

Wednesday, 10th August 2005

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Subject: Final Research Report

To Whom It May Concern:

The final report of my research conducted during the summer of 2005 is enclosed. It outlines the adsorption and reaction of acetaldehyde on two different nanoparticulate surfaces: 2%Cr-SrTiO₃ and 2.5%Sb-2%Cr-SrTiO₃. Not only has this work provided valuable information on these catalytic surfaces, but it has also allowed us the opportunity to explore the formulation and synthesis of these materials.

The findings show that the incorporation of antimony as well as chromium in the strontium titanate system does provide some additional reactivity. The literature suggests that this is through the elimination of oxygen vacancies and other defects that are caused by a charge imbalance when only chromium is doped. In addition, it was found that though these materials are both photocatalytic when exposed solely to visible light, the rate of reaction may well be higher for when UV wavelengths are also present.

These findings provide a solid basis for further work in this area. Experiments using crotonaldehyde as well as an acetate species will likely shed additional light on the mechanisms of reactions on these nanoparticles. Temperature programmed desorption studies would most assuredly offer an in-depth look at the products of these catalytic reactions.

If you have questions concerning anything in this report, please contact me at (620) 240-6830 or via email at raybrian@earthlink.net. I would like to thank Dr. Ibeh, Dr. Donovan, Dr. Hensley, Dr. Beyle and the rest of the REU/RET 2005 fellows for their feedback that helped shape and fine tune this report. I would like to acknowledge my special thanks to Dr. Dilip Paul for his guidance and patience with me as my faculty advisor.

Thank you,

Brian Ray
PSU-CNCMM/ONR: 2005 REU Fellow

Enclosed: Final Research Report

Pittsburg State University
Center for Nanocomposite and Multiuse Materials
Research Experience for Undergraduates Program
Summer of 2005

The Synthesis and Characterization of A.P. 2%Cr-SrTiO₃
and A.P. 2.5%Sb-2%Cr-SrTiO₃ Nanoparticles
and Their Applications Towards Adsorption and
Decomposition of Acetaldehyde

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On:
10 August 2005

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SUMMARY

The reactions of acetaldehyde on 2 mixed metal oxide nanoparticle surfaces were studied using in situ FTIR and mass spectroscopy. The mixed metal oxides chosen were 2.5%Sb-2%Cr-SrTiO₃ and 2%Cr-SrTiO₃ obtained with thanks from the labs of Dr. Kenneth Klabunde at Kansas State University. It was found that both surfaces adsorbed acetaldehyde through irreversible mechanisms involving surface hydroxyl groups. Upon exposure to ~15Torr of oxygen but in the absence of anything but minimal ambient light, no change in reaction was recorded indicating the necessity of light as an activating factor for the catalytic properties of these nanoparticles. Upon exposure to the visible spectrum, reactions resulting in acetate species were observed on both samples with some differences. It was generally found that some additional reactivity was afforded by the incorporation of a charge balancing species such as antimony. Significant addition reactivity was observed when the spectrum of incoming light was widened to include wavelengths as low as 300nm.

INTRODUCTION

Nanoparticles are a group of materials defined primarily by the fact each unit is on the order of 1-100nm on a side. When compared to regular size crystals who have dimensions on the order of 100's of nanometers or more, the nanoparticles' extreme surface area to volume ratio, sometimes a billion times that of their larger analogs, make them especially reactive. This makes them of special interest to surface science. A number of groups are currently making nanoparticles and doing basic characterization and testing, but due to the fact that this is a relatively new field, little mechanistic work has yet been done [2].

Aldehydes, including but not limited to acetaldehyde and formaldehyde, are the most prevalent harmful chemical in today's modern households. They can be found in everything from gasoline to coffee and fruit [7]. Their decomposition into less harmful or neutral chemical species is an area of major interest and one focus of this research. Acetaldehyde, being one of the most abundant of this group, was chosen as our target chemical and dosed onto the surface of the nanoparticles with crotonaldehyde being used in some later trials due to its likelihood as a product derived from the acetaldehyde reactions [1].

The use of light to energize a catalyst is the primary reason for the incorporation and/or impregnation of these substances with transition metals and/or other elements [2]. It is believed that wavelengths of light in the UV-visible region of the electromagnetic spectrum may promote electrons from the valence to the more reactive conduction band of these metals, which may then react directly with chemicals on the surface or be passed to the titania substrate, increasing its reactivity and catalytic properties.

In addition, the opportunity for the development of solid catalysts in the manufacturing of products of aldol condensation reactions is prime. This fact is emphasized in the work of G.J. Kelly and S.D. Jackson [2].

