Probing the Performance of Mixed-Phase Titanium Dioxide Photocatalysts: Synthesis, Characterization, Testing

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Abstract

The performance of mixed-phase TiO_2 was observed in an effort to test its practical use as a semiconductor photocatalyst. Synthesis of mixed-phase TiO_2, characterization using x-ray diffraction analysis, monitoring testing using the gas chromatography-FID, and testing gas phase reactor were four techniques used in this research to evaluate mixed-phase TiO_2. Synthesis of mixed-phase materials was completed in order to compare performance with the commercially prepared and widely available Degussa P25. Since we were not able to successfully make a TiO_2 sol during this research process, a previously prepared sol coated on ceramic tile was studied using x-ray diffraction. This characterization allowed us to identify rutile and anatase peaks within the samples. In order to test performance, a sample of Degussa P25 was used in a gas phase reactor that

was built during the research period. Acetaldehyde was used as a model reactant. Our testing found that acetaldehyde was fully oxidized within 20 minutes of being injected into the gas phase reactor. Gas chromatography–FID (GC-FID) was used in order to monitor the presence of acetaldehyde. Future research should include testing of non-commercially made TiO_2. Experimental protocol should also be improved in order to have more samples taken from the reactor within the first 20 minutes of reaction time.

Introduction

The degradation of air and water contaminants and the search for new energy sources have long been the object of research for environmental advocates as well as environmental engineers. The environmental application of semiconductor photocatalysis is a well-studied option in supplying solar power energy as well as in the remediation of hazardous wastes in contaminated groundwater and polluted air.[1] Research interests have grown so that the application of semiconductor photocatalysis is the subject of more than 200 published papers a month in recent years. Iron oxide, cadmium sulfide, zinc sulfide, and titanium dioxide are all types of semiconductor photocatalysts that have been used in past research. However, in this particular research, mixed-phase titanium dioxide (TiO_2) has been the primary photocatalyst of interest. Studies have shown that mixtures of anatase and rutile TiO_2 perform better than either individual rutile or anatase phases of TiO_2.[2] Our research sought to probe the performance of mixed-phase TiO_2 through synthesis in the lab, characterization of catalysts using x-ray diffraction, testing performance using a gas phase reactor, and monitoring by GC-FID.

Background

Previous research has shown that the mixed-phase TiO_2, Degussa P25, is a common standard for semiconductor photocatalysis and its environmental applications. TiO_2 is biologically inert, stable with respect to photo corrosion and chemical corrosion, and inexpensive.[3] TiO_2 is widely studied in two mineral phases, anatase and rutile. Anatase is regarded as the photoactive phase of TiO_2[4] and has a band gap of 3.2 eV corresponding to the use of ultraviolet light to excite electrons (Figure 1). Rutile, the second phase of TiO_2, generally exhibits lower catalytic activity and has a band gap of 3.0 eV. Rutile is the thermodynamically stable form of titania <cap needed?> and has a very organized, almost cube-like structure (Figure 2).[5] Although recent studies have shown smaller particles of rutile, it is generally at least 200 nm or larger in size. Degussa P25, a commercially produced form of titanium dioxide and reference catalyst in this research, is composed of both phases — 80 percent anatase and 20 percent rutile. The interaction between these phases at interfaces (Figure 4) is believed to be the source of its increased activity.

Semiconductor photocatalysis's major advantage is the conversion of light into chemical energy. This can lead to such diverse applications as solar energy storage, self-cleaning surfaces, environmental remediation, and chemical synthesis. Typically, energy (such as ultraviolet light) is used to excite electrons. When light of high enough energy is used, electrons are promoted from the semiconductor valence band to the conduction band (Figure 5). To produce chemical energy and catalytic activity, it is important to prevent the electron from recombining with the valence band hole.[6]

Most semiconductor photocatalytic events end in recombination of the electron instead of producing chemical energy. Therefore, research involving titanium dioxide focuses on making the catalyst more active and efficient in ultraviolet as well as visible light. By making the catalyst more active in visible light, the process is more practical for use in gas and water waste purification, energy renewal, and storage. The purpose of this research was to test the performance of mixed-phase TiO_2 derived from sol and then compare it to commercially produced Degussa P25.

