# Stereoselective hydrogenation of 11-hexadecyne-1-ol on supported copper catalysts

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Hydrogenation of 11-hexadecyne-1-ol on 5—30 % copper catalysts supported on $\gamma$-$Al_2O_3$ and $MgCO_3$ results in cis-11-hexadecene-1-ol in 100 % yield. Hydrogenation does not occur on 5—30 % Cu/ZnO catalysts. The difference in behavior of the catalysts is connected with the valent state of copper on the surface and different hydrogen chemisorption.

**Key words:** 11-hexadecyne-1-ol, stereoselective hydrogenation; cis-11-hexadecene-1-ol; copper catalysts, zero-valent state of copper; concerted addition.

Stereoselective hydrogenation of acetylenic compounds containing more than ten C atoms over copper catalysts has not been studied, while a limited number of publications on the hydrogenation of short-chain ($C_2$—$C_6$) alkynes to cis-olefins over Cu are known.[1—3]

In this work, regularities of stereoselective hydrogenation of 11-hexadecyne-1-ol (**1**) on copper catalysts supported on different carriers were studied. An attempt was undertaken to estimate the dependence of the yield of cis-11-hexadecene-1-ol (**2**) on physicochemical characteristics of the supported copper catalysts.

## Experimental

Hydrogenation was carried out using a high-pressure kinetic setup in the temperature range 353—423 K and pressures 4—8 MPa in an ethanol solution. Alcohol **1** was purified to a chromatographically pure grade.

The copper catalysts on the $\gamma$-$Al_2O_3$, $MgCO_3$, and ZnO carriers were prepared according to the procedure developed by the authors.\* The copper content was varied from 1 to 30 %.

X-ray diffraction (XRD) analysis of the catalysts was carried out on a Dron-4 diffractometer with filtered Cu-K$\alpha$ radiation (30 kV, 20 mA). X-ray photoelectron spectra (XPS) of the copper catalysts were recorded on an ES-2402 instrument with a magnesium cathode. A sample was placed into a chamber of the spectrometer under a layer of absolute ethanol.

Surface area and porosity were determined on an Accusorb-2100 sorptometer by physical adsorption of nitrogen (BET method). The ESR spectra were recorded on a Jeol JESME-3x spectrometer at ~20 C. Electron microscopic measurements were carried out by a transmission method on an EM-125 electron microscope.

Thermal desorption of hydrogen from the copper catalysts was carried out as previously described.[4]

Analysis of alcohol **1** and the products of its hydrogenation was carried out on a Tsvet-500 chromatograph (a flame-ionization detector, glass capillary column 50 m × 0.25 mm, stationary phase OV-101). The products of hydrogenation of **1** were previously acetylated.

## Results and Discussion

Hydrogenation of 11-hexadecyne-1-ol over all $\gamma$-$Al_2O_3$ supported catalysts, which contained from 5 to 30 % of copper, at hydrogen pressure of 8 MPa and 393 K resulted in compound **2** in 100 % yield (Table 1). The yield of **2** did not change and remained equal to 100 % when the temperature rose up to 423 K and under a pressure of 8 MPa. A quantitative yield of cis-olefinic alcohol was also obtained over copper catalysts supported on $MgCO_3$, which contained 10—30 % of copper, under the similar regime of hydrogenation (Table 2). Quite different results were obtained on the copper catalysts supported on zinc oxide. If the catalyst contained from 10 to 30 % of copper, the yields of cis-11-hexadecene-1-ol varied from 2 to 7 %, and 98—93 % of the starting alcohol **1** remained in the catalysate (Table 3). The reaction virtually did not occur with the samples of 5 % Cu/ZnO composition, and only traces of the cis-olefinic alcohol were formed. Total conversion of the unsaturated compound on the Cu/ZnO catalysts was not achieved even in the case of hydrogenation of low-molecular alkyne, 2-hexyne, at 393 K and 8 MPa.