As the opportunities offered by nanoparticles have become more and more apparent research into methods of their synthesis has also garnered a great deal of attention. One major technique for the creation of nanoparticles is the use of a sol-gel system and hypercritical drying. In this method, the hydrolysis of a metal alkyl oxide in a suitable solvent is carried out to create a sol-gel. To remove the solvent without its capillary pressures tearing the gel latticework apart, the gel is taken to a pressure and temperature above the critical pressure and temperature of the

solvent. Then the solvent is allowed to flow away as a supercritical fluid with the properties of a gas and no capillary forces, leaving the nanoparticles intact [3].

Of course all of the above statements concern the development of nanocomposites and especially multiuse materials. Not only can nanoparticles and nanowires imbue composites with greater strength and lighter weight and such, but they may also be able to offer other properties as well, even when incorporated in composites, such as the ability to detoxify nerve agents or household hazards.

LITERATURE REVIEW

Major Articles:

“Acetaldehyde Reactions Over the Uranium Oxide System” [1]

This journal article analyzes the reactions of acetaldehyde on 3 different types of uranium oxide surfaces and under different conditions. The article provides useful information on acetaldehyde on metal oxide systems including tables of infrared spectral assignments.

“Aldol Condensation of Aldehydes and Ketones over Solid Base Catalysts” [2]

This anthology article provides useful mechanistic and band-gap examples and data concerning metal oxide systems and the reactions of aldehydes and ketones over them.

“Aldol Condensation of Acetaldehyde to Form High Molecular Weight Compounds on TiO₂” [5]

This article discusses the reactivity of DeGussa P25 TiO₂ as opposed to TiO₂ from other sources. It lists the anatase to rutile crystal system ratio as being 75% to 25%. In addition, it lists SiO₂, Al₂O₃, and trace amounts of Fe₂O₃ as impurities found in P25 titania. The greater activity in the adsorption and catalysis of organics of P25 TiO₂ is attributed to its increased concentration of acidic sites.

Major Schools of Thought:

Concerning the reactivity of nanoparticles versus bulk materials the predominating conception is that it is the dramatically increased surface area of the material per unit volume that accounts for much of the increase. In addition, some work has been done concerning how the structure of specific nanomaterials may cause them to have reactivity levels higher than other particles of the same material with greater surface area per unit volume [6].

The incorporation of transition metals and other elements into nanoparticle crystal networks has been used as a route to increase catalytic activity through decreases in the valence to conduction band gap. With TiO₂, due to its ability to only absorb UV light, specific elements with band gaps of approximately 3eV have been focused on because that is approximately the amount energy UV photons can give [2]. Several studies have found that the incorporation of chromium benefits from the doping of another metal such as antimony or nickel which can serve to preserve the charge balance and prevent the formation of Cr⁶⁺ and oxygen defects [9, 10].

Summary of and Significance of Problem:

Nanoparticles and the composites made of them are an exciting and opportunity rich field of chemistry. Today's market-place demands results tailored to the client's needs. In order to tailor-make chemicals one must have an understanding of how the chemicals to be used act and interact. In other words, one must understand the mechanisms of the chemicals. This is why in

order to meet the market's need for tailor-made nanoparticles for their new composites, as strong a comprehension as possible must be developed of how these particles work and why. Thus far the mechanisms of nanoparticle reactivity are only barely understood. This means that this is an area ripe for development and the concomitant nanocomposite development that follows.

Acetaldehyde is a "probable human carcinogen" according to the EPA and is "ubiquitous" due in part to its appearance in coffee, vehicle exhaust, fruits, etc... [7]. The safe removal of or detoxification of these chemicals, possibly through decomposition on a catalytic nanoparticle surface, is therefore a prime concern with regard to household safety.

In addition, the formation of certain important compounds such as furan on nanoparticles offer great opportunities for the development of reusable, solid catalysts in industries swamped by the overhead of non-reusable, toxic liquid catalysts [2].

In research conducted by Dr. Dilip Paul in association with Dr. John Yates Jr., the use of nanoparticulate matter was tested in the decomposition of a mustard gas simulant [8]. Additionally, Klabunde et al have done testing on the biocidal properties of nanoparticles and halogenated nanoparticles [12].

METHODOLOGY

Materials and Equipment:

For the *in situ* infrared studies, a Mattson Research Series RS_10000 FTIR with a liquid nitrogen cooled detector and manually translatable stage was used. WinFirst v.2.10 software was used to operate the spectrometer and for some data plotting purposes. Origin 6.1 was also used as a plotting application. Microsoft's Excel software was used for some data manipulation and calculations.

Reactions were carried out in a stainless steel reaction cell with KBr windows for the passage of the IR beam and a quartz window for the UV exposure. The cell utilized differential pumping from a Pfeiffer-Balzers turbomolecular pump and a Duo Seal mechanical vacuum pump to reach pressures as low as 10 nanoTorr. Samples were pressed onto 100 x 100, plain, 0.002 inch tungsten mesh from the Unique Wire Weaving company and held in the chamber with a nickel clamp. Temperatures were monitored using an E-type thermocouple. Heating was done using electrical resistivity with a 50 amp power driver built by the University of Pittsburgh and Honeywell controller.