Approach

Our initial approach for comparing the performance of mixed-phase TiO_2 to Degussa P25 involved three steps: the synthesis of TiO_2, characterizing mixed-phase TiO_2, and testing the material. The synthesis involved making samples that would form both anatase and rutile phases using a sol gel procedure or vapor deposition. X-ray diffraction would allow for analysis of our mixed-phase TiO_2 catalyst and comparison to Degussa P25. Finally, testing the catalyst using a gas phase reactor and GC-FID would allow us to compare our sample to the activity of mixed-phase TiO_2 to Degussa P25 as a reference catalyst.

Synthesis

Techniques to make the sample TiO_2 were taken from previously published materials. Our first attempt at making TiO_2 involved synthesis at low temperature. Titanium (IV) isopropoxide was added to water cooled to 4° C. Hydrochloric acid was added as an acid

catalyst. The solution was left overnight; owing to the reactivity of the titanium isopropoxide and water, titanium dioxide particles were much larger than desired. The solution was then placed in the centrifuge in order to separate larger TiO_2 particles. The solution remaining colloidal was then purified using dialysis, but the sample did not gel. A second synthetic procedure was used that involved dissolving titanium (IV) isopropoxide in a 1 to 10 solution of isopropanol. This second batch of TiO_2 also had larger than expected particles and failed to make a TiO_2 sol gel. Vapor deposition was not available for testing.

Characterization: X-Ray Diffraction

In order to identify whether the compound we synthesized was in fact mixed-phase TiO_2, x-ray diffraction analysis was used. Small samples of previously prepared TiO_2 and Degussa P25 were suspended in ethanol, placed on a glass slide, and analyzed using the x-ray diffractor. A plot of each analysis was taken from 20 to 60 degrees. Significant peaks of anatase and rutile were found in a sample of TiO_2 ceramic tile baked at 100° C (Figure 6). At 500° C there are only rutile peaks observed (Figure 7). As a reference, commercially prepared Degussa P25 was also analyzed using x-ray diffraction (Figure 8).

Testing: Gas Chromatography–FID/Gas Phase Reactor

A gas phase reactor was built from Teflon in order to test our photocatalysts (Figure 5). In order to test the performance of the reactor, a sample of Degussa P25 was suspended in ethanol and placed on a one-inch square glass plate. The glass sample was then placed inside the gas phase reactor, and a two-inch square optical filter covered our sample and

sealed the reactor. A 100 µL sample of acetaldehyde was injected into the septum port of the reactor. A 10 µL sample was syringed from the opposite septum port every five minutes. Each sample was then injected into a GC-FID in order to monitor the reactant concentration. After 20 minutes, there was no detectable acetaldehyde from the gas phase reactor. The data from the GC-FID show the decrease of acetaldehyde over a period of 20 minutes (Figure 10). The data from the gas phase reactor and GC-FID were compared with a standard acetaldehyde curve that was constructed using the gas chromatograph (Figure 11).

Results

Although the synthesis of TiO_2 sol gel in this particular research was unsuccessful, our data from the gas phase reactor show that commercially prepared mixed-phase TiO_2 is active in the oxidation of acetaldehyde. Our data show that acetaldehyde was no longer detected after 20 minutes. Our protocol for testing for the presence of acetaldehyde included taking a 10 µL sample of vapor from the gas phase reactor every 5 minutes and then injecting it into the gas chromatographer–FID. The average retention time for the acetaldehyde peak was 9.3 minutes. We were not able to take more than three accurate samples within the first 20 minutes due to the retention time of the gas chromatograph. The unavailability of acceptable ways to store more than three acetaldehyde samples at a time also prevented more data from being recorded. The high activity rate that the acetaldehyde showed will lead us to explore protocol improvements. Although only three

data points were collected, we were able to determine the amount of acetaldehyde in the gas phase reactor at specific times.

Conclusions

The Degussa P25 mixed-phase TiO_2 had a high performance level in the oxidation of acetaldehyde when reacted with an ultraviolet light of 365 nm. The standard acetaldehyde curve allowed for the measurement of moles of acetaldehyde from the gas reactor within each sample. Future projects would include testing other mixed-phase catalysts that have been synthesized. It would be necessary to improve the experimental protocol when using the gas phase reactor so that more measurements of acetaldehyde can be taken within the first 20 minutes of reaction. It also would be necessary to have a standard attenuation and range setting for the gas chromatograph so that peak areas of acetaldehyde could routinely be used to find the molar ratio during reactions.

