Walter Reppe Revival – Identification and Genesis of Copper Acetylides $\text{Cu}_2\text{C}_2$ as Active Species in Ethynylation Reactions

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Supporting Information

Supporting data

XRD of standard catalysts after drying and calcination

Figure S1: Powder diffractograms of Cu35Bi4-80 (just dried), Cu35Bi4-450 and Cu35Bi4-700. Cu2(NO3)(OH)3 (triangles)[1], CuO (dots)[2] and SiO2 (stars)[3] serve as reference. The samples were calcined for 4 h with a heating rate of 2.5 K/min in air. Diffractograms are recorded with an angle range between 5° and 70° in steps of 0.008°.

The sample, that is just dried at 80 °C (Cu35Bi4-80), consists of basic copper nitrate (Cu2(NO3)(OH)3) which is the main product of the co-precipitation. The calcined samples (calcination at 450 and 700°C) contain CuO whereby Cu35Bi4-700 shows the narrowest reflexes.

Structural characterization data of the calcined catalysts

Table S1: BET surface area (SA_BET) in m²/g, pore volume (V_pore) in cc/g and pore radii (r_pore) in nm of the different Cu/Bi catalysts. The surface area as well as the mean pore size and the mean pore volume are determined by N2 physisorption (BJH/BET method). The error is estimated to be between 5-10%.[4] Cu (a) and Bi (b) loadings in wt.% determined by ICP-OES. The relative error is determined to be around 5% including the preparation and the ICP-OES measurement itself. Crystallite sizes (Size_crys) were calculated with the Scherrer equation of Cu35Bi4-80, Cu35Bi4-450 and Cu35Bi4-700.[5] The reflexes at 12.8 2θ and 25.7 2θ of Cu35Bi4-80 and the reflexes at 35.4 2θ and 38.7 2θ of the calcined samples (Cu35Bi4-450, Cu35Bi4-700) served for the determination of the crystallite sizes (see Figure S1).

| Sample       | SA_BET | V_pore | r_pore | Cu[a] | Bi[b] | Size_crys |
|--------------|--------|--------|--------|-------|-------|-----------|
| Cu35Bi4-80   | 171    | 0.49   | 1.69   | 33.3  | 4.4   | 43.2 ± 3.1|
| Cu35Bi4-450  | 115    | 0.24   | 1.88   | 35.3  | 4.1   | 14.1 ± 1.3|
| Cu35Bi4-700  | 25     | 0.12   | 1.69   | 35.3  | 4.6   | 20.2 ± 2.0|

After drying, Cu35Bi4-80 consists of particles with a crystallite size of around 43 nm. For medium temperature calcination (450°C) the crystallite sizes are in the range of 14 nm, but increase as expected for calcination at 700°C.

Higher calcination temperatures reduce the BET surface area (171 m²/g for Cu35Bi4-80 to 25 m²/g for Cu35Bi4-700). This is caused by pore blocking through larger CuO particles and by disruption of the
porous SiO$_2$ structure. The pore volumes increase or decrease in the same course as the surface area while the pore radii remain constant. The Cu and Bi loadings determined by ICP-OES fit well with the aimed loadings meaning that the co-precipitation method is reliable.

**Raman spectra of the calcined pre-catalysts**

![Raman spectra](image)

*Figure S2*: Raman spectra of the pre-catalysts Cu$_{35}$Bi$_4$-80, Cu$_{35}$Bi$_4$-450 and Cu$_{35}$Bi$_4$-700 in the range from 150 cm$^{-1}$ to 1800 cm$^{-1}$. The reference spectra are taken from the RRUFF database. The laser intensity was 0.015 mW and the wavelength of the laser is 532 nm. An objective with 50x magnification is used. The standard scanning time is 5 sec with 10 repetitions.

