Video Article

Heterogeneous Catalysis

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Abstract

Catalysis is among the most important fields of modern technology and presently accounts for approximately 35% of the gross domestic product (GDP) and sustenance of approximately 33% of the global population through fertilizers produced via the Haber process.[1] Catalysts are systems that facilitate chemical reactions by lowering the activation energy and influencing the selectivity. Catalysis will be a central technology in addressing the energy and environmental challenges of modern times.

Video Link

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Introduction

Heterogeneous catalysts typically consist of a nanoscale catalytic entity (typically a metal) dispersed on a support material (typically carbon or metal oxide), which increases the surface area and often imparts some stability against aggregation of the nanoparticles. The catalyst nanoparticle has active sites on its surface, where the reaction takes place. Depending on the reaction, these active sites could be planar faces or crystal edges on the surface of the particle. Typically, smaller nanoparticles have higher catalytic activity**,** due to the higher amount of surface atoms per mole of catalyst.[2]

The reaction on the catalyst surface begins with adsorption of the reagents to the active site, followed by the reaction on the surface. The surface reaction can occur between one adsorbed species and one in the bulk, called the Eley-Rideal mechanism, or between two adsorbed species, called the Langmuir-Hinshelwood mechanism. The reacted species then desorbs from the surface into the bulk.[2]

Supported nanoscale palladium particles have shown activity in many important catalytic reactions and represent a model system for demonstrating a heterogeneous catalyst. Palladium based catalyst research efforts are broad and have ranged from upgrading of biomass to the decomposition of chemical dyes in wastewater streams. The use of palladium catalysts as a representative for heterogeneous catalysts is desirable because it allows facile separation of the catalyst from the products.[2]

Here, the heterogeneous catalyst consists of nanoscale palladium particles dispersed on a high surface area carbon support. Presently, several supported palladium catalysts are commercially available. In this educational article, two commercially available supported palladium materials are used, 1% palladium supported on active carbon and 0.5% palladium supported on granular carbon. Another material, active carbon, is used as a control experiment. The reduction of 4-nitrophenol is chosen for the catalytic reaction because it is easy to work with and the results are visible through a color change. This experimental protocol provides a very clear visual demonstration of a typical catalytic reaction.

Protocol

1. Preparation of 4-Nitrophenol Solution Mixed with Sodium Borohydride

1. Weigh 14 mg of 4-nitrophenol and dissolve in 10 ml of DI water in a glass vial.
2. Weigh 57 mg of sodium borohydride and dissolve in 15 ml of DI water.
3. Mix the two solutions and magnetic stir for 30 min at room temperature to a uniform solution. Lab coat, safety goggle and gloves are needed as standard protocol protection.

2. Preparation of Catalyst Solution

1. Weigh 10 mg of palladium on active carbon and palladium on granular carbon respectively. Weigh 10 mg of active carbon as control group.
2. Transfer weighed catalysts to a vial and add 100 ml of DI water to each vial.
3. Sonicate the vials with an output power of 135 W for 10 min until catalysts are well distributed in water.

3. Catalytic Reduction of 4-Nitrophenol

1. Measure 1.15 ml of prepared 4-nitrophenol and sodium borohydride solution, transfer to a 5 ml glass vial.
2. Record the color of solution in the vial, wait 10 minutes and record if there is any change in the color of solution.
3. Add 1 ml of prepared palladium on active carbon catalyst solution to the vial, shake the vial by hand for 20 s. Observe reaction for 20 min, record when solution color starts to change and when solution color completely fades to transparent.
4. Repeat same procedure with the palladium on granular carbon catalyst solution.
5. Repeat same procedure with the active carbon catalyst solution.
6. Compare the color change between three catalysts after 0 min, 5 min, 10 min, 15 min, and 20 min of reaction time. To quantify this change, measure UV-Vis spectra of the sample during the 20 min reaction interval.

Representative Results

The reduction of 4-nitrophenol with a catalyst is a benchmark reaction in the literature for evaluating catalyst performance and measuring kinetics. Prior to the addition of catalyst, the color of the solution is light yellow, which corresponds to the 4-nitrophenol ion in alkaline conditions. Without the addition of a catalyst, the yellow color does not fade away, this indicates that the mixture system of 4-nitrophenol and sodium borohydride is stable.

After the addition of palladium on active carbon and palladium on granular carbon catalyst solutions, the yellow color of 4-nitrophenol solution gradually fades. At a time scale of approximately 20 min, the solution becomes colorless, suggesting a complete reduction of 4-nitrophenol by the catalyst.

After the addition of the active carbon solution, with no catalyst, the yellow color of 4-nitrophenol remains unaltered within the 20 minute reaction window. Carbon acts only as a support material for palladium, so carbon by itself does not demonstrate any catalytic effect on the reaction. The control group here shows that nanoscale palladium particles supported on carbon is an active catalyst while the carbon itself is not a catalyst. This control experiment also shows that the 4-nitrophenol is not simply absorbed by the carbon and removed from the solution.