According to the XPS data, copper metal occurs preferentially on the surface of the Cu/$\gamma$-$Al_2O_3$ catalysts and only ~5 % copper exists in an ionic state ($Cu^{2+}$). It was shown by X-ray electronography that the Cu/$\gamma$-$Al_2O_3$ catalysts consist of copper metal and a small amount of

**Table 1.** Hydrogenation of 11-hexadecyne-1-ol over Cu/γ-Al₂O₃ catalysts in ethanol

| [Cu]* (%) | $S$/m² g⁻¹ | $T$/K | $p_{H_2}$/MPa | τ/min | Composition of catalysate (%)** | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | | | 2 | 1 |
| 5 | 95 | 353 | 8 | 300 | — | 100 |
| | | 373 | 8 | 300 | 20 | 80 |
| | | 393 | 8 | 240 | 100 | — |
| | | 423 | 8 | 220 | 100 | — |
| 10 | 90 | 353 | 8 | 300 | — | 100 |
| | | 373 | 8 | 300 | — | 78 |
| | | 393 | 8 | 135 | 100 | — |
| | | 423 | 8 | 120 | 100 | — |
| 20 | 80 | 353 | 8 | 300 | — | 100 |
| | | 373 | 8 | 310 | 19 | 81 |
| | | 393 | 8 | 170 | 100 | — |
| | | 423 | 8 | 130 | 100 | — |
| 30 | 55 | 353 | 8 | 300 | — | 100 |
| | | 373 | 8 | 300 | 20 | 80 |
| | | 393 | 8 | 180 | 100 | — |
| | | 423 | 8 | 150 | 100 | — |
| 5 | 95 | 393 | 4 | 300 | — | 100 |
| | | 395 | 6 | 320 | 18 | 82 |
| | | 393 | 8 | 240 | 100 | — |
| | | 393 | 10 | — | — | — |
| 10 | 90 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 315 | 20 | 80 |
| | | 393 | 8 | 135 | 100 | — |
| | | 393 | 10 | 45 | 100 | — |
| 20 | 80 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 310 | 21 | 79 |
| | | 393 | 8 | 170 | 100 | — |
| | | 393 | 10 | 65 | 100 | — |
| 30 | 55 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 300 | 21 | 79 |
| | | 393 | 8 | 180 | 100 | — |
| | | 393 | 10 | 120 | 100 | — |

* Here and further (Tables 2, 3, and 5) [Cu] is the copper content in the catalyst. ** According to GLC data.

nonstoichiometric spinel $CuAl_2O_4$. The formation of the spinel was confirmed by the ESR data. A weak signal of $Cu^{2+}$ in the γ-Al₂O₃ lattice was registered in the spectrum of the 10 % Cu/γ-Al₂O₃ sample.

On the surface of the Cu/MgCO₃ catalysts, mainly $Cu^0$ was observed, but in the samples containing 20 and 30 % of copper, the presence of ~6 % $Cu^{2+}$ was found. According to the literature data,[5,6] the formation of the difficult-to-reduce structure CuOMg is possible on the surface of the Cu/MgCO₃ catalysts, whereas in the bulk of the samples copper occurs in a metal state.

According to the electron microscopic data, all samples of the copper catalysts contain both highly disperse particles with sizes of 40—60 Å and dense aggregates, whose sizes are equal to 2000—3000 Å and sometimes reach several microns. With an increase in the copper content in the catalysts, a tendency toward the growth of such large dense species was observed.

According to the XPS data, there is no copper on the surface of the sample of 5 % Cu/ZnO composition. At the same time, when the catalysts contained from 10 to 30 % copper, $Cu^0$ and ~20 % $Cu^{2+}$ were observed on the surface. This is in agreement with the literature data[5] that points to the stabilization of ionic state of copper due to the presence of ZnO, and hence only partial reduction of copper occurs in the copper—zinc catalysts. Thus, the surface of the Cu/ZnO catalysts contains significantly less $Cu^0$ than the surface of the Cu/MgCO₃ and Cu/γ-Al₂O₃ catalysts. When the Cu/ZnO samples were treated with a hydrogen flow and then the reduction temperature was increased to 723 K, the Cu—Zn intermetallide readily formed (according to the XRD analysis data). As a result, there was virtually no pure metal copper on the surface, and the conversion of 2-hexyne upon hydrogenation was equal only to 48—49 %.

