8-2008

Zeolite-Based Nanosized Ti02 Photocatalytic Paper for Antimicrobial Barrier and Toxin Passivation in Packaging: Design, Synthesis and Characterization

Seonghyuk Ko

Western Michigan University

Follow this and additional works at: https://scholarworks.wmich.edu/dissertations

Part of the Engineering Commons

Recommended Citation
https://scholarworks.wmich.edu/dissertations/785

This Dissertation-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Dissertations by an authorized administrator of ScholarWorks at WMU. For more information, please contact maira.bundza@wmich.edu.
ZEOLITE-BASED NANOSIZED TiO$_2$ PHOTOCATALYTIC PAPER FOR ANTIMICROBIAL BARRIER AND TOXIN PASSIVATION IN PACKAGING: DESIGN, SYNTHESIS AND CHARACTERIZATION

by

Seonghyuk Ko

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Paper Engineering, Chemical Engineering and Imaging
Dr. Paul D. Fleming, Advisor

Western Michigan University
Kalamazoo, Michigan
August 2008
 INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI Microform 3323526
Copyright 2008 by ProQuest LLC.
All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 E. Eisenhower Parkway
PO Box 1346
Ann Arbor, MI 48106-1346
ACKNOWLEDGMENTS

I would like to express my deepest gratitude to academic advisor, Dr. Pual D. Fleming, for his worthy advice, assistance and guidance through my research years. I would also like to extend my sincere thanks to my committee members, Dr. Margaret K. Joyce and Dr. Pnina Ari-Gur, for their professional suggestions and review of my dissertation.

I especially wish to thank National Council for Air and Stream Improvement Inc. (NCASI) for their thoughtful consideration and financial support during the course of my doctoral program. Special thanks to Dr. John Cameron, Dr. Jan Pekarovic and Mr. Matt Stoops for helping me in use of instruments and laboratory set up. Many thanks to my family friends and colleagues in PCI department for making enjoyable time and all their help.

I cannot express the depth of my gratitude in words to my mother and my parents-in-law, for all the love and their affection and I cannot think of any way right now to return their great love and sacrifice for me. I also give thanks to my sister’s and brothers-in-law for their persistent interest and support. Finally, I give heartfelt thanks to my lovely wife, Hyunjung, and my lovely sons, Yoonwoo and Geonwoo, for all their sacrifice, quite patience and constant encouragement.

Seonghyuk Ko
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS................................................................................. ii</td>
</tr>
<tr>
<td>LIST OF TABLES......................................................................................... viii</td>
</tr>
<tr>
<td>LIST OF FIGURES......................................................................................... ix</td>
</tr>
<tr>
<td>CHAPTER</td>
</tr>
<tr>
<td>I. INTRODUCTION......................................................................................... 1</td>
</tr>
<tr>
<td>References..................................................................................................... 7</td>
</tr>
<tr>
<td>II. LITERATURE REVIEW.............................................................................. 12</td>
</tr>
<tr>
<td>Photocatalyst and Photocatalysis.............................................................. 12</td>
</tr>
<tr>
<td>What is the photocatalyst?.......................................................................... 12</td>
</tr>
<tr>
<td>Crystalline structure of TiO₂.................................................................... 13</td>
</tr>
<tr>
<td>Basic principles of photocatalysis............................................................ 15</td>
</tr>
<tr>
<td>Environmental applications of TiO₂ photocatalyst.................................... 18</td>
</tr>
<tr>
<td>Zeolite: Principles and Applications......................................................... 20</td>
</tr>
<tr>
<td>Zeolite composition and structure............................................................. 20</td>
</tr>
<tr>
<td>Industrial applications of zeolites............................................................. 22</td>
</tr>
<tr>
<td>Natural zeolite and its use in papermaking and paper coating.................. 25</td>
</tr>
<tr>
<td>Photocatalytic Paper................................................................................... 27</td>
</tr>
</tbody>
</table>
Table of Contents-Continued

CHAPTER

<table>
<thead>
<tr>
<th>Definition and overview</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation methods of photocatalytic paper</td>
<td>29</td>
</tr>
<tr>
<td>Applications of photocatalytic paper</td>
<td>30</td>
</tr>
<tr>
<td>References</td>
<td>31</td>
</tr>
</tbody>
</table>

III. RESEARCH SCOPE AND OBJECTIVES | 41 |

IV. EXPERIMENTALs | 43 |

<p>| Materials | 43 |
| Synthesis of Photocatalytic Materials | 43 |
| TiO₂ colloidal nanoparticles | 43 |
| Zeolite-based photocatalyst | 44 |
| Photocatalytic Papermaking | 45 |
| Determination of TiO₂ retention | 45 |
| Preparation of photocatalytic paper | 46 |
| Characterization of Photocatalyst-Based Materials | 47 |
| Crystallographic examination | 47 |
| Particle size measurement | 48 |
| Optical properties of TiO₂ nanoparticles | 48 |
| Morphology of photocatalytic papers | 48 |
| Evaluation of Photocatalytic Activity | 49 |
| References | 50 |</p>
<table>
<thead>
<tr>
<th>CHAPTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>V. SYNTHETIC BEHAVIOR AND PHOTOCATALYTIC ACTIVITY OF NANOCRYSTALLINE TiO₂ FROM SOL-GEL DERIVED COLLOIDS .........................................................</td>
</tr>
<tr>
<td>Introduction .................................................................</td>
</tr>
<tr>
<td>Experimental .................................................................</td>
</tr>
<tr>
<td>Results and Discussion .................. ................................</td>
</tr>
<tr>
<td>Conclusions .................................................................</td>
</tr>
<tr>
<td>References .................................................................</td>
</tr>
<tr>
<td>Appendix .................................................................</td>
</tr>
<tr>
<td>DLS Distribution and TEM Image of Colloidal TiO₂ Nanoparticles.........................................................</td>
</tr>
<tr>
<td>VI. OPTIMIZATION OF OPTICAL PROPERTIES AND PHOTOCATALYTIC ACTIVITY OF POLYCRYSTALLINE TiO₂ NANOPARTICLES TOWARD PHOTOCATALYTIC PAPER .........................................................</td>
</tr>
<tr>
<td>Introduction .................................................................</td>
</tr>
<tr>
<td>Experimental .................................................................</td>
</tr>
<tr>
<td>Sample preparation .................................................................</td>
</tr>
<tr>
<td>Characterization of TiO₂ .........................................................</td>
</tr>
<tr>
<td>Evaluation of photocatalysis .........................................................</td>
</tr>
<tr>
<td>Results and Discussion .................. ................................</td>
</tr>
<tr>
<td>XRD patterns and crystalline phase transition .................. ................................</td>
</tr>
<tr>
<td>Optical properties .................................................................</td>
</tr>
<tr>
<td>Table of Contents-Continued</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>CHAPTER</td>
</tr>
<tr>
<td>Photocatalytic Activity</td>
</tr>
<tr>
<td>Conclusion</td>
</tr>
<tr>
<td>References</td>
</tr>
<tr>
<td>VII. PREPARATION AND STUDY OF VOC REMOVAL OF NANO TITANIA PHOTOCATALYTIC PAPER USING A NATURAL ZEOLITE MICROPARTICULATE SYSTEM</td>
</tr>
<tr>
<td>Introduction</td>
</tr>
<tr>
<td>Experimental</td>
</tr>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>Characterization of TiO₂ nanoparticles</td>
</tr>
<tr>
<td>Retention of TiO₂</td>
</tr>
<tr>
<td>Preparation of photocatalytic paper</td>
</tr>
<tr>
<td>Evaluation of photocatalysis</td>
</tr>
<tr>
<td>Results and Discussion</td>
</tr>
<tr>
<td>TiO₂ photocatalyst characterization</td>
</tr>
<tr>
<td>TiO₂ retention</td>
</tr>
<tr>
<td>Photocatalytic activity</td>
</tr>
<tr>
<td>Conclusion</td>
</tr>
<tr>
<td>References</td>
</tr>
<tr>
<td>Appendices</td>
</tr>
<tr>
<td>A. The Effect of TiO₂ and Natural Zeolite Contents on Retention Rate</td>
</tr>
</tbody>
</table>
Table of Contents-Continued

CHAPTER

B. The Effect of Cationic Starch Contents on TiO₂ Retention Rate ................................................................. 99

C. The Effect of Cationic Polymer (C-PAM) on TiO₂ Retention Rate ............................................................... 100

VIII. NATURAL ZEOLITE-BASED NANO TiO₂ PHOTOCATALYTIC PAPER: PREPARATION, CHARACTERIZATION AND PHOTOCATALYSIS ASSESSMENT ......................................................... 101

Introduction .................................................................................................................................................. 102

Experimental ............................................................................................................................................. 105

Materials .................................................................................................................................................. 105

Combination of TiO₂ and natural zeolite ............................................................................................... 106

Preparation of photocatalytic paper ...................................................................................................... 106

Characterization ..................................................................................................................................... 107

Evaluation of photocatalytic activity .................................................................................................... 108

Results and Discussion .......................................................................................................................... 108

Characterization of zeolite-based TiO₂ ................................................................................................. 108

Morphology of photocatalytic paper .................................................................................................... 112

Evaluation of photocatalytic activity .................................................................................................... 114

Conclusion ............................................................................................................................................. 117

References ............................................................................................................................................... 117

IX. CONCLUSION ....................................................................................................................................... 122
LIST OF TABLES