The byproducts formed from the reaction between TiO_2 and acetaldehyde would also need to be studied in future research. Settings of the chromatograph will need to be made to detect each gas, including acetaldehyde as well as formic acid, formaldehyde, acetic acid, methanol, and any other byproducts that may result from the reaction with TiO_2. Future research should also include testing other synthesized catalysts in the gas phase reactor that have been synthesized using the sol gel method as well as vapor deposition. These catalysts should also be analyzed in order to optimize the catalyst for reactions in

visible light so that they can used in more practical industrial, commercial, and environmental applications.

References

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Table 1: Parameters of the gas chromatograph used during detection of acetaldehyde.

Apparatus	**Setting**
Oven Temperature	80° C
Column Head Pressure	150 kPa
Injection Volume	10-30 µL
Attenuation	0
Range	5

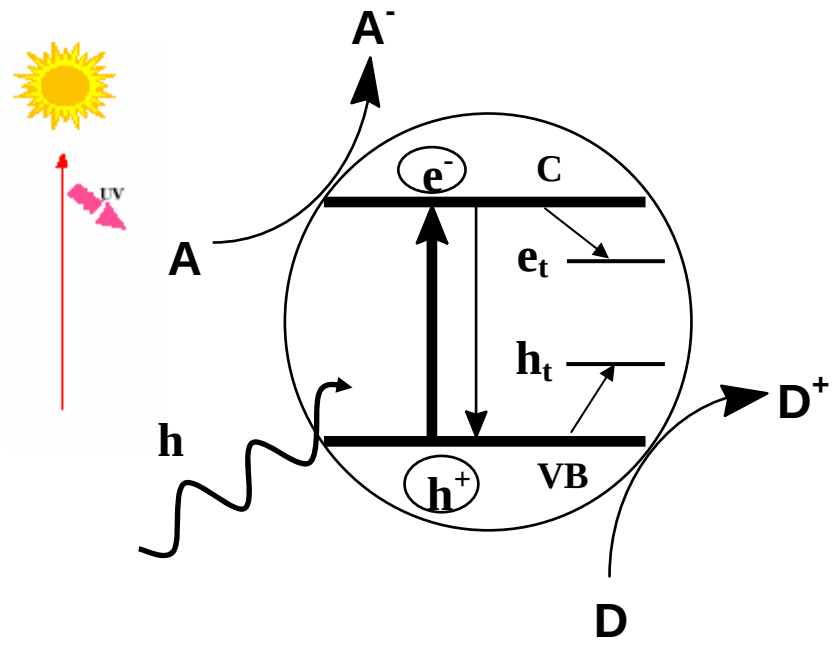

Figure 1: Schematic of photocatalytic semiconductor. [UV energy is used to promote electrons from valence band to conduction band.]

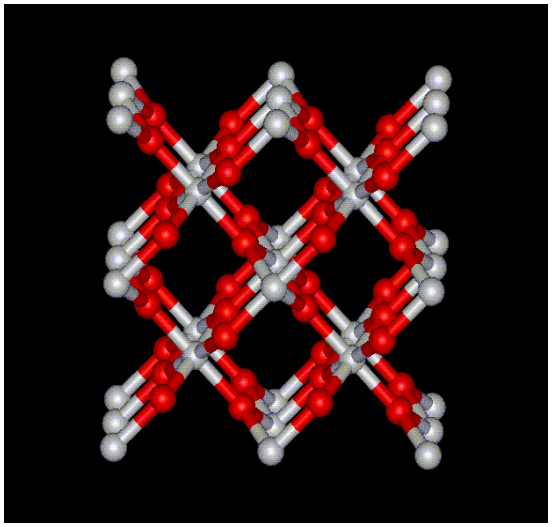

Figure 2: Rutile structure of titanium dioxide. Rutile, the second phase of TiO_2, generally exhibits lower catalytic activity and has a band gap of 3.0 eV. Rutile is the thermodynamically stable form of Titania and has a very organized, almost cube-like structure.

