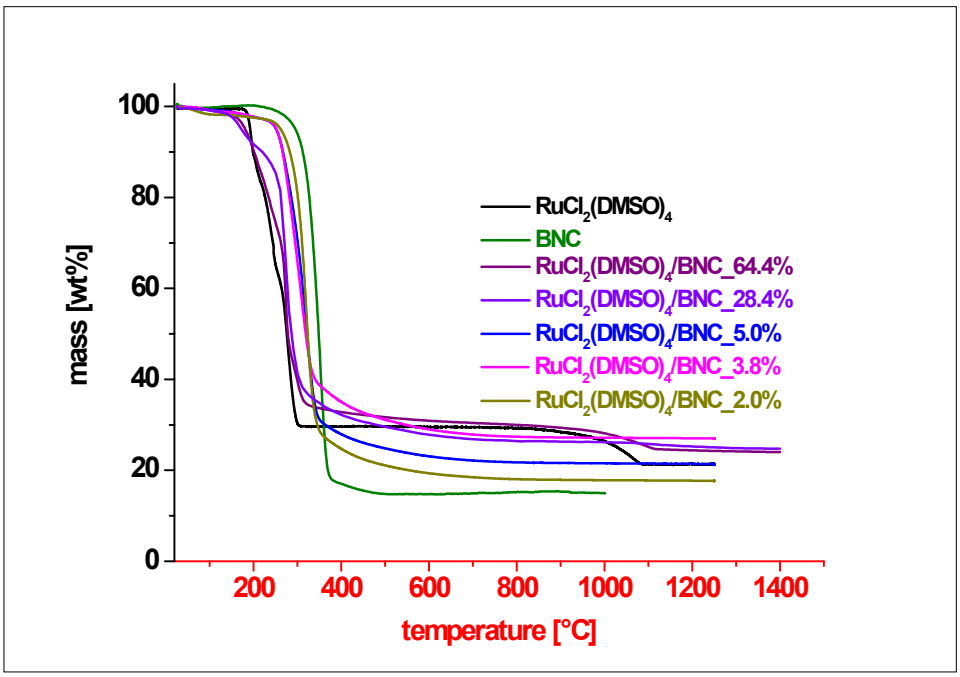

Figure C Thermogravimetric measurements of $RuCl_2(DMSO)_4$/BNC_2.0% - 64.4% in comparison to BNC and $RuCl_2(DMSO)_4$ under Ar atmosphere. Higher concentration of the Ru-precursor shifts the decomposition onset temperature to lower temperatures.