The spectra of the calcined (Cu$_{35}$Bi$_4$-450, Cu$_{35}$Bi$_4$-700) samples fit well with the CuO reference spectrum, especially the signals at 298 cm$^{-1}$ and 607 cm$^{-1}$. Also, the signals of Cu$_{35}$Bi$_4$-80 match to the signals of the Cu$_2$NO$_3$(OH)$_3$ reference. Particularly the three signals between 415 and 513 cm$^{-1}$ and the signal at 1051 cm$^{-1}$ are in good agreement with the reference signals. Both reference spectra are taken from the RRUFF database. Tenorite serves as CuO reference and Roualte as Cu$_2$NO$_3$(OH)$_3$ reference.

**XRD of pure copper acetylde, Cu$_2$C$_2$**

![XRD](image)
**Figure S3**: Powder diffractogram of freshly prepared Cu$_2$C$_2$. The diffractogram is recorded in an angle range between 5° and 70° in steps of 0.008°. Cu$_2$C$_2$ was wetted with H$_2$O.

**Quantitative determination of copper acetylide by TG-MS**

![Diffractogram](image)

**Figure S4**: Quantification of formed Cu$_2$C$_2$ by TG-MS. The dependency of the sample weight on the sample temperature of freshly prepared SiO$_2$-supported Cu$_2$C$_2$ (25 wt.%) and of a pure SiO$_2$ reference sample (background) are shown. The sample was heated to 1000°C under synthetic air at a rate of 10 K/min. Additionally, the measured ion current for m/z = 44 (CO$_2$) obtained by MS is depicted.

Three SiO$_2$ supported Cu$_2$C$_2$ samples with different loadings (5 wt.%, 15 wt.%, 25 wt.%) were synthesized to evaluate the reliability of the TG method. The samples were heated to 1000°C with 5 K/min in synthetic air. The gas phase was analyzed using a mass spectrometer. The sample temperature, the sample weight, the ion current for m/z = 44 (CO$_2$) and the reaction time for the 25 wt.% Cu$_2$C$_2$ on SiO$_2$ as well as for a pure SiO$_2$ reference sample (background) is depicted exemplarily in Figure S4.

At around 100°C the sample mass increases. It is related to the decomposition of Cu$_2$C$_2$ into Cu and C and the simultaneous oxidation of Cu(I) to Cu(II)O. The decomposition temperature of Cu$_2$C$_2$ into Cu and C is indicated at 127°C under inert conditions by Cataldo et al. and at 131 to 183°C in air by Klement et al. The decomposition of Cu$_2$C$_2$ into CuO and C is also described by Cataldo et al. After the formation of CuO, C is oxidized to CO$_2$. Consequently, the sample weight decreases. The formation of CO$_2$ is confirmed by mass spectrometry. The formation of CO$_2$ takes place at the same time as the sample weight decrease. A slight decrease of the sample weight over the whole temperature treatment is caused by desorption of surface species like water from the SiO$_2$ surface because the reference SiO$_2$ reference sample shows the same trend.
Validation of the TG-MS results

Figure S5: (a) Ratio of measured weight increase to calculated weight increase obtained by TG-MS for freshly prepared supported Cu$_2$C$_2$ on SiO$_2$ with different Cu$_2$C$_2$ loadings. (b) Ratio of weight increase to sample mass used for TG-MS for freshly prepared supported Cu$_2$C$_2$ on SiO$_2$ with different Cu$_2$C$_2$ loadings. The samples are heated to 1000°C under synthetic air at a rate of 10 K/min.

The mass increase or rather the oxidation of Cu(I) to Cu(II)O was used to calculate the amount of Cu$_2$C$_2$ of the prepared sample. In Figure S5a the ratio of the measured weight increase to the calculated weight increase of the three SiO$_2$ supported Cu$_2$C$_2$ samples with different loadings are shown. For the 5 wt.% and the 25 wt.% Cu$_2$C$_2$ samples the ratio is almost 1. Only the 15 wt.% sample differs slightly with a value of 0.85.