Dosing of the gases and evacuation was controlled and directed using a bakeable, stainless-steel UHV manifold. Pressures were monitored via an ion gauge and dual, capacitance manometer gauges.

Light exposures were done with a water-cooled, PTI short arc xenon lamp passing through a Newport 6123 liquid infrared filter. In later trials, Oriel Spectra-Physics model 59044 and 59480 long pass filters were added to limit the light to the visual and the UV-vis. ranges of 400nm to ~700nm and 300nm to ~700nm, respectively.

A Cole-Parmer 8852 sonicator was used to clean the clamp and grid prior to sample mounting. Fisher-Scientific certified spectra-analyzed acetone was used in the sonications and for cleaning the probe on which the clamp is mounted in the cell.

A MKS PPT Residual Gas Analyzer/quadrupole mass spectrometer was used for the mass spectral studies.

Thermocouple wire leads, chromel and constantan, were welded to the mesh and thermocouple using a Rocky Mountain 506 Dial-a-Weld pulsation welding device.

Dry ice and acetone were used as cryogenic agents for the cooling of the cell through thermal conduction. Compressed nitrogen was used when needed as a purging agent.

P25 DeGussa Aerosil® titanium dioxide was used as one surface. The other nanoparticles used were obtained from Dr. Kenneth Klabunde and his research group and company in Manhattan, KS where they were manufactured using the sol-gel method.

Procedure:

Synthesis

The sol-gel method of nanoparticle synthesis utilized in the creation of all the particles used in this study begins with the hydrolysis of a metal-alkyl-oxide (Ti-O-R or Sr-O-R) in presence of a solvent solution under an inert atmosphere. This step is done slowly so as to allow the newly formed metal hydroxide to react with the remaining metal-alkyl-oxide resulting in the formation of a metal oxide framework and alcohol.

Once fully reacted, the solvent must be removed from the gel. This must be done at temperatures and pressures above the critical temperature and pressure of the chosen solvents to prevent capillary forces from collapsing the framework into much larger crystals. A Parr reactor is used for this purpose. A stirring mechanism incorporated into the reactor allows for the physical breakdown of the latticework during solvent removal.

Once done, the nanoparticles are calcined in the presence of oxygen at 773 K. It should be noted that, though, we have gained knowledge concerning the production of nanoparticles and synthesized the gel precursor, all the nanoparticles used in these experiments came from the lab of Dr. Kenneth Klabunde at Kansas State University.

In Situ FTIR

The samples were pressed onto a 1" x 1.125" section of tungsten mesh under 10,000 lbs of pressure between two stainless steel cubes and mounted into the reaction vessel. The vessel was then attached to the UHV line and heated to 373 K internally and 323 K externally while under evacuation. After several hours at this temperature, the sample was taken to 473 K and left overnight.

The next day the external heating was removed and the grid and sample spectra were taken at 473 K. The sample was then heated to 573, 673, and 773 K. Each temperature was held for approximately an hour and followed by a cooling to 473 K for the taking of an IR spectrum. At 773 K, 15-20 Torr of oxygen was dosed and left in the reaction vessel for 15 minutes. The gas was then evacuated and the sample heated another 50 to 100 K for a half hour. The sample was then cooled to 473 K for a final dehydroxylation spectrum and then to room temperature.

The cell was cooled to approximately 233 K and exposed to acetaldehyde or crotonaldehyde in a series of 3-5 dosings. IR spectra, 250-300 scans per, were taken one after another during the exposure period and for approximately 30 minutes after the final exposure. The gas phase aldehydes were then evacuated and the sample was warmed in 5 K increments to 273 K. 15-20 Torr of oxygen was then introduced to the cell and spectra were taken over the next hour or so. The arc lamp was then ignited and the sample exposed to it through the quartz window of the cell with spectra being continually taken. The temperature of the cell was controlled as much as ambient conditions would allow. Temperatures were usually maintained within ± 5 K of 273 K. Ambient heat, the presence of gas in the reaction cell, imperfections in the thermocouple weld, and the heat of the lamp were the primary causes of this variation in temperature.

