

Special  
Issue

# 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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**Abstract:** More than six decades after proposing copper acetylide,  $\text{Cu}_2\text{C}_2$ , as catalytically active species in ethynylation reactions by Walter Reppe, the explosive species have been experimentally identified and investigated during catalysis in detail now. Taking into account specific safety precautions, unequivocal qualitative characterization was achieved by Raman spectroscopy and X-ray powder diffraction of supported copper catalysts  $\text{Cu}/\text{Bi}/\text{SiO}_2$  during and after activation and catalysis in comparison to bulk  $\text{Cu}_2\text{C}_2$  materials. Quantification of  $\text{Cu}_2\text{C}_2$  succeeded by thermal analysis and Raman spectroscopy. Its formation in aqueous suspension is studied starting from copper(II) oxide catalysts including dissolution, reduction and precipitation steps. Copper acetylide formation can be correlated with catalytic performance in the ethynylation of formaldehyde to 1,4-butyne-1,3-diol.

The structurally complex polynuclear explosive copper acetylide,  $\text{Cu}_2\text{C}_2$ , was proposed and generally accepted as active species in copper catalyzed reactions with acetylene in the literature more than six decades ago, but it has never been experimentally proven and investigated in detail up to now. Walter Reppe et al. assumed that the active species in ethynylation reactions could consist of three acetylene molecules coordinated to a  $\text{Cu}_2\text{C}_2$  molecule ( $\text{Cu}_2\text{C}_2 \cdot 3\text{C}_2\text{H}_2$ ). The

reaction scheme for the industrially important ethynylation reaction of formaldehyde to 1,4-butyne-1,3-diol is depicted in Scheme 1.<sup>[1]</sup>

In industrial processes, 1,4-butyne-1,3-diol is hydrogenated to either 1,4-butanediol or 1,4-butenediol, which are used for production of solvents (e.g. tetrahydrofuran), Vitamin B6 and other chemicals.<sup>[2]</sup>

W. Reppe et al. developed  $\text{Cu}/\text{Bi}/\text{SiO}_2$  catalysts that are still successfully used in current industrial processes. The most commonly applied pre-catalysts are based on  $\text{CuO}$ .<sup>[1]</sup> Most of them are supported catalysts, where  $\text{Cu}_2\text{C}_2$  is probably formed during activation and stable under reaction conditions. Still missing identification and characterization of these active species may be due to (i) the explosive properties of  $\text{Cu}_2\text{C}_2$ , which is only stable under wet conditions and in diluted state, (ii) limited availability of suitable analytical tools, (iii) its ill-defined polymeric structure, also known from more defined analogous inorganic " $\text{Cu}_2\text{C}_2$ "-compounds<sup>[3]</sup> and (iv) challenges with its in situ formation in a complex 3-phase aqueous slurry during catalysis.

In contrast to this limited understanding of the catalyst, there is a clearly increased interest in application of acetylene based processes like the ethynylation of formaldehyde to 1,4-butyne-1,3-diol as alternative to petrol chemistry for countries with large coal reserves. This is reflected by an increased number of recent scientific investigations on supported oxide catalysts and structure-activity relationships. The influence of bismuth is studied by Yang et al. who propose that bismuth weakens the interaction between  $\text{CuO}$  and the support and promotes the dispersion of  $\text{CuO}$ .<sup>[4]</sup> The influence of chlorine was investigated by Gao et al.<sup>[5]</sup> Wang et al. investigated the influence of Bi and they conclude that a strong  $\text{CuO}-\text{Bi}_2\text{O}_3$  interaction leads to a stabilization of  $\text{Cu(I)}$ , being important for the formation of active  $\text{Cu}_2\text{C}_2$  species.<sup>[6]</sup> W. Reppe proposed that Bi inhibit the formation of cuprene which plugs the pipes in the industrial process.<sup>[7]</sup> A relationship between catalytic activity and unspecified  $\text{Cu(I)}$

