

Application of Heterogeneous Copper Catalyst in a Continuous Flow Process: Dehydrogenation of Cyclohexanol

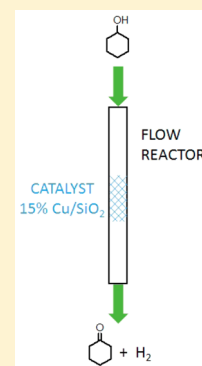
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S Supporting Information

ABSTRACT: In this laboratory experiment, the synthesis of a supported solid catalyst (Cu/SiO₂) and its application in the dehydrogenation of cyclohexanol performed under flow conditions was studied. The experiment was planned for a group of two or three students for two 6 h long sessions. The copper catalyst was synthesized using incipient wetness impregnation of the silica support with copper(II) nitrate trihydrate as the precursor of the active phase. It was then dried, calcined, and reduced. Each step of the synthesis was characterized by color change. The catalytic reaction was performed as a continuous process in a flow reactor, and the postreaction mixture was analyzed using gas chromatography. The laboratory experiment showed practical aspects of heterogeneous catalysis and encouraged students to seek alternative, environmentally friendly methods of organic compound synthesis.

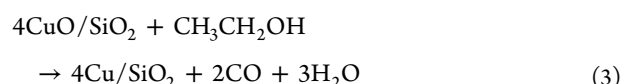
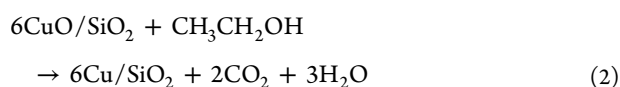
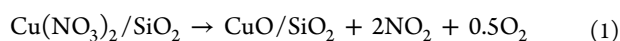


KEYWORDS: Laboratory Instruction, Hands-On Learning/Manipulatives, Catalysis, Oxidation/Reduction, Synthesis

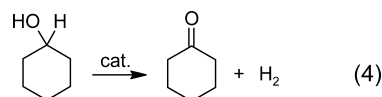
INTRODUCTION

"Catalysis is a phenomenon by which chemical reactions are accelerated by small quantities of foreign substances, called *catalysts*".¹ If a catalyst and reactants are in different phases (solid–liquid, solid–gas, or liquid–gas), the process is called *heterogeneous catalysis*.² The majority (80%) of the industrial processes are conducted over solid heterogeneous catalysts.^{1,3} Several examples concerning heterogeneous catalysis have already been described in this *Journal*: hydrogenation of ethene and 1-butene over palladium catalyst,^{4,5} methanol synthesis (platinum catalyst),⁶ Friedel–Crafts alkylation (aluminum catalyst),⁷ or oxidation of methanol to formaldehyde (copper catalyst).^{8,9} Some metal-based catalysts require a support, which improves their mechanical resistance and dispersion of the active phase; these are called supported catalysts.^{4–6}

In the experiment conducted with students, first a supported metal catalyst—Cu/SiO₂—was synthesized. The active phase of the catalyst was copper; silica played the role of a support. The catalyst was prepared using incipient wetness impregnation, which is one of the classical methods for preparation of solid catalysts.^{2,3,10} After the impregnation, the catalyst was calcined (eq 1) and reduced (eqs 2 and 3):



The subsequent part of the experiment was the application of the prepared copper catalyst in the dehydrogenation reaction. The reaction was performed in a flow reactor (continuous process), with reagents in the gas phase. Many industrial processes are designed as continuous processes, which is why it is important to make students familiar with the idea of such a process. For this experiment the dehydrogenation of cyclohexanol to cyclohexanone (eq 4) had been chosen as the test reaction for the catalyst. The product of the reaction (or its mixture with cyclohexanol) can be used in the production of ϵ -caprolactam and adipic acid, and then Nylon 6.6.¹¹

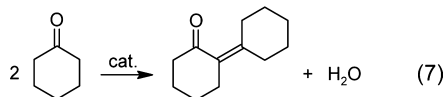
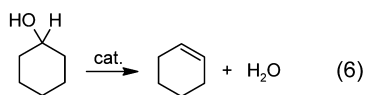
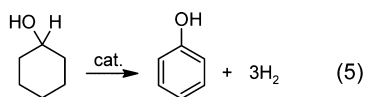


