

08-21-2006

TO,
Dr. Christopher C. Ibeh, Director
Center for Nanocomposites & Multifunctional Materials (CNCMM)
Professor, Plastics Engineering Technology
Pittsburg State University
Pittsburg, KS 66762

Re: Research paper on **Photoinduced Chemical Reaction on TiO₂-SiO₂**
Nanocomposites.

Dear Dr. Ibeh,

I would like to submit the research paper on the above mentioned topic as a part of 2006 PSU-CNCMM REU/RET ETHICS PROGRAM. I would like to thank you and the executive board of the CNCMM for giving me this wonderful opportunity to participate in the fellowship program for the summer 2006.

The main objective of the research paper is to study the photoinduced chemical behavior of TiO₂-SiO₂ nanocomposites on the surface of the acetaldehyde and to find out the possible application for the protection of the environment.

If you have further queries, please contact me at mlaxmi55@hotmail.com

Thanking You.

Yours' Sincerely,

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**PHOTOINDUCED CHEMICAL REACTION ON TiO₂-SiO₂
NANOCOMPOSITES**

(2006 PSU-CNCMM REU/RET SUMMER PROGRAM)

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1. ABSTRACT

TiO₂-SiO₂ has been one of the most important nanosized mixed metal oxide due to its catalytic and photocatalytic behavior. High surface area of the TiO₂-SiO₂ exhibits photooxidation and photoreduction capabilities. Hence, the synthesis of TiO₂-SiO₂ by the co-precipitation or the sol-gel technique is also important. Further, the adsorption of acetaldehyde on the surface of TiO₂-SiO₂, mixed metal oxide has been studied by transmission infrared spectroscopy. It has been observed that adsorption of acetaldehyde on the surface of mixed metal oxide occurs by the characteristic feature of the Si-OH and Ti-OH.

2. INTRODUCTION

Definition

There is always the need of the new development in the modern industries especially in the field of nanotechnology. Nano means the smallest particle, the unit of which is 10⁻⁹m. Nanomaterials possess the unique properties which are determined by the surface area and the size. These Nanomaterials are intermediate between the single atom and the single crystal structure.

Objectives

The importance of the study of the nanosized materials in the field of Science and technology leads many researchers to the new techniques and its application. The effect of the nano size and the process of synthesis play an important role for the study of nanocomposites. The advancement of the nanocrystals research contributed to the production of the different nano materials, its measurement in nano scale, the better understanding of their properties and the control of the synthesis of the nanomaterials.

Significance of study

One of the most important properties of nanomaterials is size dependent effect in which high distribution of electrons confines the quantized energy levels and is used in the semiconductors and optoelectronics. The semiconductor nanomaterials have interesting optical properties as the size decreases the space between energy levels increases. The electrical properties of the nanomaterials also change with the decrease in size. The surface area of the nanoparticle increases with the decrease in size which influences the chemical properties of the nanomaterials.

The metal oxide and mixed metal oxides are very important as the naomaterials, since these oxides exhibit the very diverse properties, these compounds are being used for the development of the nanomaterials. These oxides can behave as a catalyst, photocatalyst, photoelectric and dielectric [1]. Some of these oxides are semiconductor and some are superconductor as well. TiO₂ is the inert oxide and exhibits the semi conductive properties. It has wide band gap of 3.2 ev [2] .The highly dispersed nanosized TiO₂ with high surface area of SiO₂ may possess both high photo-oxidation and high photo-reduction capabilities. The interaction between the interface of two metal oxides lead to the formation of Ti-O-Si bonds which has some modification in the electronic structure.

Highly porous oxides like silica and titania are considered as a good catalyst as they possess high surface area. Further, they can be applied as low loss electronic devices due to its low dielectric constant. These materials are synthesized by sol-gel technique which is the most widely used technique and better than the conventional technique based on the solid state reaction.