Mass Spectral Study of Residual Gases and Desorbed Species

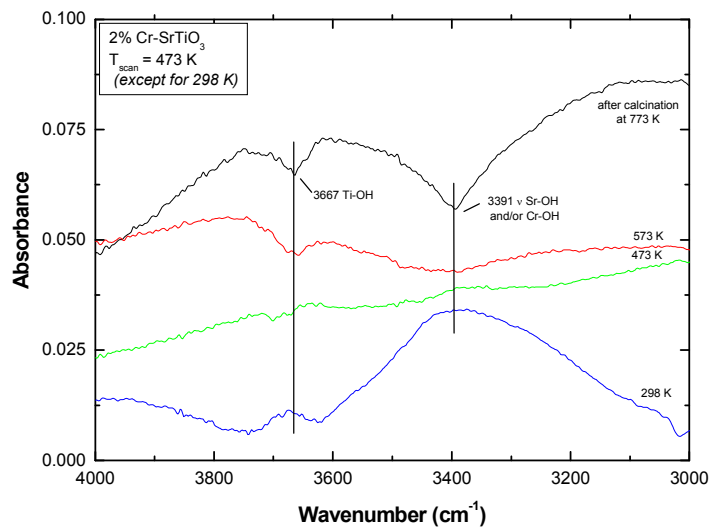
After the photooxidation, a mass spectral study was done. Early experiments used simple mass spectral plots, but the later experiments benefited from temperature programmed desorption (TPD) studies. Some data from these will be used as reinforcing material, but the in-depth discussion of these is beyond the scope of this work.

RESULTS/DISCUSSION

Dehydroxylation:

2%Cr-SrTiO₃

The dehydroxylation as a function of temperature and calcination on chromium incorporated SrTiO₃ can be seen in Figure#1. Decreasing negative peaks at 3667cm⁻¹ and 3391cm⁻¹ can be seen forming as the temperature was increased and calcination was undergone. These correspond to the stretching modes of the titania hydroxyl groups and strontium/chromium perturbed titania hydroxyl groups, respectively.



Figure#1: Dehydroxylation as a Function of Temperature and Calcination on 2%Cr-SrTiO₃ Nanoparticles

2.5%Sb-2%Cr-SrTiO₃

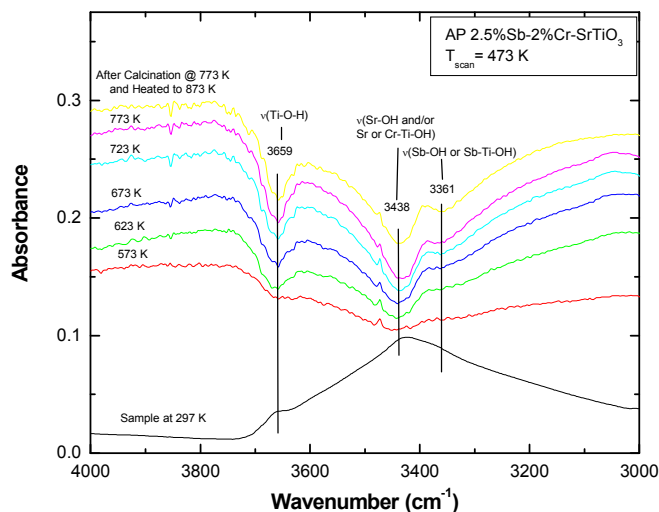
When antimony is incorporated into the nanoparticle, three negative features develop with increasing temperature and calcination. The first is at 3659cm⁻¹ and represents the stretching mode of the titania hydroxyl groups. The peak at 3438cm⁻¹ represents the strontium and/or chromium perturbed titania hydroxyl groups, and the last peak at 3361cm⁻¹, which is absent on the Cr-SrTiO₃, appears to be either an antimony perturbed titania hydroxyl group or a surface antimony hydroxyl group. These features can be seen in Figure#2.

Adsorption, Evacuation, and Warming prior to Dark Oxidation:

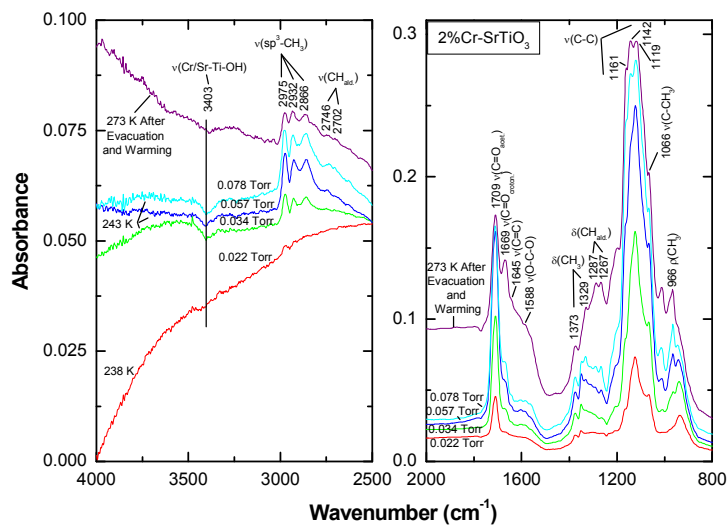
2%Cr-SrTiO₃

As acetaldehyde was sequentially dosed onto the Cr-SrTiO₃ nanoparticle surface a number of distinct bands can be seen. There is a slight negative feature at 3403cm⁻¹, which corresponds to the chromium/strontium perturbed titania hydroxyl groups. This indicates they place some role, though apparently not a large one, in acetaldehyde adsorption. The peaks from 2975cm⁻¹ to 2702cm⁻¹ represent the stretching modes of the methyl groups and the C-H of the aldehyde. The carbonyl stretches of acetaldehyde and in the later spectra crotonaldehyde can be found at 1709cm⁻¹ and 1669cm⁻¹, respectively. At 1645cm⁻¹, the C=C stretch of crotonaldehyde

