

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Microwave Synthesis of Copper Phyllosilicates as Effective Catalysts for Hydrogenation of C≡C Bonds

Shesterkina, Anastasiya; Vikanova, Kseniia; Kostyukhin, Egor; Strekalova, Anna; Shuvalova, Elena; Kapustin, Gennady; Salmi, Tapio

Published in:
Molecules

DOI:
[10.3390/molecules27030988](https://doi.org/10.3390/molecules27030988)

Published: 01/02/2022

Document Version
Final published version

Document License
CC BY

[Link to publication](#)

Please cite the original version:

Shesterkina, A., Vikanova, K., Kostyukhin, E., Strekalova, A., Shuvalova, E., Kapustin, G., & Salmi, T. (2022). Microwave Synthesis of Copper Phyllosilicates as Effective Catalysts for Hydrogenation of C≡C Bonds. *Molecules*, 27(3), Article 988. <https://doi.org/10.3390/molecules27030988>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Article

Microwave Synthesis of Copper Phyllosilicates as Effective Catalysts for Hydrogenation of C≡C Bonds

Anastasiya Shesterkina ^{1,2,*}, Kseniia Vikanova ², Egor Kostyukhin ² , Anna Strelkova ^{1,2}, Elena Shuvalova ², Gennady Kapustin ² and Tapio Salmi ³

¹ Laboratory of Nanochemistry and Ecology, National University of Science and Technology MISiS, 6 Leninsky Prospect, 119049 Moscow, Russia; anna.strelkova1994@mail.ru

² N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospect, 119991 Moscow, Russia; ks.vikanova@gmail.com (K.V.); kostyuhin.egor@gmail.com (E.K.); evshouvalova@yandex.ru (E.S.); gik@ioc.ac.ru (G.K.)

³ Laboratory of Industrial Chemistry and Reaction Engineering, Abo Akademi University, 3 Tuomiokirkontori, FI-20500 Turku, Finland; tapio.salmi@abo.fi

* Correspondence: anastasiia.strelkova@mail.ru

Abstract: For the first time, the new microwave-assisted method for the synthesis of copper phyllosilicates on a commercial SiO₂ carrier was developed. The application of microwave synthesis allowed to decrease the synthesis time from 9 to 6 h compared to the traditional DPU method of preparing chrysocolla. The synthesized catalysts were studied by N₂ adsorption, TEM and XRD methods. Catalysts prepared by microwave method are highly effective in the selective hydrogenation of the C≡C bond in 1,4-butyne-1,3-diol to 1,4-butanediol and 2-phenylethynylaniline with a selectivity of 96.5% and 100% at full conversion for 2 and 0.5 h of the reaction, respectively.

Keywords: microwave synthesis; copper phyllosilicate; selective hydrogenation; 1,4-butyne-1,3-diol; 1,4-butanediol



Citation: Shesterkina, A.; Vikanova, K.; Kostyukhin, E.; Strelkova, A.; Shuvalova, E.; Kapustin, G.; Salmi, T. Microwave Synthesis of Copper Phyllosilicates as Effective Catalysts for Hydrogenation of C≡C Bonds. *Molecules* **2022**, *27*, 988. <https://doi.org/10.3390/molecules27030988>

Academic Editor: Yuanfu Chen

Received: 25 December 2021

Accepted: 28 January 2022

Published: 1 February 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Copper and copper-containing materials are widely used in catalytic processes due to their electronic structure, which allows varying the oxidation state of copper from Cu³⁺ to Cu⁰ [1], high activity in both hydrogenation [2,3] and oxidation [4,5] reactions, and relatively low cost compared to noble metals. Among the diversity of different copper catalytic systems, copper phyllosilicates occupy a special place due to their unique structure. Copper phyllosilicate, or chrysocolla, is a silica-supported copper material with a sandwich structure consisting of octahedra CuO₆ layers possessed between tetrahedra SiO₄ layers [6]. In contrast to traditional SiO₂-supported copper oxide, phyllosilicate has an improved thermal stability, higher copper species dispersion, and larger specific surface area due to its layered structure [7–9].

The synthesis of such structured materials is not a trivial task. Among the methods for preparing phyllosilicates, it is worth noting an ion exchange [10], an ammonia evaporation [11], and the sol–gel [12] methods. However, the simplest and most convenient method is the traditional thermal hydrolysis of urea, which makes it possible to obtain phyllosilicate particles of small size [13]. The main disadvantage of this technique is the synthesis time: the decomposition of urea in solution proceeds slowly and depends on its concentration in the solution. Wei Di et al. [14] noted that complete urea hydrolysis takes 24 h during 35%Cu/SiO₂ catalyst synthesis at urea: copper ratio 3:1. Hong Du et al. [15] also pointed out that 18%Cu/SiO₂ phyllosilicate preparation by this method at urea: copper ratio 2:1 proceeds within 24 h to achieve full urea thermal decomposition. Krijn P.de Jong and co-authors [16] reported that complete copper phyllosilicate formation occurs for 7 days during urea thermal hydrolysis at urea: Cu ratio 1:1.