2.1 Comparison of Rutile and Anatase Crystalline Properties .................. 14
2.2 Primary Process and Time Domains in Titania-Catalyzed Mineralization of Organic Pollutants ...................................................... 17
2.3 Selected Applications of Photocatalysis ........................................ 19
2.4 Pore Types and Diameters in Zeolites ......................................... 23
2.5 Major Commercial Process Based on Zeolite Catalysts ................. 24
2.6 The Expanding Applications of Photocatalytic Paper .................... 31
4.1 Experimental Factors for TiO\textsubscript{2} Colloidal Nanoparticles .......... 44
4.2 Factors and Levels for the $2^3$ Factorial Design in TiO\textsubscript{2} Retention Test .................................................................................................. 46
5.1 Experimental Factors for TiO\textsubscript{2} Colloidal Nanoparticles and Their Particle Size .............................................................................. 55
7.1 Factors and Levels for the $2^3$ Factorial Experimental Design .......... 89
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>TiO$_2$ crystal structures: Rutile (left) and Anatase (right)</td>
<td>14</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic mechanism of photocatalytic process over TiO$_2$</td>
<td>16</td>
</tr>
<tr>
<td>2.3</td>
<td>Illustration of three- and two-dimensional zeolite framework</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Framework structures of selected zeolites</td>
<td>23</td>
</tr>
<tr>
<td>2.5</td>
<td>Framework structure of Clinoptilolite</td>
<td>26</td>
</tr>
<tr>
<td>2.6</td>
<td>Photocatalysis process on photocatalytic paper</td>
<td>28</td>
</tr>
<tr>
<td>5.1</td>
<td>Representative TEM images of TiO$_2$ colloidal nanoparticles and DLS particle diameter distribution (the upper insert); (A) DOE #2, scale bar=10nm, (B) DOE #5, scale bar=50nm.</td>
<td>56</td>
</tr>
<tr>
<td>5.2</td>
<td>XRD diffraction patterns of as-prepared TiO$_2$ nanoparticles; (A) DOE #2, (B) DOE #5</td>
<td>58</td>
</tr>
<tr>
<td>5.3</td>
<td>The relationship of particle growth and rutile weight fraction as a function of annealing temperature</td>
<td>59</td>
</tr>
<tr>
<td>5.4</td>
<td>Photodegradation of gaseous toluene under UV irradiation</td>
<td>60</td>
</tr>
<tr>
<td>6.1</td>
<td>XRD patterns of phase modulated P25 TiO$_2$ nanoparticles</td>
<td>72</td>
</tr>
<tr>
<td>6.2</td>
<td>Crystallite fractions of TiO$_2$ nanoparticles annealed at varied temperature</td>
<td>73</td>
</tr>
<tr>
<td>6.3</td>
<td>Opacity and brightness of TiO$_2$ nanoparticles according to different rutile fractions</td>
<td>74</td>
</tr>
<tr>
<td>6.4</td>
<td>Diagram of CI$E_L<em>a</em>b*$ values of TiO$_2$ nanoparticles with different rutile weight fraction</td>
<td>75</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>6.5</td>
<td>Photodegradation of toluene with varied crystalline phase of TiO₂ nanoparticles under UV irradiation</td>
<td>77</td>
</tr>
<tr>
<td>7.1</td>
<td>XRD pattern of Degussa P25 TiO₂ powder.</td>
<td>87</td>
</tr>
<tr>
<td>7.2</td>
<td>Representative TEM images of P25 TiO₂ nanoparticles; scale bar=50nm.</td>
<td>88</td>
</tr>
<tr>
<td>7.3</td>
<td>TiO₂ retention values in bleached softwood pulp with varying retention aids; CSF=430 ml, 750rpm</td>
<td>90</td>
</tr>
<tr>
<td>7.4</td>
<td>Main effect and interaction plot for TiO₂ retention (%) in natural zeolite microparticle system</td>
<td>91</td>
</tr>
<tr>
<td>7.5</td>
<td>Photodecomposition of gaseous toluene by nano TiO₂ photocatalytic sheets.</td>
<td>93</td>
</tr>
<tr>
<td>8.1</td>
<td>XRD patterns of natural zeolite-based TiO₂ with varying calcination temperature</td>
<td>110</td>
</tr>
<tr>
<td>8.2</td>
<td>Representative TEM images of TiO₂ nanoparticles on natural zeolite at different calcination temperature; (A) no calcination, (B) 600°C and (C) 800°C, scale bar = 50nm</td>
<td>111</td>
</tr>
<tr>
<td>8.3</td>
<td>SEM images of photocatalytic papers; (A) blank sheet, (B) P25 TiO₂/natural zeolite sheet, (C) natural zeolite-based nano TiO₂ paper and (D) Ahlstrom sample.</td>
<td>113</td>
</tr>
<tr>
<td>8.4</td>
<td>Decomposition of gaseous toluene on photocatalytic papers under UV irradiation</td>
<td>115</td>
</tr>
<tr>
<td>8.5</td>
<td>Comparison of toluene photodegradation by different types of photocatalytic papers</td>
<td>116</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Titanium dioxide (TiO₂) has been widely used for two major purposes, an opacifying pigment and photocatalytic agent [1]. Due to its unique optical properties of a high refractive index and whiteness, TiO₂ has long been used in applications requiring high opacity and brightness such as coatings, paints, plastics, inks, and paper [2]. However, because of its relatively high cost compared to other pigments, such as clay and calcium carbonate, its use in papermaking and coating has been limited to high valued products [3]. Of great interest to many R&D communities in academia and industry is to improve TiO₂ performance to meet the ideal requirements of high optical properties and lower cost.

By contrast, since the remarkable discovery of the Fujishima-Honda effect, that is the photoinduced splitting of water into hydrogen on titania electrodes using only light in 1972 [4], there have been huge breakthroughs achieved, both scientifically and practically, in various applications of semiconductor photocatalysis. In particular, nanocrystalline TiO₂ has recently drawn enormous attention among the possible photocatalytic semiconductor materials, because of their photosensitive, inexpensive, non-toxic and chemically stable characteristics [5-8]. Examples include solar cells [9-11], fuel cells [12-13], optical sensors [14-16], hygienic disinfection [17-20], self-cleaning [21] and extensive environmental cleanup for both air pollutants [22-24] and wastewater [25-27], which is often referred to as “Light Cleaning” [1].

TiO₂ is well known to have three main crystalline structures, which
have different optical and physical properties, namely anatase, brookite and rutile [1]. For the photocatalytic oxidation, anatase is superior to the others, because its conduction band is favorably located to support sufficient conjugation involving electrons and it also can generate very stable peroxide radicals on the surface during the oxidation reaction [28]. Anatase is typically transformed to rutile with an increase in temperature, because the surface free energy has to be minimized to become thermodynamically stable and rutile is the most stable at high temperature among the three main phases [29]. As noticed, different structures govern dissimilar optical and physical properties, which lead to different applications. Indeed, TiO$_2$ is a material that highly depends on its crystalline phase to determine its pigment and photocatalyst properties.

Photocatalysis occurs when a photocatalyst, such as titanium dioxide, is exposed to photons with at least as much energy as the band gap energy of the photocatalyst. When the band gap energy is exceeded, the material forms electron-hole pairs, which are sets of negatively charged electrons and positively charged vacancies, where the electrons used to be. In general, the holes react with H$_2$O to form hydroxyl (OH$^-$) radicals, which lead to an oxidation reaction of a variety of contaminants, such as environmental pollutants and microorganisms [1, 30]. In other words, the oxidizing power of these radicals is the means by which organic chemicals are degraded during photocatalysis, whether in aqueous and gaseous media.

Out of this variety of TiO$_2$-based applications, there has been an emerging interest in attempting to create innovative applications to increase the value of functional paper, named photocatalytic paper, for deodorizing,
disinfection, disintegration of toxins. Photocatalytic paper has been defined as a smart paper that has a light-activated catalytic function to decompose organic pollutants and kill pathogens [31]. Of specific interests are two possible applications, antimicrobial active and VOCs removing paper. In recent years, food-borne microbial outbreaks have been an issue and it is important to promote developing the next generation of materials incorporating anti-bacterial properties in active food packaging [32-33]. This is an advanced packaging system functionalized by interacting package components with food products to satisfy demands for fresh-like foods safe from pathogens [34]. More recently, a new bioactive paper and its packaging has been designed and developed to detect and deactivate any pathogens, such as E-coli and salmonella, borne by food, air and water [35]. Therefore, it would not be an overstatement to say that photocatalytic paper can be used in such new applications as antimicrobial food packaging, bioactive conjugated catalytic paper, as well as toxin passivation and deodorizing paper.

As an effective means of decomposing organic compounds, it is of particular interest to immobilize nanosized TiO2 particles on such supporting or anchoring materials as silica [36-37], glass beads [38,39], alumina [39], fiber glass [40], clay [41] and zeolite [42-43] with the ultimate aim of intact photoactivity and the enhancement of photocatalytic efficiency. Of various supports, zeolites have been found to be more favorable to be used for supporting TiO2, due to their unique crystal structure and uniform nanoscaled pores and channels, which lead to large surface area and induce synergetic adsorption effect of organic matters in turn. A great deal of
previous works has been performed on synthetic zeolites, for instance, HZSM-5 [44], Y zeolite [45] and MCM-41 zeolite [46], because of the relatively larger surface area and supercages in the infrastructure which enable the trapping of TiO₂ nanoparticles.

As distinct from synthetic zeolites, however, natural zeolite provides significant advantages of cost, it’s naturally abundant and is more easily accessible. Surprisingly, though, relatively few studies have been devoted to the anchoring and incorporation of TiO₂ on natural zeolite. Moreover, attempts to use natural zeolite in paper making and coating has been performed recently and it was revealed that natural zeolite pigment makes it possible to significantly improve the print quality of ink jet and digital papers and it is also efficient for filler retention enhancement [47-51]. It is therefore expected that natural zeolite plays important roles between fibers and TiO₂ particles, not only as an effective microparticle retention aid, but as a photocatalytic activity enhancer as well in photocatalytic paper. It is worthwhile, thus, to investigate the integration of natural zeolite and nanosized TiO₂ and to evaluate the photocatalytic activity of photocatalytic paper containing as-prepared natural zeolite-based nano TiO₂. These studies have not, so far, been noticed, nor have they been researched in detail in the area of photocatalytic paper.

The present work aims to design, synthesize and characterize newly developed natural zeolite-nano titania composites and to develop novel photocatalytic papers having the functions of disinfection and decomposition of organic contaminants. In line with these purposes, this research generated the following journal articles referred to as Papers I-IV: (I) Synthetic behavior

In paper I, colloidal titania nanoparticles were synthesized by the sol-gel process based on an experimental design and as-prepared TiO$_2$ nanoparticles were comprehensively characterized from primitive colloids to solid nanoparticles with regard to particle size and photocatalytic activity. Compared to well-known Degussa P25 TiO$_2$, which is the most widely used product in photocatalysis process, TiC$_2$ nanoparticles obtained from this work were determined to have an optimal synthetic passage that surpassed P25 TiO$_2$ in photocatalytic activity of toluene removal as one representative of VOCs.

The goal of the paper II was to optimize the ratio of crystalline phases of polycrystalline TiO$_2$ nanoparticles to satisfy required optical properties, such as opacity, brightness and L*a*b* values, while maintaining high photocatalytic activity. TiO$_2$ nanoparticles were treated by heat to vary the crystalline fraction of anatase and rutile, and subsequently, the crystalline phase of the as-modulated TiO$_2$ samples were used after deposition onto filter paper. Structural change and optical analyses of the TiO$_2$ particles were carried out with various characterization tools such as XRD, BNL Dyano 10 Opacimeter, Technidyne Brightimeter and X-rite 530 SpectroDensitometer,
while at the same time their photocatalytic activity was also evaluated with toluene decomposition. As a result, the optimal ranges of crystalline phase fraction for influencing both the optical properties and photocatalytic activity are suggested in detail.

Paper III deals with nanosized TiO$_2$ photocatalytic paper prepared by a natural zeolite microparticulate system and its photocatalytic performance in VOC decomposition. In order to confirm the importance of natural zeolite, the retention of TiO$_2$ nanoparticles was first tested with a dynamic drainage jar (Britt Jar$^\text{TM}$[52]) according to the factorial experimental design and factors influencing retention of TiO$_2$ nanoparticles discussed by using statistical analysis tools. TiO$_2$ nanoparticles used in this study were characterized by TEM and XRD and the photocatalytic effect was evaluated by toluene removal with a gas chromatograph.