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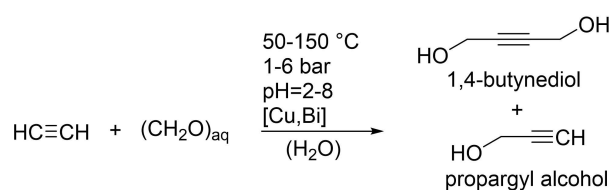
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**Scheme 1.** Ethynylation reaction of acetylene and formaldehyde to 1,4-butyne-1,3-diol and propargyl alcohol including the parameter range applied in industrial processes.<sup>[1]</sup>

surface centers (amorphous active cuprous species) was derived from infrared spectroscopic experiments (CO adsorption), one of the very few studies of spent catalysts in the literature proposing a reaction mechanism.<sup>[8]</sup>

In all former experimental studies, the focus was on the characteristics of the pre-catalysts only (supported copper(II) oxides). The present study shall bridge the gap between these pre-catalysts and catalysis by focusing on the active species "Cu<sub>2</sub>C<sub>2</sub>" formed under activation conditions. We learned to work safely with the explosive Cu<sub>2</sub>C<sub>2</sub> species in the activated, working and spent catalyst and identified Raman spectroscopy and X-ray powder diffraction (XRD) as most suitable methods for its characterization. Cu<sub>2</sub>C<sub>2</sub> was doubtlessly identified and even quantified (thermogravimetry, TG, and Raman spectroscopy) in the activated and working catalysts, allowing correlation between the progress of the reaction and the catalytic performance. Moreover, Cu<sub>2</sub>C<sub>2</sub> formation could be followed during typical activation procedures in the complex solid-liquid-gas systems. All experiments were performed with silica supported industrial-like Cu/Bi catalysts and wherever necessary or possible with pure (bulk) or supported Cu<sub>2</sub>C<sub>2</sub> for comparison.

**Preparation and characterization of the pre-catalysts:** The SiO<sub>2</sub> supported Cu/Bi catalysts were prepared by co-precipitation in close analogy to industrial catalysts. The standard loading of industrial catalysts is 30–60 wt% Cu and 2–4 wt% Bi.<sup>[1c,9]</sup> X-ray powder diffractograms of a standard catalyst containing 35 wt% Cu and 4 wt% Bi after drying (80 °C) and after calcination (4 h; 450 °C (=standard calcination temperature), and 700 °C, denoted as Cu35Bi4-450 etc.) are given in Figure S1.

The sample dried at 80 °C (Cu35Bi4-80) consists of basic copper nitrate (Cu<sub>2</sub>NO<sub>3</sub>(OH)<sub>3</sub>), the main product of co-precipitation. The calcined samples contain CuO. Table S1 summarizes crystallite sizes calculated by Scherrer equation.<sup>[10]</sup>

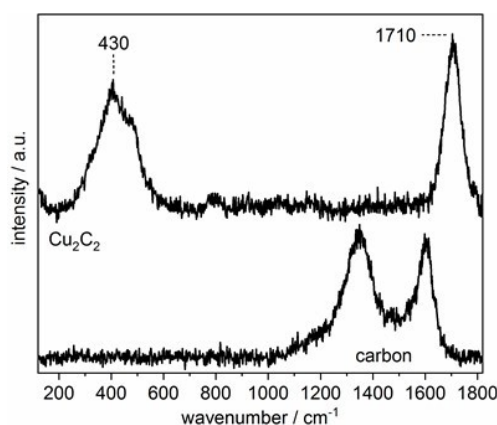
Surface areas, pore sizes and pore volumes of the catalysts as well as the real Cu and Bi loadings (ICP-OES) are summarized in Supporting Information Table S1 too. As expected, the higher calcination temperature reduces the BET surface area. The Raman spectra of the catalyst after different thermal treatment are shown in Figure S2. The spectra of the calcined samples fit well with the CuO reference spectrum. The signals of Cu35Bi4-80 match a Cu<sub>2</sub>NO<sub>3</sub>(OH)<sub>3</sub> reference.

