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Synthesis of Semiconductor Nanoparticles and Their Reactivity toward the Photocatalytic Oxidation of Toxic Organic Chemicals

Dear Dr. Ibeh:

I am pleased to present my 2006 Research Paper to the REU-RET Program. I have synthesized and characterized Rh doped TiO_2 and SrTiO_3 nanoparticles. The decomposition of toxic organic compounds in these nanoparticles offer many advantages in understanding the semiconductor properties. The investigation of the reaction mechanism was carried out using a specially designed reactor where temperature and pressure could be easily varied as needed under reaction conditions. The results in this study are invaluable in determining the role of rhodium in the decomposition of toxic organic compounds.

I hope this report will help educate you, along with others, about this new study on nanoparticle decomposition of acetaldehyde. Thank you for the opportunity to work on such an advanced technological project. I also thank my research advisor, Dr. Paul, for his continuous assistance and graduate assistant, Chih-Ang Chang, for his constant support. If you have any questions, please contact me by email or telephone.

Respectfully,

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Synthesis of Semiconductor Nanoparticles and Their Reactivity toward the Photocatalytic
Oxidation of Toxic Organic Chemicals

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Abstract

Nanoparticles are the future. These very small particles are the latest technology, because of the extremely different properties they possess compared to their regular particle. Scientists are still trying to find out how nanoparticles react. With the support of the Office of Naval Research, this study is to see how nanoparticles affect the decomposition of acetaldehyde, a common pollutant. The procedure is performed using an Infrared Spectrometer. At 173 K, the absorption levels were very low compared to the high levels at 233 K. This finding shows that higher temperatures correspond directly to a higher decomposition of acetaldehyde. In comparing Rh-SrTiO₃ and Rh/TiO₂, the mixture containing strontium proved to play a more significant role in the degradation of the pollutant in dark oxidation and UV-visible photooxidation. Also, for 2.5% Rh-SrTiO₃, UV-Visible photooxidation concluded to be as effective as the thermal reaction in forming acetate species.

Introduction

Nanoparticles offer an exciting addition to the field of Chemistry with such a vast behavioral difference compared to their regular sized particles. The synthesis and characterization of nanoparticles allow scientists to ‘design’ a particle for any purpose or for multiple purposes. However, in order to devise such particles, nanoparticles must be studied to understand their behavior under certain conditions. However, few studies on nanoparticle reactivity are being done today because of the scarcity of equipment allowing an open field for development of this technology.

Acetaldehyde, CH₃CHO, is a toxic organic compound and used as model pollutant for experimental purposes. It is a strategic goal to find a solution, possibly through the use of catalytic nanoparticles, of detoxifying this pollutant. Titanium dioxide or Titania (TiO₂) is the nanoparticle to which acetaldehyde is bonded. It was chosen for this study because it is known as “one of the most active and efficient semiconductors” (Reztsova). Electron transfer from the valence band to the conduction band occurs when titanium dioxide is exposed to ultraviolet light and the photon energy is equivalent to the band gap.

Rhodium and strontium are other metals synthesized with titanium dioxide in order to study the effects of noble metals on the decomposition of acetaldehyde. “The addition of metals, such as Pt, Au, and Pd, on TiO₂ may provide two types of enhancement effects...which improves the degradation rate” (Sano). Rhodium, a noble metal along with the other metals previously mentioned, was used and synthesized with titanium dioxide because of its ability to decrease the band gap allowing visible light absorption to increase (Demydov). It also facilitates hydro carbon oxidation by breaking the C-H bond of acetaldehyde and also by bonding well to carbon monoxide. Strontium is a noble metal indicating that it an excellent metal to synthesize with titanium dioxide because it narrows the band gap for photooxidation, allowing electrons to easily cross the band gap.

Vaidyanathan Subramanian performed a similar study incorporating gold with titanium dioxide instead of rhodium. Rhodium and gold are both noble metals and are used, in both studies, to synthesize with titanium dioxide. Noble metals are used to improve the photooxidation of the semiconductor by creating electron holes and exciting electrons from the valence band to the conduction band. Under photooxidation, gold incorporated with titanium dioxide had a poor “photocatalytic perform in the UV region” (Subramanian) which “decreased significantly” (Subramanian) compared to the titanium dioxide without the gold.

The purpose of this study is to gain a further understanding of the decomposition of acetaldehyde. It is imperative to find a way to neutralize it by means of detoxification in order to study the reactivity of nanoparticles. This paper will explain how titanium dioxide is synthesized as well as describing the theories behind this compound. Also, the individual effects of rhodium and strontium incorporated with titanium dioxide on acetaldehyde will be analyzed.

Literature Review

1. Paul, Dilip K, Todd H. Ballinger, and John T. Yates, Jr. “Rhodium Surface Chemistry on a Chemically Modified Al_2O_3 Support.” Journal of Physical Chemistry. 1990. 4617-4622.

This study was conducted to find the effect rhodium would have on the Al_2O_3 nanoparticle’s decomposition of acetaldehyde. The significance of this study is to establish rhodium’s effect in the decomposition of pollutants and possible role in assisting decontamination means in chemical warfare. Paul, Ballinger, and Yates have performed many studies and papers in an attempt to find the most efficient nanoparticle’s performance in decomposing acetaldehyde and continue to do so today.

This paper analyzes rhodium and its ability to remove OH groups while oppressing CO molecules that try to destroy rhodium. It claims that rhodium is the most effective metal for reducing oxides of nitrogen into nitrogen gas. During the oxidation process, $\text{Rh}(\text{CO})_2$ is formed in the presence of carbon monoxide. Carbon monoxide and isolated OH groups can contribute in the detoxification of rhodium. This process can be reversed by the reduction process using hydrogen which takes $\text{Rh}(\text{CO})_2$ back to rhodium.