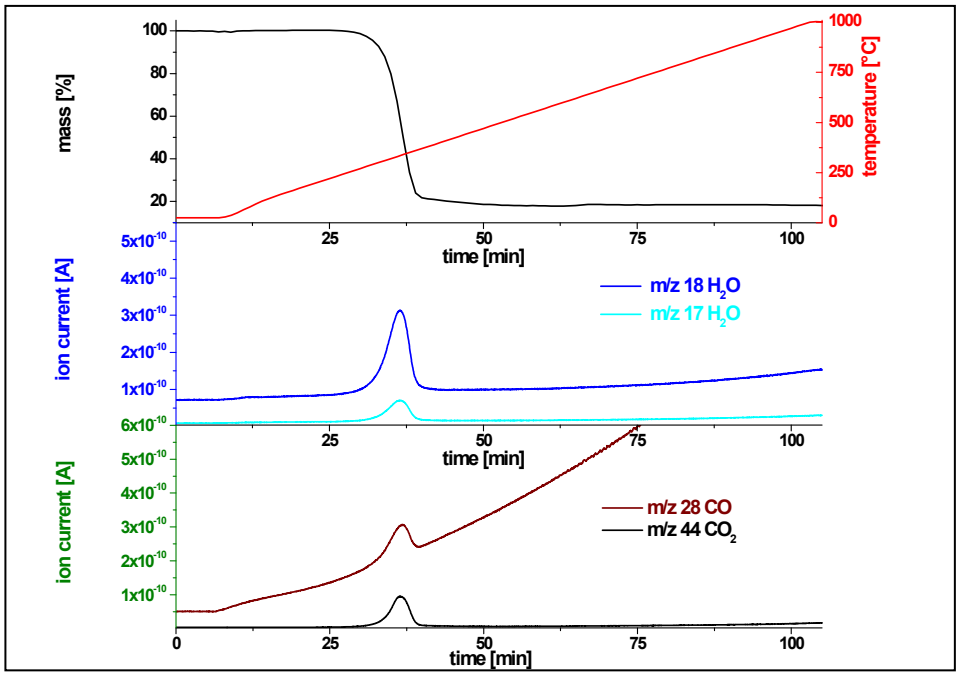

Figure D TGA-MS measurement of BNC up to 1000 °C under Ar atmosphere. m/z 18 and m/z 17 are indicating water. Areas underneath the Peaks of m/e 28 and m/e 44 are almost equal; hence CO_2 and CO were released.

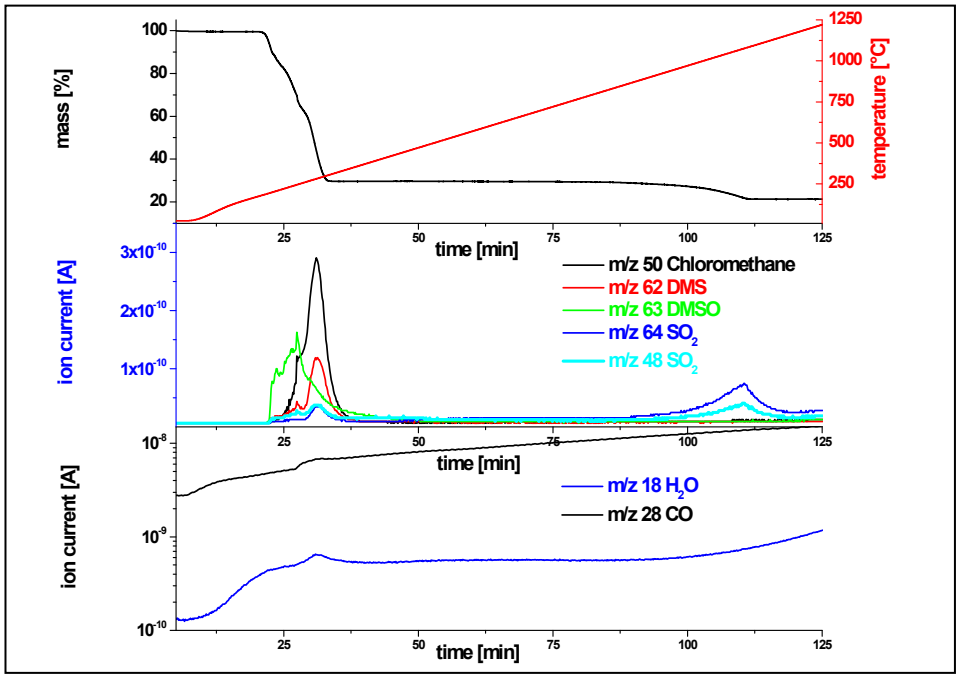

Figure E TGA-MS measurement of $RuCl_2(DMSO)_4$ up to 1250 °C under Ar atmosphere. m/z 50 for CH_2Cl; m/z 62 for DMS; m/z 63 DMSO; m/z 64 and m/z 48 for SO_2; m/z 18 for H_2O; m/z 28 CO;.