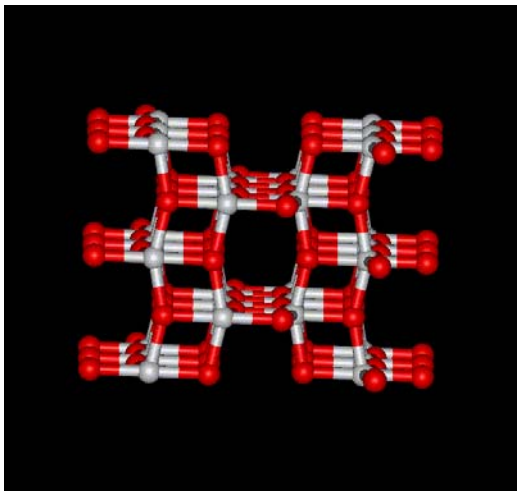

Figure 3: Anatase structure of titanium dioxide. Anatase, one of the three mineral forms of titanium dioxide, is found as small, isolated, and sharply developed crystals. Like rutile, a more commonly occurring modification of titanium dioxide, it crystallizes in the tetragonal system.

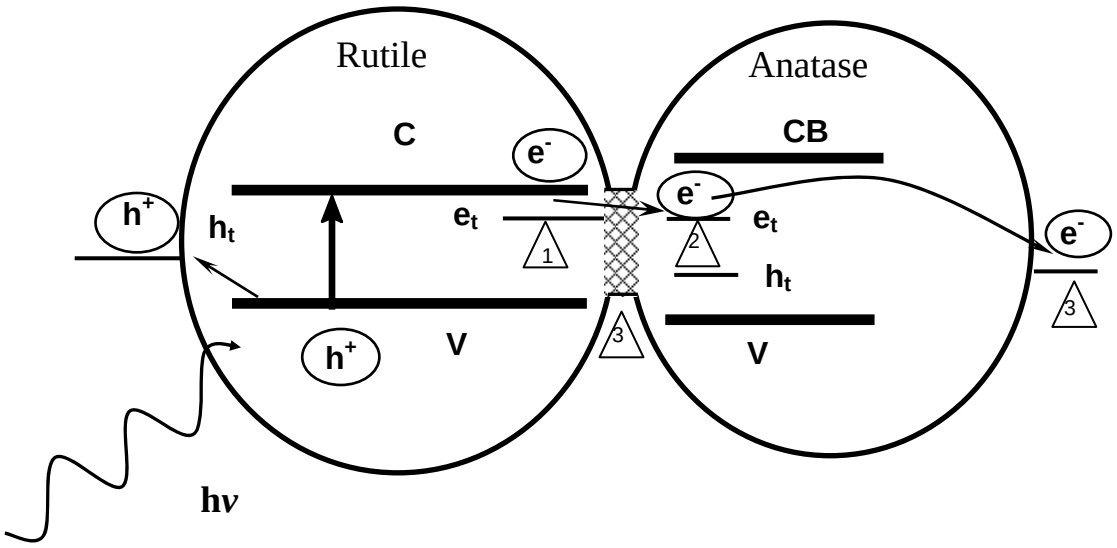

Figure 4: Interaction between rutile and anatase phases. The “3” of the diagram points to the interaction between the phases. The interaction between these phases at interfaces is believed to be the source of its increased photocatalytic activity.