There are many different methods for the synthesis of these nanomaterials such as the solid-state reaction, sol-gel technique, aerogel technique etc. The sol-gel technique is the widely used technique for the preparation of the nanomaterials as it is convenient and thus produced nanomaterials exhibit the high surface area as well.

Thus synthesized metal oxides are studied for the reaction on the surface of the oxygenated hydrocarbons. These materials can be used for the protection of the environment by the reduction or the decomposition of the toxic components[3,4]. The photolytic process can be used for the detoxification of these toxic compounds which decompose the pollutants into the CO_2 , H_2O and N_2 . The discovery of the photochemical water splitting on the titanium dioxide leads to the possibility for the application of these semiconductor metal oxides for the catalysis induced by the light irradiation. Thus the study of the chemistry of the acetaldehyde on the surface of SiO_2 - TiO_2 nanocomposites has been introduced during the adsorption and the photochemical reaction by using FT-IR spectroscopy. The high resolution of this technique has been successful in providing the invaluable information.

4. LITERATURE REVIEW

Metal oxides and mixed metal oxides have been established as the nanomaterials due to its unique properties. They exhibit high mechanical, thermal and chemical stability. These are very good catalyst due to the high surface area.

There is a wide application of these oxide materials as photoelectric, piezoelectric and dielectric materials. Many of the oxides such as SiO_2 and TiO_2 are semiconductors and have a perovskite structure.

There are different methods for the synthesis of these oxide nanomaterials. Conventional method of the preparation of titanates is the solid state synthesis in which grinding is repeated and calcined above 1000 C of the metal carbonate and titanium dioxide. The major advantage of this method is inexpensive, simple and easy. However, these oxides have very low surface area and not homogenous. The preparation of the barium titanate is carried out by using solid state reaction method.

Another method of preparation is the sol-gel method in which gel is produced by mixing two metal alkoxides, a mixture of metal salt and metal alkoxide or a mixture of metal hydroxide and metal alkoxides. The crystalline structure of thus prepared oxides is obtained by calcinations of the dried gel. The major advantage of this method is

homogeneity and the high surface area of the sample obtained. Some of the oxides prepared from this method are $V_2O_5-TiO_2$, SiO_2-TiO_2 and $Nb_2O_5-TiO_2$. These oxides may suffer from the phase segregation as the pore structure becomes non-uniform[5].

Many other wet methods are used for the preparation of these metal oxides. Oxides prepared by these methods have several advantages over the traditionally prepared oxides as they have higher homogeneity, higher surface area and relatively higher reactivity.

5. METHODOLOGY

The development of the titanate materials as the nanocomposites, following three steps are very important; Synthesis, Characterization and the application.

There are different methods for the synthesis of the titanate nanomaterials as previously mentioned solid-state reaction, sol-gel technique or the aerogel technique.

Sol-gel technique is one of the most convenient methods for the synthesis of the oxide nanomaterials. For the preparation of the SiO_2-TiO_2 , following reagents and materials are used.

Materials/Reagents used:

- a) Ethanol
- b) Toluene
- c) Titanium Hydropropoxide
- d) Tetraethoxysilane
- e) Distilled water
- f) Nitrogen
- g) Conical flask
- h) Hot plate with stirrer
- i) Syringe
- j) Timer

Procedures:

The synthesis is performed by mixing ethanol and titanium Hydropropoxide in a conical flask by continuous stirring. After 5 minutes Tetramethoxysilane was added along with the toluene. There should be the continuous bubbling of nitrogen and water was added dropwise so that the slow hydrolysis of alkoxides followed by the gelation takes place. Thus formed oxides exhibit the network structure. The ethanol and toluene used should be in the ratio 1:1.5. Care should be taken while adding water dropwise and the flow of nitrogen should be optimum. The main purpose of the synthesis using this technique is the controlled hydrolysis of the metal alkoxides in the organic solvents. This process leads to the formation of the hydroxyl bridges and the oxygen bridges.