can be seen forming as a shoulder peak. Another shoulder peak at 1588cm^{-1} is believed to be an adsorbed acetate species' O-C-O stretching mode. The bending/deformation modes of acetaldehyde's and crotonaldehyde's CH_3 's and CH aldehydes appear between 1373cm^{-1} and 1267cm^{-1} . The carbon-carbon stretching modes of both acetaldehyde and crotonaldehyde occur in the 1161cm^{-1} to 1066cm^{-1} region and form a large peak complex. The final peak is the rocking deformation mode found at 966cm^{-1} in Figure#3. The fact that these peaks do not depreciate significantly upon evacuation indicates that the species observed after evacuation are surface and not gaseous in nature and that the adsorption is to an extent irreversible. No significant formation of crotonaldehyde was seen until the sample was warmed above $\sim 252\text{ K}$.



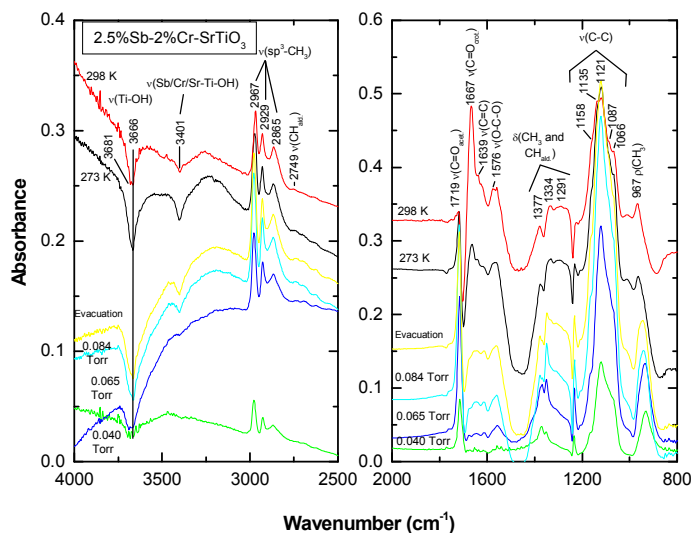
Figure#2: Dehydroxylation as a Function of Temperature and Calcination on 2.5%Sb-2%Cr-SrTiO₃ Nanoparticles



Figure#3: Adsorption, Evacuation, and Warming prior to Dark Oxidation on 2%Cr-SrTiO₃ Nanoparticles

2.5%Sb-2%Cr-SrTiO₃

The analogous spectra for the Sb-Cr-SrTiO₃ sample can be found in Figure #4. Similar trends are seen here as were seen on the Cr-SrTiO₃ with a few exceptions. There is a significant negative feature between the 1719cm⁻¹ $\nu(\text{C}=\text{O})$ of acetaldehyde and 1667cm⁻¹ $\nu(\text{C}=\text{O})$ of crotonaldehyde. This is a surface artifact, not shown, that was not removed by calcination. In addition, the hydroxyl features not only appear at 3666cm⁻¹ and 3401cm⁻¹ but are more significant than on the chromium incorporated sample. This is most likely a function of the amount of sample present on the grid and not a real difference between the adsorption of acetaldehyde on the two samples. The rest of the major groups that were present on the chromium-incorporated sample can be seen on the antimony/chromium sample as well. A significant difference between the two experiments was that the antimony/chromium sample was taken to room temperature, 298 K, prior to dark oxidation while the chromium only sample was stopped at 273 K.