Observation of the UV-Vis absorption spectra indicates a gradual decrease at around 400 nm while increasing at around 300 nm. This change is indicative of the reduction of 4-nitrophenol during the process. The relative concentration of 4-nitrophenol is represented by the relative intensity of the absorption at 400 nm. A plot $\ln(A_t/A_0)$ vs. time shows the reaction proceeding in a quantified way. A representative plot is shown in **Figure 1**.

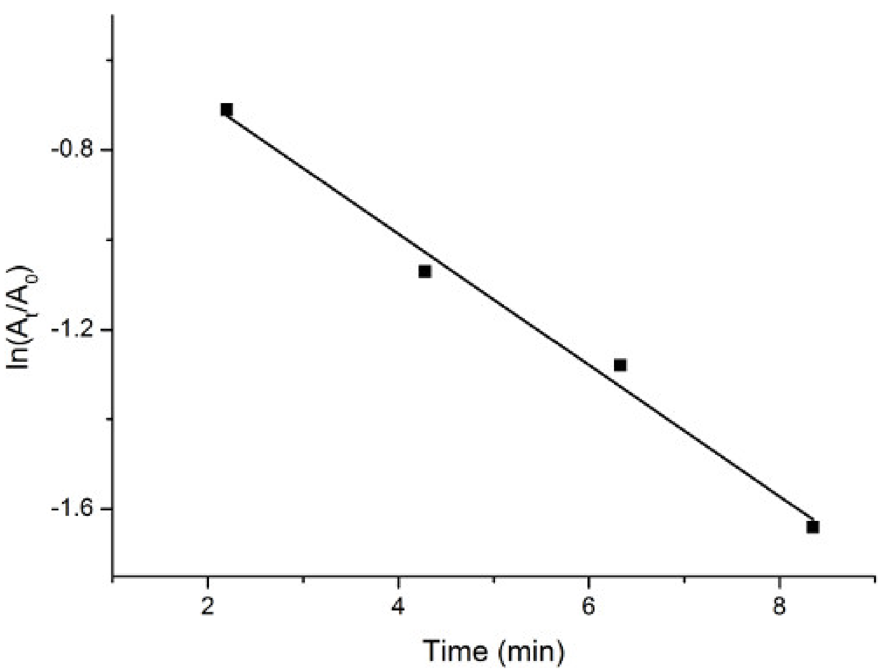

Figure 1. Plot of absorption vs. time during the reduction of 4-nitrophenol by the palladium catalyst on active carbon.

For both palladium catalysts used, there is no difference between their color change behavior and their spectra. This result indicates palladium is active in catalytic reduction of 4-nitrophenol regardless of whether it is supported on active carbon or granular carbon.

Discussion

As a benchmark reaction, the catalytic application of nanoscale palladium particles can be extended to other fields. Similar to the reduction of 4-nitrophenol, which is a colorometric (the reaction is observed as a color change), the hydrogenation of chemical dyes can be accomplished with the same protocol. Chemical hydrogenation processes are very important in many industrial reactions as well as waste disposal. Researchers have found applications of catalysts in hydrogenation reactions in fields such as petrochemicals. In the United States, benzene production reached 415,144 million gallons during fourth quarter in 2010, where hydrogenation process played an important role.

In the presence of a palladium catalyst and a basic environment, C-C coupling reactions occur between aryl/vinyl halides and alkenes.[3,4] This reaction is known as the Heck Reaction. C-C coupling reactions are of vital importance to solving the energy challenges now facing society. The implication is so important that the 2010 Nobel Prize in chemistry was awarded for work on palladium catalyzed cross coupling reaction. Catalysts are also used in the synthesis of polymer nanoparticles. In this application, polymer branches are mixed with a catalyst in order to induce the formation of star particles.[5] Finally, catalysts are found widely in nature, and drive biological reactions. Here, they naturally exist as shape specific enzymes.[6]

References

1. Armor, J. What is catalysis? *North American Catalysis Society.* (2008).
2. Thomas, J.M., Thomas, W.J. Principles and Practice of Heterogeneous Catalysis. *Wiley-VCH.* Germany (2015).
3. Heck, R.F., Nolley, J.P. Palladium-catalyzed v Vinylic Hydrogen Substitution Reactions with Aryl, Benzyl and Styryl Halides. *J. Org. Chem.* **37** (14), (1972).
4. Oberholzer, M., Frech, C. M. Mizoroki-Heck Cross-coupling Reactions Catalyzed by Dichloro{bis[1,1',1''-(phosphinetriyl)tripiperidine]}palladium Under Mild Reaction Conditions. *J. Vis. Exp.* (85), e51444, (2014).
5. Liu, J., Gao, A. X., Johnson, J. A. Particles without a Box: Brush-first Synthesis of Photodegradable PEG Star Polymers under Ambient Conditions. *J. Vis. Exp.* (80), e50874, (2013).
6. Fowler, M. L., Ingram-Smith, C. J., Smith, K. S. Direct Detection of the Acetate-forming Activity of the Enzyme Acetate Kinase. *J. Vis. Exp.* (58), e3474, (2011).