In Figure S5b the ratio of the weight increases to the amount of sample used for the TGA is depicted. The linear dependency of the ratio to the Cu$_2$C$_2$ loading can be clearly figured out. Hence, the TGA method is a suitable and reliable technique to determine the amount of formed Cu$_2$C$_2$. The TGA measurements were carried out with supported Cu$_2$C$_2$ because of the explosive character of dry, pure Cu$_2$C$_2$ and to compare the results with supported Cu/Bi catalysts.

Reduction of Cu(II) studied by EPR spectroscopy

EPR spectroscopy has the advantage that it is possible to determine the oxidation states of components in solutions, solids or even slurries. In Figure S6, the EPR spectra of the reaction of CuCl$_2$ with formaldehyde are depicted. Cu(II) has a nuclear spin of I=3/2. Therefore, four signals should appear for the parallel and the vertical portion. If Cu(II) is reduced to Cu(I) the Cu(II) signals should disappear. Since Cu(I) is EPR inactive, no further signals should appear. It can be clearly seen in both Figures (S10a and S10b) that in all spectra Cu(II) is present. The g-values of g‖ = 2.40823 and g┴ = 2.07525 are in accordance to literature.[8] The intensity of the signals do not decrease during the reaction neither at 25°C nor at 100°C. Therefore, the reduction of Cu(II) to Cu(I) does not take place under these conditions and it cannot be confirmed that formaldehyde acts as reducing reagent.

In Figure S7, the EPR spectra of the reaction of CuCl$_2$ with formaldehyde and additional acetylene are shown. Reduction of Cu(II) does not take place at 25°C during the first 15 min (Figure S7a). After that (between 15 min and 30 min) Cu(II) is reduced indicated by the decrease of the Cu(II) signals. Cu(II) is completely converted to Cu(I) after 45 min. Simultaneously a new species is formed with a g-value of 2.00259 and corresponds to a carbon based radical. Compared to that the reduction at 100°C takes place substantially faster (Figure S7b). Already after 2 min a complete reduction of Cu(II) to Cu(I) is achieved and the new species is formed.

To strengthen the obtained results the reduction behavior of a solid Cu/Bi catalyst (Cu35Bi4-450) was investigated doing the same experiments at 100°C. The results are depicted in Figure S8.
During the purging period with N₂ only formaldehyde and no acetylene are present. Hence, the reduction from Cu(II) to Cu(I) does not take place. After the addition of acetylene the intensity of the Cu(II) signals decrease and Cu(II) is reduced to Cu(I). The new species with a g-value = 2.00259 is formed as soon as the reduction occurs. This is in accordance with the results obtained with CuCl₂ solution. However, the decrease of the Cu(II) signals is hardly visible in the EPR spectra shown in Figure S8a. Therefore, the double integrals of the Cu(II) signals calculated from the spectra of Figure S8a at different reaction times are shown in Figure S8b. The decrease of Cu(II) and consequently the reduction of Cu(II) to Cu(I) induced by acetylene can clearly be figured out by the decrease of the double integrals of the Cu(II) signals after the addition of acetylene (right part in Figure S8b). With ongoing activation time Cu(II) is further converted into Cu(I).

In addition, the reduction behavior of Cu₃5Bi₄₋₄₅₀ was investigated only with acetylene as reducing agent (without formaldehyde) to exclude that a combination of formaldehyde and acetylene is necessary for the reduction of Cu(II). It turns out that acetylene itself is capable of reducing Cu(II) to Cu(I). It agrees with Brameld et al. They reported that Cu₂C₂ can be synthesized from Cu(II) solutions without formaldehyde.

**Figure S6:** Anisotropic EPR spectra (T<sub>recorded</sub> = -120°C) of CuCl₂ in formaldehyde solution at 25 °C (a) and 100°C (b) for different reaction times. Samples were taken after different reaction times with a syringe and are transferred into capillaries that were placed in EPR tubes.