Figure#4: Adsorption, Evacuation, and Warming prior to Dark Oxidation on 2.5%Sb-2%Cr-SrTiO₃ Nanoparticles

Dark Oxidation:

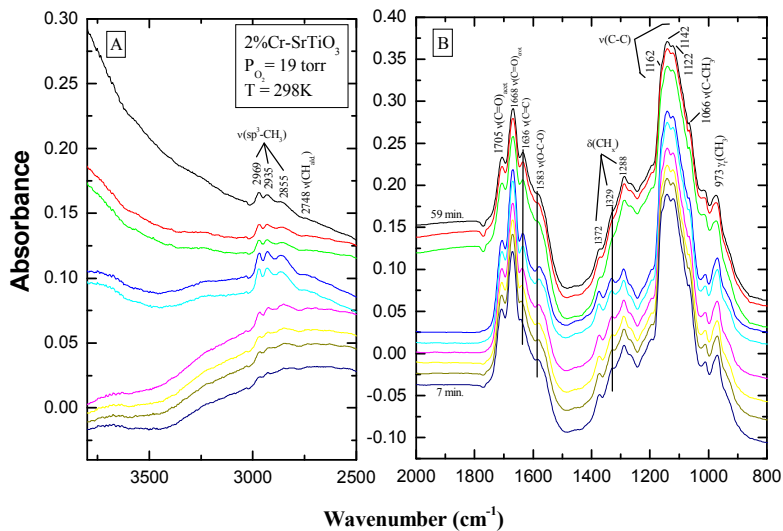
2%Cr-SrTiO₃

The most noticeable thing during the entire course of the dark oxidation in presence of oxygen was the lack of change in the spectrum. The 1669cm⁻¹ crotonaldehyde carbonyl stretch did become predominant over the 1705cm⁻¹ acetaldehyde carbonyl stretch, but this was mostly due to the temperature increase prior to the oxygen introduction and not the oxidation itself. This indicates that the presence of an oxidative atmosphere is not enough to engage the catalytic properties of the nanoparticles. See Figure#5.

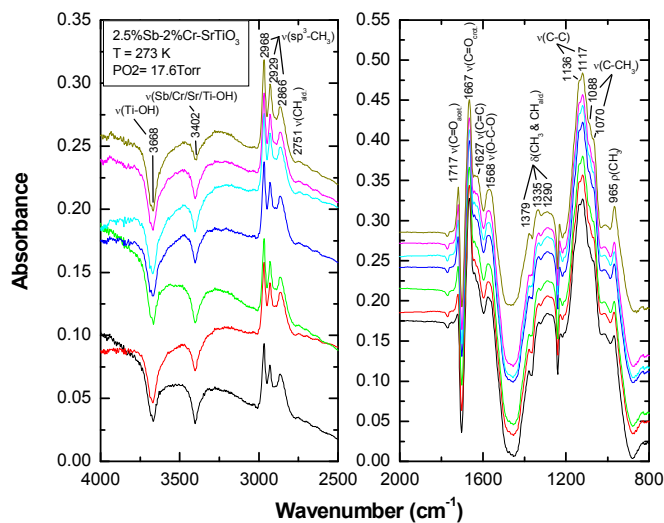
2.5%Sb-2%Cr-SrTiO₃

The antimony/chromium sample also experienced no significant changes with the addition of oxygen. See Figure#6 for the spectra of this. It should be noted that this section of

the reaction was carried out on this sample at 298 K while the same section on the chromium only sample was done at 273 K.



Figure#5: Dark Oxidation as a Function of Time at Constant Temperature on 2%Cr-SrTiO₃ Nanoparticles



Figure#6: Dark Oxidation as a Function of Time at Constant Temperature on 2.5%Sb-2%Cr-SrTiO₃ Nanoparticles

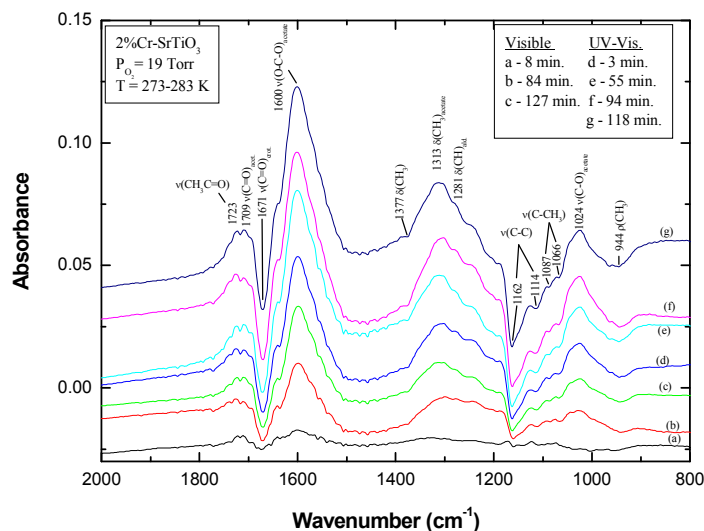
Photooxidation:

There were two parts to the photooxidation. In the beginning, filters were used to restrict the spectrum of the incoming light from the lamp to between ~400nm and ~700nm, the visible range. After 2 hours, some of the filters were removed to open up the spectrum of incoming light to include all the way down to 300nm, a portion of the ultraviolet spectrum. As expected

with photooxidation there was evolution carbon dioxide, but for reasons concerning space, that section of the spectra was not shown.