Thus obtained powdered sample by using the sol-gel technique followed by supercritical drying is used for the study of the effect photoinduced chemical reaction based on the FT-IR Technology. The powdered sample was pressed on to the tungsten grid at 12000lbs/in² by using the hydraulic press. The grid was supported in the center by using nickel clamps. E-Type thermocouple is used spot welded at the center of the top of the grid which is used for the temperature controller. Cooling was performed by using the liquid nitrogen. The IR Cell is connected to the high vacuum system, equipped with quadruple mass spectrometer. The base pressure was maintained below 10⁻⁸ torr using a Pfeiffer Vacuum turbo molecular pump. The pressure was measured by a capacitance manometer. The differentially pumped KBr windows of the IR cell are mounted on the concentric Viton O-rings to prevent the leaks. The IR cell is further connected with the computer controlled translation system which make the cell capable to move +_ 1um in the horizontal and vertical direction and also possible to study two sample at a time. 1000W Xenon Arc lamp was used as a light source and the IR spectra were obtained with dry CO₂ free air purged FT-IR spectrometer. The spectra of the background and the sample were taken and the ratio was calculated.

The sample pressed in the tungsten grid is first heated for about half an hour at high temperature ~600 C to get rid of the contamination of hydrocarbon in the pressure of O₂. It was then heated at about 600-650 C to remove the excess O₂ which may lead to the formation of the defect sites. Cooling of the sample was performed by using liquid nitrogen and left overnight. The FT-IR study of adsorption of the acetaldehyde was carried out at different conditions i.e. temperature, Dark oxidation, Visible-light oxidation and UV-visible light oxidation.

6. RESULTS AND DISCUSSIONS

i) Acetaldehyde adsorption over TiO₂-SiO₂ at 233K:

Figure 1 shows the background spectra of the TiO₂-SiO₂ at 233K before exposure to the acetaldehyde. The Infrared feature of OH region at 3749 cm⁻¹ can be assigned as the ν (OH) mode for the isolated hydroxyl groups bound to Si atoms. However, in a recent TiO₂ study by Panayotov and Yates determined the small feature at 3700 cm⁻¹ is due to the isolated Ti-OH groups[6]. So, the 49 cm⁻¹ red shift might be due to the effect of Si on OH. The IR spectrum at 3475 cm⁻¹ can be assigned as the OH group bound to either Ti or Si atoms. The dominant spectral features at 3010 cm⁻¹, 2990 cm⁻¹ and 2914 cm⁻¹ can be assigned to ν (CH₃) for the adsorption of acetaldehyde on the surface of TiO₂-SiO₂. The mode at 2868 cm⁻¹ is due to the overtone for Delta (CH) mode. The depletion of isolated Ti-OH at 3749 cm⁻¹ shows the formation of H-bond through the oxygen of the carbonyl group [TiOH...O=C(H)CH₃]. Upon evacuation for 30 minutes at 1x10⁻⁶ torr, no apparent changes in spectral behavior were observed. The most probable configuration for the irreversibly bound CH₃CHO species is due to the interaction of the partially negatively charged oxygen moiety of the acetaldehyde with the positively charged hydrogen moiety to the surface of the hydroxyl groups. Further this configuration is most probable because of the gas phase of the acetaldehyde which has dipole moment 2.7 Debye. The minor

frequency changes and the intensity in the ν (CH_3) and δ (CH_3) vibrational modes are due to the local mode of the character of the CH_3 groups. The fingerprint region at 1706 cm^{-1} and the shoulder feature at 1684 cm^{-1} can be assigned for the $\nu(\text{C}=\text{O})$. The spectra at 1427 cm^{-1} , 1415 cm^{-1} and 1403 cm^{-1} can be assigned for the ν (OCO) towards the adsorption of the acetaldehyde on the surface of $\text{TiO}_2\text{-SiO}_2$. Further, 1380 cm^{-1} and 1352 cm^{-1} can be assigned for the δ (CH) and δ (CH_3) respectively.