**Model compounds: pure and supported copper acetylide, Cu<sub>2</sub>C<sub>2</sub>:** Besides the industrial-like Cu/Bi catalyst, pure Cu<sub>2</sub>C<sub>2</sub> was synthesized and characterized for direct comparison, taking account of safety measures. Characterization of Cu<sub>2</sub>C<sub>2</sub> is challenging due to its explosive decomposition in dry state. Characterization techniques are preferred, which allow to work in (aqueous) suspension or at least in wet state. Raman spectroscopy was found to best meet all the demands. Besides experimental advantages compared to infrared, Raman allows to identify the characteristic C≡C- and C–H-bond vibrations separately from water. Supported Cu<sub>2</sub>C<sub>2</sub> catalysts were found to be comparatively stable at dry (ambient) conditions at least up to moderate loadings.

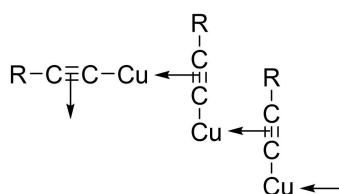
In Figure 1, the Raman spectrum of the freshly prepared pure Cu<sub>2</sub>C<sub>2</sub> is shown in comparison to a typical carbon reference (with typical D-peak at 1350 cm<sup>-1</sup> and G-peak at 1600 cm<sup>-1</sup>).<sup>[12]</sup>

Signals arise at 430 cm<sup>-1</sup> including a shoulder at higher wavenumbers and at 1710 cm<sup>-1</sup>. The signal at 430 cm<sup>-1</sup> corresponds to the Cu–C bond. Garbuzova et al. and Aleksanyan et al. indicate the same wavenumber for Cu–C σ-bonds in other copper(I) acetylide compounds as for example (phenylethynyl)copper(I) (PEC, (CuC≡CPh)<sub>x</sub>).<sup>[3a,b]</sup> The signal at 1710 cm<sup>-1</sup> corresponds to the C≡C bond and is surprisingly shifted; C≡C-bonds are rather expected at 2100 cm<sup>-1</sup>. Aleksanyan et al. found C≡C bond wavenumbers being lower on average by 180–200 cm<sup>-1</sup> compared to the corresponding alkyne precursor molecules in other copper(I) acetylide compounds.<sup>[3b]</sup> Sladkov et al. propose that the C≡C bond in copper(I) acetylide compounds can be shifted towards lower frequencies by up to 300 cm<sup>-1</sup> because of the decreasing order of the C≡C bond.<sup>[3d]</sup> The even larger difference for Cu<sub>2</sub>C<sub>2</sub> found in this investigation can be explained by additional bonding partners. In contrast to the molecular model compounds discussed above, triply bound carbons do not only coordinate to one copper but to two, i.e. on both sides of the C≡C bond in addition to π-bond coordination. The further decrease of the bond order (1710 cm<sup>-1</sup>) is thus reasonable.

Crystalline Cu<sub>2</sub>C<sub>2</sub> can also be identified by X-ray powder diffraction.<sup>[13]</sup> The powder diffractogram of pure Cu<sub>2</sub>C<sub>2</sub> is given in Figure S3. The pattern obtained for the freshly prepared Cu<sub>2</sub>C<sub>2</sub> match well with the pattern published by Judai et al.,<sup>[13]</sup> who also calculated the structure of lowest energy of Cu<sub>2</sub>C<sub>2</sub> via DFT based on alkali metal acetylide compounds. Bond lengths of 1.29 Å between triple and double bonds were predicted. The C<sub>2</sub>-unit is surrounded by four end-on and four side-on coordinated Cu atoms.<sup>[13]</sup> Several other polymer-like structures of copper acetylides were published.<sup>[3a,d,14]</sup> A general formula is given in Scheme 2 for illustration.



**Figure 1.** Raman spectrum of freshly prepared Cu<sub>2</sub>C<sub>2</sub> (aqueous suspension) from 115 cm<sup>-1</sup> to 1880 cm<sup>-1</sup>. For comparison, a carbon reference (activated charcoal from FLUKA) spectrum is shown. Spectra of CaC<sub>2</sub> or Li<sub>2</sub>C<sub>2</sub> are similar to Cu<sub>2</sub>C<sub>2</sub> and show characteristic signals below 500 cm<sup>-1</sup> and at around 1870 cm<sup>-1</sup>.<sup>[11]</sup> The whole spectrum of Cu<sub>2</sub>C<sub>2</sub> in the range between 150 and 2850 cm<sup>-1</sup> is depicted in Figure S14.