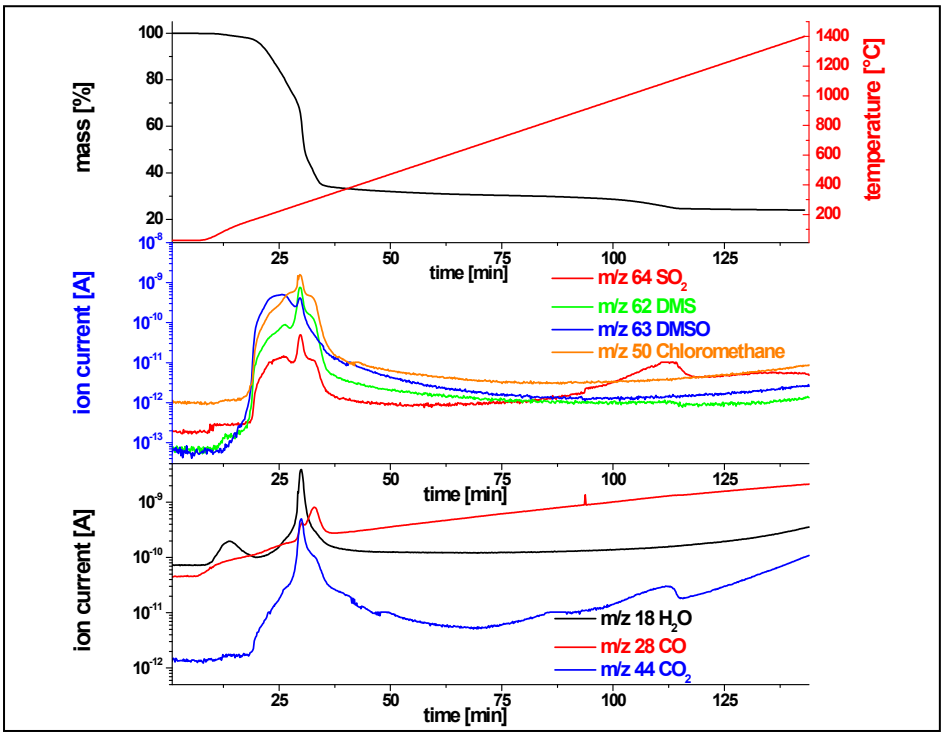

Figure F TGA-MS measurement of Ru/p-BNC_64.4% up to 1400 °C under Ar atmosphere. m/z 50 for CH_3Cl; m/z 62 for DMS; m/z 63 DMSO; m/z 64 SO_2; m/z 18 for H_2O; m/z 28 CO; m/z 44 for CO_2. For a better overview of the decomposition process the ion currents of the MS-signals are shown in logarithmical scale.