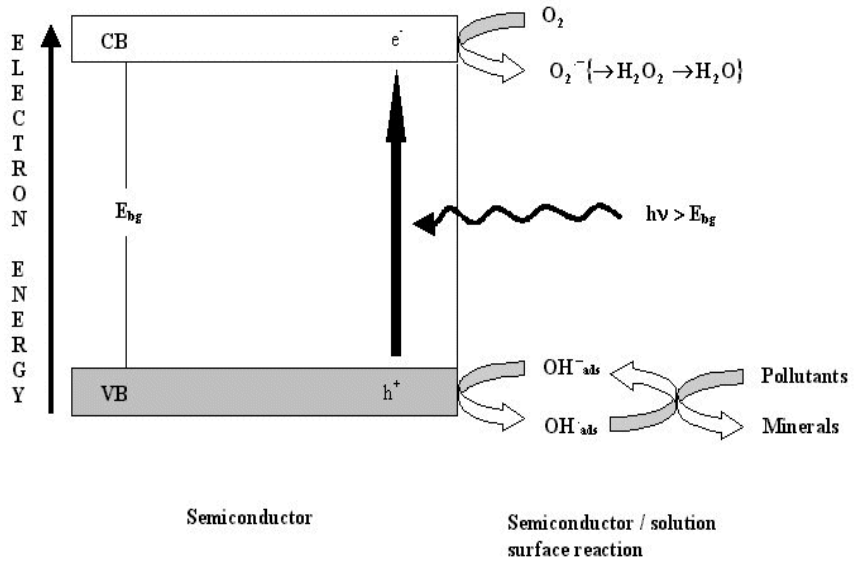

Figure 5: Diagram of photocatalytic activity. Typically, energy (such as ultraviolet light) is used to excite electrons. When light of high enough energy is used, electrons are promoted from the semiconductor valence band to the conduction band, which then encourages oxidation.

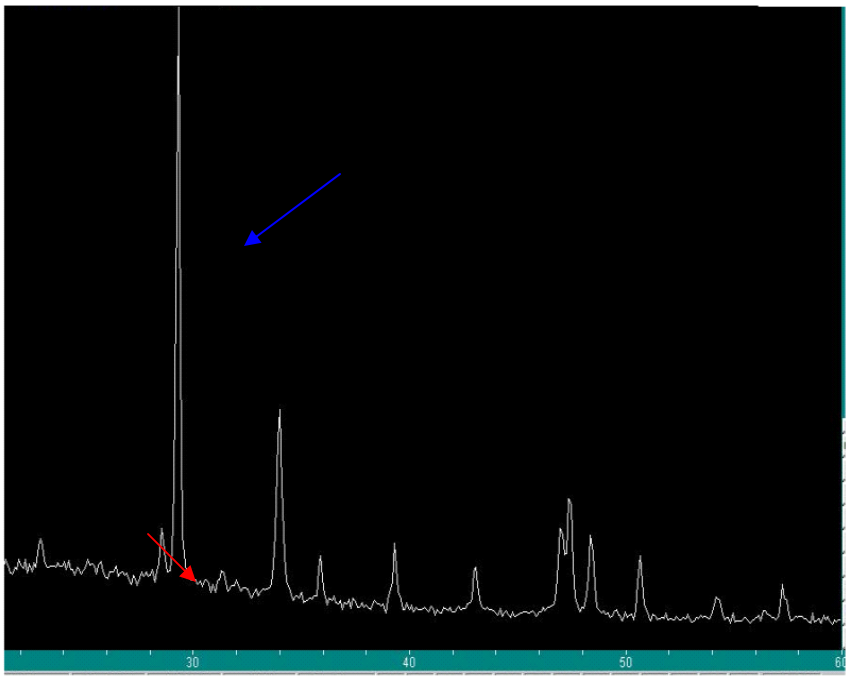

Figure 6: X-Ray diffraction of coated tile baked at 100° C.