A variety of catalysts are used in the dehydrogenation of cyclohexanol to cyclohexanone;¹² among them there are copper-based catalysts (e.g., Cu/SiO₂, Cu/MgO, Cu/ZnO).^{13–18} The support and the preparation method play a crucial role in the selectivity of these catalysts in the dehydrogenation of cyclohexanol.^{13,14} Apart from the dehydrogenation into cyclohexanone, the dehydrogenation of a

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cyclohexane ring can occur (phenol is a product: eq 5). Cyclohexanol can also dehydrate (cyclohexene is formed: eq 6). In some cases subsequent condensation of cyclohexanone is also possible (e.g., 2-cyclohexylidenecyclohexan-1-one is formed: eq 7).



The dehydration of cyclohexanol is connected with the acid properties of the support; the condensation reaction is possible when a basic support is used (e.g., MgO). Concurrently, there is a discussion about whether monovalent copper (Cu^+) or metallic copper (Cu^0) plays the main role in the formation of cyclohexanone and phenol.^{15–17} In this case, the opinions of the various research groups are divided.

The aim of the experiment was to familiarize students with the concept of the synthesis of a solid catalyst and conduct a reaction under flow conditions, which is important from the point of view of chemical technology, as most laboratory reactors are batch-type reactors.

EXPERIMENTAL OVERVIEW

The laboratory experiment was planned for a group of two or three students. The work was divided into 2 days: 6 h each day. During the first day of the experiment the catalyst was synthesized; during the second day the catalytic reaction was performed.

15 wt % Cu/SiO_2 was synthesized using incipient wetness impregnation. The precursor of the active phase was copper(II) nitrate trihydrate. SiO_2 was impregnated with a water solution of the precursor, then dried (80 °C, 1 h), calcined in a stream of air (450 °C, 1 h), and reduced with ethanol (350 °C, 2 h).

Thus, prepared catalyst was used in the catalytic reaction, i.e., dehydrogenation of cyclohexanol. The reaction was performed in a flow reactor at three different temperatures, namely, 200, 250, and 300 °C (the temperatures were chosen on the basis of the boiling point of the reagents). Liquid cyclohexanol was dosed into the electrically heated reactor and evaporated in its upper part, and the cyclohexanol vapor went through the catalyst bed kept at a given temperature.

The reaction products were analyzed by GC. The detailed experimental procedure is given in the [Supporting Information](#) in the student handout.

HAZARDS

Safety goggles, lab coats, and gloves are recommended during the whole laboratory experiment. Students should avoid contact with all utilized chemical substances. Cyclohexanol is highly toxic (if swallowed or inhaled), is considered a skin irritant, and is flammable. Ethanol is an eye irritant and a flammable liquid. Copper(II) nitrate trihydrate is an oxidizing agent, may cause eye damage, and is a skin irritant. Calcination and reduction of the precatalyst, as well as the catalytic reaction, should be

performed under a hood. During the catalyst synthesis NO_2 , CO_2 , and CO are formed (during calcination and reduction). Vertical tube electric furnace and drying oven represent a burn hazard.

RESULTS AND DISCUSSION

The catalyst was synthesized using a classical method: incipient wetness impregnation. At every step of the synthesis the catalyst had a different color (Figure 1). The support was

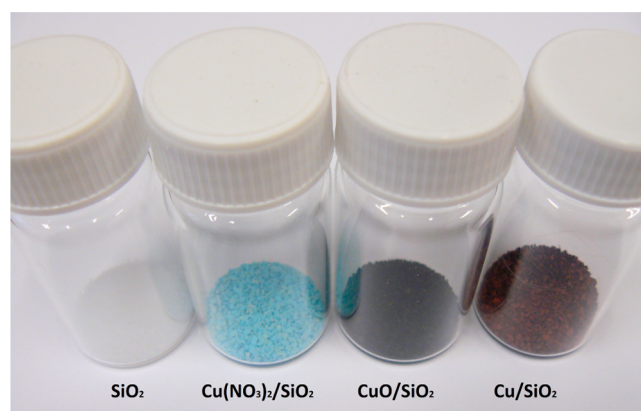


Figure 1. Synthesis of the catalyst: subsequent stages.