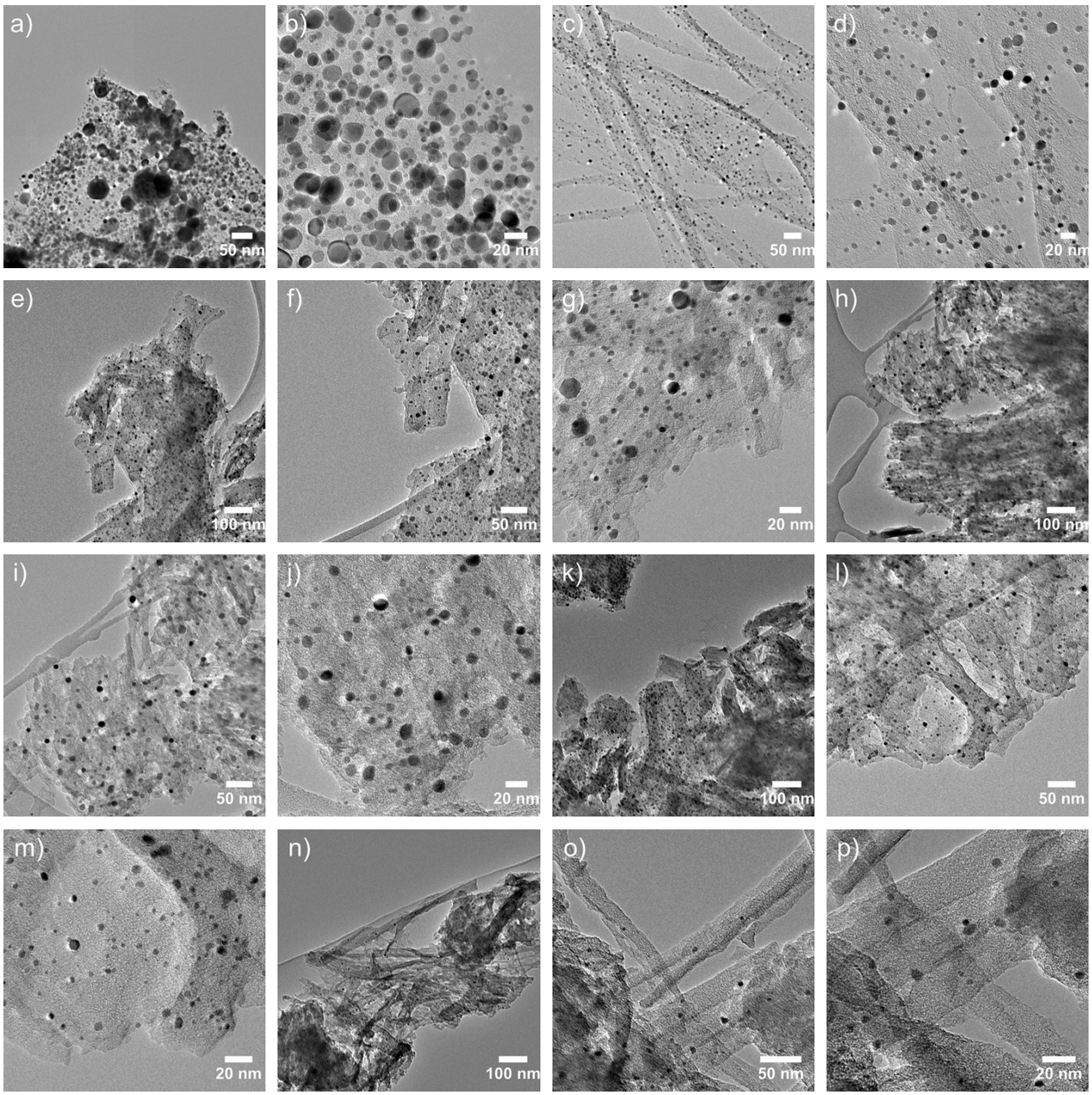

Figure G TEM images of carbon supported Ru-clusters: a, b: Ru/p-BNC_64.4%; c, d: Ru/p-BNC_28.3%; e, f, g: Ru/p-BNC_5.0%; h, i, j: Ru/p-BNC_5.0% after catalytical tests; k, l, m: Ru/p-BNC_3.8%; n, o, p: Ru/p-BNC_2.0%

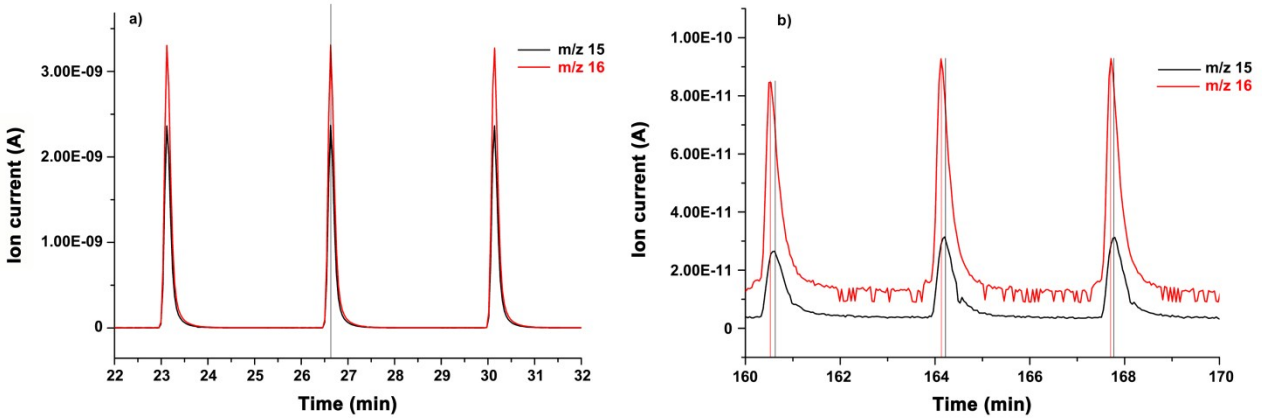

Figure H a) Mass spectrum of methane calibration pulses to determine the ratio of the peak areas for m/z values 15 and 16. The vertical black line indicates the same peak positions. b) Pulse experiment with Ru/p-BNC_3.8%: carbon monoxide pulses with hydrogen as carrier gas. Due to reaction with the catalyst, carbon monoxide (m/z 16) is reduced to methane (m/z 15, 16). The black and red vertical lines illustrate the delayed detection of methane.