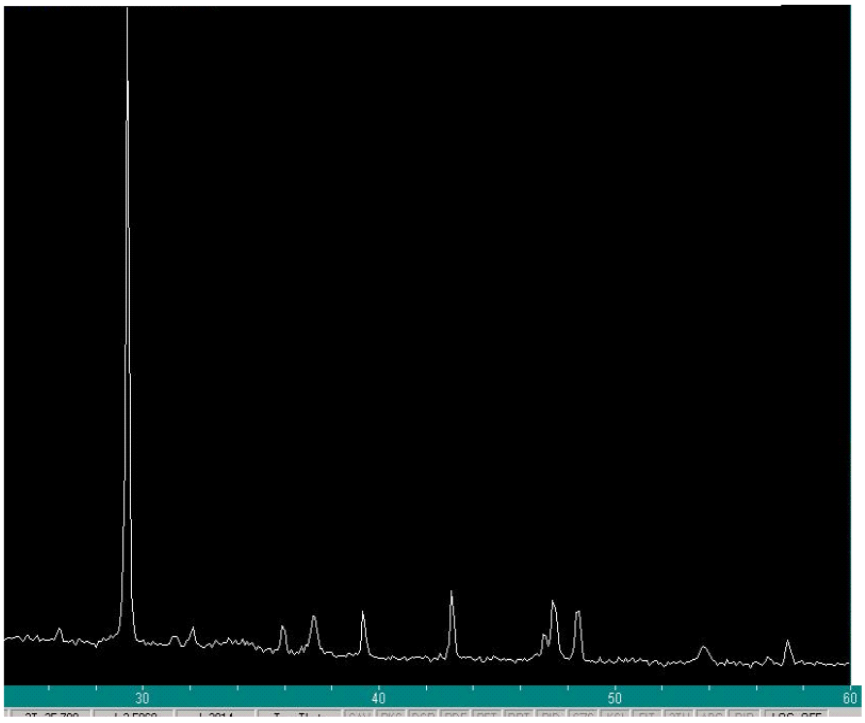

Figure 7: X-Ray Diffraction of coated tile baked at 500° C.

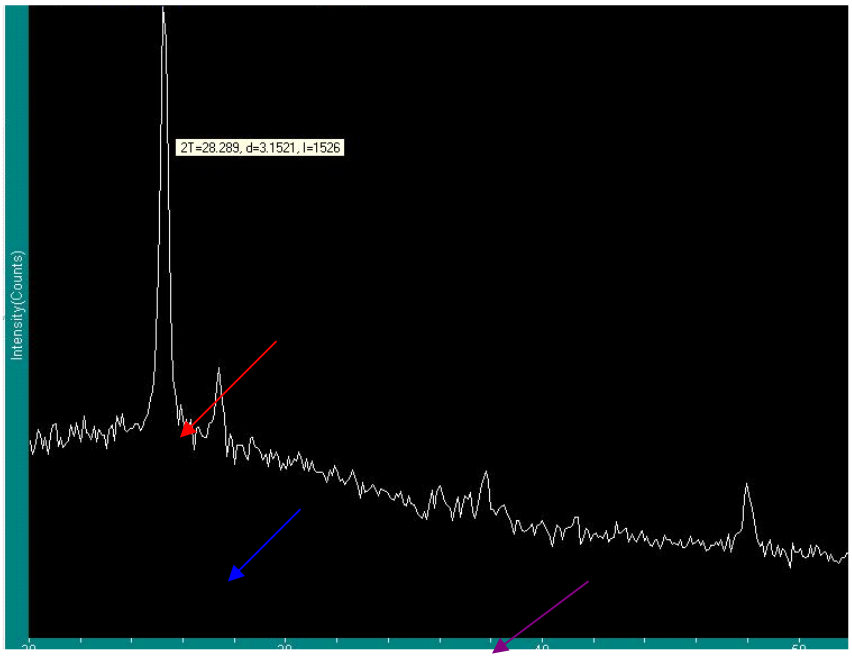

Figure 8: X-Ray Diffraction of commercially prepared Degussa P25.

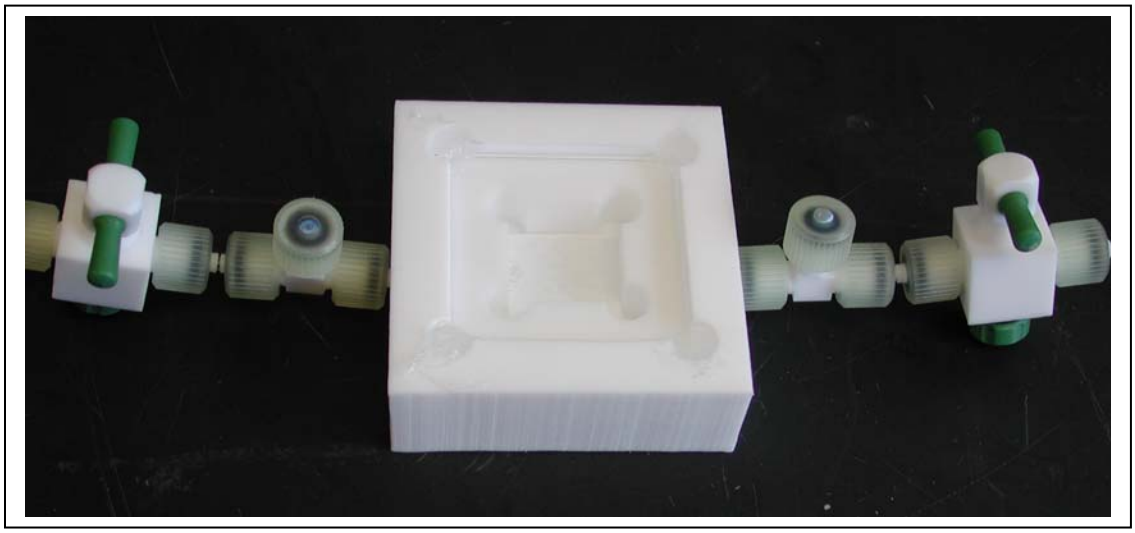

Figure 9: Gas phase reactor.