Scheme 2. General structure of Cu acetylides, R=Cu, H, organic group.<sup>[3d]</sup>

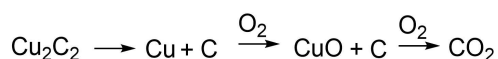
The proposed structures match well with results obtained by Raman spectroscopy. The signal at  $1710\text{ cm}^{-1}$  corresponds to the  $\text{C}_2$ -building block representing the triple bond with decreased order caused by the  $\pi$ -bonded Cu atoms. The broad signal at  $430\text{ cm}^{-1}$  corresponds to the Cu–C- $\sigma$ -bond. The broadness of the signal including the shoulder is caused by the variation of bond strengths between Cu and C and Cu and triple bonds.

Besides the structural identification, the amount of  $\text{Cu}_2\text{C}_2$  formed is of particular interest for catalytic properties. Thermogravimetric analysis coupled with mass spectrometry (TG-MS) was found to be the most useful approach to quantify  $\text{Cu}_2\text{C}_2$ . A method was developed based on the decomposition of  $\text{Cu}_2\text{C}_2$  in an oxygen containing atmosphere leading to different defined decomposition reactions (Scheme 3) and corresponding mass changes of the sample allowing determination of the initial acetylide amount.<sup>[3c,15]</sup>

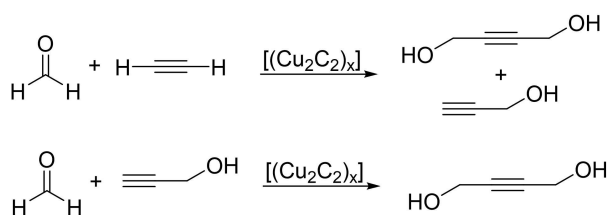
The TG results of supported  $\text{Cu}_2\text{C}_2$  samples with different CuO loadings (5 wt%, 15 wt%, 25 wt%) are exemplarily shown in Figure S4 together with a detailed description of the procedure. The mass increase by oxidation of Cu(I) to Cu(II)O was used to calculate the amount of  $\text{Cu}_2\text{C}_2$  in the catalysts. The validation of the TG-MS results is demonstrated in Figure S5. All experiments were carried out with supported  $\text{Cu}_2\text{C}_2$  only, because of the explosive decomposition of pure dry  $\text{Cu}_2\text{C}_2$ .

#### Ethynylation of formaldehyde catalyzed by (bulk) $\text{Cu}_2\text{C}_2$ :

The activation and reaction conditions are selected to be as equal/comparable as possible to the industrial process. The reaction of formaldehyde and acetylene to 1,4-butyndiol was



Scheme 3. Proposed reactions occurring during thermogravimetry of  $\text{Cu}_2\text{C}_2$  supported on  $\text{SiO}_2$ .<sup>[3c]</sup>



Scheme 4. Reactions during catalytic ethynylation of formaldehyde.

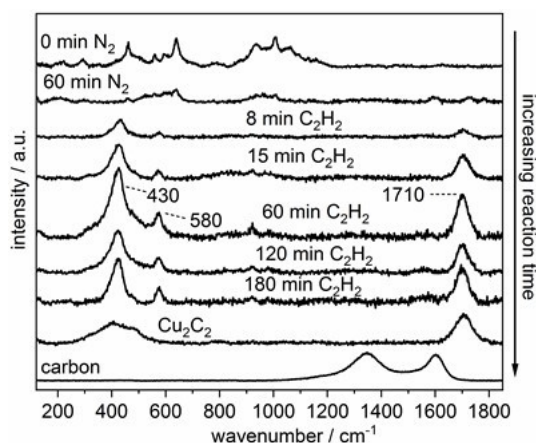
carried out at  $100^\circ\text{C}$  under slight pressure of acetylene (1.2 bar).<sup>[1]</sup> The reactions occurring under these conditions are summarized in scheme 4.

Before the reaction can start, the CuO precursor must be activated, i.e. the pre-catalyst is transformed into the active species  $\text{Cu}_2\text{C}_2$ . Industrially this is carried out either separately before the reaction or in situ during the reaction by adding new substrate and catalyst precursor to the reaction slurry. A typical activation time is 5 h.<sup>[1c]</sup> During the activation both reactants are present and reaction conditions are applied. Due to the importance of this activation process for the formation and properties of  $\text{Cu}_2\text{C}_2$ , we investigated this particular step in detail.