Because of rhodium’s reactive properties in being a photocatalyst, it makes the element an attractive addition to other nanoparticles such as TiO_2 . Although rhodium may be able to decrease the gap between the valence and conduction band in ultraviolet light

photooxidation, it must be matched with another nanoparticle that can decrease the gap under other conditions such as TiO₂.

2. Sano, T., et al. "Photocatalytic Degradation of Gaseous Acetaldehyde on TiO₂ with Photodeposited Metal and Metal Oxides." Journal of Photochemistry and Photobiology. 2003. 93-98.

Sano's study was conducted to find whether TiO₂ or metal deposited TiO₂ would aid better in the decomposition of acetaldehyde. Before the study, TiO₂ was regarded as one of the most efficient semiconductors in the decomposition of acetaldehyde; however, they did not know if they could increase its efficiency by the addition of a noble metal. The significance of this study is to conclude that noble metals synthesized with TiO₂ become better semiconductors rather than pure TiO₂ resulting in a further decomposition of acetaldehyde. Dr. Sano has written numerous papers regarding the behavior of TiO₂ nanoparticles and their behavior towards the photocatalytic decomposition of acetaldehyde.

This paper describes the activity of TiO₂ at both room and elevated temperatures. It analyzes the effects these temperatures have on the photocatalytic decomposition of acetaldehyde. Secondly, it compares the TiO₂ results with that of TiO₂ synthesized with a transition metal. The paper concluded that the metal deposited TiO₂ decomposed acetaldehyde more than that of pure TiO₂. Also, higher temperatures increased the degradation rate of acetaldehyde and the production rate of carbon dioxide.

Platinum was the transition metal synthesized with TiO₂. It was found that the oxidation state of the metal controlled the signal intensities in electron spin resonance. Without light, platinum did help with the degradation of acetaldehyde. However, in order to decompose acetaldehyde to its complete mineralization, UV light photooxidation was used.

3. Subramanian, Vaidyanathan, Eduardo E. Wolf, and Prashant V. Kamat. "Influence of Metal/Metal Ion Concentration on the Photocatalytic Activity of TiO₂-Au Composite Nanoparticles." Langmuir. 2003. 469-474.

Subramanian, Eduardo, and Prashant have conducted many experiments to study the photocatalytic behavior of nanoparticles and are still conducting studies today in order to find a nanoparticle capable of decomposing pollutants used in chemical warfare. By

synthesizing Ag, Pt, and Au with SrTiO₃, they were able to conclude which of the three nanoparticles decomposed the furthest.

In photocatalysis, Ag- SrTiO₃ was the most promising mixture for photocatalytic purposes under UV-visible light whereas Au and Pt showed almost no effect. The mixture with Ag showed a 12% increase in pollutant decomposition when UV-visible light exposure exceeded 180 minutes. The significance of this study is becoming aware of three additional noble metals decomposition capability for the specified pollutant.

Synthesis of Rhodium Corporated Titanium Oxide

The synthesis of rhodium corporated titanium oxide is a simple process, only taking one day. The nanoparticle desired was 2.5% Rh/TiO₂. Using 100 mg of TiO₂, it was calculated to use 6.537 mg of RhCl₃· 3H₂O. The RhCl₃·3H₂O was then added to 5 milliliters of water dropwise. The solution was then stirred to make the solution as evenly distributed as possible. The solution was then placed in a Stable-Therm laboratory oven.

Synthesis of Strontium Titanate

The synthesis of rhodium corporated strontium titanate, performed at Kansas State University, has several steps including a three day process. A titanium alkoxide is put into a mixture of ethanol and toluene while the strontium metal is mixed with ethanol and toluene in a separate solution. Ethanol and toluene solvents are used in the process because they are both highly volatile substances that will not react with the gel themselves, but simply assist in the transformation as well as behaving well under high pressures. The two mixtures are then put together and hydrolyzed with water, slowly by drops to transform the solution into a “three dimensional polymeric network from metal alkoxides” (Demydov). The process involves using supercritical drying for solvent removal which allows the solvents to be removed while keeping the nanoparticles from ‘collapsing’ and keep their unique properties such as “high porosity, small crystallite sizes, and large surface area” (Dmydov). The solution is cooked for four hours to remove all of the solvent, leaving only the nanoparticle.

Methodology

Equipment Used

Kansas State University
Synthesis and Characterization Purpose

1. Parr Reactor
2. Calcination oven
3. XRD
4. Surface area analyzer
5. UV-Visible light spectrometer

Pittsburg State University

1. Ultra high vacuum system
2. FT-IR (Fourier Transform Infrared) Spectrometer, Mattson

Instrument

Used to receive infrared data using Winfirst software

3. Xenon short arc and Filters, LPS-220
4. 100 watt UV lamp
5. Hydraulic press
6. Honeywell UDC 3000 Temperature Controller

Used to heat and maintain sample's temperature as needed in reaction

7. OriginPro 6.

Used for manipulating Infrared spectrometer data

8. Sonicator FS14H, Fisher Scientific

Used for cleaning the sample holder and Tungsten grid

9. Rocky Mountain 506 Welder

Used for welding thermocouple wires onto upper cell

10. Newport Universal Motion Controller/Driver, Model ESP300

Used for moving cell to exact locations of grid or sample

11. Vacuum Gauge Controller, Model 307, Granville-Phillips

Used for monitoring pressure of the cell and line

Materials Used

1. Nanomaterial 2.5% Rh-SrTiO₃, SrTiO₃, 2.5%Rh/TiO₂, TiO₂

2. Photoetched Tungsten, .002" thick
Used to hold sample, 58% transmission
3. Acetone A19-1, Fisher Scientific
Used for cleaning of grid and cell
4. Liquid Nitrogen
Used for conduction cooling
5. E-type Thermocouple (.12mm constant and chromega wires)
6. High purity hydrogen gas
7. High purity oxygen gas (99.999%), Matheson
8. High purity acetaldehyde (99%), Aldrich Chemical