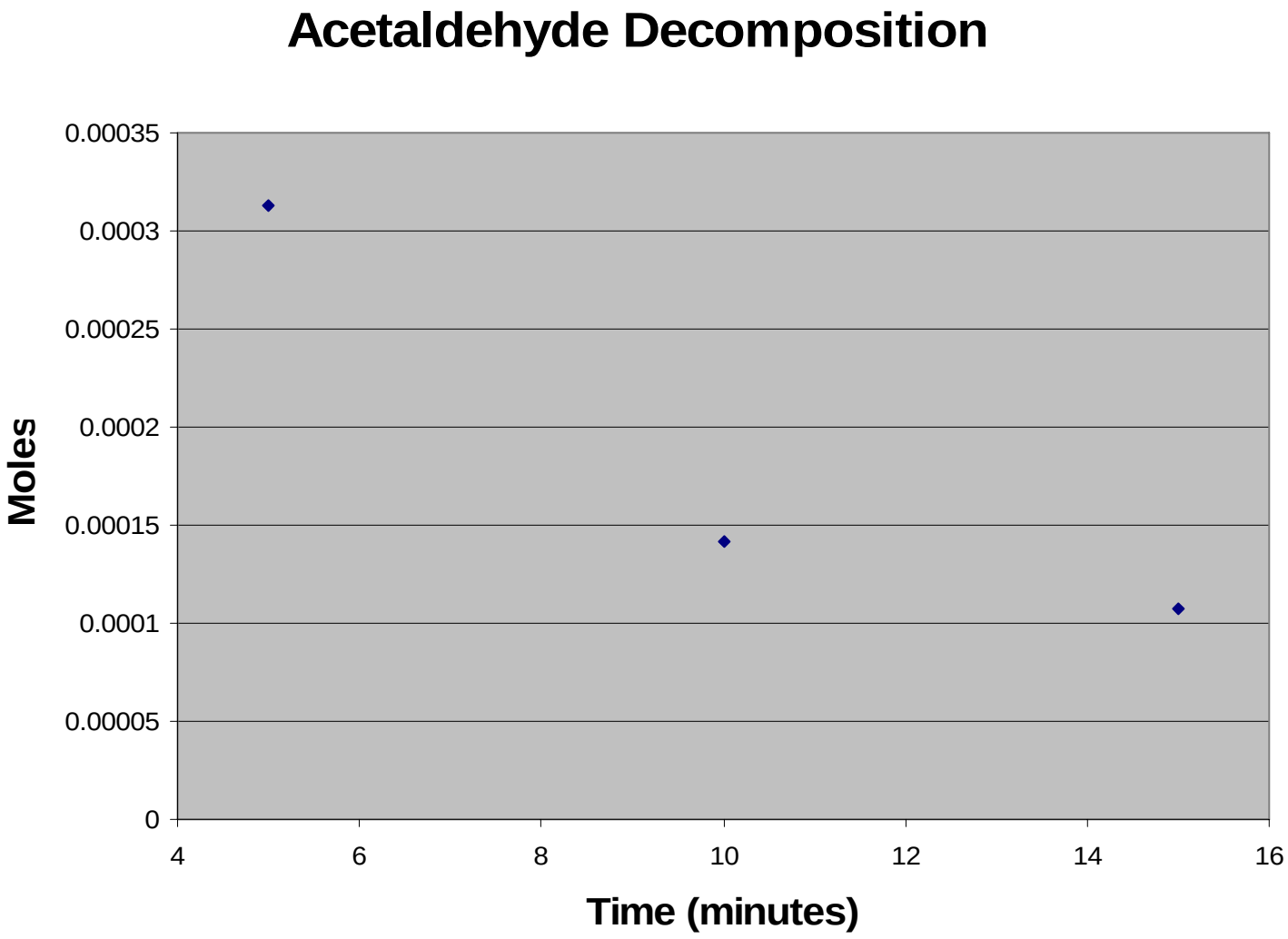

Figure 10: Graph of gas phase reactor acetaldehyde decomposition moles vs. time.