Paper IV describes how to synthesize and characterize nano TiO$_2$-supported natural zeolite from sol-gel derived nano titania colloids and to use as-fabricated zeolite-based TiO$_2$ nanoparticles in preparation of photocatalytic paper using a microparticle retention system. Photocatalytic performance on VOC decomposition was evaluated with gaseous toluene, and to compare photocatalytic activity, two different types of photocatalytic papers were also tested, Ahalstrom commercial photocatalytic non-woven paper and a lab-sample made using Degussa P25 TiO$_2$, which is the most referred to TiO$_2$ pigment for photocatalysis. In the end, the phenomenon of enhanced photocatalysis, as well as, the physical properties of both zeolite-TiO$_2$ hybrid material and its photocatalytic paper were shown and discussed. Indeed, the results in this paper bring us much closer to understanding the
potential of photocatalytic paper and to the day when photocatalytic paper might move beyond fantasy.

References


[52] TAPPI test method T 261 cm-00, Fines fraction by weight of paper stock by wet screening
CHAPTER II

LITERATURE REVIEW

Photocatalyst and Photocatalysis

What is a photocatalyst?

A photocatalyst is generally defined as a material that has an ability to induce chemical reactions of substances of interest adsorbed on the surface by light-generated active radicals and photocatalysis primarily refers to the chemical transformations of reactive species occurring on the photocatalyst in the presence of the proper light energy [1].

Semiconductors, which have band gaps between conduction and valence bands, are the most common materials used in photocatalysis [1]. Due to such unique physical properties of semiconductor as light absorbers, charge excitation and transport and advantaged combination characteristic of electronic structure, metal oxide semiconductors are of great advantaged to photocatalysis agents [2-4]. Among various semiconductor materials, titanium dioxide (TiO$_2$) has been widely used as the most effective photocatalyst, which is well-defined photoinduced oxidative and reductive processes resulting from creating charge carriers on titania surface [5].

In particular, since an epoch-making discovery of TiO$_2$ photoelectrochemical water splitting and hydrogen production using light in 1972 [6], which also referred to as the Fujishima-Honda effect, there have been huge breakthroughs, both scientifically and practically, in various applications of semiconductor photocatalysis. Such research is of constant interest in the field of hydrogen generation by water splitting [7-8],
alternative energy [9-13], sensors [14-16], disinfection [17-20] and extensive environmental cleanup [21-29]. On these wide applications, nanocrystalline TiO\textsubscript{2} has been unchallenged among other semiconductor materials, largely because of their photosensitivity, low cost, easy availability, non-toxicity, chemical and biological stability, even in extreme chemical conditions [30-35].

Crystalline structures of TiO\textsubscript{2}

Titanium dioxide is well known to have three main crystalline structures, which have different optical and physical properties, namely anatase, rutile and brookite. The brookite, which has a structure belonging to the orthombic crystal system, is usually not used because it is extremely difficult to synthesize pure brookite without coexistence of rutile or anatase phase on single particle. For this reason, although the brookite-type TiO\textsubscript{2} has proper band gap energy (3.14 ev) between anatase and rutile, application of brookite TiO\textsubscript{2} has been highly limited and only found in nature [4].

On the other hand, both anatase and rutile TiO\textsubscript{2} are more common to investigate in industrial and experimental applications and are also easier to make. Diebold [36] has recently reviewed the basic structural characteristics of both anatase and rutile TiO\textsubscript{2}, which can be classified into distorted octahedron crystals. Two different crystal structures of anatase and rutile are shown in Figure 2.1 and their different physical properties are summarized in Table 2.1.
Figure 2.1. TiO$_2$ crystal structures: Rutile (left) and Anatase (right). Source: http://ruby.colorado.edu/~smyth/min/tio2.html

Table 2.1. Comparison of Rutile and Anatase Crystalline Properties
Source: TiO$_2$ Photocatalysis: Fundamentals and Applications, pp 125

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rutile</th>
<th>Anatase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline form</td>
<td>Tetragonal system</td>
<td>Tetragonal system</td>
</tr>
<tr>
<td>Band Gap $E$</td>
<td>3.0 eV</td>
<td>3.2 eV</td>
</tr>
<tr>
<td>Corresponding Wavelength</td>
<td>413 nm</td>
<td>388 nm</td>
</tr>
<tr>
<td>Lattice constant $a$</td>
<td>4.58 Å</td>
<td>3.78 Å</td>
</tr>
<tr>
<td>Lattice constant $c$</td>
<td>2.95 Å</td>
<td>9.49 Å</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.71</td>
<td>2.52</td>
</tr>
<tr>
<td>Hardness</td>
<td>6.0-7.0</td>
<td>5.5-6.0</td>
</tr>
<tr>
<td>Permittivity</td>
<td>114</td>
<td>31</td>
</tr>
<tr>
<td>Melting point</td>
<td>1858°C</td>
<td>Changes to Rutile at high temperature.</td>
</tr>
</tbody>
</table>

It is generally known that anatase is transformed to rutile with an
increase in temperature, because the surface free energy has to be minimized to become thermodynamically stable and rutile is the most stable at high temperature among the three main phases [37]. It is also of importance that anatase is more photoactive than the rutile phase, mostly due to the different characteristics of energy levels in the conduction band (CB), as will be more discussed in the mechanism study, the CB energy for rutile is lower in the energy diagram than that of anatase, indicating insufficient reducing potential to produce a superoxide (O$_2^-$) from molecular oxygen (O$_2$). The superoxide turned out to be one of the important reactant species with the holes and hydroxyl radicals in photooxidative degradation of organic contaminants.

As is well known, different structures govern dissimilar optical and physical properties, which lead to different applications by definition. Indeed, TiO$_2$ is a material that highly depends on its crystalline phase to determine its pigment and photocatalyst properties.

Basic principles of photocatalysis

Photocatalysis occurs when a photocatalyst such as titanium dioxide, also known as titania, is exposed to photons with at least as much energy as the band gap energy of the photocatalyst. Band gap energy between valence and conduction band means the minimum light energy required to excite the electrons from the valence band to the conduction band, which makes semiconductor materials electrically conductive [38]. Figure 2.2 gives a conceptual mechanism of titania-assisted photocatalytic process on TiO$_2$. When the band gap energy is exceeded under 380 nm, the material forms
electron(e\textsuperscript{-})-hole(h\textsuperscript{+}) pairs, which are sets of negatively charged electrons and positively charged vacancies where the electrons used to be. In general, the holes react with H\textsubscript{2}O to form hydroxyl (\textsuperscript{·}OH) radicals on valence band, which lead to an oxidation reaction of a variety kind of contaminants, such as environmental pollutants and microorganisms [39]. In other words, the oxidizing power of these radicals is the means by which organic chemicals are degraded during photocatalysis, regardless of both aqueous and gaseous surroundings of TiO\textsubscript{2}. On the other hand, electrons (e\textsuperscript{-}) produced concurrently react with oxygen in the atmosphere to create activated oxygen, the superoxide radical anion (O\textsubscript{2}\textsuperscript{−}), acting as a reductant.

![Figure 2.2. Schematic mechanism of photocatalytic process over TiO\textsubscript{2}.](http://www.nanoin.com)

A number of fundamental mechanistic studies have been conducted on photodecomposition of organic compounds over TiO\textsubscript{2} surfaces [40-42] and the featured time for each primary elementary process has been described as
shown in Table 2.2. The steps of photocatalytic reactions from activation by UV light to decompose organic compounds can be reasonably simplified as follows; [1, 43-44]

\[
\text{TiO}_2 + h\nu \rightarrow h^+ + e^- \quad (1)
\]

\[
\text{OH}^- + h^+ \rightarrow \text{OH} \text{ (hydroxyl radical)} \quad (2)
\]

\[
\text{O}_{2\text{ads}} + e^- \rightarrow \text{O}_{2\text{ads}}^- \text{ (superoxide anion radical)} \quad (3)
\]

\[
\text{OH} + \text{pollutant} + \text{O}_2 \rightarrow \text{products (CO}_2, \text{H}_2\text{O, etc.)} \quad (4)
\]

<table>
<thead>
<tr>
<th>Primary Process</th>
<th>Characteristic time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge carrier generation</td>
<td>Fs (very fast)</td>
</tr>
<tr>
<td>(\text{TiO}_2 + h\nu \rightarrow e^- + h^+)</td>
<td></td>
</tr>
<tr>
<td>Charge carrier trapping</td>
<td>10 ns (fast)</td>
</tr>
<tr>
<td>(h^+ + \Rightarrow \text{Ti}^{IV}OH \rightarrow {\Rightarrow \text{Ti}^{IV}OH^{+}})</td>
<td>100 ps (shallow trap; dynamic equilibrium)</td>
</tr>
<tr>
<td>(e^- + \Rightarrow \text{Ti}^{IV}OH \Leftrightarrow {\Rightarrow \text{TiOH}^{m}})</td>
<td></td>
</tr>
<tr>
<td>(e^- + \Rightarrow \text{Ti}^{IV} \rightarrow \text{Ti}^{III})</td>
<td>10 ns (deep trap)</td>
</tr>
<tr>
<td>Charge carrier combination</td>
<td>100 ns (slow)</td>
</tr>
<tr>
<td>(e^- + {\Rightarrow \text{Ti}^{IV}OH^{+}} \rightarrow \Rightarrow \text{Ti}^{IV}OH)</td>
<td>10 ns (fast)</td>
</tr>
<tr>
<td>(h^+ + \Rightarrow \text{Ti}^{III}OH \rightarrow \text{Ti}^{IV}OH)</td>
<td></td>
</tr>
<tr>
<td>Interfacial charge transfer</td>
<td>100 ns (slow)</td>
</tr>
<tr>
<td>{\text{Ti}^{IV}OH^{+}} + \text{organic molecule} \rightarrow \Rightarrow \text{Ti}^{IV}OH^{+} \text{ oxidized molecule}</td>
<td>mili second (very slow)</td>
</tr>
<tr>
<td>{\Rightarrow \text{Ti}^{III}OH} + \text{O}_2 \rightarrow \Rightarrow \text{Ti}^{IV}OH^{+} + \text{O}_2^{-})</td>
<td></td>
</tr>
</tbody>
</table>
Environmental applications of TiO$_2$ photocatalyst

Titanium dioxide (TiO$_2$) is one of the basic materials that are found easily in our circumstance and daily life. Due to its superior optical properties of a high refractive index and whiteness, TiO$_2$ has long been engaged in such applications requiring high opacity and brightness as coatings, paints, plastics, ink, cosmetics and paper [45-46].