Procedure

The experiment procedure was performed in a stainless steel infrared cell with a temperature range from 180 K – 2000 K. The upper cell was cleaned with acetone while the nickel clamp and screws were removed and placed in the Sonicator for ten minutes to remove any loose pollutants. The .002" tungsten was cut into a 1" x 1" square. Similarly, the thermocouple wires (constant and chromega) were cut into three inch segments. Constant and chromega wires are E-type wires and are used because of their temperature range, -200° C - 1000° C. The two wires are then crossed at the end to make an "X" and welded together. Then the wires are welded to the square grid. After weighing the sample and grid separately, the sample is pressed onto the grid using a hydraulic press and 10,000 PSI for five minutes. The grid and sample are weighed together, and the actual weight of the sample is calculated. Clamps are then attached to the upper cell power rods, and the grid and sample are screwed into the clamp. Again, the welder is used to attach the thermocouple wires to the thermocouple feedthrough on the upper cell. The upper cell is then mounted onto the lower cell and evacuated over night at room temperature.

The sample is slowly heated to 500° C to dehydroxylate the sample. Oxidation is then performed on the sample using 10.0 Torr. Then, the sample is reduced twice using 100.0 Torr. of hydrogen. Afterwards, the sample undergoes calcination in the presence of oxygen (approximately 10 Torr.) at a high temperature to remove C-H bonding on the surface for 20 minutes. The sample is then conduction cooled using liquid nitrogen before dosed with acetaldehyde. Acetaldehyde has a boiling point of 20.1°C making a lower temperature more attractive for dosing the pollutant. The sample is exposed to acetaldehyde eight times using pressures of .75, 1.3, 2.0, 3.0, 5.0, 7.0, 10.0, and 12.0 Torr., respectively. Then, spectrometer scans are taken to see what surface bonds acetaldehyde and the nanoparticle have made. The sample is then exposed to 15 Torr. of oxygen to perform dark oxidation as spectrometer scans are taken every 3 minutes to observe the change in bonds as time

progresses. Visible light is then projected onto the sample with spectrometer scans taken every 3 minutes for an hour for photooxidation. UV-visible light photooxidation is then performed on the sample for approximately 7.5 hours and then left overnight without light. Carbon monoxide is then dosed to see what bonds show up with rhodium, because of carbon monoxide characteristic of bonding well to transition metals. Therefore, it forms many bonds with the various rhodium ions on the surface.

All spectrometer readings are then ratioed with the beginning spectrometer reading before any dosing using the Winfirst Program. These readings are then categorized and displayed as Dark Oxidation, Visible Light Photooxidation, and UV-Visible Light Photooxidation using OriginPro.

Results and Discussion

Figure One: Adsorption of Acetaldehyde as a Function of Pressure

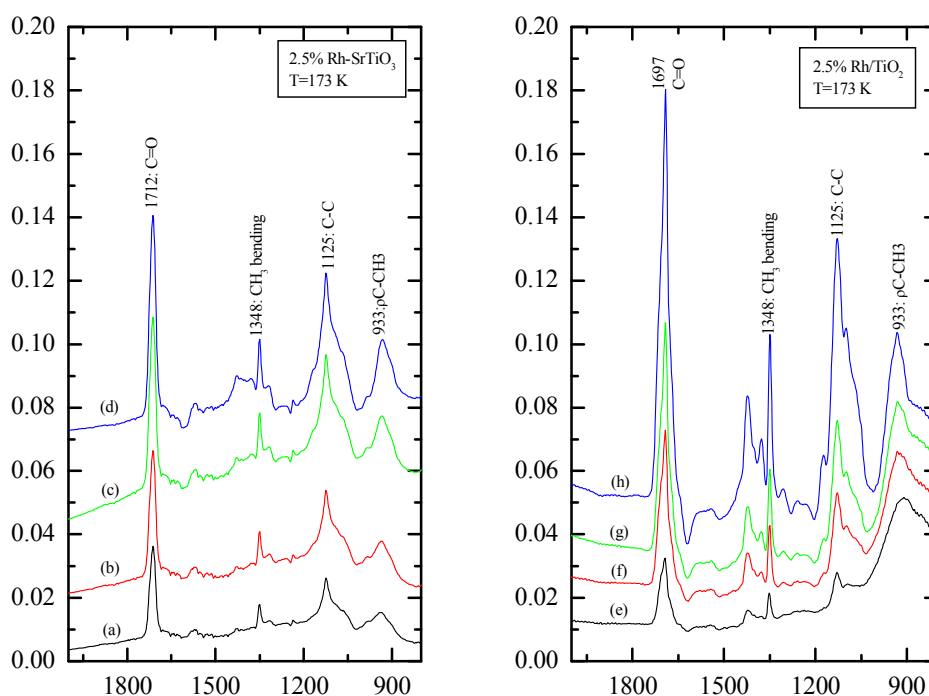


Figure 1 shows the development of IR spectra as acetaldehyde is introduced to the nanoparticle surface at different pressures: (a) .38 Torr, (b) .58 Torr, (c) .77 Torr, (d) 1.0 Torr, (e) .35 Torr, (f) .55 Torr, (g) .70 Torr, and (h) .92 Torr. The wave number (cm^{-1}) of the peak is represented by the x-axis and the absorbance level by the y-axis. When comparing the adsorption of acetaldehyde on the surface on both Rh-SrTiO₃ and Rh/TiO₂, the spectras have similar shapes. However, the amount of acetaldehyde adsorption is very different on the two charts.