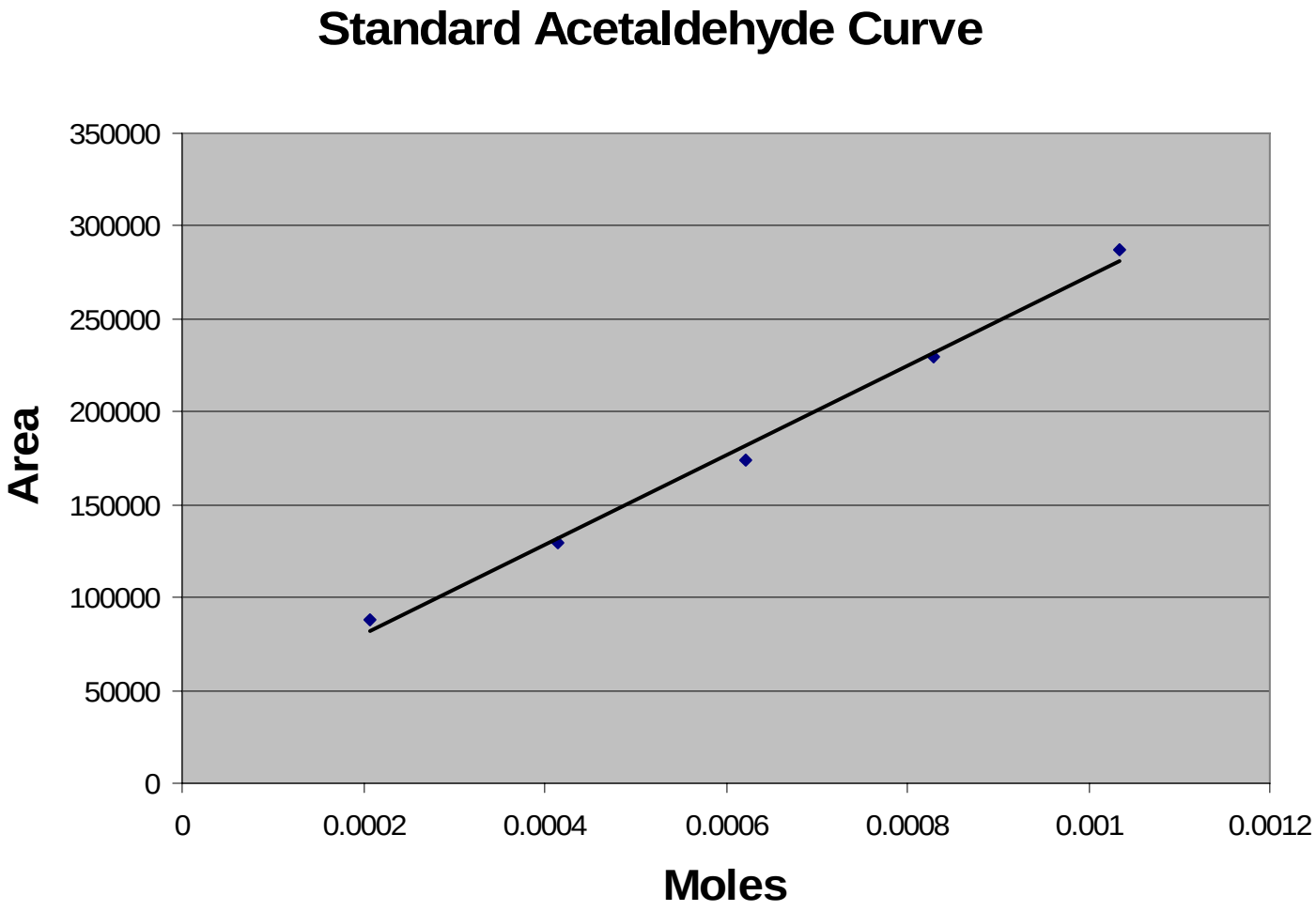

Figure 11: Standard acetaldehyde graph taken from GC-FID.