*Formation of  $\text{Cu}_2\text{C}_2$  under typical reaction conditions (catalyst activation).* Pre-reduction of Cu(II) to Cu(I) is the first step necessary to form the  $\text{Cu}_2\text{C}_2$  phase. In the literature it is generally accepted<sup>[5]</sup> that formaldehyde acts as reducing agent being oxidized to formic acid. There are however no studies investigating this reduction. We investigated the reduction of Cu(II) to Cu(I) by EPR spectroscopy, which allows the simultaneous observation of paramagnetic Cu(II) species dissolved in solution, as a solid as well as at interfaces. A first series of experiments (Figure S6) shows clearly that reduction of Cu(II) to Cu(I) does not take place, neither at temperatures of 25 nor at  $100^\circ\text{C}$ , i.e. formaldehyde does not act as reducing reagent for Cu(II) under typical reaction conditions. When acetylene is added (Figure S7), Cu(II) chloride is slowly reduced to Cu(I) at  $25^\circ\text{C}$  in 45 min and very fast and completely within 2 min at  $100^\circ\text{C}$ . Analogous reduction experiments with the standard catalyst Cu35Bi4-450 performed at  $100^\circ\text{C}$  (Figure S8) show that the intensities of the Cu(II)-EPR signals (double integrals of the “powder” EPR spectra) decrease slowly over time (by about 20% per hour). Additional experiments showed that the CuO catalyst can be reduced by acetylene alone (without formaldehyde) at  $100^\circ\text{C}$  too. This agrees with reports of Brameld et al., who synthesized copper acetylides from Cu(II) solutions with acetylene.<sup>[16]</sup>

Formation of  $\text{Cu}_2\text{C}_2$  as function of activation time can be traced by Raman spectroscopy (Figure 2). The Raman spectra of the activated Cu35Bi4-80 catalyst (not calcined), i.e. starting from supported basic copper nitrate ( $\text{Cu}_2\text{NO}_3(\text{OH})_3$ ) are shown after certain reaction times.

During the purging period under  $\text{N}_2$  (two top spectra), only signals of  $\text{Cu}_2\text{NO}_3(\text{OH})_3$  appear. Addition of acetylene gives rise to two signals at  $430\text{ cm}^{-1}$  (Cu–C bond) and  $1710\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C}$ -bond) of  $\text{Cu}_2\text{C}_2$ . Under acetylene gas, the signals get more pronounced over time and a third signal becomes visible at  $580\text{ cm}^{-1}$ . The signal at  $430\text{ cm}^{-1}$  of the activated catalyst is narrower and more intense than the signal of the reference (supported  $\text{Cu}_2\text{C}_2$  is seemingly structurally better defined or crystalline). The signal at  $580\text{ cm}^{-1}$  can only be observed with the activated catalyst and corresponds to a  $\equiv\text{C}-\text{C}$ -bond<sup>[3a]</sup> indicating that coupling products like Cu polyynides were formed. Controlled deposition of  $\text{Cu}_2\text{C}_2$  in contrast to fast precipitation of pure  $\text{Cu}_2\text{C}_2$  (reference) from Cu(I) solutions without reactants (formaldehyde) is the probable reason for these differences.



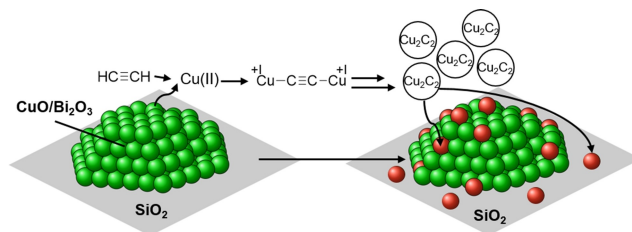
**Figure 2.** Raman spectra of the Cu<sub>35</sub>Bi<sub>4</sub>-80 catalyst after certain activation times. Freshly prepared Cu<sub>2</sub>C<sub>2</sub> and carbon (last two spectra) serve as reference.