On both charts, the peaks of acetaldehyde all increase as pressure increases. When analyzing Rh-SrTiO₃, the highest absorbance level is at 1712 cm⁻¹ for aldehyde with an absorbance of .06. The ν (C=O) mode at 1697 cm⁻¹ for Rh/TiO₂ is of an absorbance of .10 proving that acetaldehyde bonds stronger to the surface of Rh/TiO₂ than Rh-SrTiO₃. The 1348 cm⁻¹, 1125 cm⁻¹, and 933 cm⁻¹ modes correspond to CH₃, ν (C-C), and C-CH₃ bonds of the acetaldehyde compound. As seen in the figure, all of the peaks for Rh-TiO₂ are larger than those of Rh-SrTiO₃ including the 1125 cm⁻¹ mode of .05 absorbance for Rh-SrTiO₃, but .075 absorbance for Rh-TiO₂ presenting, once again, that acetaldehyde bonds more to the surface of Rh/TiO₂ rather than Rh-SrTiO₃.

Figure Two: Dark Oxidation as a Function of Temperature

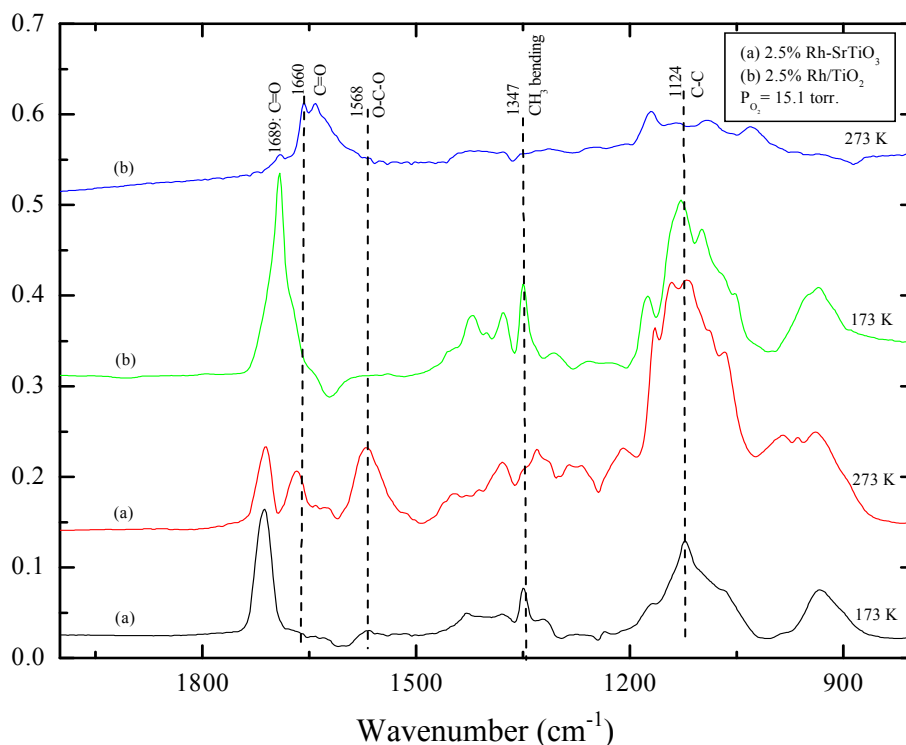


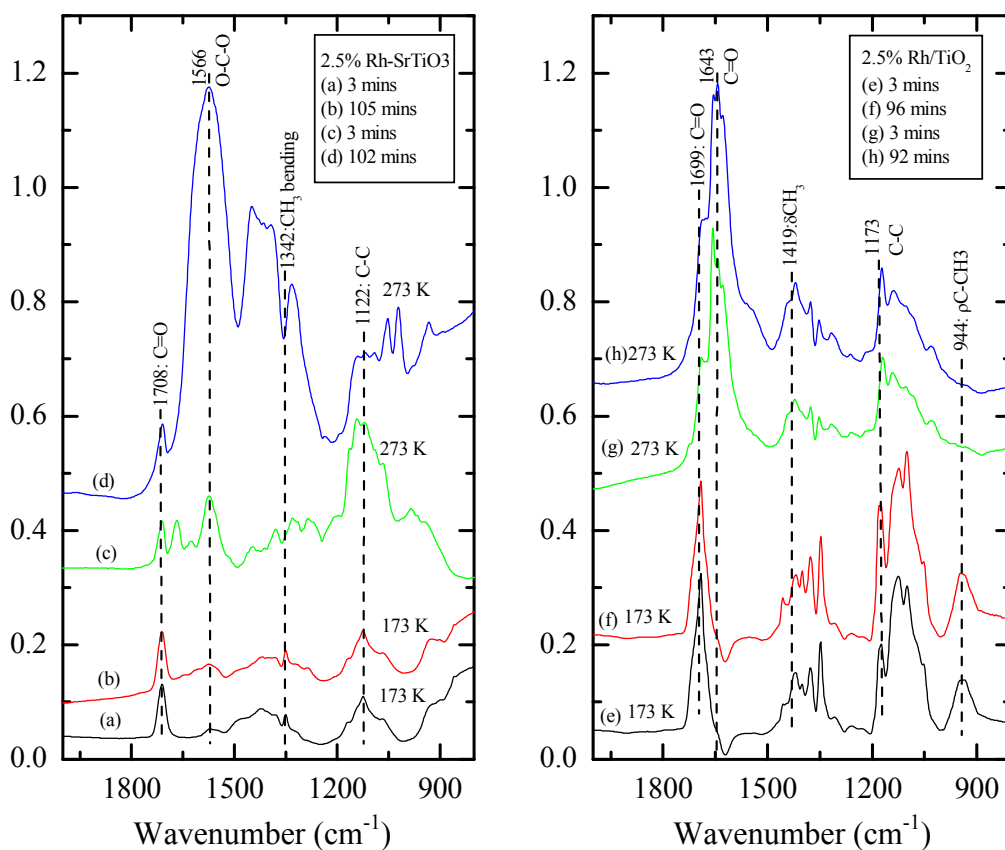
Figure 2 shows the development of IR spectra as oxygen is introduced to the nanoparticle surface at a pressure of 15.1 Torr. and observed as a function of temperature. The wave number (cm⁻¹) of the peak is represented by the x-axis and the absorbance level by the y-axis. The mode of 1689 cm⁻¹ shows the ν (C=O) bond for aldehyde, a part of acetaldehyde. For Rh-SrTiO₃, the 1689 cm⁻¹ band decreases as 1660 cm⁻¹ ν (C=O) bond for crotonaldehyde increases. This transformation indicates the breakdown of acetaldehyde, but into another toxic compound. Rh/TiO₂ performs a similar process of