2%Cr-SrTiO₃

Once the light was turned on, a reaction can be seen taking place. The crotonaldehyde carbonyl stretch at 1671cm⁻¹ can be seen to decrease in relationship to an incoming peak at 1600cm⁻¹. This peak is believed to be the O-C-O asymmetric stretch of an acetate species that is forming [11]. A methyl group deformation mode for this species appears at 1313cm⁻¹ and its C-O stretching mode can be seen coming in at 1024cm⁻¹. At 1723cm⁻¹, an incoming feature was detected that can be attributed to surface bound acetaldehyde species with the hydrogen abstracted from the aldehyde carbon, CH₃C=O. In Figure#7, the decrease in the crotonaldehyde carbonyl stretch is accompanied by decreases in all the acetaldehyde and crotonaldehyde carbon-carbon, single-bond stretches between 1162cm⁻¹ and 1066cm⁻¹ and the methyl deformation mode at 1377cm⁻¹. Note that the spectra were cut off above 2000cm⁻¹ due to the lack of any changes in the features beyond the range shown.



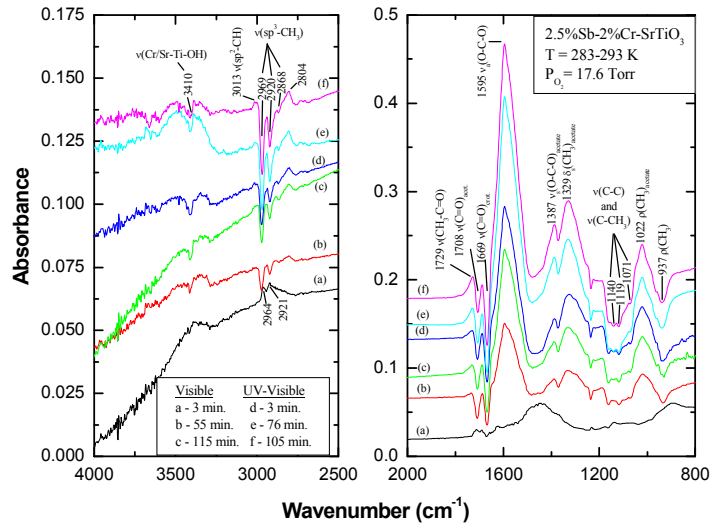
Figure#7: Visible and UV-Visible Photooxidation on 2%Cr-SrTiO₃ Nanoparticles

2.5%Sb-2%Cr-SrTiO₃

A similar reaction to what occurred on the chromium only sample occurred on the antimony/chromium sample but with some significant differences. Negative features were seen for the sp³-hybridized carbon-hydrogen stretches between 2969cm⁻¹ and 2868cm⁻¹ and for the carbonyl stretches of acetaldehyde and crotonaldehyde at 1708cm⁻¹ and 1669cm⁻¹, respectively. This is an area of difference between the 2 samples. The chromium sample saw no decrease in the carbonyl stretch of acetaldehyde but the sample with antimony and chromium experience a significant decrease in both acetaldehyde and crotonaldehyde carbonyls.

Though the basic reaction taking place does not appear to change with the addition of the ultraviolet light, the fact that, after the initial concentrations of reactants has decreased due to visible light photooxidation, not only did the reaction not slow down but appears to have

increased in rate suggests that ultraviolet light is at least as good at activating the photocatalyst if not more effective than visible light only.



Figure#8: Visible and UV-Visible Photooxidation as a Function of Time on 2.5%Sb-2%Cr-SrTiO₃

CONCLUSIONS

As predicted by the literature, the addition of antimony to the chromium doped strontium titanate nanoparticles did offer greater catalytic activity. The products of the reactions, though, appear to be the same or at least within the same chemical group. Dark oxidation resulted in no significant catalysis indicating that the electron promotion via visible and/or UV light is necessary to activate the catalyst. While visible light alone was found to be sufficient to enable catalysis, the addition of ultraviolet wavelengths appears to increase the photocatalysis noticeably.

RECOMMENDATIONS

Thanks to the funding of this program and other sources, an actuator/linear stage setup, a die capable of pressing multiple samples on a single piece of tungsten mesh, and a second turbo pump were purchased. This will greatly increase the effectiveness and efficiency of future *in situ* FTIR studies. To match these increased data acquisition capabilities, work is needed and in progress on increasing the capabilities for data compilation and analysis.

In addition, opportunities exist for the further familiarization with and use of the TPD capabilities of the quadrapole mass spectrometer, which could provide beneficial information about products of these catalyzed reactions.

Collaboration with KSU to make nanoparticles using their Parr reactors for the hypercritical drying stage offers great promise for the expansion of PSU's nanoparticle work and expansion of a synergistic relationship between nanoparticle synthesis and characterization efforts and nanocomposite development on the PSU campus.