The progressive formation of crystalline Cu<sub>2</sub>C<sub>2</sub> is additionally confirmed by XRD of suspensions taken at different times during activation procedure (Figure S9–S11). Quantitative determination of Cu<sub>2</sub>C<sub>2</sub> amounts by thermal analysis (Figure S12) shows that conversion of the Cu(II) precursor occurs continuously and is completed depending on calcination conditions, latest after 5–6 hours, which corresponds to activation times in patents.<sup>[1c]</sup>

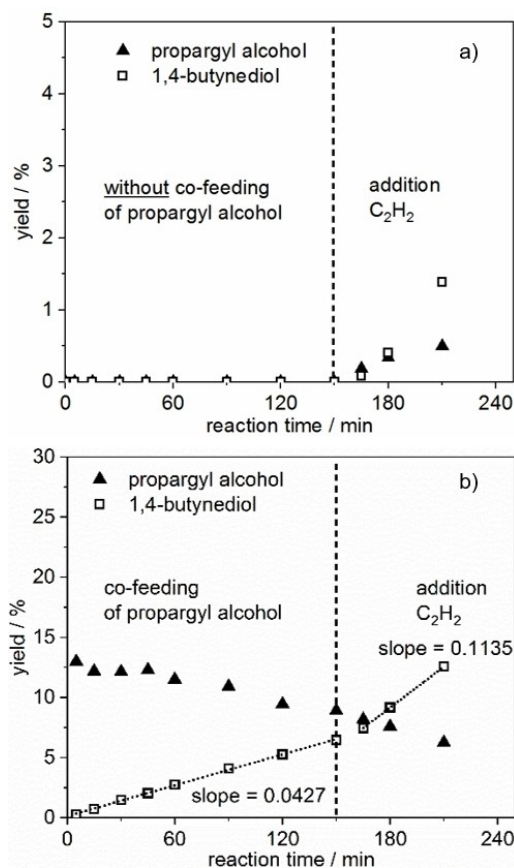
In order to study the Cu<sub>2</sub>C<sub>2</sub> formation mechanism during activation, the copper content in solution has been determined by ICP-OES as function of time (Figure S13 for the dried (non-calcined) catalyst); the results were confirmed by conductivity measurements of the solutions with a Cu(II) specific electrode (Figure S13b). During N<sub>2</sub> purging, copper leaches from the Cu/Bi catalysts into the reaction medium (e.g. up to 12 ppm = about 0.1% of the total copper content with Cu<sub>35</sub>Bi<sub>4</sub>-80, but up to 10 times less for catalysts calcined). This agrees with structural changes of the catalysts observed by Raman spectroscopy (Figure 2). With addition of C<sub>2</sub>H<sub>2</sub> gas, the Cu(II) concentration drops almost to zero indicating that sparingly soluble Cu<sub>2</sub>C<sub>2</sub> is precipitated. Raman spectroscopy and XRD revealed (Figure 2, Figure S9–11) that formation of Cu<sub>2</sub>C<sub>2</sub> gradually occurs during activation (ca. 5 h). Copper acetylides are supposedly formed from temporarily dissolved copper, the permanent copper concentration during activation is determined to be 0.3 ppm. This also agrees with the gradual formation of Cu<sub>2</sub>C<sub>2</sub> and offers an interesting starting point to optimize the final activated catalyst. The proposed model is illustrated in Figure 3.

**Copper(I) acetylide activity in ethynylation reactions:** Figure 4 shows the yields of propargyl alcohol and 1,4-butyne-1,3-diol in the ethynylation of formaldehyde in the presence of (bulk) Cu<sub>2</sub>C<sub>2</sub>.

Formaldehyde and Cu<sub>2</sub>C<sub>2</sub> are not converted (stoichiometrically) to either propargyl alcohol or 1,4-butyne-1,3-diol in the absence of acetylene (a, left). After the addition of acetylene, 1,4-butyne-1,3-diol and propargyl alcohol are formed. Cu<sub>2</sub>C<sub>2</sub> is not a reaction intermediate but acts as catalyst. Part b) also shows



**Figure 3.** Probable formation of Cu<sub>2</sub>C<sub>2</sub> during the activation of a Cu/Bi/SiO<sub>2</sub> catalyst by copper(II) leaching, reduction and re-deposition onto the support under typical activation conditions.