On the other hand, the development of chemical technology requires the use of new, modern approaches to the synthesis of materials. The use of the microwave (MW) irradiation during the synthesis of catalytic systems can significantly accelerate the decomposition of the precursors used subsequently reducing the preparation time, which, in some cases, can also lead to a decrease in the size of the deposited particles in comparison with conventional synthesis methods [17–19].

In this work, for the first time, the synthesis of copper phyllosilicates (chrysocolla) with 10% wt. Cu loading based on commercial SiO₂ support was performed using the microwave-assisted (MW) deposition–precipitation with urea method. The morphological and textural properties of the samples obtained under the microwave irradiation were compared with the samples prepared by the traditional DPU method. The catalytic properties of the synthesized materials were investigated in the selective liquid-phase hydrogenation of unsaturated compounds.

2. Results

2.1. Physico-Chemical Properties of Catalysts

Copper-containing catalysts with the copper phyllosilicate structure obtained by thermal deposition–precipitation with urea were previously studied in detail by our group and investigated in the hydrogenation reaction of nitro compounds [20]. Here, for the synthesis of chrysocolla microwave irradiation was used for the decomposition of urea for the first time and the physicochemical and catalytic properties were compared with catalysts obtained by the traditional DPU method in the selective hydrogenation of different unsaturated compounds.

The phase composition of all the prepared samples was estimated by X-ray diffraction (XRD) analysis. XRD profiles of samples exhibited a main peak at 2Θ of 22° , which corresponded to commercial amorphous silica, and no obvious peaks corresponding to CuO and Cu₂O for the calcined catalysts were detected. On both XRD profiles of the dry 10%Cu/SiO₂-DPU and 10%Cu/SiO₂-MW (Figure 1) samples, there are broadened reflexes at values of 2Θ at 30.5° , 35.8° , and 56.9° , which ideally agree with the standard reflexes of the (132), (023), and (360) chrysocolla planes. This indicates that copper nanoparticles are strongly dispersed over the surface of the carrier. The dried sample obtained under microwave conditions is slightly more crystallized compared to the DPU catalyst. After calcination at 300°C in air, the chrysocolla phase was preserved in all samples. Thus, the microwave-assisted synthesis with urea makes it possible to obtain copper-containing catalysts of the chrysocolla structure for 6 h by one-pot synthesis without further calcination.

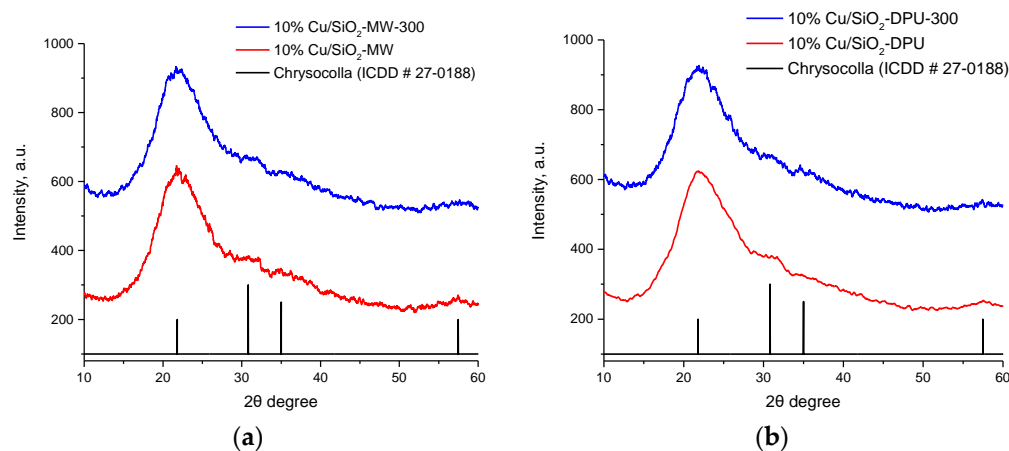


Figure 1. XRD profiles for dry and calcined 10%Cu/SiO₂ samples obtained by microwave synthesis (a) and DPU method (b).

The textural properties of the two types of catalysts were presented in Table 1 and Figure 2. The N₂ adsorption–desorption isotherms of the samples obtained by DPU and microwave-assisted methods with subsequent drying and calcination are shown in Figure 2a,b. The shape of the adsorption curves in all cases belongs to type IV according to the IUPAC classification [21], which indicates the predominance of the mesoporous structure in all samples [22]. Comparison of the synthesized samples isotherms with that of the pure SiO₂-KSKG has shown the formation of additional narrow mesopores $d = 2\text{--}6\text{ nm}$ during the copper deposition which are absent in the carrier. The formation of new pores leads to an increase in the specific surface area of the obtained catalysts (Table 1) relative to the SiO₂ support. The change in the textural characteristics of the synthesized copper-containing samples relative to the initial carrier gives reason to believe that the obtained catalysts have a hierarchical trimodal micro-meso-macro-porous structure. The synthesized catalysts differed in color; the MW samples had a light blue coloration, and the DPU samples were blue-greenish in color (Figure 3). The high specific surface area of copper-containing samples and the color from blue to olive is explained by the presence of copper phyllosilicates, as described in the work [23].

Table 1. Texture properties of the synthesized samples.