Another area of work that needs attention is the characterization of more nanoparticle surfaces. This is traditionally done with pyridine or carbon monoxide. Basic characterization on many has already been done using the extensive capabilities of KSU and Dr. Klabunde's lab, but further study into the mechanics of the interaction of surface features and target chemicals could still be carried further.

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APPLICATIONS of METAL-INCORPORATED TITANIUM DIOXIDE NANOPARTICLES

So what good are chemically active nanoparticles? That is a very good question, and I am glad you have asked it.

General Statement on Nanoparticle Research's Importance to Nanocomposites and Multiuse Materials:

The CNCMM has as one of its core goals, the development and synthesis of multiuse materials. If a nanoparticle were incorporated into a nanocomposite such that it improved the physical properties of the polymer (i.e. tensile strength, Young's modulus, ...) and that also maintained some sort of useful chemical reactivity, this would definitely be a multiuse material and of great interest depending on the specific end properties and capabilities of the nanocomposite. In addition, the reactivity of the nanoparticles in any nanocomposite is going to be of interest because of their integral nature in the material. If the nanoparticles react with and break down the polymer, the composite will fail. That is of course bad, unless one was looking for a material that would work for a certain amount of time and then intentionally disintegrate (i.e. dissolving stitches, and the like).

Specific Applications of Metal-Incorporated TiO₂ Nanoparticles Currently Being Researched or Already Seeing Use:

Work done by Dr. Dilip Paul at the University of Pittsburgh targeted the use of nanoparticles in **chemical warfare decomposition** [8], and research by Dr. K. Klabunde of Kansas State University illustrated the biocidal abilities, specifically the **bactericidal** activities, of halogen exposed MgO nanoparticles [12].



Cover of August 30, 2002 Langmuir 18(17)

Solar power is another area where strontium incorporated titanium dioxides have been investigated as possible catalysts due their water splitting ability under UV radiation [10]. As only a small percentage of light that reaches the earth is UV, the real need is for a visible light active material that can catalyze the reaction. The incorporation of metals such as Sr, Cr, Sb, Ni, etc... is viewed by many to be an area likely to produce significant results in the search for a material to fill this need due to electron band-gap reduction aided by the presence of the metals. Due to its longevity and lack of reliance on refueling the Navy has shown interest in the use of solar power for certain applications and any increases in the efficiency of photovoltaic cells can only work to expand their usefulness to our armed

forces [13, 14]. Some research in this area is planned by Dr. Dilip Paul in conjunction with Dr. Klabunde in the near future.

G.J. Kelly and S.D. Jackson point out in their article “Aldol Condensation of Aldehydes and Ketones over Solid base catalysis” that over 1.5 million tones of “key compounds” are made each year through condensation reactions but that in many cases up to ~30% of the final product cost is “product purification, recovery and waste treatment”, which are necessary due to the use of liquid catalysts [2]. As less than a tenth of the processes used to produce these chemicals use **solid base catalysts** such as nanoparticles, this an area ripe with opportunity. Just think if one could build piping that would not only be a structural element of a plant but actually the reactor and the catalyst as well.

Like their chemical relatives zeolites, nanoparticles have the capacity to trap chemicals on their surface and in the pores of the clusters they form. This capacity is being investigated by Dr. Klabunde’s labs at KSU for the possibility of a **smoke removal system**. The system would disperse a nanoparticle into an area overcome by smoke. The nanoparticles would adsorb/absorb the particulate smoke matter while remaining biologically benign with regard to humans and eventually be removed via a vacuum or other system. The system envisioned would be of special interest to the Navy for 2 major reasons: 1) most deaths in fires are due to smoke inhalation and such and not from direct contact with the fire itself, 2) fire on-board a marine vessel is one of the greatest dangers faced by naval vessels.

In an age where **stealth** is of concern even to Naval vessels (click on the Lockheed stealth submarine below to see more on stealth ships), great advances have been made in reducing the radar, acoustic and other signatures of our vessels. One region of the spectra where



not much in the way of real camouflage has been designed is in the infrared. Research is being conducted at Klabunde’s KSU laboratory into the use of nanowires to absorb the infrared emissions of objects and thus make them **invisible to IR detection**. Not only could this be useful in passive camouflage but could make heat-seeking armaments all the less effective.

Currently a TiO₂ nanoparticle embedded glaze is being used by a number of Japanese firms as a coating on their **tiles and toilets** that make the items effectively **self-cleaning** when they are

given some amount of UV illumination. In addition, the Japanese firm TOTO’s Sanigloss® surface on some of its toilets is smooth at the nano-level, which aids in self-cleaning by making it that much more difficult for anything to stick to the surface.

See http://www.toto.co.jp/hydro_e/index.htm for more on this.

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