During the last two decades, especially as a photocatalytic semiconductor material, TiO$_2$ has became more attractive as a promising means of environmental purification attributing to exceptional characteristics, to be exact, it is photosensitive to promote photooxidation at room temperature, it is inexpensive, non-toxic and chemically stable, no chemicals needed in the photocatalytic system to complete photodegradation and wide range of pollutants of our choice can be decomposed by this system [28-33]. These benefits have led to its broad applications [5-27] and a diversity of TiO$_2$-based photocatalytic products has been commercialized since the mid-1990s. The volume of markets and industries has been growing in prominence both environmental and bactericidal applications, as listed in Table 2.3.
Table 2.3. Selected Applications of Photocatalysis

<table>
<thead>
<tr>
<th>Property</th>
<th>Category</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-Cleaning</td>
<td>Materials for residential and office buildings</td>
<td>Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminum siding</td>
</tr>
<tr>
<td></td>
<td>Indoor and outdoor lamps and related systems</td>
<td>Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass</td>
</tr>
<tr>
<td></td>
<td>Materials for roads</td>
<td>Tunnel wall, soundproofed wall, traffic signs and reflectors</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>Tent material, cloth for hospital garments and uniforms and spray coating for cars</td>
</tr>
<tr>
<td>Air Cleaning</td>
<td>Indoor air cleaners</td>
<td>Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories</td>
</tr>
<tr>
<td></td>
<td>Outdoor air purifiers</td>
<td>Concrete for highways, roadways and footpaths</td>
</tr>
<tr>
<td>Water Purification</td>
<td>Drinking water</td>
<td>River water, ground water, lakes and water-storage tanks</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>Fish feeding ranks, drainage water and industrial wastewater</td>
</tr>
<tr>
<td>Antitumor</td>
<td>Cancer therapy</td>
<td>Endoscopic-like instruments</td>
</tr>
<tr>
<td>Self-sterilizing</td>
<td>Hospital</td>
<td>Tiles and coatings to cover the floor, walls and ceiling of operation rooms, hospital garments and uniforms</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>Public restroom, pet breeding rooms</td>
</tr>
</tbody>
</table>
Zeolite: Principles and Applications

Zeolite composition and structure

The zeolite is named after the two Greek words, boils for ‘Zeo’ and stones for ‘lithos’ [47]. By Smith in 1971 [48], a zeolite has been conceptually defined as:

*a crystalline aluminosilicate with a tetrahedral framework structure enclosing cavities occupied by cations and water molecules, both of which have enough freedom of movement to permit cation exchange and reversible dehydration.*

According to the above definition, zeolites are highly crystalline aluminosilicate materials with well-defined pore structure originating from a three dimensional framework of SiO4 and AlO4 tetrahedra [49-50]. Figure 2.3 depicts the framework structure of zeolite. Either a Si4+ or an Al3+ can be located within the tetrahedral sites, which are formed by sharing the oxygen atoms between interconnected tetrahedra, and thus it sometimes called TO4- tetrahedral, where T is silicon or aluminum. Due to the unbalance charge between (AlO4)5- and (SiO4)4+, zeolite is structurally negative charged and thus extra counterions are required to the AlO- to produce electrical neutrality that make zeolite ion-exchangeable [51].

Zeolites are exemplified by structure formula consisting of the crystallographic unit cell as follows;

\[ M_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]_{w}H_2O \]  

(5)

where \( n \) is the cation (M) balance, \( w \) is the number of water molecules per unit cell, \( x \) and \( y \) are total number of tetrahedral per unit cell and \( x/y \) is a ratio of Si/Al in framework referring to as zeolite composition [52]. The cations are feasible to exchange with either proton or transition metals,
accordingly properties of zeolite can be modified by the type of cation. The chemical elements used normally in cation exchange are NH$_4^+$, H$^+$, tetramethylammonium (TMA$^+$), the rare-earth and noble metal ions, the alkaline (Na$^+$, K$^+$, Rb$^+$, Cs$^+$) and alkaline earth (Mg$^+$, Ca$^+$) ion and other nitrogen-containing organic cations [53-54]. It is quite pronounced that the different arrangement of tetrahedra give rise to myriads of open framework structures, which determine the pore structure, the size and shape of channels and cages with high surface area. Three dimensional frameworks ultimately consist of channels and interconnected voids or cages.

![Diagram](image)

Figure 2.3. Illustration of three- and two-dimensional zeolite framework. Source [57]: Trends in Analytical Chemistry, Vol. 25, No. 1, 2006 pp25

There are various factors influencing the characteristics of zeolite, to be exact, they extensively depend on the structure of framework, channel size and shape, the ordering and local environment of T-atoms and the size and location of cations within the framework [55-56]. It is therefore extremely
important to recognize the structural properties of zeolites in perception of phenomena associating with catalytic reactivity and adsorptive features as a diffusion medium, sorbent and molecular sieve.

Industrial applications of zeolites

A large number of zeolites have been proposed and 40 known natural zeolites and about 200 zeolites that are not naturally occurring have been synthesized with varied Si/Al ratios [58]. Of the great variety of zeolites, just a few types, mostly synthetic and synthetic-analog natural zeolites, are commercially found in industrial applications. For the industrial catalytic process, zeolites having medium to large pore size are of intense interest and such zeolites belong to a group of 10 or 12 member rings of oxygen atoms with relatively high Si/Al ratio [59]. In general, the pore structure differs considerably from one zeolite to another and its pore diameter is varied by the free aperture arising from 4, 6, 8, 10, 12 or 18 member rings of oxygen atoms. Extra-large pores that consist of more than 12 member rings and mesoporous zeolites have been recently synthesized [60-61]. Zeolites of high current interest in the major industrial process include zeolite Y and mordenite, which have a 12 member ring and zeolite ZSM-5, which has a 10 member ring system. Table 2.4 lists the pore diameters in zeolites and Figure 2.4 shows pictorial structures of selected zeolites.
Table 2.4. Pore Types and Diameters in Zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Pore Type</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Y</td>
<td>Interconnected</td>
<td>7.4 Å diameter pore</td>
</tr>
<tr>
<td></td>
<td>Spherical Supercage</td>
<td>11.8 Å diameter cavity</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Interconnected</td>
<td>5.5 Å x 5.6 Å opening</td>
</tr>
<tr>
<td></td>
<td>Channels</td>
<td>5.1 Å x 5.5 Å opening</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Interconnected</td>
<td>6.5 Å x 7.0 Å channel</td>
</tr>
<tr>
<td></td>
<td>Channels</td>
<td>2.6 Å x 5.7 Å channel</td>
</tr>
<tr>
<td>Beta-Zeolite</td>
<td>Interconnected</td>
<td>7.6 Å x 6.4 Å channel</td>
</tr>
<tr>
<td></td>
<td>Channels</td>
<td>5.5 Å x 5.5 Å channel</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Interconnected</td>
<td>4.1 Å diameter pore</td>
</tr>
<tr>
<td></td>
<td>α-cage</td>
<td>11 Å diameter cavity</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Mesoporous</td>
<td>3~10 nm</td>
</tr>
</tbody>
</table>

Figure 2.4. Framework structures of selected zeolites.
Zeolites have been of great interest as catalysts and adsorptive materials for the last four decades, because of their high surface area, activity, confinement and unusual selectivity, frequently called molecular sieve property, mostly related to solid acid catalyzed processes, for example, isomerization, cracking, hydrocracking, etc [64-65]. The catalytic active sites of zeolite are originated from imbalanced charge in the framework between Si and Al ions that make them amphoteric, including Lewis- and Bröntsted-acid sites [66]. All heterogeneous catalysis of zeolite takes place at acidic sites in the channels, cavities or cages formed by interconnected three dimensional frameworks [67-68]. The major commercial industrial processes based on zeolite catalysts are listed in Table 2.5.

Table 2.5. Major Commercial Process Based on Zeolite Catalysts
Source: Zeolite Catalysis: Principles and Applications, pp 241

<table>
<thead>
<tr>
<th>Process</th>
<th>Zeolite</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic Cracking</td>
<td>Faujasite (Zeolite X or Y)</td>
<td>Gasoline, Fuel oil</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>Faujasite (Zeolite X or Y)</td>
<td>Kerosene, Jet fuel, BTX</td>
</tr>
<tr>
<td>Hydroisomerization</td>
<td>Mordenite</td>
<td>i-Hexane, Heptane</td>
</tr>
<tr>
<td>Iso/n-paraffin separation</td>
<td>Ca⁺- Zeolite A</td>
<td>Pure n-paraffin</td>
</tr>
<tr>
<td>Dewaxing</td>
<td>ZSM-5, Mordenite</td>
<td>Lubes</td>
</tr>
<tr>
<td>Olefin Drying</td>
<td>K⁺- Zeolite A</td>
<td>Polyolefin feed</td>
</tr>
<tr>
<td>Benzene Alkylation</td>
<td>ZSM-5</td>
<td>Styrene</td>
</tr>
<tr>
<td>Xylene Isomerization</td>
<td>ZSM-5</td>
<td>p-Xylene</td>
</tr>
</tbody>
</table>
Natural zeolite and its use in papermaking and paper coating

Natural zeolite has been practically used to control malodor arising from enclosed livestock-breeding spots, such as cat litter, pet shops, kennels and zoos. By and large, natural zeolite has all the advantages of inexpensive cost and abundant reserves, while it has relatively smaller channels, difficulty in purification and inconsistent properties compared with uniform synthetic zeolite. Due to high sorption capacity and its modification by selective cation-exchange [69], however, natural zeolite has been recently well demonstrated for the application of environmental remediation [70-71], especially adsorption process of organic and heavy metals [72] and gas separation [73].

Clinoptilolite, one of the most frequently occurring natural zeolite among more than 40 natural zeolite minerals, is a representative natural zeolite that has been thoroughly studied for modification of its chemical-physical properties [74-75]. Figure 2.5 shows clinoptilolite framework model. The structure of clinoptilolite has a rigid two-dimensional channel system that can be usually occupied by water, cations ion-exchanged and other organic molecules. Two cages in a three-dimensional network are created by intersections of interconnected channels and water and adsorptive materials freely go in and out of pores, without damage to the crystalline structure [76].

With regard to papermaking and coating, an interesting application of this natural zeolite has been announced with two potential uses; low-cost microparticle retention aid in papermaking and purified pigment for ink jet coating [77]. It was revealed that a highly purified clinoptilolite zeolite pigment makes it possible to significantly improve printing quality and economics in ink jet and digital printing and it also may be suitable as a
complementary pigment to make coated paper and paperboard for water-based gravure and flexography. The results of this work has been patented by Klass and Joyce [78-80].