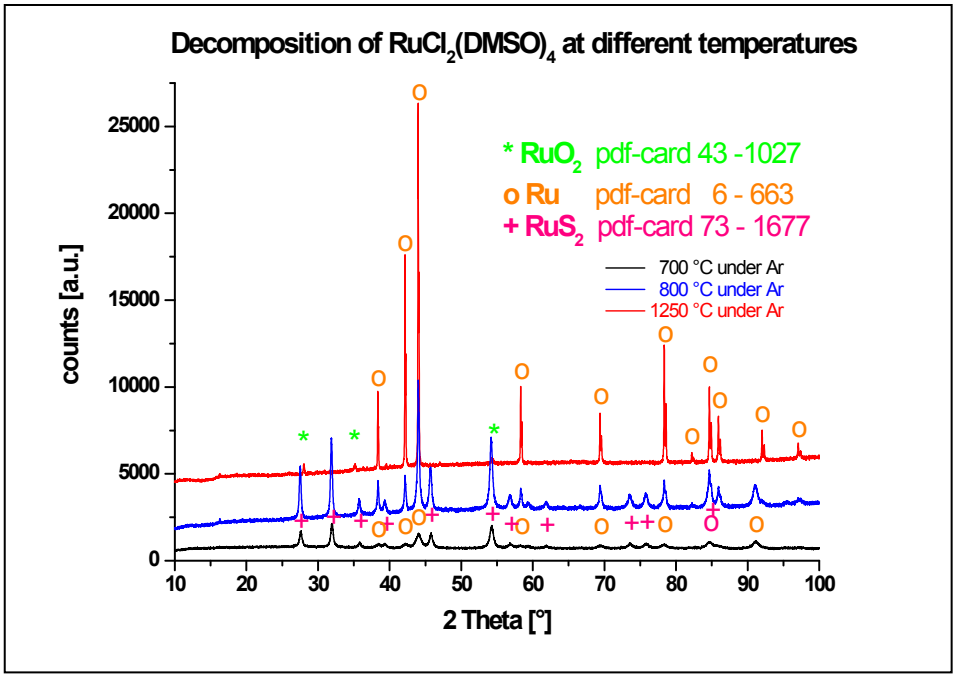

Figure I Powder diffractions of decomposition products from $RuCl_2(DMSO)_4$ at different temperatures (under Ar flow).

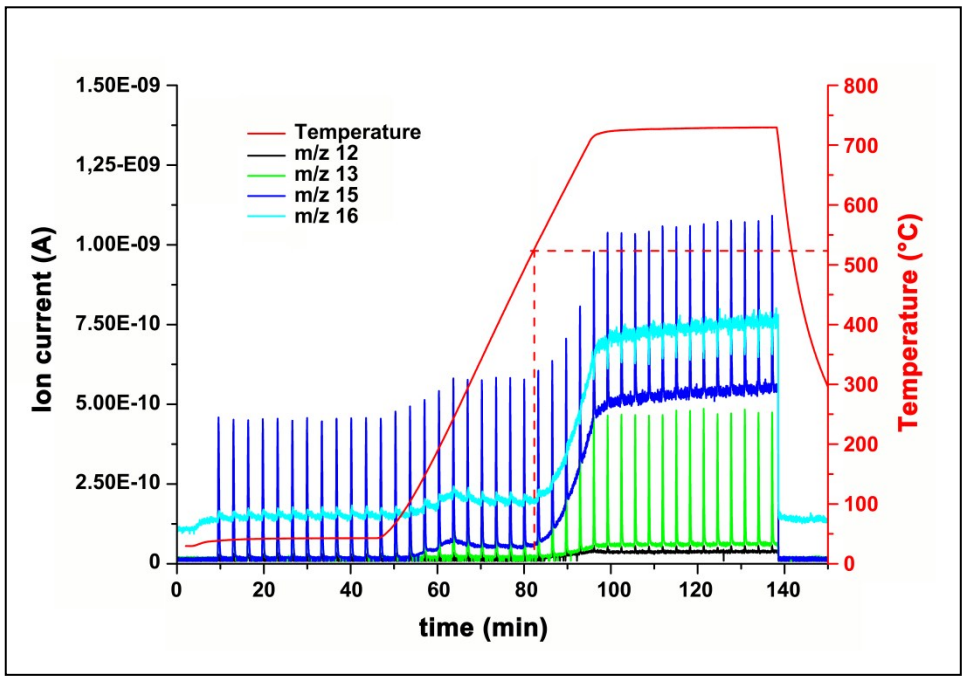

Figure J Pulse experiment of Ru/p-BNC_3.8%. The sample was heated up to 800 °C (oven temperature, 10K/min) in an Ar/H2 (5%) gas atmosphere (30ml/min). Every 3 min an injection of nitrogen (pulse volume 0.9200 ml) takes place. At ~ 525 °C (dashed line), hydrogen reduces the carbon support material to form methane (increase of m/z: 16, 15, 14, 13, 12). m/z 14 is not displayed for reasons of clarity (nitrogen: m/z 28, 14)