**Figure S7:** Anisotropic EPR spectra (T<sub>recorded</sub> = -120°C) of CuCl₂ in formaldehyde solution and acetylene at 25 °C (a) and 100°C (b) for different reaction times. Samples were taken after different reaction times with a syringe and are transferred into capillaries that were placed in EPR tubes.
Figure S8: a) Anisotropic EPR spectra (T_{record} = -120°C) of separated Cu35Bi4-450 catalyst after different reaction times. In the first 60 min the set-up is purged with N\textsubscript{2} before switching to acetylene. The activation is carried out at 100°C with 1.1 bar acetylene. The dashed line separates the N\textsubscript{2}-purging period (60 min) from the activation with acetylene. The activation is carried out at 100°C with 1.1 bar acetylene. Samples were taken after different reaction times with a syringe and are transferred into capillaries that were placed in EPR tubes.

XRD of activated catalysts

The time course of the formation of Cu\textsubscript{2}C\textsubscript{2} can also be observed via X-Ray diffraction. The Cu\textsubscript{2}NO\textsubscript{3}(OH)\textsubscript{3} (Cu35Bi4-80, Figure S9) or rather the CuO reflexes of the pre-catalysts (Cu35Bi4-450, Cu35Bi4-700, Cu35Bi4-700) decrease during the activation because of the formation of Cu\textsubscript{2}C\textsubscript{2}, which leads to the consumption of the precursor phases. The effect that Cu\textsubscript{2}C\textsubscript{2} is formed directly at the beginning of the activation and that the formation takes place much faster for Cu35Bi4-80 compared to Cu35Bi4-700 can be confirmed by XRD.

Figure S9: Powder diffractionograms of spent Cu35Bi4-80 after different activation time. The samples were taken during activation with a syringe and they are measured in dry state. The powder diffractionograms of freshly prepared Cu\textsubscript{2}C\textsubscript{2} and of the dried catalyst before the catalytic reaction serve as reference. Diffractionograms are recorded in an angle range between 5° and 70° in steps of 0.008°.
Figure S10: Powder diffractograms of spent Cu35Bi4-450 after different activation time. The samples were taken during activation with a syringe and they are measured in dry state. The powder diffractograms of freshly prepared Cu_{2}C_{2} and of the calcined catalyst before the catalytic reaction serve as reference. Diffractograms are recorded in an angle range between 5° and 70° in steps of 0.008°.

Figure S11: Powder diffractograms of spent Cu35Bi4-700 after different activation time. The samples were taken during activation with a syringe and they are measured in dry state. The powder diffractograms of freshly prepared Cu_{2}C_{2} and of the calcined catalyst before the catalytic reaction serve as reference. Diffractograms are recorded in an angle range between 5° and 70° in steps of 0.008°.

**TGA of activated catalysts**

Cu(II) is not converted into Cu_{2}C_{2} during the purging period because acetylene is not present. Cu_{2}C_{2} is formed as soon as acetylene is introduced and consequently Cu(II) from the catalyst precursor is consumed. The conversion of Cu(II) of the catalyst precursors and consequently the continuously formation of Cu_{2}C_{2} during the activation is in agreement with the obtained X-Ray diffraction results. 91% of the overall Cu(II) amount is converted into Cu_{2}C_{2} after 4 h reaction time using Cu_{35}Bi_{4}-80 and Cu_{35}Bi_{4}-700. The initialization period is very pronounced using Cu_{35}Bi_{4}-700, confirming the results obtained by XRD. After that, the Cu_{2}C_{2} formation rate increase linearly.
Figure S12: Conversion of Cu(II) of the initial Cu/Bi/SiO$_2$ catalysts (dried at 80 °C or calcined at 700°C) into Cu$_2$C$_2$ measured by TGA. The samples were heated to 1000°C under synthetic air at a rate of 10 K/min during the TGA. The activation of the catalysts were carried out at 100°C with 1.1 bar acetylene. Samples were taken during the activation to separate the catalyst.