colorless. After impregnation of the support with a solution of copper(II) nitrate, the resulting precatalyst— $\text{Cu}(\text{NO}_3)_2/\text{SiO}_2$ —was blue. This was because copper(II) nitrate was present. Then, during the calcination, copper(II) oxide was formed (eq 1), which was why the precatalyst— CuO/SiO_2 —became black. At the very end, copper(II) oxide was reduced (eq 2 or 3). In the experiment, ethanol was used as the reductant. Students obtained a dark-red catalyst, Cu/SiO_2 ; the color is characteristic for dispersed elemental copper, although elemental copper in a form of a strip is yellow.^{19,20} The pronounced color change observed during the preparation of the catalyst not only added to the educational aspects of this experiment (giving the opportunity to discuss the reasons for the changes of colors) but also provided students with a confirmation that the desired transition occurred.

The prepared catalyst was used in a catalytic reaction: dehydrogenation of cyclohexanol to cyclohexanone (eq 4). During the reaction the dehydration of cyclohexanol into cyclohexene was also observed (eq 6).

The average values from the results obtained by students in the academic year 2014/2015 are given in Figure 2. It can be seen that the conversion of cyclohexanol increases steeply with temperature. The yield of cyclohexanone follows the conversion. It is the main product of the reaction; at 300 °C its yield reaches approximately 82%. Cyclohexene is formed in the whole range of temperatures, although its yield never exceeds 5%, even at the highest reaction temperature. In all performed reactions heavy products are also formed, however their total yield reaches less than 5%. The students were not required to identify the remaining signals found in the obtained chromatogram.

CONCLUSIONS

The experiment can be used as an effective teaching tool in a chemical technology laboratory. It gives students hands-on knowledge of catalyst preparation and the modes of performing

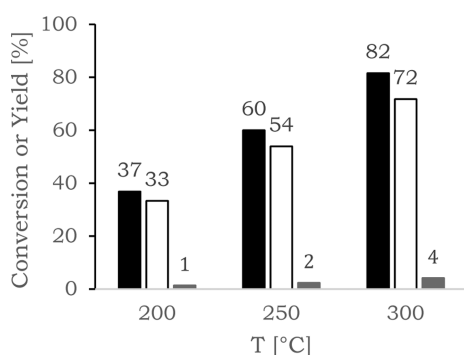


Figure 2. Results of the experiments obtained by students in the academic year 2014/2015 (6 student groups, spring semester). Values were calculated based on the average peak areas obtained from three injections of 0.2 μL of a solution collected during 10 min of reaction after collecting the forerun; for details see student handout. Black: average conversion of cyclohexanol. White: average yield of cyclohexanone. Gray: average yield of cyclohexene.

chemical processes. The catalyst is synthesized using a very common method of obtaining a heterogeneous catalyst. The catalytic reaction is carried out in a flow mode of reaction that is characteristic for many large-scale processes. Analyses of reaction products are performed using gas chromatography. The experiment is easy to handle; all reagents are commercially available.

On the basis of the results of the prelaboratory quiz and final report, the instructor will check if the students met the following learning outcomes. The students will be able to

- Implement incipient wetness impregnation to synthesize a heterogeneous supported catalyst.
- Deconstruct a continuous heterogeneous catalytic reaction under flow conditions.
- Explain how temperature influences the kinetics of a specific catalytic reaction.
- Apply gas chromatography to determine the composition of a postreaction mixture.
- Differentiate between the conversion of the substrate and selectivity of a catalytic reaction.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00849.