Sample	S_{BET} , m ² /g	V_{tot} , cm ³ /g	V_{meso} , cm ³ /g	V_{micro} (<i>t</i> -Plot), cm ³ /g	D_{av} , nm
10%Cu/SiO ₂ -MW	303	0.862	0.853	0.0021	1–2, 2–25
10%Cu/SiO ₂ -MW-300	299	0.857	0.848	0.0047	1–2, 2–25
10%Cu/SiO ₂ -DPU	333	0.857	0.844	0.0017	1–2, 2–25
10%Cu/SiO ₂ -DPU-300	323	0.863	0.851	0.0049	1–2, 2–25
SiO ₂ -KSKG	244	0.782	0.773	0.0065	6–18

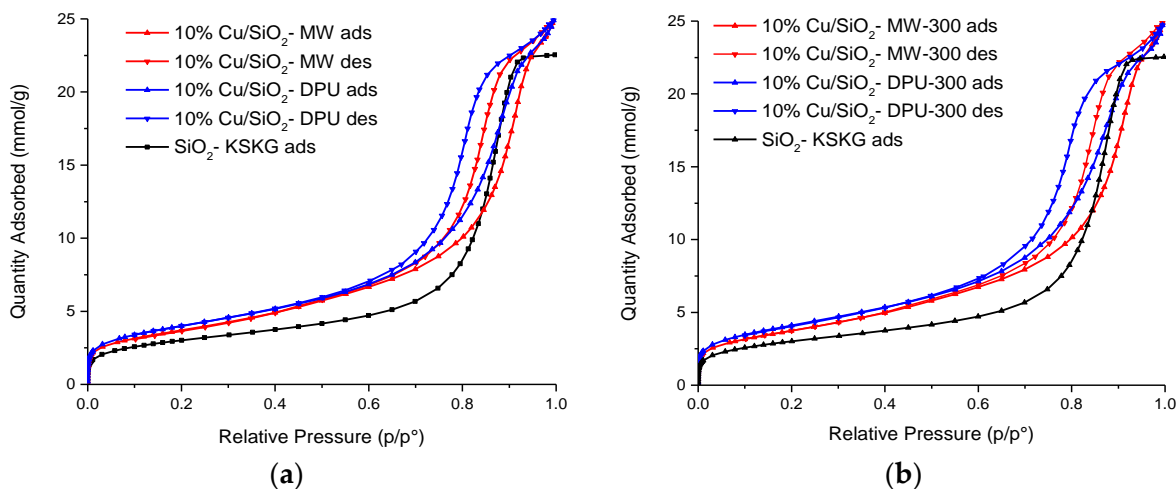


Figure 2. N₂ adsorption–desorption isotherms of prepared catalysts: dried samples (a) and calcined at 300 °C samples (b).

The shape of the hysteresis loops of all catalysts is located between the H1 and H2 types according to the IUPAC classification [24]. This may indicate the presence of various shape pores in the samples: both cylindrical and bottle-shaped [25]. The calculated values of the pore volume and pore size distribution for samples synthesized by the MW method are higher compared to the DPU samples (Figure 3, Table 1). The calcination of samples leads to an increase in micropores volume, and a decrease in surface area relative to dry samples. Thus, it can be noted that the use of the MW-assisted method leads to an increase in volume of micropores compared to the samples obtained by the DPU method and, at the same time, noticeably reduce the synthesis time of the materials.

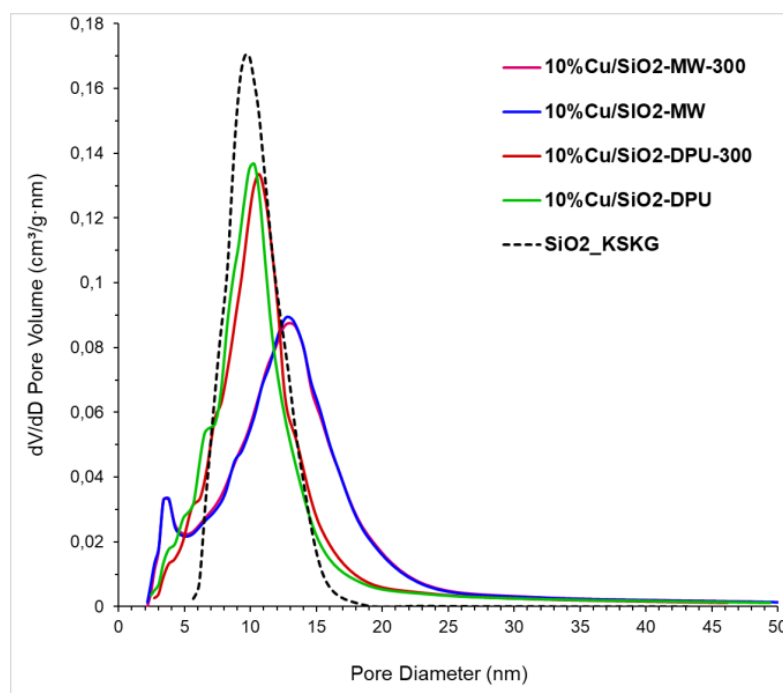
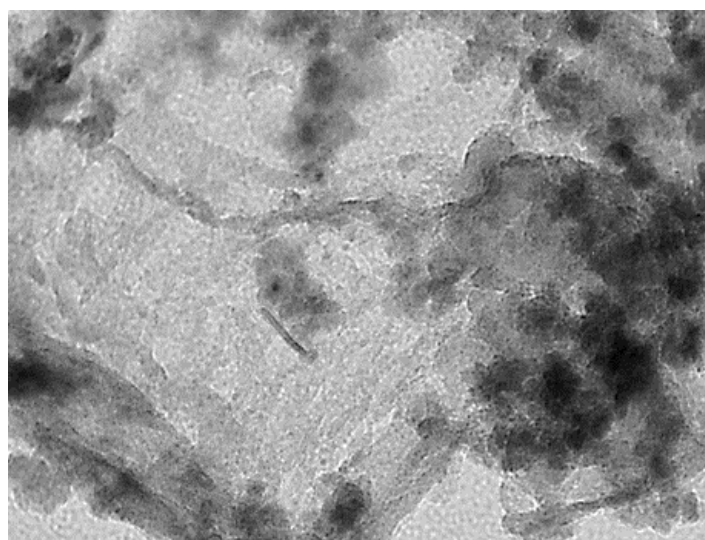