![Clinoptilolite Framework Structure](http://www.zeoponix.com/zeolite.htm)

**Figure 2.5. Framework structure of Clinoptilolite.**
*Source: [http://www.zeoponix.com/zeolite.htm](http://www.zeoponix.com/zeolite.htm)*

Natural zeolite has also been tested as a retention aid in papermaking because it showed high self retaining characteristics in uncoated paper to get rid of print-thorough. The evaluation of retention effect was confirmed by comparing it to bentonite and silica used typically in microparticle retention systems and it was evident that natural zeolite performs outstandingly as a microparticle retention aid in both alkaline and acid papermaking furnishes. Another patent was issued from this line of work with clinoptilolite zeolite [81].
Photocatalytic Paper

Definition and overview

By Pelton, Geng and Brook [82], photocatalytic paper is defined as paper and non-woven fabrics that have a light-activated catalytic function to decompose organic pollutants and kill pathogens. Figure 2.6 illustrates briefly how photocatalytic paper functions. Since the first photoactive TiO$_2$ containing paper introduced by Matsubara et al. in 1995 [83], a few publications and patents have been announced as already summarized elsewhere [82]. H. Tanaka et al [84-88] have successfully prepared different types of photocatalytic paper composites with a dual polymeric retention system, using TiO$_2$ supported on the ceramic fibers. These were shown to remove effectively hazardous chemicals both bisphenol A in wastewater and indoor air pollutants such as acetaldehyde and toluene. The kinetic study of TiO$_2$ containing paper on the photooxidation of ketones was also performed in the gaseous phase and it was shown that water vapor tends to adsorb competitively with ketones and thereby, significantly affects the adsorption behavior on TiO$_2$ particles [89].

In addition, for a photocatalytic removal of nitrogen oxides (NO$_x$), different TiO$_2$ sheets have been prepared and reported that both photocatalytic papers combined with zeolite A [90] and treated with alkaline metal compounds including CaO, MgO, CaCO$_3$, Al$_2$O$_3$ and Fe$_2$O$_3$ [91] were substantially effective for NO$_x$ photodegradation. More recently, it was revealed that void structures of photocatalytic paper have considerable influence on the photocatalytic function [92].
To the best of knowledge, commercial photocatalytic paper is developed and produced by three different companies, namely, Nippon Paper Group (Tokyo, Japan), Ahlstrom (Helsinki, Finland) and Ein Co. Ltd (Gifu, Japan). Nippon paper has announced the development of a new photocatalytic newsprint with an air purification effect [93] and more recently presented a photocatalytic coated paper based on TiO₂ converged technology [94]. Another Japanese company, Ein Co. Ltd. has patented [95] their own technique, specifically focused on environmental technology and developed a photocatalytic pulp, which can be applied for various types of products. Ahlstrom [96], on the other hand, has produced TiO₂ immobilized non-woven paper with an inorganic binder and N. Barka et al [97] has examined photocatalytic decomposition of Rhodamine B using coated TiO₂.
photocatalyst on non-woven paper with an aqueous phase colloidal SiO$_2$ as an inorganic binder. As a result, they were determined the factors influencing the rate of photocatalytic degradation and their sensitivity on photocatalytic performance for the non-woven TiO$_2$ paper. Besides, A. Aguedach et al [98] also found that the photodegradation rate of azo dye, such as reactive black 5 (RB 5), is strongly affected by the ionic strength in dye solution when TiO$_2$ is coated on the non-woven paper with silica binder.

Preparation methods of photocatalytic paper

The approaches of the photocatalytic paper are largely classified into wet-end papermaking and paper coating. For wet-end papermaking, TiO$_2$ powders are deposited on the fibers with retention aids, which are chemicals, such as inorganic salts, natural or synthetic polymers, added to the papermaking stock to improve the retainability of fiber fines, mineral fillers and other additives [99]. It is thus important to retain TiO$_2$ (nano) particles in the paper sheet formed on the forming machine with a fast drainage process in using the traditional papermaking process. However, since it is normally possible to come about fiber-fiber or fines-fines flocculation by high molecular weight retention aids, it should be identified that TiO$_2$ particles are embedded in the fiber matrix as long as possible during the sheet formation. By the wet-end papermaking technique, the TiO$_2$ contents in photocatalytic paper are less likely to exist at the surface, more likely to be in its interior because drainage forces compel fillers to draw out into the fiber web.

In paper coatings, TiO$_2$ has been considered as an essential pigment to provide desirable optical properties, such as opacity and brightness, in
coating formulation generally mixing with other additives, which are principally used for improving the printability of coated paper. Genuinely, TiO₂ is the material that has two sides, but one set of properties and photoactivity, one side of intrinsic characteristics, has been an occasionally regarded factor that should be controlled for a quite long time, because it tends to deteriorate the quality of coating, printing and more seriously, paper itself by photocatalysis. Nonetheless, a number of TiO₂ coated samples focused on photocatalytic effect have been presented [90,100] using either paper or non-woven substrates, since coating readily increases the opportunity for contacting organic contaminants with TiO₂ particles as well as uniform distribution on the paper surface. In this sense, it would be interesting to see an air-purifying paper (Nippon Paper Industries) developed through the combination of pre-binding titania with an inorganic binder, which is a smaller inorganic material even than TiO₂ particles, prior to coating the substrate [101].

Applications of photocatalytic paper

It is generally conceded that photocatalytic paper is reasonably applicable to environmental and hygienic purposes, in short, degradation and disinfection. Moreover, photocatalytic paper, combined with high performance filter paper secures a healthful life in virtue of photodestructuring various pathogens and germs, hazardous organic molecules and obnoxious substances. The applications of photocatalytic paper based on either paper or non-woven substrate have been spreading to predominantly indoor air purification, sanitary product and food packaging.
The expanding applications of this unique paper are summarized in Table 2.6.

Table 2.6. The Expanding Applications of Photocatalytic Paper

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Function</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indoor Air Purification</td>
<td>Purifying hazardous materials and germs floating in the air</td>
<td>Wallpaper, screen, lighting, sliding door paper, sliding screen paper</td>
</tr>
<tr>
<td></td>
<td>Relieving sick building syndrome (SBS)</td>
<td></td>
</tr>
<tr>
<td>Hygiene (Individual &amp; Public)</td>
<td>Disinfection</td>
<td>Mask, paper diaper, tissue paper, hand towel, toilet sheet, poster/calendar, dust box, paper cover, etc.</td>
</tr>
<tr>
<td></td>
<td>Antimicrobacterial</td>
<td></td>
</tr>
<tr>
<td>Food Packaging</td>
<td>Resistant to food poisoning</td>
<td>Wrapping paper, paper cup, napkin, safe milk package, paper sheet for fresh fish, meat, uncooked gift, fruits, etc.</td>
</tr>
<tr>
<td></td>
<td>Disinfection &amp; Antibacterial</td>
<td></td>
</tr>
</tbody>
</table>

References


CHAPTER III

RESEARCH SCOPE AND OBJECTIVES

The current study is focused on: 1) synthesizing colloidal nano-titania and its supported zeolite, 2) characterizing as-prepared materials and evaluating their photocatalytic efficiency, and 3) preparing photocatalytic paper of developed zeolite-based nano-TiO$_2$ and investigating its potential for photodecomposition of organic contaminants.

This research was principally carried out in two ways: The first was to synthesize, to characterize and to optimize the optical and photocatalytic properties of the titania nanocrystalline material from sol-gel derived TiO$_2$ colloidal nanoparticles, and the second aimed to prepare, to estimate the suitability of natural zeolite microparticle systems, and to develop a novel zeolite-based nanosized TiO$_2$ photocatalytic paper for disinfection and toxin passivation in packaging.

The outlines of the objectives of this research are as follows:
1. To study sol-gel synthetic routes to obtain high photoactive TiO$_2$ nanopowders from colloidal titania nano sol,
2. To optimize the effect of crystalline phase, which influences the optical properties, as well as the photocatalytic activity, of polycrystalline TiO$_2$ nanoparticles,
3. To determine the availability of natural zeolite for retaining TiO$_2$ in a fiber matrix, when it is used in a microparticle retention system for wet-end papermaking technique,
4. To characterize the newly developed natural zelite-TiO$_2$ hybrid material, and

5. To investigate the photoactivity and physical properties of novel photocatalytic paper made by using as-prepared TiO$_2$ nanoparticles-supported on natural zeolite.
CHAPTER IV

EXPERIMENTALS

Materials

Titanium tetra-isopropoxide (TTIP 99%), ACS reagent grade 2-propanol and hydrochloric acid (HCl) were used as received from Aldrich in the preparation of sol-gel derived TiO₂ colloids. Natural zeolite (clinoptilolite, ZOBRITE™) was provided by ZO mineral partners. The pulp used for the photocatalytic paper was bleached softwood northern kraft pulp and all of the pulps were refined to a Canadian Standard Freeness (CSF) of approximately 430 ml according to Technical Association of the Pulp and Paper Industry (TAPPI) test methods T 227 [1] and T 248 [2]. Cationic starch and cationic polyacrylamide (C-PAM, Core Shell 61607; NALCO) were also used as flocculants in natural zeolite microparticle retention systems. Nanosized P25 bimodal TiO₂ (Degussa, 22 nm, 50 m²/g, 70% anatase and 30% rutile), which is the most commonly referred to photocatalytic material, was employed as a comparative specimen as a photocatalysis agent. Non-woven photocatalytic paper was purchased from Ahlstrom (France, BR 1048-075, 75g/m²).

Synthesis of Photocatalytic Materials

TiO₂ colloidal nanoparticles

Colloidal TiO₂ particles were prepared by the acid catalyzed hydrolysis of titanium tetra-isopropoxide (TTIP 99%, Aldrich) dissolved in 2-propanol with vigorous stirring for 4-5 hrs to further peptization, based on
the design of experiments established with 3 factors and 2 levels. All reagents were used as received and detailed experimental conditions are given in Table 4.1.

Table 4.1. Experimental Factors for TiO$_2$ Colloidal Nanoparticles

<table>
<thead>
<tr>
<th>Run #</th>
<th>TTIP (M)</th>
<th>HCl (M)</th>
<th>Peptization Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>0.1</td>
<td>Room</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.1</td>
<td>Room</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
<td>0.2</td>
<td>Room</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.2</td>
<td>Room</td>
</tr>
</tbody>
</table>

Zeolite-based photocatalyst

A few nanometers sized TiO$_2$ colloidal nanoparticles were made thorough a sol-gel synthetic route in which acid catalyzed hydrolysis of titanium tetra-isopropoxide dissolved in 2-propanol. Briefly, in a typical synthesis of zeolite-based TiO$_2$ photocatalyst, 10 ml of 0.5 M TTIP solution in 2-propanol was added slowly drop by drop to 2 ml of 0.1M HCl in 88 ml of 2-propanol under vigorous stirring at 0°C. Continuous stirring was carried out for 4-6 hrs to further peptization, and the obtained particle size in a transparent TiO$_2$ sol was 2-3 nm on an average. Natural zeolite was
subsequently mixed thoroughly with as-prepared titania sol by stirring and removed completely from the solvent by evaporation. TiO₂ impregnated natural zeolite was then collected and dried at 110°C followed by post-calcination at 300°C to 800°C to induce the crystallinity of TiO₂ on zeolite.