**Table 2.** Hydrogenation of 11-hexadecyne-1-ol over Cu/MgCO₃ catalysts in ethanol

| [Cu] (%) | $S$/m² g⁻¹ | $T$/K | $p_{H_2}$/MPa | τ/min | Composition of catalysate (%)* | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | | | 2 | 1 |
| 5 | 19.4 | 353 | 8 | 300 | 10 | 90 |
| | | 373 | 8 | 300 | 72 | 28 |
| | | 393 | 8 | 300 | 98 | 2 |
| 10 | 12.0 | 353 | 8 | 300 | 32 | 68 |
| | | 373 | 8 | 300 | 79 | 21 |
| | | 393 | 8 | 230 | 100 | — |
| 20 | 8.0 | 353 | 8 | 300 | 30 | 70 |
| | | 373 | 8 | 300 | 75 | 25 |
| | | 393 | 8 | 200 | 100 | — |
| 30 | 6.0 | 353 | 8 | 300 | 27 | 73 |
| | | 373 | 8 | 300 | 76 | 24 |
| | | 393 | 8 | 160 | 100 | — |
| 5 | 19.4 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 300 | 2 | 98 |
| | | 393 | 8 | 300 | 98 | 2 |
| 10 | 12.0 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 300 | 14 | 86 |
| | | 393 | 8 | 230 | 100 | — |
| 20 | 8.0 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 300 | 12 | 88 |
| | | 393 | 8 | 200 | 100 | |
| 30 | 6.0 | 393 | 4 | 300 | — | 100 |
| | | 393 | 6 | 300 | 11 | 89 |
| | | 393 | 8 | 160 | 100 | — |

* According to GLC data.

**Table 3.** Hydrogenation of 11-hexadecyne-1-ol over Cu/ZnO catalysts in ethanol ($p_{H_2}$ = MPa, 393 K)

| [Cu] (%) | $S$/m² g⁻¹ | τ/min | Composition of catalysate (%)* | |
| --- | --- | --- | --- | --- |
| | | | 2 | 1 |
| 5 | 1.0 | 300 | Traces | 100 |
| 10 | 3.0 | 270 | 2 | 98 |
| 20 | — | 240 | 3 | 97 |
| 30 | — | 220 | 7 | 93 |

* According to GLC data.

Table 4. Thermal desorption of hydrogen from supported copper catalysts used for hydrogenation of 11-hexadecyne-1-ol

| Catalyst | Temperature intervals of hydrogen desorption/K | | | $V_{H_2}^{\Sigma*}$ /cm$^3$ (g Cat)$^{-1}$ | Yield of 2 (%) | $w$ /cm$^3$ min$^{-1}$ g$^{-1}$ |
|---|---|---|---|---|---|---|
| | I | II | III | | | |
| 10 % Cu/γ-Al$_2$O$_3$ | 183—298 | 298—463 | | 0.052 | 100 | 4.0 |
| 10 % Cu/MgCO$_3$ | 183—298 | | 403—873 | 0.033 | 100 | 2.7 |
| 10 % Cu/ZnO | 183—298 | 298—403 | | 0.008 | 2 | 0.05 |
| 30 % Cu/γ-Al$_2$O$_3$ | 183—298 | 298—473 | | 0.049 | 100 | 2.0 |

* The sum amount of hydrogen.

Hydrogen is known[6,7] to be weakly chemisorbed on copper, but we found no quantitative data on the adsorption of $H_2$ on copper catalysts in the literature. In this connection, we studied thermal desorption of hydrogen from the copper catalysts contained 10 % Cu and supported on γ-Al$_2$O$_3$, MgCO$_3$, and ZnO. Table 4 presents the results. As seen from these data, a carrier crucially affects the temperature of desorption and the specific chemisorption of $H_2$. The catalysts can be arranged in the following sequence with respect to the specific chemisorption: 10 % Cu/γ-Al$_2$O$_3$ > 10 % Cu/MgCO$_3$ > 10 % Cu/ZnO. The rates of hydrogenation of 11-hexadecyne-1-ol (see Tables 1—3) and the values of surface area ($S$) of the catalysts change in the same sequence.

The content of zero-valent copper decreases on going from Cu/γ-Al$_2$O$_3$ to Cu/ZnO catalysts; the chemisorption of hydrogen decreases correspondingly. Since the activation of hydrogen occurs on Cu$^0$ (see Ref. 8), a decrease in the amount of the zero-valent copper on the surface reduces the possibility of adsorption and hydrogen activation.