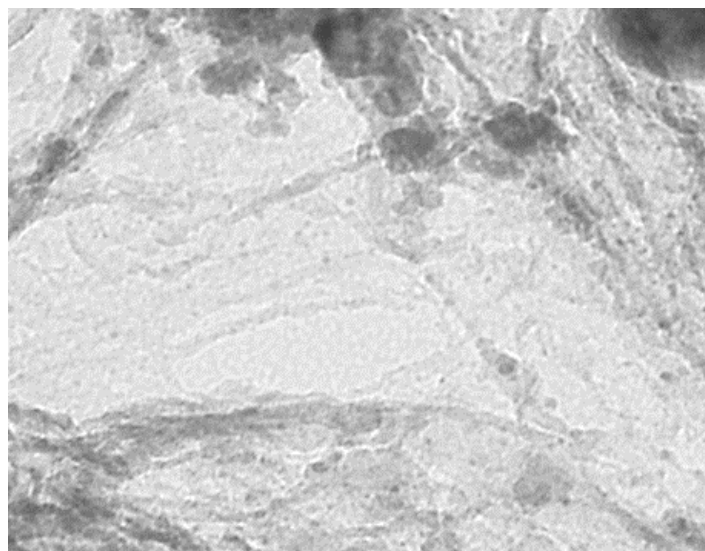
Figure 3. Pore size distributions of the 10%Cu/SiO₂ catalysts.

The TEM images of calcined catalysts are presented in Figure 4. Microphotographs of both catalysts show the presence of highly dispersed spherical nanoparticles. In addition, filamentous morphology can be seen, which also confirms the formation of chrysocolla, previously noted by XRD [26]. Statistical results calculated on the 200 particles showed that the sizes of copper particles in 10%Cu/SiO₂-MW-300 ranged from 4.3 to 5 nm, which was smaller and more uniform than that of the DPU catalyst, where the average particle size was about 7 nm.



(a)

Figure 4. Cont.



(b)

Figure 4. TEM images of calcined 10%Cu/SiO₂ catalysts obtained by microwave-assisted synthesis (a) and DPU method (b).

2.2. Catalytic Properties in the Selective Hydrogenation of Unsaturated Compounds

The effect of the samples' preparation method on their catalytic properties was investigated in unsaturated compound hydrogenation reactions. Earlier in our works [27,28], it was shown that, on copper phyllosilicates catalysts obtained by the DPU method, the best catalytic performance in hydrogenation reactions was achieved at temperatures of 150–170 °C and H₂ pressure up to 2 MPa.

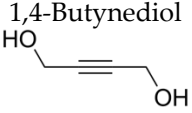
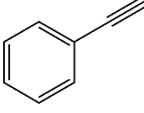
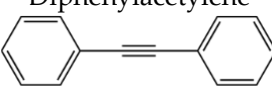
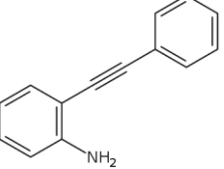
In the hydrogenation of 1,4-butyndiol at temperature of 120 °C, no conversion was detected in the presence of the 10%Cu/SiO₂-DPU-300 catalyst (Table 2), which might be explained by the fact that, according to TPR-H₂ studies, the beginning of the reduction of the chrysocolla-like structure begins only above 150 °C. Thus, the optimal reaction temperature for acetylene alcohol hydrogenation was 150 °C.

According to the experimental data presented in Table 2, all synthesized chrysocolla-like samples are catalytically active under selected reaction conditions. However, the catalytic behavior of the obtained Cu/SiO₂ samples differ somewhat depending on the synthesis method. Comparison of low-percentage samples showed that on a dry 5%Cu/SiO₂-MW sample, the full conversion of 1,4-butyndiol is achieved in 4 h of reaction with high selectivity (90.2%) for the target 1,4-butenediol.