Photocatalytic Papermaking

Determination of TiO₂ retention

A dynamic drainage device [3], typically called a Britt Jar (Electrocraft, Motomatic II), was used to simulate the main and interactive factors in microparticle retention systems involving cationic starch and polyacrylamide and to determine the effect of natural zeolite for TiO₂ retention in the fiber matrix. As indicated in TAPPI test method T261 [4], paper stock was prepared with 500 mL of 0.5% pulp consistency and filler retention was tested at 750 rpm repetitively at each Britt Jar run with varying dosing level of retention aids based on the design of experiments. A 2³ factorial model was designed in this study and variables and levels are listed in Table 4.2. The amount of TiO₂ loaded to paper stock was fixed at 10% of pulp consistency. The TiO₂ filler retention was determined by the following formula [5];

\[
R_{TiO₂} (%) = \left(1 - \frac{M_w}{M_H}\right) \times 100 \quad (4.1)
\]

where \(R_{TiO₂}\) is the retention rate of TiO₂ nanoparticles, \(M_w\) is the solid weight of filtrate in the drainage and \(M_H\) is the original solid weight of the pulp slurry stock, respectively. The main effects and interaction factors were analyzed to identify the most significant factors influencing TiO₂ retention in
the pulp using MINITAB 14 software (Minitab Institute, USA).

Table 4.2. Factors and Levels for the $2^3$ Factorial Design in TiO$_2$ Retention Test

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
<th>Variable*</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>Natural Zeolite (%)</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>Cationic Starch (%)</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>Cationic Polyacrylamide (%)</td>
<td>0</td>
</tr>
</tbody>
</table>

* weigh percent versus 0.3% pulp contents
* Basis on 10% TiO$_2$ addition level

Preparation of photocatalytic paper

Photocatalytic papers of various TiO$_2$ photocatalysts with approximate 100 g/m$^2$ basis weight were prepared according to TAPPI test methods T 205 [6]. The pulp was mechanically refined to a Canadian Standard Freeness (CSF) of approximately 430 ml as formally designated in TAPPI test methods T 227 [7] and T 248 [8], prior to be blended with other materials. As-prepared zeolite-based TiO$_2$ was added to the pulp suspension with stirring, followed by the addition of cationic starch and cationic polyacrylamide (C-PAM) for the enhancement of retention. In the case of P25 containing paper, natural zeolite was combined with pulp suspension at the last step of dosing. Optimum levels of each retention aid were determined from the Britt Jar experiments. The addition level of each retention aid was 10% photocatalyst, 0.5% cationic starch, 0.1% C-PAM and, when needed, 2% natural zeolite in that order versus 0.3% pulp consistency (3 g dry pulp/L). All lab-made sheets were uniformly formed on a 200 wire mesh in a standard handsheet forming...
machine and dried under standard conditions given in TAPPI T 402 [9] for at least 24 hrs before it was used for the photocatalysis.

Characterization of Photocatalyst-Based Materials

Crystallographic Examination

The X-ray diffraction (XRD) analysis was performed with a Diano X-ray Diffractometer at room temperature using 20 Kw Cu-Kα radiation (λ=0.15418 nm) to survey the crystal structure, approximate crystalline size and integrity of raw natural zeolite and TiO₂ nanoparticles. All peaks were identified using MDI Jade 5.0 software (Materials Data Inc. USA). The average crystallite size of the samples was roughly calculated using the Scherrer equation [10] based on the X-ray line broadening technique as follows;

\[ t = \frac{0.9\lambda}{B\cos\theta_b} \]  

(4.2)

where \( t \) is the diameter of the particle, \( \lambda \) is the wavelength of X-rays, \( B \) is the full width of diffraction lines at half of maximum intensity (radians), and \( \theta_b \) is the diffraction angle corresponding to the maximum peak.

The crystalline phase fraction was also calculated by the following formula, which has been described elsewhere [11].

\[ W_R = \frac{1}{1+0.8\left(\frac{I_A}{I_R}\right)} \]

(4.3)

where \( W_R \) is the percentage of rutile phase, and \( I_A \) and \( I_R \) are the intensities of
anatase (101) and rutile (110) diffraction, respectively.

Particle size measurement

The particle size distribution of the colloidal samples was obtained by a Dynamic Light Scattering (DLS) particle size analyzer (NICOMP, λ=632.8 nm, He-Ne laser). Transmission electron microscope (TEM) images were taken with a JEOL transmission electron microscope (JEM-1230) to confirm the accuracy of DLS values for colloids. The samples for TEM measurement were prepared by dropping a tiny amount of each sample using a micropipette on a Formvar/carbon-coated copper grid (01814F, Ted Pella) and drying in air for at least 1 hour before imaging. Three typical regions of each sample were imaged at 300,000~500,000X magnification.

Optical properties of TiO₂ nanoparticles

The optical properties of the TiO₂ nanopowders deposited on the paper were characterized with regard to opacity, brightness and CIEL*a*b* values and each optical property was tested by an opacimeter (BNL-2 Opacimeter, Diano Corp.), a Brightimeter (Brightimeter Micro S-5, Technidyne Corp.) and an X-rite 530 SpectroDensitometer, respectively. All of the measurements were repeated 10 times for each sample and the average values were calculated and reported.

Morphology of photocatalytic papers

The surface morphologies of various photocatalytic handsheets including example of commercial photocatalytic paper (Ahlstrom, France, BR
were observed by scanning electron microscopy (SEM, Akashi ISI-DS 130) after gold sputtering on the specimen. The voltage set to accelerate electrons was 12 kV and three typical SEM images were taken at 50~1000X magnification in each sample under vacuum.

Evaluation of Photocatalytic Activity

To investigate the photoreactivity of photocatalytic material and its lab-made photocatalytic handsheets, toluene was chosen as a representative compound among various indoor VOC chemicals. Photocatalytic decomposition of gas-phase toluene was carried out in a 1L glass photoreactor under UV light irradiation (EIKO blacklight lamp, 4W, \(\lambda=365\)nm) with circular photocatalyst handsheet (11.29cm in diameter). Specifically, in the TiO\(_2\) nanoparticles experiments, 0.1 g of each TiO\(_2\) powder sample was deposited on the filter paper substrate (Whatman Qualitative, Grade #2) instead of placing on the photocatalytic handsheet. For the quantitative analysis of varying toluene concentrations through the entire experimental time, regardless of UV irradiation, gas samples were withdrawn from a sampling port attached to the reactor and injected into the Gas Chromatograph (GC, SRI 8610C) equipped with a Flame Ionization Detector (FID) and a 30m x 0.25 mm fused silica capillary column (Quadrex Corp.). All samples were tested three times to verify the photodegradation effect and the results were within 5% of standard deviations.
References


[2] TAPPI test method T 248 sp-00, Laboratory beating of pulp (PFI mill method)

[3] TAPPI test method T 248 sp-00, Laboratory beating of pulp (PFI mill method)

[4] TAPPI test method T 261 cm-00, Fines fraction by weight of paper stock by wet screening


[6] TAPPI test method T 205 sp-02, Forming handsheets for physical tests of pulp


[8] TAPPI test method T 248 sp-00, Laboratory beating of pulp (PFI mill method)


The characteristics of TiO₂ nanoparticles in a sol-gel synthetic route, from the colloidal to nanopowder, were investigated based on a factorial experimental design. The as-prepared nanosized TiO₂ was characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Various initial sizes of colloidal nanoparticles ranging between 2.5±0.1 nm and 14.3±0.9 nm were synthesized. It was revealed that the different passages exist between the disparately synthesized colloidal particles on the crystalline phase transformation and particle growth along with annealing temperatures. The photocatalytic activity of pure anatase TiO₂ nanoparticles prepared from optimal synthetic colloids was better than that of commercially available Degussa P25 TiO₂ in toluene removal.

Keywords: TiO₂ nanoparticles, design of experiment, sol-gel, photocatalytic activity, crystalline phase

Introduction

Recently, nanocrystalline TiO₂ has received enormous attention as the
most promising photocatalytic material, as it is photosensitive, inexpensive, non-toxic and chemically stable [1-4]. Of the three main crystalline phases of TiO₂, anatase, rutile and brookite, it is also generally well known that anatase TiO₂-based photocatalyst is more effective than the other phases in decomposing harmful organic compounds [5-6]. Referring to the physical properties of TiO₂ in terms of crystalline structures, there is no wonder that anatase will be transformed to rutile with increase of temperature, because the surface free energy has to be minimized to become thermodynamically stable and rutile is the most stable among the three main phases [6-7] at high temperature. With the level of nanometer scale of particle size, photocatalytic activity is enhanced due to not only the large surface-to-volume ratio, but also band gap widening by the quantum size effect [8-9]. For these reasons, proper control of the size at the level of nano and crystalline structure of TiO₂ in the process of preparation is essential for photocatalytic characteristics.

TiO₂ nanoparticles have been prepared successfully through a variety of methods, such as the sol-gel process [10-11], solvothermal treatments [12], laser pyrolysis [13], hydrothermal method [14], reverse microemulsion method [15], and flame synthesis [16]. Among all synthetic methods, the sol-gel process is still considered as one of the most attractive methods, due to such unique advantages as low-temperature processing, simple, convenient and great flexibility at the stage of preparing TiO₂ samples, either powder or film, with high purity [17]. However, it is recognized as one of the main drawbacks that sol-gel derived TiO₂ is amorphous and needs further heat treatment to obtain crystallization, which can be also accompanied by particle size growth [18]. It is, therefore of practical significance to not only explore
the mechanism of phase transformation for initial colloids to post-synthesized TiO$_2$ nanoparticles in a sol-gel synthetic route, but also to study the particle growth accompanying the phase transition, in order to modulate properly the particle size and crystalline type, and eventually optimize the photocatalytic activity. In the present study, colloidal titania nanoparticles were prepared by the sol-gel process, according to a design of experiments and the resultant TiO$_2$ nanoparticles were systematically characterized from primitive colloids to solid nanoparticles with its photocatalytic activity. As a result, by comparing to well-known commercially available Degussa P25 TiO$_2$, higher photocatalytic effects were achieved with optimal synthetic colloidal-prepared samples.

Experimental

Colloidal TiO$_2$ particles were prepared by the acid catalyzed hydrolysis of titanium tetra-isopropoxide (TTIP 99%, Aldrich) dissolved in 2-propanol with a vigorous stirring for 4-5 hrs to further peptization, based on the design of experiments established with 3 factors and 2 levels. All reagents were used as received and detailed experimental conditions are given in Table 5.1.

In order to investigate the phase transformation and particle size change of TiO$_2$ nanostructures, along with different annealing temperatures, nanocrystalline TiO$_2$ powder samples were prepared by evaporating solvent from colloidal suspensions, without any heating (at room temperature), followed by post-calcination in air.

The particle size distribution of the colloidal samples was obtained by
Dynamic Light Scattering (DLS) particle size analyzer (NICOMP, $\lambda=632.8$ nm, He-Ne laser). Transmission electron micrograph (TEM) images were taken with a JEOL transmission electron microscope (JEM-1230) to confirm the accuracy of DLS values for colloids. The samples for TEM measurement were prepared by dropping a tiny amount of each sample using a micropipette on a Formvar/carbon-coated copper grid (01814F, Ted Pella) and drying in air for at least 1hr before imaging. Three typical regions of each sample were imaged at 500,000X magnification. The X-ray diffraction (XRD) analysis was performed with a Diano X-ray Diffractometer using Cu-Kα radiation ($\lambda=0.15418$ nm).