Sample	Gas	Temperatrure	D-band		G-band		
			Peak [cm^{-1}]	FHWM [cm^{-1}]	Peak [cm^{-1}]	FHWM [cm^{-1}]	Raman band ratio $A_{D\text{-}band}/A_{G\text{-}band}$
p-BNC	N2	1250 °C	1350±1	165.3±20.0	1590±3	93.5±4.4	3.27±0.17
p-BNC	N2	1400 °C	1344±1	120.5±1.7	1592±1	82.1±6.3	3.00±0.04
p-BNC	Ar	1250 °C	1348±1	154.3±0.1	1589±1	93.1±2.0	2.94±0.26
p-BNC	Ar	1400 °C	1345±1	121.1±3.7	1596±3	68.8±8.6	2.71±0.17
Ru/p-BNC_3.8	N2	1250 °C	1347±1	154.1±4.2	1593±1	87.7±1.1	3.48±0.13
Ru/p-BNC_3.8	N2	1400 °C	1347±2	127.5±7.1	1594±1	84.0±1.8	2.89±0.14
Ru/p-BNC_3.8	Ar	1250 °C	1349±1	167.9±8.3	1592±2	91.9±1.4	3.59±0.06
Ru/p-BNC_3.8	Ar	1400 °C	1346±3	119.4±15.4	1595±1	82.2±2.6	2.85±0.23

Table A: Raman spectroscopy data of p-BNC and Ru/p-BNC_3.8 samples, prepared under different gases and temperatures. Raman spectra of each sample were recorded at seven different positions. Each spectrum was smoothed, base line corrected and fitted with a two peak Gaussian/Lorentzian fit function.

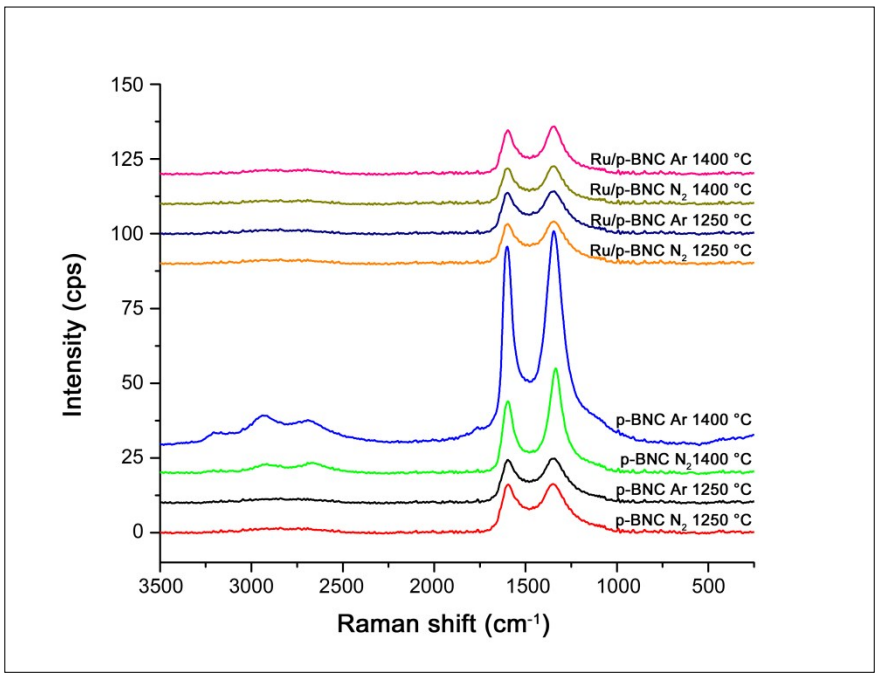

Figure K Raman spectra of p-BNC and Ru/BNC_3.8 prepared under different pyrolysis gases and at different temperatures. For clarity the spectra are stacked and the noise was smoothed with a FFT function.