converting high absorption acetaldehyde into crotonaldehyde as seen on the top two spectrums.

The 1568 cm^{-1} band seems to increase only for Rh-SrTiO₃ indicating the deformation mode of the $\nu(\text{O-C-O})$ bond in acetate formation from acetaldehyde. On the other hand, Rh/TiO₂ has a loss of peak height at 1347 cm^{-1} with the raise of temperature indicating the loss of the CH₃ mode of acetaldehyde as the 1689 cm^{-1} bond of acetaldehyde decreases. Both of the acetaldehyde peaks at 1689 cm^{-1} and 1345 cm^{-1} are contributing to the formation of crotonaldehyde at 1660 cm^{-1} for Rh/TiO₂.

The 1124 cm^{-1} mode can be the $\nu(\text{C-C})$ bond of acetaldehyde, crotonaldehyde, acetate, or crotonate. For increasing temperature of Rh-SrTiO₃, the aldehyde is decreasing as crotonaldehyde and acetate are increasing; therefore, the increase of the 1124 cm^{-1} band could be due to the increase of crotonaldehyde or acetate. For Rh/TiO₂, aldehyde and acetate are decreasing which signifies that the increase of the 1124 cm^{-1} band must be due to the increase of crotonaldehyde.

Figure Three: UV-Visible Light Photooxidation as a function of Time



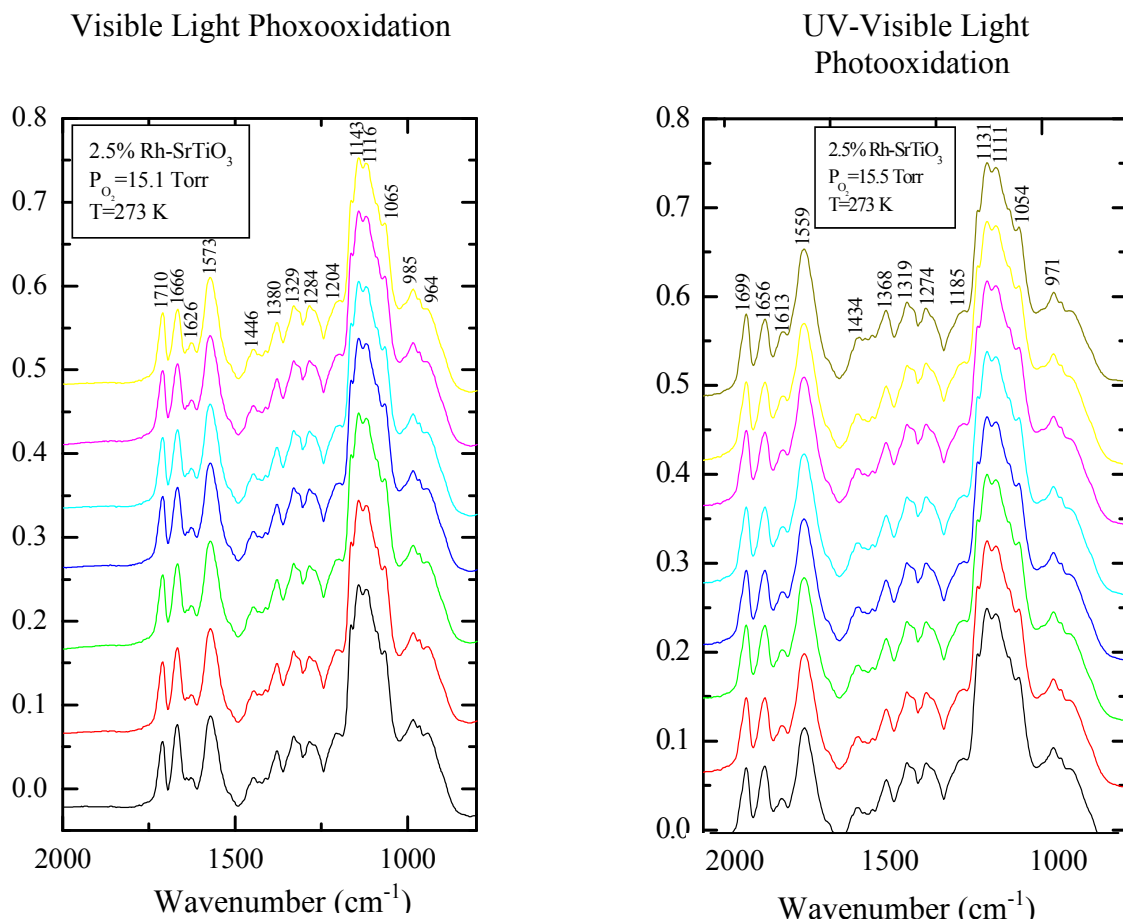
In figure three the UV-Visible light photooxidation process is shown as a function of time for both Rh-SrTiO₃ and Rh-TiO₂ under temperatures 173 K and 273 K. The wave number (cm⁻¹) of the peak is represented by the x-axis and the absorbance level by the y-axis. If inspecting Rh-SrTiO₃ at 173 K, the 1708 cm⁻¹ peak ν (C=O) appears to decrease slightly with time as does the 1342 cm⁻¹ δ (CH₃) peak. 1708 cm⁻¹ represents aldehyde decreasing while 1342 cm⁻¹ represents the CH₃ bond in acetaldehyde. At this same temperature, Rh/TiO₂ has peaks 1699 cm⁻¹, 1173 cm⁻¹, and 944 cm⁻¹ all staying relatively the same absorbance level as time goes on from (e) to (f). This data shows that at low temperatures, Rh/TiO₂ does not effect ν (C=O) and ν (C-C) bonds of acetaldehyde at 1699 cm⁻¹ and 1173 cm⁻¹. In the 273 K spectra of Rh-SrTiO₃, the 1566 cm⁻¹ peak for acetate increases significantly from an absorbance level of .12 to .25 as time goes on. Along with the formation of acetate is the increase in absorbance level of crotonate. At 273 K, Rh/TiO₂ has an increase in acetaldehyde (1643 cm⁻¹) as well as crotonate (1419 cm⁻¹).