**Figure 4.** (a) Reaction of formaldehyde with pure (bulk) Cu<sub>2</sub>C<sub>2</sub> as catalyst and (b) reaction of formaldehyde and propargyl alcohol with Cu<sub>2</sub>C<sub>2</sub> as catalyst.

that the addition of propargyl alcohol to the reaction mixture leads to formation of 1,4-butyne-1,3-diol in the presence of Cu<sub>2</sub>C<sub>2</sub>, i.e. Cu<sub>2</sub>C<sub>2</sub> acts as catalyst for conversion of the intermediate propargyl alcohol too. 1,4-butyne-1,3-diol yield increases faster when acetylene is present. The results fit well with kinetic studies of Kiyama et al. who obtained a zero order reaction based on formaldehyde.<sup>[17]</sup>

The experiments were also conducted with the supported Cu<sub>2</sub>C<sub>2</sub> catalyst Cu<sub>35</sub>Bi<sub>4</sub>-450 (Figure 5). During the N<sub>2</sub> purging period no products are formed. After the addition of acetylene, the catalyst is activated forming Cu<sub>2</sub>C<sub>2</sub>, which catalyzes the production of propargyl alcohol and 1,4-butyne-1,3-diol after an

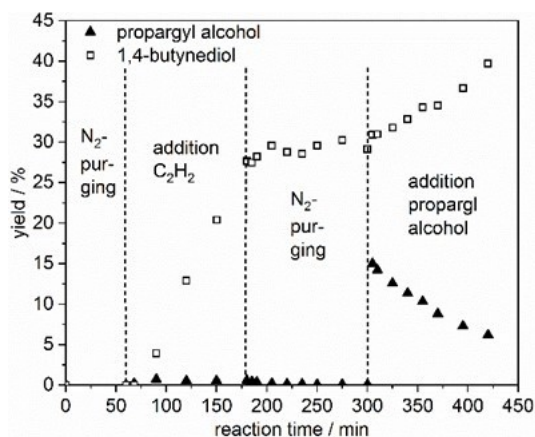


Figure 5. Reaction of formaldehyde with Cu35Bi4-450 as catalyst.

induction period (about 20 min.). The yield of the intermediate propargyl alcohol is very low in accordance with former kinetic investigations. When acetylene is replaced by N<sub>2</sub> after 180 min, yields do not increase. Addition of propargyl alcohol after 300 min leads to the formation of 1,4-butyndiol again and underlines that Cu<sub>2</sub>C<sub>2</sub> represents the active phase in the ethynylation reaction.

The reaction kinetics during activation is shown in Figure 6 for the CuO/Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalysts after drying at 80 °C (Cu35Bi4-80) and after calcination (Cu35Bi4-450). A number of interesting information can be concluded: the catalyst without calcination does not show an activation period, i.e. formation of the product(s) starts immediately after introduction of C<sub>2</sub>H<sub>2</sub>. The calcined catalyst has an induction period of about 20 min. This is in agreement with the observation that the formation of Cu<sub>2</sub>C<sub>2</sub> is faster for the non-calcined catalyst starting from (supported) basic copper nitrate (Cu<sub>2</sub>NO<sub>3</sub>(OH)<sub>3</sub>) than from copper oxide. This is in agreement with the differences in the dissolved copper amount and supports the leaching mechanism for the Cu<sub>2</sub>C<sub>2</sub> formation. The reaction rate (slope) is higher

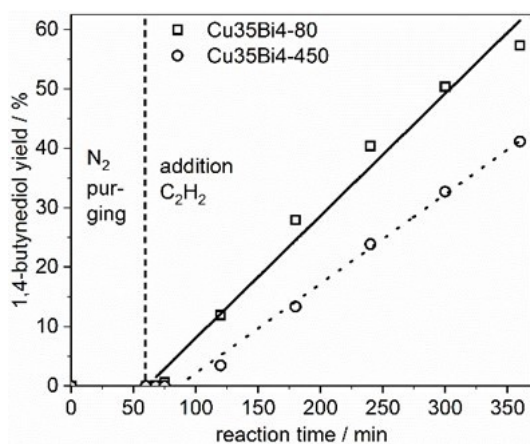


Figure 6. Reaction kinetics of supported copper oxide catalysts calcined at different temperatures (80 °C, 450 °C).