To evaluate the photoreactivity, photocatalytic decomposition of gas-phase toluene was carried out in a 1L glass photoreactor under UV light irradiation (EIKO blacklight lamp, 4W, $\lambda=365$ nm). 0.1 g of each TiO₂ powder sample, deposited on the filter paper substrate (Whatman Qualitative, Grade #2), was used in the removal of toluene. During the irradiation, a gas sample was withdrawn from a sampling port attached to the reactor and injected into the Gas Chromatography (GC, SRI 8610C) equipped with a Flame Ionization Detector (FID) and a 30 m x 0.25 mm fused silica capillary column (Quadrex Corp.). Degussa P25 TiO₂, which is the most commonly used for photocatalysis, was employed as a reference for comparison.

Results and Discussion

Table 5.1 gives the factors and levels used for synthesizing colloidal titania nanoparticles with the particle size measured by the DLS technique as a response on this experimental design. Hereafter, colloidal samples will be
denoted as DOE Run #, like DOE#2, according to the number of the experimental run. The colloidal particles obtained from entire runs were in the range of 2~14nm size. It was found that the peptization temperature is significant to determine the size of nanoparticles and the smallest colloidal nanoparticles are produced in 0.5M TTIP and 0.1M HCl under 0°C. Considering the titanium alkoxide goes through hydrolysis, polymerization and condensation to determine the particle size during the sol-gel process [19], it should be noted that the temperature for these reactions is a critical factor in determining the colloidal particle size. Representative TEM images of the as-prepared TiO$_2$ shown in Figure 5.1 unveil that the titania particles in Figure 5.1(A) are distinctly smaller than those of Figure 5.1(B), resulting from DOE #5, which is consistent with the DLS measurements (See more data in appendix).

Table 5.1. Experimental Factors for TiO$_2$ Colloidal Nanoparticles and Their Particle Size

<table>
<thead>
<tr>
<th>Run #</th>
<th>TTIP (M)</th>
<th>HCl (M)</th>
<th>Peptization Temp (°C)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.1</td>
<td>0</td>
<td>6.5 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.1</td>
<td>0</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.2</td>
<td>0</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.2</td>
<td>0</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>0.1</td>
<td>Room</td>
<td>8.5 ± 0.5</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.1</td>
<td>Room</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
<td>0.2</td>
<td>Room</td>
<td>14.3 ± 0.9</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.2</td>
<td>Room</td>
<td>6.8 ± 0.5</td>
</tr>
</tbody>
</table>
Figure 5.1. Representative TEM images of TiO$_2$ colloidal nanoparticles and DLS particle diameter distribution (the upper insert); (A) DOE #2, scale bar=10nm, (B) DOE #5, scale bar=50nm.

Figure 5.2 shows XRD patterns of TiO$_2$ nanoparticles annealed at different temperatures ranging from 300°C to 800°C in order to investigate phase transformation and particle size change as well. DOE #2 and #5
colloidal samples in Table 1 were chosen for this study named as powder A and B. Diffraction peaks correspond to a reference pattern (ICDD 21-2172) of crystalline titanium dioxide. The average single particle size of the prepared TiO\textsubscript{2} was calculated from the X-ray line broadening technique using the Scherrer equation [20]. As seen in Figure 5.2, both of the samples have only the anatase phase up to 500°C annealing temperature. However, they show different trends of phase transition above 600°C, which was the temperature the rutile phase appears slightly in powder B. It is evident that the behavior of crystalline phase transformations, which include transformation sequence and starting point of change, varied with primary size of colloidal nanoparticles. The anatase phase was completely transformed to a rutile phase at 800°C of annealing temperature in both of the powders.

The correlation of phase transition with particle size change as a function of annealing temperature is shown in Figure 5.3. The rutile weight fraction was calculated by the following formula [21].

\[ W_R = \frac{1}{1 + 0.8 \left( \frac{I_A}{I_R} \right)} \]  

(5.1)

where \( W_R \) is the rutile weight fraction and \( I_A \) and \( I_R \) are the diffraction peak intensities of anatase (101) and rutile (110), respectively. On the basis of the Scherrer equation [20], single particle size of DOE #2 has been roughly estimated and conspicuously increased to about 16.4 nm maximum in anatase phase from 2.5 nm colloidal particles. Indeed, it is a general tendency that not only TiO\textsubscript{2} particle growth, but crystalline structure also changes from
amorphous to anatase, then into rutile, as annealing temperature increases [6].

![XRD diffraction patterns](image)

Figure 5.2. XRD diffraction patterns of as-prepared TiO₂ nanoparticles; (A) DOE #2, (B) DOE #5.

It is also possible to weigh a coarsening mechanism, when the colloidal material evolved into a crystalline phase for different types of powder TiO₂ nanoparticles. Banfield et al. reported that different coarsening pathways exist between different particle sizes in thermal stability of
nanoparticle phase transformations [22-23], and thus, it is entirely noticeable that the nature of primary colloidal particles definitely affects both the particle propagation and features of crystalline structure transformations.

Figure 5.3. The relationship of particle growth and rutile weight fraction as a function of annealing temperature.

For the photocatalytic activity, toluene was used as a model compound to compare as-prepared TiO\(_2\) with commercial Degussa P25 TiO\(_2\), which consists of 70% anatase and 30% rutile phase and the results are shown in Figure 5.4. DOE #2 sample annealed at 600°C, which has only anatase phase of about 14.8 nm, was chosen for this work. As observed in Fig. 4, photoactivity of as-prepared TiO\(_2\) surpasses that of the P25 TiO\(_2\). According to previous reports [24-25], the degree of anatase crystallinity is positively correlated with the efficiency of the titania for photocatalytic degradation of organic pollutants in that fewer defects in the crystalline frame contribute to
prohibition of recombination of photosensitized electron-hole pairs. Moreover, it has been revealed that the photoactivity of Degussa P25 is mainly attributed to the anatase phase resulting from the undesirable fact that the anatase grains have been separated from the rutile grains [26]. Accordingly, it is more evident that as-prepared anatase TiO₂ was highly crystallized with less defects, resulting in enhancement of photocatalytic activity. Consequently, based on these facts, this result supports the conclusion that the photocatalytic effect is synergistically enhanced with the degree of crystallization and nanosized particles for pure anatase nanocrystalline titania in toluene decomposition.

Figure 5.4. Photodegradation of gaseous toluene under UV irradiation.

Conclusions

The synthetic characteristics of nanosized TiO₂ have been studied from sol-gel derived colloidal nanoparticles prepared through the experimental
design approach. A few nanometers size of colloidal samples, which are in the range of 2.5 nm to 14.3 nm determined predominantly by media temperature, were synthesized followed by annealing at various temperatures. The evolution of crystalline phases and growth showed different-behavior sequences with different primary sizes of colloidal nanoparticles and it was confirmed that varying primitive properties of TiO$_2$ colloidal particles has an impact on the behavior of the crystalline phase transition and coarsening mechanisms as well. The photocatalytic activity of the selected as-prepared TiO$_2$ nanoparticles, which are comprised of only anatase phase, was more potent compared to that of Degussa P25 TiO$_2$ in toluene decomposition on a paper substrate.

References


Appendix

DLS Distribution and TEM Image of Colloidal TiO₂ Nanoparticles

DOE 1 Run #3

Intensity-Wt NICOMP Distribution

![Intensity-Wt NICOMP Distribution Graph]

3.1 ± 0.1 nm

Diameter (nm)
DOE 1 Run #8

Intensity-Wt NICOMP Distribution

![Graph showing intensity-weighted NICOMP distribution with a peak at 6.8 ± 0.5 nm.]

Diameter (nm)
Nanocrystalline TiO$_2$ has attracted much attention both as a photocatalytic agent and an opacifying pigment, due to its photosensitivity, high refractive index, non-toxicity and chemical stability. Recently, its applications have been extended to a photocatalytic paper that can effectively decompose toxins and kill pathogens. Herein, we have investigated the effect of the crystalline phase of TiO$_2$ nanoparticles to optimize the optical properties, as well as photocatalytic activity, as it is deposited onto a paper substrate. Six different crystallite fractions of anatase and rutile were prepared for this study. The structural change and particle size were characterized by X-ray diffraction (XRD). Optical properties including opacity, brightness and CIEL*a*b* values were tested using a BNL Dyano 10 Opacimeter, Technidyne Brightimeter and X-rite 530 SpectroDensitometer. Photocatalytic activity was evaluated by measuring toluene removal, using gas chromatography (GC). It was found that a specific ratio of two different crystalline phases exists to ensure relatively higher optical properties and photoactivity as well, and consequently, the optimum value of phase fraction was in the range of 0.48 rutile:0.52 anatase and 0.71rutile:0.29anatase.
Introduction

Titanium dioxide (TiO₂) has been largely used for an opacifying pigment and photocatalytic agent [1]. Due to unique optical properties of a high refractive index and whiteness, TiO₂ has long been engaged in such applications, requiring high opacity and brightness as coatings, paints, plastics, ink and paper [2]. In addition, during the last two decades, especially as a photocatalytic semiconductor material, nanocrystalline TiO₂ has drawn enormous attentions as it is photosensitive, inexpensive, non-toxic and chemically stable [3-6] and these benefits have led to its wide applications, for example, solar cell [7-8], optical sensors [9], hygienic products [10] and extensive environmental cleanup for both air pollutants [11-12] and wastewater [13-14].

Of a variety of TiO₂-based applications, there has been growing interest in recent years to extend the application and value of functional paper, named as photocatalytic paper, which is defined as paper that has a light-activated catalytic function to decompose organic pollutants and kill pathogens [15]. Since the first photoactive TiO₂ containing paper introduced by Matsubara et al. in 1995 [16], a few publications and patents have been announced as already summarized elsewhere [15]. H. Tanaka’s research group has successfully prepared different types of photocatalytic paper composites with a dual polymeric retention system using, TiO₂ supported on the inorganic fibers [17-19]. These were found to remove hazardous chemicals
both bisphenol A in wastewater and indoor air pollutants such as acetaldehyde and toluene. In addition, the void structure effect has recently been investigated and a kinetic study of TiO₂ containing paper on the VOC decomposition with photocatalytic activity has been reported [20-21].

TiO₂ is well known to have three main crystalline structures, which have different optical and physical properties, namely anatase, brookite and rutile [1]. Due to its higher surface area, anatase has higher photoactivity and also, anatase is transformed to rutile with an increase in temperature, because the surface free energy has to be minimized to become thermodynamically stable and rutile is the most stable at high temperature among three main phases [22]. As noticed, different structures govern dissimilar optical and physical properties, which lead to different applications by definition. Indeed, TiO₂ is a material that highly depends on its crystalline phase to determine its pigment and photocatalyst properties.