Temperature

Temperature plays a critical role in the analysis of decomposing acetaldehyde. In both dark oxidation and photooxidation, the temperature's position can be seen. In dark oxidation, both the Rh-SrTiO₃ and Rh/TiO₂ particles' absorption level of acetaldehyde at 273 K is significantly smaller than that at 173 K. Also, Rh-SrTiO₃ sees an increase in the ν (O-C-O) bond of acetate whereas Rh/TiO₂ results in an increase in the ν (C=O) bond of crotonaldehyde. Although both particles have different decompositions of acetaldehyde, both have a higher rate of degradation of acetaldehyde at the higher temperatures pushing the reaction further as the absorption of acetaldehyde decreases.

In photooxidation, temperature continues to play a key role in the decomposition of acetaldehyde. The ν (C=O) bond of acetaldehyde continues to decrease even more than during the dark oxidation process. However, the phenomenal play is the increase in the ν (O-C-O) bond of acetate that can be seen in figure 3 for Rh-SrTiO₃. Also, the ν (C-C) bond at 1122 cm⁻¹ increases most likely corresponding to the increase in acetate. Now, discussing Rh/TiO₂, acetaldehyde decomposes more so in crotonaldehyde rather than acetate. However, the important note here being that the mixture becomes rid of the 933 cm⁻¹ band of C-CH₃ of acetaldehyde completely. Overall, it can be concluded that performing dark oxidation and photooxidation at higher temperatures will conclude a higher degradation rate of acetaldehyde.

Figure Four



In figure four, the Visible and UV-Visible light photooxidation spectrums can be seen as a function of time. The process is shown as a function of time for Rh-SrTiO₂ at a temperature of 273 K to analyze the effect of visible and uv-visible light individually. The wave number (cm⁻¹) of the peak is represented by the x-axis and the absorbance level by the y-axis.

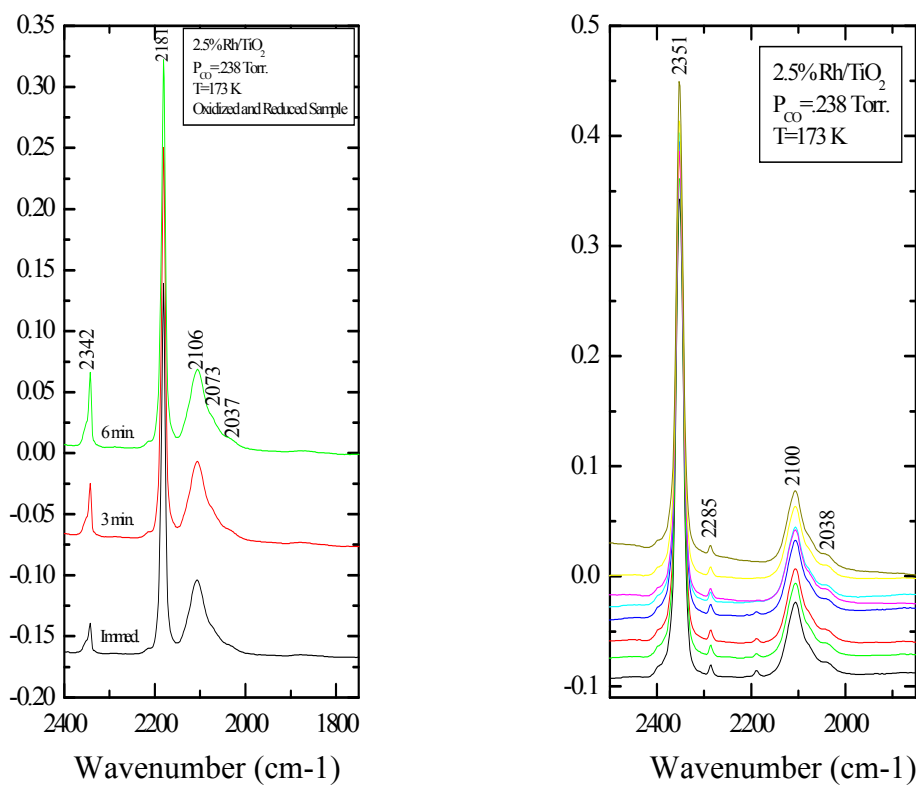
When comparing the visible and uv-visible spectrums of Rh-SrTiO₃, the first noticeable difference is the absence of the 1710 cm⁻¹ peak in the uv-visible spectrum. In this experiment, acetaldehyde is completely decomposed into other products. UV-visible photooxidation has higher absorbance levels for both the ν (C=O) bond of crotonaldehyde at ~1656 cm⁻¹, ν (O-C-O) bond in acetate (1559 cm⁻¹) as well as the ν (C-C) bond at 1111 cm⁻¹ or 1116 cm⁻¹. The ν (C-C) bond can, again, be related to the increase in acetate and crotonaldehyde for the uv-visible spectrum. Therefore, it can be concluded that the more effective catalyst would be the uv light by its performance in degrading the acetaldehyde farther into acetate and crotonaldehyde than the visible light alone.

