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

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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):

\[
\text{Cu(NO}_3\text{)}_2/\text{SiO}_2 \rightarrow \text{CuO/SiO}_2 + 2\text{NO}_2 + 0.5\text{O}_2
\]  

(1)

\[
6\text{CuO/SiO}_2 + \text{CH}_3\text{CH}_2\text{OH}
\rightarrow 6\text{Cu/SiO}_2 + 2\text{CO}_2 + 3\text{H}_2\text{O}
\]  

(2)

\[
4\text{CuO/SiO}_2 + \text{CH}_3\text{CH}_2\text{OH}
\rightarrow 4\text{Cu/SiO}_2 + 2\text{CO} + 3\text{H}_2\text{O}
\]  

(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

\[
\text{HO} + \text{H}_2 \rightarrow \text{O} + \text{H}_2
\]  

(4)

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
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-cyclohexylidencyclohexan-1-one is formed: eq 7).

\[
\begin{align*}
\text{HO} & \quad \text{cat} \quad \text{H} \quad \text{OH} \\
\text{HO} & \quad \text{cat} \quad \text{O} \quad \text{H} + 3\text{H}_2 \\
2 & \quad \text{cat} \quad \text{O} \quad \text{O} + \text{H}_2\text{O}
\end{align*}
\]

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 (Cu⁰) 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 colorless. After impregnation of the support with a solution of copper(II) nitrate, the resulting precatalyst—Cu(NO\(_3\))\(_2\)/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
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REFERENCES