Increasing the copper content in the samples to 10 wt.% leads to an increase of the activity of catalysts obtained both in microwave-assisted and thermal DPU methods. However, calcination of catalysts in air contributes to an increase in both the activity and selectivity of the process. The best catalytic properties under the selected reaction conditions were obtained in the presence of a 10%Cu/SiO₂-MW-300 catalyst, while the full conversion of 1,4-butyndiol was achieved in 2 h with selectivity for 1,4-butenediol of 96.5%. The catalyst recyclization have shown the negligible drop of 1,4-butenediol selectivity from 96.5% to 91.2% after the third cycle at full substrate conversion.

Moreover, the catalyst with the higher catalytic performance (10%Cu/SiO₂-MW-300) was examined in the reactions of selective hydrogenation of arylacetylenes of various structures (Table 2). Phenylacetylene is a highly reactive compound, and its full conversion was achieved in 0.5 h with a 75.2% styrene selectivity. The relatively low activity and very low selectivity toward stilbene in the diphenylacetylene hydrogenation are associated with its poor solubility in ethanol, which leads to an instant hydrogenation of C≡C to C-C bond. The complete conversion of 2-phenylethynylaniline was achieved in just 0.5 h at a temperature of 160 °C with the 2-(2-phenyl-ethen-1-yl)-aniline selectivity of 100%.

Table 2. Catalytic properties of chrysocolla-like Cu/SiO₂ catalyst samples obtained by MW and DPU methods in the selective hydrogenation of unsaturated compounds.

Substrate	Catalyst	Reaction Temperature, °C	Reaction Time, h	Conversion, %	Selectivity to C=C Bond, %	
1,4-Butynediol 	5%Cu/SiO ₂ -MW	150	2	41.8	95.6	
		120	4	100	90.2	
	5%Cu/SiO ₂ -DPU	120	0.5	0	0	
		150	0.5	17.5	100	
		150	2	40.6	94.1	
		150	4	90.5	89.4	
		150	3	100	96.5	
		150	2	100	96.3	
Phenylacetylene 	10%Cu/SiO ₂ -MW-300	170	0.5	99.5	75.2	
		Diphenylacetylene 	140	0.5	3.9	35
			160	0.5	10.2	20.5
			170	0.5	20	24.8
2-Phenylethynylaniline 	10%Cu/SiO ₂ -MW-300	140	0.5	20	100	
		160	0.5	99.5	100	

Reaction conditions: a 0.2 M substrate solution in ethanol (15 mL), H₂ pressure 1 MPa, 120–170 °C.

3. Materials and Methods

The Cu/SiO₂ catalysts were obtained by deposition–precipitation with urea by microwave synthesis (MW) and thermal hydrolysis (DPU). The synthesis of 10%Cu/SiO₂—MW catalyst was carried out in a laboratory microwave system Multiwave Pro (Anton-Paar) under irradiation (2.45 GHz) with urea in four autoclave-type Teflon vessels for 6 h. In a typical synthetic experiment, each vessel was filled with 50 mL of a mixture of decarbonated water and certain volume of 1M Cu(NO₃)₂ (Acros Organics, 99+%) solution, prepared in advance. Then, fine powder of SiO₂ (Acros Organics, S_{BET} = 244 m² g^{−1}) was added into the solution and stirred. In 15 min, urea (molar ratio urea:copper was equal 6) was added into the obtained colloid solution. Then, vessels filled with the above solution were placed into microwave system and heated up to 93 °C for 6 h. The power of microwave radiation during the synthesis was controlled automatically and was in the range of 70–80 W. The pressure of the system was increased by 4.6 bars, indicating a urea decomposition process. After the synthesis the obtained, the precipitate was separated from the mother liquor by centrifugation (10,000 rpm, 10 min) and washed 2–3 times with 40 mL of decarbonated water. The mother liquor was investigated for the deposition of Cu²⁺ ions onto the support by a qualitative reaction with 1M NH₄OH solution. The absence of blue coloration confirmed the complete deposition of the precursor onto the support surface. After each wash, the precipitate was separated by centrifugation. The sample was dried under a vacuum

on a rotary evaporator at 40 °C and a pressure of 40 mbar for 2 h and then dried at 110 °C in an oven for 5 h. The dry sample was additionally calcined in an air atmosphere at a temperature of 300 °C for 3 h (in a muffle furnace). Catalysts with a copper content of 5wt.% were obtained using a similar technique. Dry microwave samples were marked as xCu/SiO₂-MW, and the calcined samples were marked as xCu/SiO₂-MW-300, where x is the mass percentage of Cu (5 or 10 wt.%).

To compare the catalytic and physical–chemical properties, 5–10% Cu/SiO₂ catalysts with a chrysocolla structure were prepared by deposition–precipitation of Cu(NO₃)₂ on the outer surface of the SiO₂ support using thermal hydrolysis of urea (DPU). A detailed method of preparation is described in our previously published article [25]. Decarbonized distilled water (46.8 mL), 1 M Cu(NO₃) solution (3.2 mL), and 1.13 g urea were used for the initial solution for 10%Cu/SiO₂-DPU sample. However, it should be noted that a longer time of 9 h relative to the MW method is required for the complete deposition of copper ions into the carrier structure by DPU method. The DPU samples were thermally treated according to a similar MW-samples procedure. Dry DPU samples were marked as xCu/SiO₂-DPU, and the calcined samples were marked as xCu/SiO₂-DPU-300, where x is the mass percentage of Cu (5 or 10 wt.%).