Determination of Cu(II) in solution

During the activation of a Cu35Bi4-80 catalyst samples of the reaction slurry were taken and the copper content in solution was determined by elemental analysis via ICP-OES. The overall reaction volume is 100 mL. In Figure S13a the ratio in percentage of the amount of leached copper to the amount of the overall copper content in the catalyst is shown as well as the Cu leaching percentage. Additionally, the Cu(II) concentration in solution is measured by a specific Cu(II) electrode (Figure S13b).

During the purging period copper from the Cu/Bi catalyst leaches and dissolves in the reaction medium. The leaching of Cu(II) leads to structural changes of the catalyst which was already observed by Raman spectroscopy. The copper leaching can be confirmed by the conductivity measurement (Figure S13b). After the addition of the catalysts the conductivity increases (after 10 minutes in Figure S13b). The maximum amount of dissolved Cu is most likely defined by the ratio between dissolved Cu(II) and Cu(II) which precipitates as Cu(OH)$_2$ under these conditions (pH = 7). The leached copper must have an oxidation state of II because the electrode used for this experiment is only sensitive for Cu(II) ions. After
starting the activation by switching to \( \text{C}_2\text{H}_2 \) gas the Cu(II) concentration drops almost to zero indicating that \( \text{Cu}_2\text{C}_2 \) is formed.

Raman spectra of Cu(I) acetylide

![Raman spectrum of freshly prepared Cu(2)C2 (aqueous suspension) from 115 cm\(^{-1}\) to 2850 cm\(^{-1}\).]

Fig. S14: Raman spectrum of freshly prepared Cu(2)C2 (aqueous suspension) from 115 cm\(^{-1}\) to 2850 cm\(^{-1}\).

Methods

Caution: Due to the fact that Cu acetylide compounds are to some extend unstable against heat and impacts, proper safety precautions should be taken when handling the materials. Especially dry samples are able to explode under the influence of impact or heat. Wearing protective equipment is recommended for the handling of any explosive materials. All Cu acetylides samples or activated catalysts used in this work are disarmed by carefully addition of nitric acid.

General

Chemicals
All chemicals were used without further purification.

Preparation of pure and silica supported \( \text{Cu}_2\text{C}_2 \)^{[9]}

In a glovebox 2.50 g copper(I) chloride is weighed in a Schlenk tube and 50 mL of a 25 wt.% ammonia solution are added. The Schlenk tube is purged with nitrogen via a septum for 8 min before switching to acetylene. Immediately a red to brown solid precipitates. After 2 h reaction time, the Schlenk tube is purged with nitrogen again to remove the remaining acetylene. The precipitate is washed with water and methanol. The only difference between the preparation of pure copper(I) acetylide to supported one is the addition of silica to the 50 mL ammonia solution. Be careful because copper(I) acetylide is highly explosive at dry condition!

Preparation of copper-bismuth-silica catalyst
The catalysts were synthesized by a common co-precipitation procedure.{[10]} Catalysts containing 5, 15, 25 and 35 wt.% copper are prepared. The weight percentage of bismuth is kept in a constant ratio to the weight percentage of copper of 1:8.75. \( \text{Bi}_2\text{O}_3 \) is dissolved in 2 mL of concentrated \( \text{HNO}_3 \) and added
to a solution of Cu(NO₃)₂ · 3 H₂O in water. In a second beaker, a 2 M solution of Na₂SiO₃ in water is prepared. For the co-precipitation process, 150 mL of distilled water are filled into an 800 mL beaker containing a stirring bar, a pH electrode and a thermometer and placed onto a magnetic hot plate stirrer. After heating to 60 °C, the stirring speed is set to 400 rpm and the precipitation process is started. Therefore, the 2 M solution of Na₂SiO₃ and the solution containing both Bi₂O₃ and Cu(NO₃)₂ · 3 H₂O are simultaneously added dropwise over a time frame of 20 min using two peristaltic pumps operating at a constant volumetric flow rate. During this process the pH of the reaction mixture is kept at a constant value of 7 by titration with 2 M HNO₃. The titration is controlled by a 906 Titrando titrator by Metrohm. After both precursor solutions are fully added to the reaction mixture, the titration is stopped, the stirring speed adjusted to 300 rpm and the reaction mixture aged for 60 min. The resulting precipitate is filtered off under vacuum, washed with distilled water until the electrical conductivity of the filtrate is below 4 mS · m⁻¹, dried at 80 °C overnight and calcined at 450 °C for 4 h with a heating rate of 2.5 K min⁻¹. The obtained catalyst is then sieved to give particles of a diameter d with 100 μm < d ≤ 300 μm.