Instructor notes (PDF, DOCX)

Student handout (PDF, DOCX)

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Deutschmann, O.; Knözinger, H.; Kochloeff, K. Heterogeneous Catalysis and Solid Catalysts. *Ullmann's Encyclopedia of Industrial Chemistry*. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a05_313.pub2/abstract (accessed Jun 2016).
- (2) Kolb, D. Catalysis. *J. Chem. Educ.* **1979**, *59* (11), 743–747.
- (3) de Jong, K. P. *Synthesis of Solid Catalysts*, 1st ed.; Wiley: Weinheim, Federal Republic of Germany, 2009; pp 3–10, 59–82.
- (4) Perkins, R.; Mattson, B.; Fujita, J.; Catahan, R.; Cheng, W.; Greimann, J.; Hoette, T.; Khandhar, P.; Mattson, A.; Rajani, A.; Sullivan, P.; Perkins, R. Demonstrating Heterogeneous Gas-Phase Catalysis with the Gas Reaction Catalyst Tube. *J. Chem. Educ.* **2003**, *80* (7), 768–772.
- (5) Mattson, B.; Foster, W.; Greimann, J.; Hoette, T.; Le, N.; Mirich, A.; Wankum, S.; Cabri, A.; Reichenbacher, C.; Schwanke, E. Heterogeneous Catalysis: The Horiuti-Polanyi Mechanism in an Alkene Hydrogenation. *J. Chem. Educ.* **2013**, *90* (5), 613–619.
- (6) Luengo, M. A. M.; Sermon, P. A. Experiments Illustrating Heterogeneous Catalysis. *J. Chem. Educ.* **1991**, *68* (3), 251–253.
- (7) Meeks, B. S.; Lucas, A. R. Friedel-Crafts Alkylation Using Elemental Aluminum Catalyst. *J. Chem. Educ.* **1989**, *66* (2), 176–177.
- (8) Ashmore, R. E. Visual Demonstration of the Catalytic Action of Copper on Methyl Alcohol. *J. Chem. Educ.* **1968**, *45* (4), 243.
- (9) Olsen, E. S.; Ashmore, R. E. A Modification of the Copper Catalysis Demonstration Apparatus. *J. Chem. Educ.* **1982**, *59* (12), 1042.
- (10) de Jong, K. P. Synthesis of supported catalysts. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4* (1), 55–62.
- (11) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, 3rd ed.; Wiley: Weinheim, Federal Republic of Germany, 1997; pp 239–242.
- (12) Musser, M. T. Cyclohexanol and Cyclohexanone. *Ullmann's Encyclopedia of Industrial Chemistry*. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a08_217.pub2/abstract (accessed Jun 2016).
- (13) Jeon, G. S.; Chung, J. S. Preparation and characterization of silica-supported copper catalysts for the dehydrogenation of cyclohexanol to cyclohexanone. *Appl. Catal., A* **1994**, *115* (1), 29–44.
- (14) Jeon, G. S.; Seo, G.; Chung, J. S. Dehydrogenation of cyclohexanol to cyclohexanone over Cu/SiO₂ catalysts: dispersion and catalytic activity. *Korean J. Chem. Eng.* **1996**, *13* (4), 412–414.
- (15) Fridman, V. Z.; Davydov, A. A. Dehydrogenation of cyclohexanol on copper-containing catalysts. I. The influence of the oxidation state of copper on the activity of copper sites. *J. Catal.* **2000**, *195* (1), 20–30.
- (16) Fridman, V. Z.; Davydov, A. A.; Titievsky, K. Dehydrogenation of cyclohexanol on copper-containing catalysts. II. The pathways of the cyclohexanol dehydrogenation reaction to cyclohexanone on copper-active sites in oxidation state Cu⁰ and Cu⁺. *J. Catal.* **2004**, *222* (2), 545–557.
- (17) Ji, D.; Zhu, W.; Wang, Z.; Wang, G. Dehydrogenation of cyclohexanol on Cu-ZnO/SiO₂ catalysts: the role of copper species. *Catal. Commun.* **2007**, *8* (12), 1891–1895.
- (18) Romero, A.; Santos, A.; Escrig, D.; Simón, E. Comparative dehydrogenation of cyclohexanol to cyclohexanone with commercial copper catalysts: catalytic activity and impurities formed. *Appl. Catal., A* **2011**, *392* (1–2), 19–27.
- (19) Guerrero, A. H.; Fasoli, H. J.; Costa, J. L.; de Piccardo, V. Copper Is Yellow. *J. Chem. Educ.* **1989**, *66* (5), 400.
- (20) Guerrero, A. H.; Fasoli, H. J.; Costa, J. L. Why Gold and Copper Are Colored but Silver Is Not. *J. Chem. Educ.* **1999**, *76* (2), 200.