The catalysts obtained by the two methods differed in color; photos of dry and calcined samples are presented on Figure 5. The difference in the color of the samples is probably due to the different volume of micropores.

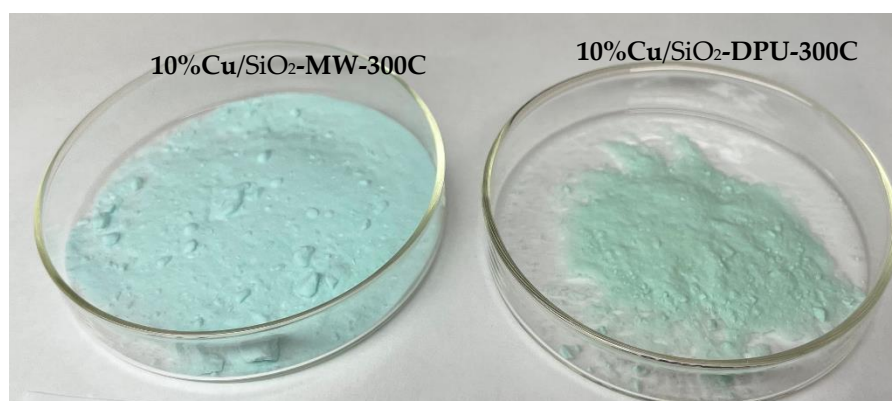


Figure 5. Photos of calcined samples 10%Cu/SiO₂ obtained by microwave (MW) and thermal (DPU) hydrolysis of urea.

Chrysocolla-like catalysts were characterized by XRD and N₂ adsorption–desorption. X-ray diffraction (XRD) were performed after drying and calcination of the samples using an ARL X'TRA diffractometer (Thermo Fisher Scientific) with CuK α radiation (40 kV, 40 mA) with a scanning rate of 1.2° per minute over the scanning range of 10 < 2 θ < 60°. ICCD data were used for the identification purpose.

The N₂ adsorption–desorption isotherms at 77 K were measured by the Micromeritics ASAP 2020 Plus System. Prior to acquisition of the adsorption isotherm, both dry and calcined samples were degassed for 3 h at 130 and 300 °C under a residual pressure of 0.8 Pa, respectively. The BET method was used to calculate the specific surface area of the sample. Pore size distributions for mesopores were determined by Barret–Joyner–Halenda (BJH) method applied to the desorption isotherms with the Harkins and Jura thickness curve. The total pore volume was evaluated at p/p₀ = 0.99. The cumulative volume at desorption in the BJH method was taken as a mesopore volume. The micropore volume was calculated as the difference between the total pore volume and the mesopore volume. The mesopore-specific surface area was calculated as cumulative at desorption in the BJH method. The micropore size distribution was calculated according to the Horwath–Kawazoe model in assumption of a cylinder shape of the pores.

The microstructure of samples was also studied by a JEM-2100 (JEOL, Tokyo, Japan) transmission electron microscope. Before measurements, the samples were mounted on 3 mm carbon-coated copper grids from a suspension in isopropanol. Images were acquired in the bright-field TEM mode at a 200 kV accelerating voltage.

The catalytic properties of the dry and calcined copper samples were investigated in the selective liquid-phase hydrogenation of unsaturated compounds with molecular hydrogen using a stainless-steel autoclave (100 mL) with a probe-withdrawing valve. The reaction conditions of hydrogenation were as follows: a 0.2 M substrate solution in ethanol (15 mL) with undecane as an internal standard, H₂ pressure 1 MPa, 150–170 °C, and 1–4 h. The stirring rate was 500 rpm (magnetic stirring). Samples of the reaction mixture were analyzed by GLPC with an internal standard method.

4. Conclusions

In this study, a new microwave-assisted method for copper phyllosilicate on a commercial SiO₂ carrier synthesis is described. The formation of the chrysocolla phase in MW samples is confirmed by the XRD and TEM results. The catalytic properties of the copper samples strongly depend on their composition and conditions of thermal treatment. The calcined samples are the most active catalysts in selective hydrogenation C≡C bonds. The best catalytic properties were obtained in the presence of a 10%Cu/SiO₂-MW-300 catalyst, the full conversion of 1,4-butyndiol on which was achieved in 2 h with a selectivity for 1,4-butenediol of 96.5%. Additionally, the 10%Cu/SiO₂-MW-300 catalyst is highly active and selective in the hydrogenation of arylacetylenes to form a C = C bond with selectivity of 75.2 and 100% to styrene and 2-(2-phenyl-ethen-1-yl)-aniline, respectively. The fast microwave synthesis method is an excellent alternative to traditional methods of synthesis of chrysocolla-like systems, which require a very long synthesis time from 9 h to several days.