**Catalytic test (activation or ethynylation)**

For a standard catalytic test 50.34 g paraformaldehyde, 10.90 g methanol and 50.34 g water are weighed in a three-necked flask, attached to the reactor setup (see below) and heated to 100 °C under reflux. NaOH (1.40 g) and NaH₂PO₄ · H₂O (4.84 g) are added as a buffer and the suspension stirred at 100 °C until a clear solution is obtained. After addition of 5.00 g catalyst (or Cu acetylide) and 1,3-propanediol (5.00 g) acting as an internal standard, the stirring speed is set to maximum and the reaction mixture purged with nitrogen for 60 min. The gas stream is then switched to acetylene to start the reaction and the reaction setup flushed with acetylene for 8 min. The pressure relieve valve is then closed, the acetylene pressure set to 1.2 bar and the reaction mixture stirred until the end of the reaction at 100 °C. At the end of the reaction, the reaction setup is cooled down and purged with nitrogen for 10 min to remove residual acetylene and reaction gases. Samples of 0.5 mL of reaction mixture are collected during the nitrogen purge phase and the reaction period using a syringe. They are used to determine the composition of the reaction mixture via GC analysis. In the case of propargyl alcohol co-feeding experiments, the amount of propargyl alcohol is added with a syringe. Catalysts separation after the activation was done via centrifugation.

A blank was carried out without any catalyst to show that no products are formed under the selected activation/reaction conditions.
Sample preparation for EPR spectroscopy
0.08 mL of the reaction suspension are filled in a capillary with a syringe. The capillaries were put into EPR tubes. The EPR tubes were purged with argon and closed.

Sample preparation for Raman spectroscopy, X-Ray diffraction and TGA
Samples of 3.5 mL of reaction mixture are collected during the purging and the reaction period. The samples were filtrated. The solids were washed with water and methanol and dried under vacuum.

Sample preparation for copper leaching measurements
To investigate copper leaching processes, the concentration of copper(II) ions dissolved in the reaction mixture is measured *in situ* during the reaction using an ion-selective electrode and by ICP-OES. First method requires using a four-necked round flask in the reactor setup instead of the three-necked flask described in the section before. A copper(II)-selective electrode by Metrohm is inserted through the additional opening and an Ag/AgCl(aq) (3 M KCl) reference electrode through the opening otherwise used for sample extraction. For the copper content determination by ICP-OES samples were taken with a syringe and the organic compounds were removed by heating at 90°C for 10 hours. The residue was dissolved with 2 mL concentrated phosphoric acid and diluted with water. 10 mL of the solution was used for the ICP-OES analysis.

Product analysis via gas chromatography
Samples of 0.5 mL of reaction mixture are transferred into a test tube. 1.5 mL acetonitrile is added to end the reaction process and precipitate buffer salts. The suspension is mixed thoroughly and filtered over activated aluminium oxide (PURALOX SCCa150/200 from SASOL Germany GmbH). The filtrate is collected in GC vials and analyzed quantitatively by gas chromatography. Gas chromatograms are recorded on an Agilent G1530A machine fitted with a TCD detector. A HP-PLOT-Q (stationary phase: solid polystyrene/divinylbenzene, length: 30 m, inner diameter: 0.32 mm, film thickness: 0.2 μm) GC column is used to separate compounds and 1,3-propanediol as internal standard for calibration.