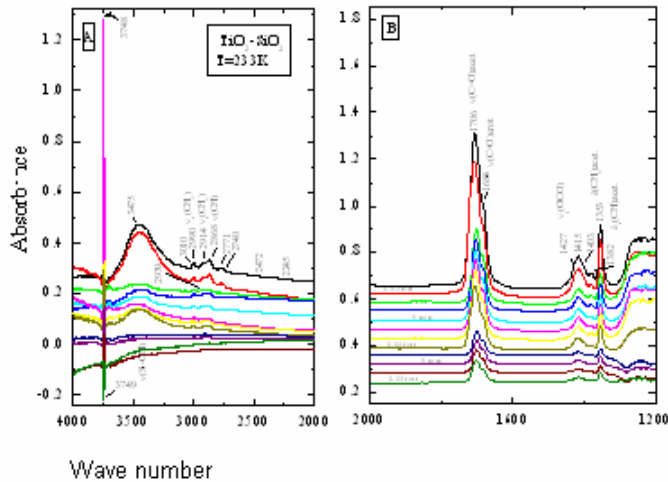


Figure 1 : Adsorption of Acetaldehyde

ii) Warming up effect of the adsorbed acetaldehyde:

As the temperature is raised from 253K to 273K, the evidence of the Aldol Condensation and the formation of crotonaldehyde can be found. The decrease in the intensities of the spectra 1702 cm^{-1} , the shoulder feature at 1682 cm^{-1} and 1353 cm^{-1} are referred to the surface bound to the acetaldehyde.

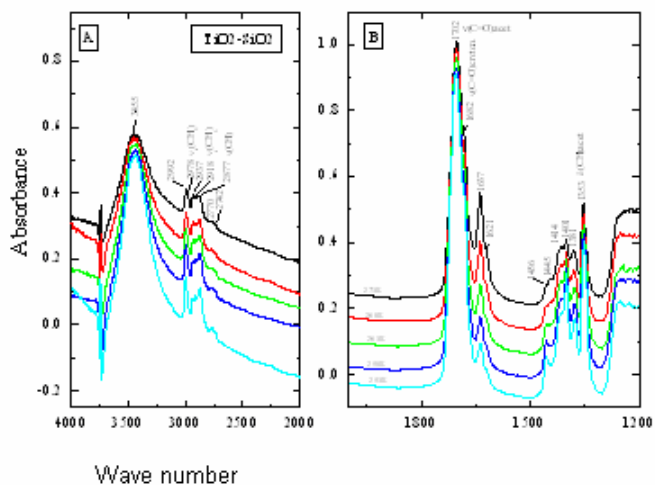


Figure 2: Warming up

iii) Dark Oxidation:

Figure 3 shows the infrared spectra obtained upon the introduction of Oxygen gas on the preadsorbed acetaldehyde at 273K. The decrease in the intensities of $\nu(\text{C}=\text{O})$ at 1706 cm^{-1} , $\delta(\text{CH}_3)$ acetate at 1456 cm^{-1} and $\delta(\text{CH})$ acetate at 1353 cm^{-1} indicate the preadsorbed acetaldehyde and the crotonaldehyde formed during the warm up. However there was no evidence for the formation of CO_2 . Further, there is no evidence for the overall changes in the integrated absorbance for both $\nu(\text{OCO})$ and $\nu(\text{CH})$ for the entire duration of the dark oxidation for 60 minutes.

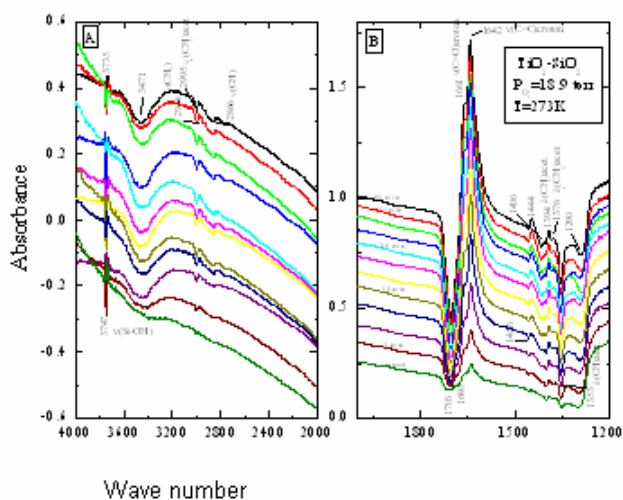


Figure 3: Dark Oxidation in presence of time

iv) Photochemical reaction:

The infrared spectra of Visible-light oxidation as a function of time do not give any significant feature for the formation of CO₂. The intensities of Si-OH at 3747 cm⁻¹ and Ti-OH at 3423 cm⁻¹ determine the adsorption of acetaldehyde.

Figure 4 shows the intensities of CH₃ vibrational modes (at 2977, 2920 and 2857 cm⁻¹) of adsorbed acetaldehyde are significant.

The gradual formation of gas phase CO₂ is observed during the UV-Visible photooxidation reaction at 272-279K. The formation of CO₂ is the final oxidation product which represents the multiple elementary photooxidation steps as acetaldehyde and crotonaldehyde are destroyed by the production of a sequence of the intermediate oxidation production. However the formation of CO is not observed during photooxidation. As the photooxidation takes place at a function of time gradual destruction of acetaldehyde and crotonaldehyde occurs forming non-toxic components.

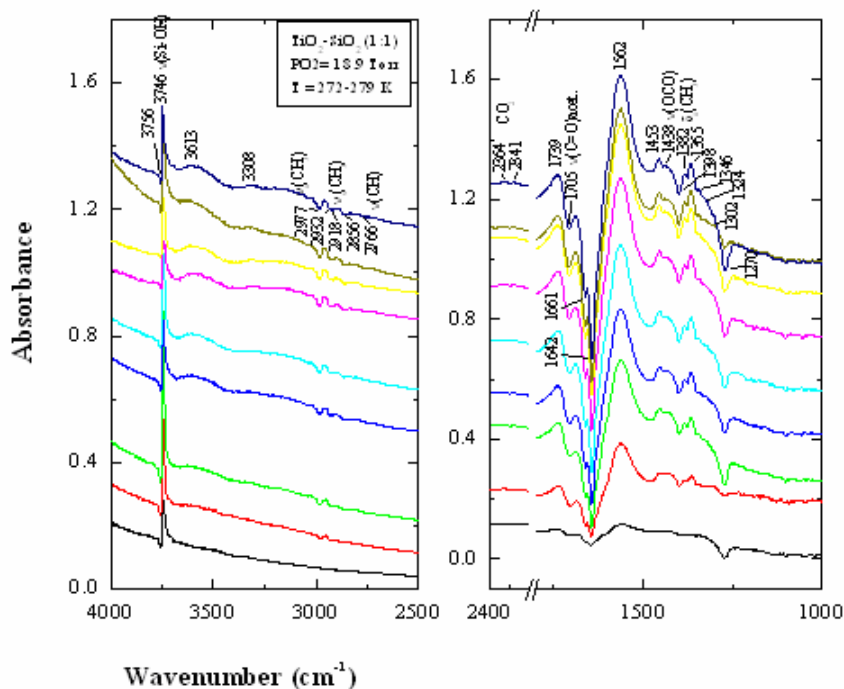


Figure 4: UV-Visible Light Oxidation as a Function of Time

7. CONCLUSIONS

The nanosized mixed metal oxide of $\text{TiO}_2\text{-SiO}_2$ can be applied for the photocatalytic oxidation of the volatile toxic organic materials due to its unique properties such as high porosity, small crystalline size and high surface area. FT-IR spectroscopy is the useful technique for the study of the photoinduced chemical reaction of acetaldehyde on the surface of $\text{TiO}_2\text{-SiO}_2$ leading to the formation of crotonaldehyde and ultimately the degradation into CO_2 .

8. REFERENCES

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