Author Contributions: Conceptualization, T.S. and A.S. (Anastasiya Shesterkina); methodology, A.S. (Anastasiya Shesterkina) and E.K.; formal analysis, G.K. and E.S.; investigation, A.S. (Anastasiya Shesterkina) and A.S. (Anna Strekalova); data curation, T.S.; writing—original draft preparation, A.S. (Anastasiya Shesterkina) and K.V.; supervision, T.S. and A.S. (Anastasiya Shesterkina); project administration, T.S.; funding acquisition, T.S. and A.S. (Anastasiya Shesterkina). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ministry of Science and Higher Education (project no. 075-15-2021-591) in part related to investigation of microwave synthesis, by the Russian Foundation for Basic Research, project no. 19-33-60001 in part related to study of thermal synthesis of catalysts of selective hydrogenation.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors are thankful to Igor V. Mishin for the study of samples by XRD analysis.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are available from the authors.

References

1. Kottappara, R.; Pillai, S.C.; Vijayan, B.K. Copper-based nanocatalysts for nitroarene reduction—A review of recent advances. *Inorg. Chem. Commun.* **2020**, *121*, 108181. [[CrossRef](#)]
2. Yue, H.; Zhao, Y.; Zhao, S.; Wang, B.; Ma, X.; Gong, J. A copper-phyllosilicate core-sheath nanoreactor for carbon-oxygen hydrogenolysis reactions. *Nat. Commun.* **2013**, *4*, 2339. [[CrossRef](#)] [[PubMed](#)]
3. Zhu, S.; Gao, X.; Zhu, Y.; Zhu, Y.; Zheng, H.; Li, Y. Promoting effect of boron oxide on Cu/SiO₂ catalyst for glycerol hydrogenolysis to 1,2-propanediol. *J. Catal.* **2013**, *303*, 70–79. [[CrossRef](#)]
4. Bozbag, S.E.; Sot, P.; Nachtegaal, M.; Ranocchiari, M.; van Bokhoven, J.A.; Mesters, C. Direct Stepwise Oxidation of Methane to Methanol over Cu-SiO₂. *ACS Catal.* **2018**, *8*, 5721–5731. [[CrossRef](#)]