For the calculation of the 1,4-butynediol and propargyl alcohol yield the molar amount of the product is calculated:

\[
n_i(t) = \frac{n_{\text{int.st}} \cdot A_{\text{int.st}}}{m_{\text{GC}}}
\]

\[n_i(t)\] = molar amount at reaction time \(t\) for component \(i\)
\[n_{\text{int.st}}\] = molar amount of the internal standard (1,3-propanediol)
\[A_{\text{int.st}}\] = area of component \(i\) obtained from the GC after reaction time \(t\)
\[m_{\text{GC}}\] = slope of the calibration curve for component \(i\) obtained from the GC

Then, the product yield is obtained as follows:

\[
Y_i = \frac{n_i(t)}{n_i,\text{max}}
\]

\[Y_i\] = yield of component \(i\)
\[n_i(t)\] = molar amount at reaction time \(t\) for component \(i\)
\[n_i,\text{max}\] = maximum molar amount of component \(i\), which can be produced (calculated from the formaldehyde concentration)

Analysis via EPR spectroscopy
EPR spectra were recorded using a JEOL JES-RE 2X spectrometer on x-band frequency at -120°C. The spectra were measured at a microwave frequency of 9.20 GHz, 5 mW, a modulation amplitude of
0.4 mT and a sweep-time of 4 min. The sweep-width is 230.430 mT at a constant time of 0.1 s and a modulation frequency of 100 kHz. The microwave frequency is determined by Advantest R5372 instrument and the temperature by a JEOL ES DVT2 thermometer which is equipped with a calibrated thermocouple. The g- and A-values are calibrated as a standard via Mn(II) (nuclear spin I = 5/2) in a magnesium(II) oxide matrix (g = 1.981).

Analysis via Raman spectroscopy
Raman spectra are recorded on an InVia Raman Microscope from Renishaw with a Newton EMCCD Camera (Spectroscopy EMCCD, width: 25.6 mm, 1600 pixel, 3 MHz) from Andor. For the measurements, a frequency-doubled Nd:YAG laser (\(\lambda=532\) nm) and an objective with 50x magnification (Leica N PLAN EPI 50x/0.75) are used. The standard laser intensity was 0.015 mW and the standard scanning time 5 sec with 10 repetitions. It is important to note that the Raman spectra must be recorded at very low laser intensities because of instability of Cu2C2 leading to fast decomposition with formation of carbon.

Analysis via X-Ray diffraction
The powdered catalyst sample is placed onto a flatbed support, inserted into the X-ray machine and measured with an Empyrean diffractometer from PANalytical (K\(_\alpha\)(Cu), \(\lambda=1.5419\), Ni as K\(_\beta\)(Cu)-filter) in reflection mode. Diffractograms are recorded in an angle range between 5° and 70° in steps of 0.008°. They are analysed using the HighScore Plus software from PANalytical. The crystallite sizes were calculated with the Scherrer equation\((5)\):

\[
L = \frac{K \lambda}{\Delta(2\theta) \cos\theta}
\]

\(\Delta(2\theta)\) = the quantity of the line broadening at half the maximum intensity (FWHM) in radians
K = shape factor (0.9 to 1)
\(\lambda\) = wavelength of the X-Ray source
\(\theta\) = Bragg angle
L = mean size of the ordered crystalline domains

Analysis of copper content via ICP-OES
The copper content was determined using an ICP-OES 700 from Agilent. A multiple element standard from Merck was used for external calibration.

Quantification of copper(I) acetylide via TGA-MS
The TGA was carried out using a STARE System TGA DSC\(^3\); TGA 2 from Mettler Toledo GmbH and the software STARESoftware version 14.000 from Mettler Toledo GmbH. The samples were heated from 25°C to 1000°C in synthetic air with a heating rate of 10 Kmin\(^{-1}\). The gas phase analysis done by MS was measured using a ThermoStar\(^\text{TM}\) from Pfeiffer Vacuum and the software QUADERA\(^\circ\) version 4.62 from INFICON Holding AG.

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