for the non-calcined catalyst ( $3.8 \text{ g}_{1,4\text{-butyndiol}} \times \text{g}_{\text{Cu}}^{-1} \times \text{h}^{-1}$ ) than for the calcined catalyst ( $3.1 \text{ g}_{1,4\text{-butyndiol}} \times \text{g}_{\text{Cu}}^{-1} \times \text{h}^{-1}$ ) up to the end of the activation period (300 min.) indicating a higher number of active species, when the catalyst is not calcined.

In summary, copper acetylides Cu<sub>2</sub>C<sub>2</sub> have been doubtlessly proven experimentally as active species (Raman, XRD) in wet supported (Cu/Bi/SiO<sub>2</sub>) and bulk copper oxide catalysts after activation and during ethynylation of formaldehyde to 1,4-butyndiol for the first time. The structurally complex compound is formed during catalyst activation in aqueous suspension by leaching of copper(II) (ICP-OES) followed by reduction and reaction with C<sub>2</sub>H<sub>2</sub> and deposition onto the support. The reducing agent is acetylene, not formaldehyde (EPR, conductivity). Correlation of properties of Cu<sub>2</sub>C<sub>2</sub> (Raman, XRD, thermal analysis) with catalytic activity support the identification of copper(I) acetylide as active species. Experimental proof and quantification of copper acetylide bridges the gap between well-characterized copper oxide pre-catalysts and its catalytic performance and allows for advanced investigations of the mechanism and more efficient parameter optimization of copper catalyzed reactions with acetylene in the future.

## Experimental Section

For more experimental details, see the Supporting Information.

CuO/Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalysts with 35 wt% Cu loading and 4 wt% Bi loading were prepared by a common co-precipitation procedure<sup>[9]</sup> based on copper nitrate, dissolved bismuth oxide and sodium silicate. Pure or SiO<sub>2</sub> supported Cu<sub>2</sub>C<sub>2</sub> was synthesized from CuCl and acetylene in ammoniacal solution.<sup>[16]</sup> XRD measurements were carried out using an *Empyrean* diffractometer from *PANalytical* in reflection mode and in an angle range between 5° and 70° in steps of 0.008°. Raman spectra were recorded on an *InVia* Raman Microscope from *Renishaw* with a laser intensity of 0.015 mW using a 532 nm laser. EPR spectroscopy was measured using a *JEOL JES-RE 2X* spectrometer on X-band frequency at -120 °C with a microwave frequency of 9.20 GHz, 5 mW, a modulation amplitude of 0.4 mT and a sweep-time of 4 min. The metal contents as well as the leached Cu amounts were determined via elemental analysis using an ICP-OES 700 from Agilent. For the conductivity measurement a copper(II)-selective electrode by *Metrohm* was inserted and an Ag/AgCl(aq) (3 M KCl) reference electrode was used. TG-MS experiments were done with a *STARe* System TGA DSC<sup>3+</sup>, TGA 2 from *Mettler Toledo GmbH* connected to a *ThermoStar*<sup>TM</sup> mass spectrometer from *Pfeiffer Vacuum*. The samples were heated from 25 °C to 1000 °C with a heating rate of 10 Kmin<sup>-1</sup> in synthetic air. The standard catalyst activation was carried out at 100 °C and 1.2 bar of acetylene for 5 h. The pH was kept constant using a NaOH/NaH<sub>2</sub>PO<sub>4</sub> buffer. For a standard activation procedure 5 g of the catalyst was applied in 100 mL of a 37% aqueous formaldehyde solution. Product analysis was done by GC using *Agilent G1530A* equipped with a TCD. The catalysts were separated with a syringe from the reaction suspension during the activation procedure. The separated catalysts were washed with water, dried under vacuum and stored in a glovebox for further characterization. The exact description of the synthesis of the catalysts, the activation procedure and the analytical methods are given in the Supporting Information.

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## Conflict of Interest

The authors declare no conflict of interest.

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