5. Song, E.H.; Wen, Z.; Jiang, Q. CO Catalytic Oxidation on Copper-Embedded Graphene. *J. Phys. Chem. C* **2011**, *115*, 3678–3683. [[CrossRef](#)]
6. To, D.-T.; Lin, Y.-C. Copper Phyllosilicates-Derived Catalysts in the Production of Alcohols from Hydrogenation of Carboxylates, Carboxylic Acids, Carbonates, Formyls, and CO₂: A Review. *Catalysts* **2021**, *11*, 255. [[CrossRef](#)]
7. Zhang, B.; Hui, S.; Zhang, S.; Ji, Y.; Li, W.; Fang, D. Effect of copper loading on texture, structure and catalytic performance of Cu/SiO₂ catalyst for hydrogenation of dimethyl oxalate to ethylene glycol. *J. Nat. Gas Chem.* **2012**, *21*, 563–570. [[CrossRef](#)]
8. Wang, X.; Ma, K.; Guo, L.; Tian, Y.; Cheng, Q.; Bai, X.; Huang, J.; Ding, T.; Li, X. Cu/ZnO/SiO₂ catalyst synthesized by reduction of ZnO-modified copper phyllosilicate for dimethyl ether steam reforming. *Appl. Catal. A Gen.* **2017**, *540*, 37–46. [[CrossRef](#)]
9. Dong, X.; Ma, X.; Xu, H.; Ge, Q. Comparative study of silica-supported copper catalysts prepared by different methods: Formation and transition of copper phyllosilicate. *Catal. Sci. Technol.* **2016**, *6*, 4151–4158. [[CrossRef](#)]
10. Li, F.; Lu, C.-S.; Li, X.-N. The effect of the amount of ammonia on the Cu⁰/Cu⁺ ratio of Cu/SiO₂ catalyst for the hydrogenation of dimethyl oxalate to ethylene glycol. *Chin. Chem. Lett.* **2014**, *25*, 1461–1465. [[CrossRef](#)]
11. Yao, Y.; Wu, X.; Chen, B.; Tu, Z.; Gutiérrez, O.Y.; Cui, Y.; Wang, J.; Huang, J.; Xu, Y.; Sun, H.; et al. Copper-Based Catalysts Confined in Carbon Nanocage Reactors for Condensed Ester Hydrogenation: Tuning Copper Species by Confined SiO₂ and Methanol Resistance. *ACS Sustain. Chem. Eng.* **2021**, *9*, 16270–16280. [[CrossRef](#)]
12. Zhang, Y.; Zheng, N.; Wang, K.; Zhang, S.; Wu, J. Effect of copper nanoparticles dispersion on catalytic performance of Cu/SiO₂ catalyst for hydrogenation of dimethyl oxalate to ethylene glycol. *J. Nanomater.* **2013**, *2013*, 629375.
13. Van der Grift, C.J.G.; Elberse, P.A.; Mulder, A.; Geus, J.W. Preparation of silica-supported copper catalysts by means of deposition-precipitation. *Appl. Catal.* **1990**, *59*, 275–289. [[CrossRef](#)]
14. Di, W.; Cheng, J.; Tian, S.; Li, J.; Chen, J.; Sun, Q. Synthesis and characterization of supported copper phyllosilicate catalysts for acetic ester hydrogenation to ethanol. *Appl. Catal. A Gen.* **2016**, *510*, 244–259. [[CrossRef](#)]
15. Du, H.; Ma, X.; Yan, P.; Jiang, M.; Zhao, Z.; Zhang, Z.C. Catalytic furfural hydrogenation to furfuryl alcohol over Cu/SiO₂ catalysts: A comparative study of the preparation methods. *Fuel Process. Technol.* **2019**, *193*, 221–231. [[CrossRef](#)]
16. Pompe, C.E.; Slagter, M.; de Jongh, P.E.; de Jong, K.P. Impact of heterogeneities in silica-supported copper catalysts on their stability for methanol synthesis. *J. Catal.* **2018**, *365*, 1–9. [[CrossRef](#)]
17. Kostyukhin, E.M.; Nissenbaum, V.D.; Abkhalimov, E.V.; Kustov, A.L.; Ershov, B.G.; Kustov, L.M. Microwave-Assisted Synthesis of Water-Dispersible Humate-Coated Magnetite Nanoparticles: Relation of Coating Process Parameters to the Properties of Nanoparticles. *Nanomaterials* **2020**, *10*, 1558. [[CrossRef](#)] [[PubMed](#)]
18. Kostyukhin, E.M.; Kustov, A.L.; Evdokimenko, N.V.; Bazlov, A.I.; Kustov, L.M. Hydrothermal microwave-assisted synthesis of LaFeO₃ catalyst for N₂O decomposition. *J. Am. Ceram. Soc.* **2021**, *104*, 492–503. [[CrossRef](#)]
19. Vikanova, K.; Redina, E.; Kapustin, G.; Nissenbaum, V.; Mishin, I.; Kostyukhin, E.; Kustov, L. Template-free one-step synthesis of micro-mesoporous CeO₂-ZrO₂ mixed oxides with a high surface area for selective hydrogenation. *Ceram. Int.* **2020**, *46*, 13980–13988. [[CrossRef](#)]
20. Kirichenko, O.A.; Shuvalova, E.V.; Strelkova, A.A.; Davshan, N.A.; Kapustin, G.I.; Nissenbaum, V.D. Catalytic Activity of Cu and Cu-Fe Hydrosilicates in Hydrogenation with Molecular Hydrogen. *Russ. J. Phys. Chem. A* **2018**, *92*, 2417–2423. [[CrossRef](#)]
21. McCusker, L.B.; Liebau, F.; Engelhardt, G. Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts. *Microporous Mesoporous Mater.* **2003**, *58*, 3–13. [[CrossRef](#)]
22. Xu, L.; Zhang, J.; Ding, J.; Liu, T.; Shi, G.; Li, X.; Dang, W.; Cheng, Y.; Guo, R. Pore Structure and Fractal Characteristics of Different Shale Lithofacies in the Dalong Formation in the Western Area of the Lower Yangtze Platform. *Minerals* **2020**, *10*, 72. [[CrossRef](#)]
23. He, L.; Chen, X.; Ma, J.; He, H.; Wang, W. Characterization and catalytic performance of sol-gel derived Cu/SiO₂ catalysts for hydrogenolysis of diethyl oxalate to ethylene glycol. *J. Sol-Gel Sci. Technol.* **2010**, *55*, 285–292. [[CrossRef](#)]
24. Sing, K.S.W.; Williams, R.T. Physisorption Hysteresis Loops and the Characterization of Nanoporous Materials. *Adsorpt. Sci. Technol.* **2004**, *22*, 773–782. [[CrossRef](#)]
25. Allothman, Z.A. A Review: Fundamental Aspects of Silicate Mesoporous Materials. *Materials* **2012**, *5*, 2874–2902. [[CrossRef](#)]
26. Chen, L.-F.; Guo, P.-J.; Qiao, M.-H.; Yan, S.-R.; Li, H.-X.; Shen, W.; Xu, H.-L.; Fan, K.-N. Cu/SiO₂ catalysts prepared by the ammonia-evaporation method: Texture, structure, and catalytic performance in hydrogenation of dimethyl oxalate to ethylene glycol. *J. Catal.* **2008**, *257*, 172–180. [[CrossRef](#)]
27. Shesterkina, A.A.; Strelkova, A.A.; Shuvalova, E.V.; Kapustin, G.I.; Tkachenko, O.P.; Kustov, L.M. CuO-Fe₂O₃ Nanoparticles Supported on SiO₂ and Al₂O₃ for Selective Hydrogenation of 2-Methyl-3-Butyn-2-ol. *Catalysts* **2021**, *11*, 625. [[CrossRef](#)]
28. Kirichenko, O.; Kapustin, G.; Nissenbaum, V.; Strelkova, A.; Shuvalova, E.; Shesterkina, A.; Kustov, L. Thermal decomposition and reducibility of silica-supported precursors of Cu, Fe and Cu-Fe nanoparticles. *J. Therm. Anal. Calorim.* **2018**, *134*, 233–251. [[CrossRef](#)]