Quantum-chemical calculations of the adsorption of 2-butyne and hydrogen on copper clusters[9] have shown that the activated adsorption of 2-butyne occurs without a barrier, while in the case of the copper surface, a transition from a molecular form of hydrogen adsorption to a chemisorption requires overcoming a significant energy barrier.

Indeed, the reaction occurs at high temperatures and high pressure of hydrogen (see Tables 1 and 2). The activation energy is equal to 53—64 kJ mol$^{-1}$ for samples of the 5—30 % Cu/γ-Al$_2$O$_3$ composition and 57—67 kJ mol$^{-1}$ for 5—30 % Cu/MgCO$_3$ samples. The order of the reaction with respect to hydrogen on the Cu/γ-Al$_2$O$_3$ and Cu/MgCO$_3$ catalysts is close to unity at pressures below 8 MPa, whereas the order of the reaction with respect to an unsaturated compound is equal or close to zero. According to the experimental data and results of calculations, an elementary act related to activation, i.e., dissociative chemisorption of hydrogen on copper, is the rate-determining step of hydrogenation at pressure below 8 MPa. Owing to the insufficient amount of copper in a zero-valent state on the surface of Cu/ZnO catalysts, the possibility of activation and specific chemisorption of hydrogen decreases, which influences the conversion of alcohol 1 and the yield of compound 2.

High selectivity of copper upon hydrogenation of the triple bond to the double one is known,[10,11] which is related first of all to the low heat of adsorption of compounds containing C=C bond on copper (~77 kJ mol$^{-1}$)[13] that is unfavorable for catalysis. The olefinic alcohol formed is practically not hydrogenated on the copper catalyst.

According to the literature data,[13] the cis-character of catalytic hydrogenation is due to the concerted addition of two activated hydrogen atoms to an unsaturated bond.

The structures
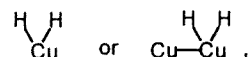


have been shown[9] to form with the highest probability upon chemisorption of hydrogen on copper. In these structures, two equivalent hydrogen atoms, which are located in close proximity to each other, are adsorbed on the copper atom. This provides the possibility of their concerted addition to the triple bond of the molecules adsorbed on copper resulting in olefinic compounds of cis-configuration. The high stereoselectivity of copper catalysts is likely to be due to the formation of stable dihydride structures on the surface that are capable of performing simultaneous addition of hydrogen atoms to the C≡C bond.

In our experiments the hydrogenation was carried out until hydrogen uptake ceased. It was found that at the pressure of hydrogen of 8 MPa and temperature of 393 K, the Cu/γ-Al$_2$O$_3$ and Cu/MgCO$_3$ catalysts absorbed much more $H_2$ than expected from the theoretical calculations. In this case, the stereoselectivity and yield of compound 2 were equal to 100 %. The amount of excess hydrogen increased with increasing metal content in the catalyst (Table 5).

It has been noted in the literature[14] that the formation of copper hydrides was possible when the just reduced finely divided copper is heated up to 250—400 °C in a hydrogen flow. Upon cooling to 333 K, the solid copper hydride decomposes, forming hydrogen and copper. One can assume that under the reaction conditions, i.e., at hydrogen pressure of 8 MPa and 393 K or higher temperature, a hydride forms that decomposes upon cooling

**Table 5.** The amount of excess hydrogen absorbed during hydrogenation of 11-hexadecyne-1-ol ($p_{H_2}$ = 8 MPa, 393 K) over $Cu/\gamma\text{-}Al_2O_3$ and $Cu/MgCO_3$ catalysts

| [Cu] | $V_{H_2}$(exc.)/cm$^3$ (g Cat)$^{-1}$ | |
|------|--------------------|------------|
| (%) | $Cu/\gamma\text{-}Al_2O_3$ | $Cu/MgCO_3$ |
| .5 | 90 | 50 |
| 10 | 95 | 50 |
| 20 | 122 | 55 |
| 30 | 140 | 68 |

of the reaction vessel. In fact, after opening of the ampoule that was cooled to 333—323 K, the intense evolution of hydrogen bubbles was observed. The surface complexes Cu—Cu (with H, H above) which were formed upon coordination of hydrogen on copper, are likely to interact with the activated triple bond, and the copper hydride does not participate in the reaction.

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