When comparing the visible light photooxidation to dark oxidation (refer to figure 2), both follow the same path in the means of decomposing acetaldehyde. Dark oxidation begins the process of turning acetaldehyde into crotonaldehyde as well as acetate. However, visible light furthers this process even more by almost doubling the absorbance of acetate as well as increasing in crotonaldehyde absorbance. The processes are very similar in their means of decomposing acetaldehyde; however, the visible light photooxidation goes farther in the process.

Figure Five

Characterization of Rhodium Surface

UV-Visible Light Photooxidation as a function of Time



In figure five, the Characterization of Rhodium Surface and UV-Visible photooxidation spectrums for 2.5% Rh/TiO₂ are displayed as a function of time with the wave number (cm⁻¹) of the peak represented by the x-axis and the absorbance level by the y-axis.

The oxidation state of rhodium can be using carbon monoxide as a probe molecule where the vibration frequencies are known. The wavenumbers where carbon monoxide bonds to rhodium can be found around the 2000 cm⁻¹-2100 cm⁻¹ range. Essentially, rhodium having an oxidation state of zero would be ideal meaning that it has been oxidized. 2106 cm⁻¹ and 2037 cm⁻¹ on the left chart represent rhodium in the +1 oxidation state. 2073 cm⁻¹

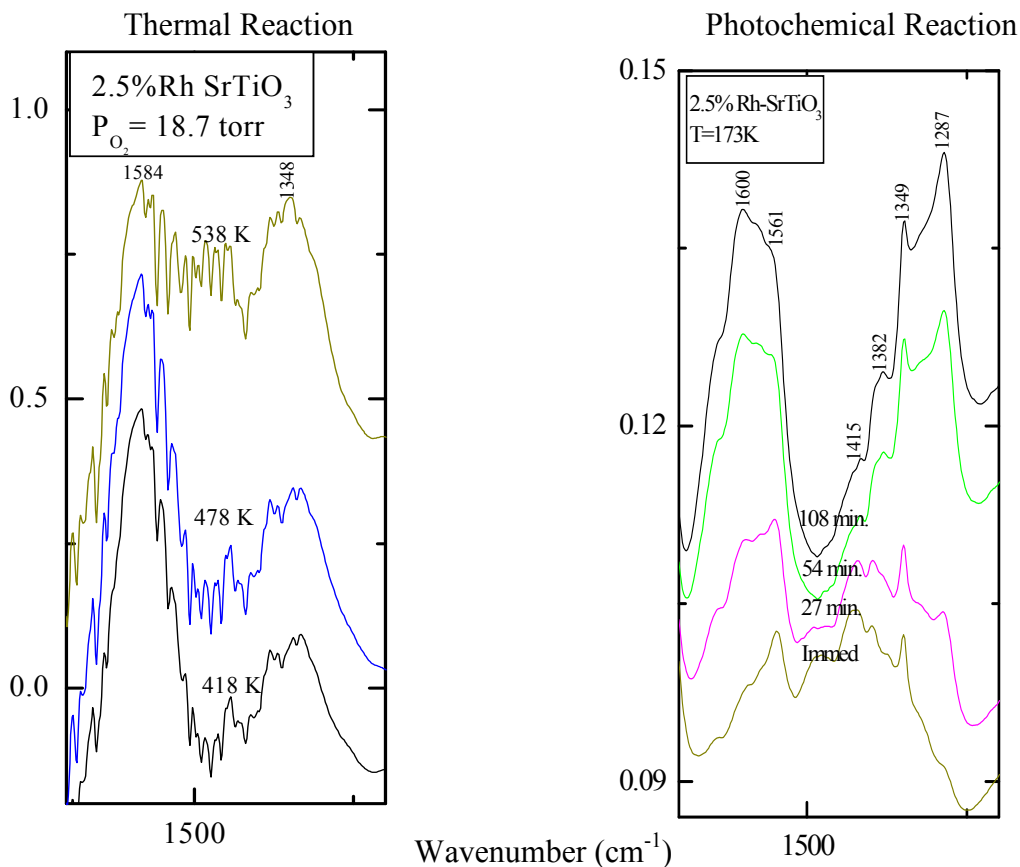
represents Rh° , a very small peak, which leads to the conclusion that rhodium exists more so in the Rh^{+1} state as it increases with time.

In decomposing acetaldehyde, products such as crotonaldehyde, acetate, and crotonate are good signs that the degradation is taking place. However, the ultimate goal is to end with a high absorbance of oxygen or carbon dioxide. The carbon dioxide wavenumber is around 2351 cm^{-1} , which is precisely what is happening in the figures above. As time increases, so does the absorbance of carbon dioxide. However, carbon dioxide is more prevalent in photooxidation than in carbon monoxide exposure. For this experiment, characterization of rhodium surface was performed prior to dark oxidation and photooxidation. In order to study the effects of the change in procedure, more experiments will be conducted to inspect this great result.

Rhodium Amount Effect in Photochemical Reactions

When deciding the percentage amount of rhodium to be synthesized with titanium dioxide or strontium titanate, the amount giving the largest decomposition of acetaldehyde would be the prime. Under ultraviolet-visible light reactions, rhodium at 2.5% proved to decrease the absorbance of acetaldehyde on the $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{C})$, and $\delta(\text{CH}_3)$ modes. These experiments were conducted at 173 K. More studies could be done at 273 K to gain more insight on whether the amount of rhodium effects the photochemical reaction.

Figure Six



In figure six, the thermal and photochemical reaction for 2.5% Rh-SrTiO₃ are compared where the wave number (cm⁻¹) of the peak represented by the x-axis and the absorbance level by the y-axis.

Rh-SrTiO₃ and Rh/TiO₂ were studied thermally and photochemically. Thermally, oxidation was performed while the temperature was raised and monitored from 298 K to 523 K. For Rh-SrTiO₃, acetaldehyde decomposed into acetate until 418 K when acetate absorption levels began to decrease. Photochemically, rhodium seems to assist in the decomposition of acetaldehyde with approximately the same amount absorbance of acetate as a thermal reaction. However, reaching carbon dioxide using low temperatures and UV-visible light is more advancing than using very high temperatures.

Conclusion

Through a detailed process, 2.5% Rh-SrTiO₃ and 2.5% Rh/TiO₂ were compared and studied through the adsorption of acetaldehyde, dark oxidation, and UV-visible light photooxidation. With dark oxidation, Rh-SrTiO₃ decomposed aldehyde into crotonaldehyde and acetate. Similarly, Rh/TiO₂ decomposed aldehyde into crotonaldehyde, but not further into crotonate or acetate. Under photooxidation Rh-SrTiO₃ successfully converts almost all of the acetaldehyde into acetate and crotonate whereas Rh/TiO₂ keeps a high absorbance of acetaldehyde and low absorbance of crotonate. Therefore, Rh-SrTiO₃ presents itself as the more effective mixture for decomposing acetaldehyde. Incorporating rhodium with strontium titanate as well as titanium dioxide helps decompose acetaldehyde in the visible light spectrum.

In the photochemical reaction, we view many variances in the adsorption levels compared to that of the dark oxidation. In the Rh-SrTiO₃ study, the ν (C=O) bond of acetaldehyde decreases indicating the decomposition of the compound. However, the ν (O-C-O) bond of acetate increases with time supporting the idea of acetaldehyde degrading into acetate. When using Rh/TiO₂, the ν (C=O) bond of acetaldehyde decreased as did Rh-SrTiO₃. In addition, the ν (C-C) bond of acetaldehyde decreased as well. However, rather than decomposing into mostly acetate, the mixture had a large increase in the ν (C=O) for crotonaldehyde. The acetaldehyde in this mixture did not breakdown as far as the Rh-SrTiO₃, but into another toxic organic compound. However, further decomposing could lead to the transformation from crotonaldehyde into crotonate.

The effect of rhodium on nanoparticles SrTiO₃ and TiO₂ can be divided into two ways. If implemented at 273 K, the majority of the reaction will take place in dark oxidation forming acetate species when dosing oxygen. Throughout photooxidation, all absorbance levels will stay constant. However, if conducted at 173 K, rhodium serves as the photocatalyst in the degrading of acetaldehyde into acetate. Without rhodium, TiO₂ cannot turn acetaldehyde into acetate. Similarly, SrTiO₃ cannot reach the acetate species without

rhodium's performance in visible light. Rhodium's role also has importance in bonding to carbon monoxide in an attempt to reach carbon dioxide as mentioned before. Rhodium helps with the decomposition of acetaldehyde in the photochemical process, but more study must be done to relay if reorganizing the steps in the procedure could lead to more absorption of carbon dioxide as mentioned earlier.

Recommendations

In the study, 2.5% Rh-SrTiO₃ and 2.5% Rh/TiO₂ were studied and compared more so to see the effect of strontium in the TiO₂ nanoparticle. Throughout the data, one can see how rhodium ineffectively assisted in the decomposition of acetaldehyde at both 173 and 273 K. Perhaps further study could be done with rhodium on the same TiO₂ nanoparticle and possibly other particles. Also, some studies are now experimenting with other transition metals such as gold, nickel, and platinum to see the effects they have on narrowing the gap between the valence band and conduction band in an attempt to decompose some pollutant as acetaldehyde. These could then be compared to the results of rhodium.

Acknowledgement

I would like to thank graduate assistant, Chih-Ang Chang, for his guidance in learning about the instrumental side of this project. Also, I would like to extend my gratitude to Dr. Paul for all of his guidance and assistance through my project. Lastly, I would not have been able to participate in this project had it not been for the CNCMM Program and the Office of Naval Research who have so graciously given me the opportunity to learn and further the knowledge known about nanoparticle's role in the decomposition of acetaldehyde. Thank you again for such a wonderful opportunity.

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