It would not be an overstatement to say that photocatalytic paper will be possibly applicable to innovative applications, for example, antimicrobial food packaging, bioactive conjugated catalytic paper, as well as toxin passivation and deodorizing paper. To the best of our knowledge, all previous attempts [15-20] have been performed by using only anatase TiO₂, due to its strong photooxidation capability among the three main different crystalline phases. However, rutile TiO₂ has the relative advantage of optical and photosensitivity, because of its exceptionally high refractive index and smaller band gap energy, which provides better visible light absorption efficiency. It is, therefore, very necessary to explore the optimum combination of bicrystalline TiO₂ to impart essential optical properties, while maintaining
the high photocatalytic function in the photocatalytic papers. To date, very little has been done in this direction.

The purpose of the present study is to optimize the ratio of crystalline phases of polycrystalline TiO$_2$ nanoparticles to assign required optical properties, such as opacity, brightness and $L^*a^*b^*$ values, and simultaneously to ensure higher photocatalytic activity. Six TiO$_2$ nanoparticles varying in different crystalline fractions of anatase and rutile were used as after deposition onto filter paper. Structural change and optical analyses of TiO$_2$ were conducted by XRD, BNL Dyano 10 Opacimeter, Technidyne Brightimeter and X-rite 530 SpectroDensitometer, while at the same time photocatalytic activity was evaluated with toluene decomposition. In the end, the optimal ranges of crystalline phase fraction for influencing both the optical properties and photocatalytic activity are suggested in detail.

Experimental

Sample preparation

Nanophase Degussa P25 TiO$_2$, which is the most commonly referred material in the field of photocatalysis, was used for this study. P25 TiO$_2$ is a bicrystalline phase of 70% anatase and 30% rutile in itself with about 20nm of average single particle size (surface area; 50m$^2$/g). Crystalline phase modulation was accomplished by heat treatment of the P25 TiO$_2$, due to the fact that anatase transformed to a rutile phase, which is more thermodynamically stable, along with heating. The heat treatment of the TiO$_2$ powder was performed in air for 4hrs at different temperatures ranging from 500C to 800C and lastly, six different TiO$_2$ nanoparticles with varying
fractions of crystal morphologies were obtained.

Characterization of TiO₂

To investigate the structural transition of TiO₂, X-ray diffraction (XRD) measurements were performed with a Diano X-ray Diffractometer at room temperature using a 20Kw Cu-Kα radiation (λ=0.15418 nm). The average crystallite size of the samples was calculated from X-ray line broadening technique using the Scherrer equation [23] as follows:

\[
t = \frac{0.9λ}{B \cosθ_B} \quad (6.1)
\]

where \( t \) is the diameter of the particle, \( λ \) is the wavelength of X-rays, \( B \) is the full width of diffraction lines at half of maximum intensity (radians), and \( θ_B \) is the diffraction angle corresponding to the maximum peak.

The crystalline phase fraction was also calculated by the following formula, which has been described elsewhere [24].

\[
W_R = \frac{1}{1 + 0.8 \left( \frac{I_A}{I_R} \right)} \quad (6.2)
\]

where \( W_R \) is the percentage of rutile phase, and \( I_A \) and \( I_R \) are the intensities of anatase (101) and rutile (110) diffraction, respectively. In each case, the baseline amount was subtracted from the peak intensities and the lowest intensity value of each series was taken to be the baseline for that sample.

The optical properties of the TiO₂ deposited onto the paper were
characterized with respect to opacity, brightness and CIEL*a*b* values and each optical property was tested with an Opacimeter (BNL-2 Opacimeter, Diano Corp.), Brightimeter (Brightimeter Micro S-5, Technidyne Corp.) and X-rite 530 SpectroDensitometer, respectively. All of the measurements were tested 10 times for each sample and the average values were calculated and reported.

Evaluation of photocatalysis

To evaluate the photoreactivity, photocatalytic decomposition of gas-phase toluene was carried out in a 1L glass photoreactor under UV light irradiation (EIKO blacklight lamp, 4W, λ=365nm). 0.1 g of each TiO₂ powder sample deposited on the filter paper substrate (Whatman Qualitative, Grade #2) was used in the removal of toluene. For the quantitative analysis of toluene concentration, during the irradiation, gas samples were withdrawn from a sampling port attached to the reactor and injected into the Gas Chromatograph (GC, SRI 8610C) equipped with a Flame Ionization Detector (FID) and a 30m x 0.25 mm fused silica capillary column (Quadrex Corp.).

Results and Discussion

XRD patterns and crystalline phase transition

Figure 6.1 shows XRD patterns for the P25 TiO₂ nanoparticles annealed at different temperatures. Diffraction peaks obviously correspond to a reference pattern (ICDD 21-2172) of crystalline titanium dioxide. It is evident that P25 is comprised of anatase and rutile phases and the crystallite structure transformed to rutile from anatase along with heat treatment. As observed in
Figure 6.1, nothing happens to the crystalline phase at a temperature of 500 °C. The diffraction intensity of the rutile phase increased at 600 °C and the anatase phase completely disappeared at 800 °C of heat treatment.

Figure 6.1. XRD patterns of phase modulated P25 TiO₂ nanoparticles.

The change in phase fraction at the different annealing temperatures is shown in Figure 6.2. With the intensity of each diffraction peak, the phase fraction has been numerically determined, which was in the range of 30% to 100% rutile phase. Based on the Scherrer equation, which has been used to roughly estimate the size of nanoparticles, the average particle size was maintained at around 20 nm through the entire range of the heat treatment.
Figure 6.2. Crystallite fractions of TiO$_2$ nanoparticles annealed at varied temperature.

Optical properties

Opacity, brightness and CIEL*a*b* values were examined from the point of view of paper coating and wet-end paper making applications and the results are shown in Figure 6.3 and Figure 6.4. Figure 6.3 shows opacity and brightness as function of rutile weight fraction. In general, it was highly expected that the pure rutile phase would give the best opacity and brightness, due to its higher refractive index and better ability to reflect radiation in comparison to the anatase form. As seen in Figure 6.3, however, proper ratios of the two crystal forms, anatase and rutile, exist in TiO$_2$. More exactly, the optimal fraction of the two crystalline phases was 0.29 anatase and 0.71 rutile for both enhanced opacity and brightness.
Figure 6.3. Opacity and brightness of TiO$_2$ nanoparticles according to different rutile fractions.

Notably, opacity is a function of refractive index relative to the air in the case of paper sheet, in other words, the greater the differences in refractive index, the higher amount of light scattering. It is also known that light scattering occurring in particles is attributed to direct reflection and diffraction as well [2]. Y. Deng et al [25], recently, reported that light
scattering efficiency of a biphasic pigment increased by reflection and refraction of light at the grain boundaries between crystals of different phases, which have different refractive indices. From the fact that anatase is the more UV region sensitive phase in terms of UV reflectance with higher surface area, it is understood that combinations with anatase could make it possible for optical properties to be strengthened due to synergetic effects of refraction, reflection and diffraction between two phases in light scattering. Figure 6.4 shows CIEL*\(a^*b^*\) values of TiO\(_2\) nanoparticles, which is the most complete color model used conventionally to describe all the colors visible to the human eye. All trends of CIEL*\(a^*b^*\) values were in good accordance with the results of opacity and brightness, which means appropriate anatase to rutile ratios will serve more sensibly neutral base color based on high whiteness.

Figure 6.4. Diagram of CIEL*\(a^*b^*\) values of TiO\(_2\) nanoparticles with different rutile weight fraction.
Photocatalytic activity

For the photocatalytic activity, toluene was used as a model compound to investigate the effect of phase transformation. Figure 6.5 shows toluene removal of phase modulated TiO₂ nanoparticles according to different rutile contents ranging from 0.3 to 1.0 weight fraction. As observed in Figure 5, residual toluene is increasing gradually by small gaps to 0.48 rutile fraction, while removal efficiency of toluene drops rapidly at 0.71 rutile and only 25% of initial toluene removed from the rutile phase only. It is highly probable that rutile TiO₂ has low photooxidation capability, because rutile has a low level conduction band, which has not enough reducing potential to produce a superoxide (O₂⁻) from molecular oxygen (O₂). It has been found that superoxide is as important as the holes and hydroxyl radicals in breaking down organic compounds [1]. As a result, photocatalytic activity is strongly dependent on the anatase phase and it is more worthwhile that rutile will be inducted as a photocatalytic inhibitor to apply where needed to protect from photodecomposition.
Figure 6.5. Photodegradation of toluene with varied crystalline phase of TiO₂ nanoparticles under UV irradiation.

Conclusion

We present here the results of measurements of optical properties and photocatalytic activity that allow us to optimize the effect of polycrystalline phases of TiO₂ nanoparticles from the point of view of principal crystal structures, anatase and rutile. Six different fractions of crystal structure of TiO₂, which are in the range of 0.7 anatase: 0.3 rutile to only rutile phase, were prepared from P25 Degussa TiO₂ by means of heat treatment at 500 °C-800 °C. For the optical properties, opacity, brightness and CIEL*a*b* values were tested and 0.71 rutile/0.29 anatase phase composition of TiO₂ was definitely superior to the others, even though pure rutile has the higher refractive index. The photocatalytic activity of the as-modulated TiO₂ nanoparticles was gradually decreased along with decreasing contents of anatase phase and photoactivity dropped largely from beyond 0.48 rutile ratio in toluene.
decomposition. Accordingly, it is obviously shown that there is an optimal range of anatase and rutile crystalline phases that possesses both better optical properties and photocatalytic activity. Consequently, it makes practically possible an optimal range of TiO₂ phase fractions in the range of 0.48 rutile:0.52 anatase and 0.71 rutile:0.29 anatase.

References


Nanosized TiO$_2$ photocatalytic papers were successfully prepared using a natural zeolite microparticle retention system in papermaking. Applying a factorial experimental design, natural zeolite is evidently confirmed as the most significant and interactive factor for increasing the TiO$_2$ retention rate in paper stock. The photocatalysis of as-prepared sheets was evaluated with toluene as one representative VOC among indoor pollutants. Under UV irradiation, it was shown to very effectively remove gaseous toluene by photodecomposition, assisted by absorption. It was revealed that natural zeolite plays an important role in both increasing retention rate of TiO$_2$ nanoparticles and enhancing photocatalytic efficiency of the paper. It is indeed sensible that the photocatalytic paper can be potentially applied for the environmental purification as well as antimicrobial passivation.

Keyword: nanosized TiO$_2$, photocatalytic paper, natural zeolite, VOC, photocatalysis, experimental design
Introduction

Since the pioneer discovery of TiO$_2$ photoelectrochemical water splitting and hydrogen production using light in 1972 [1], the Fujishima-Honda effect, there have been huge breakthroughs, both scientifically and practically, in various applications of semiconductor photocatalysis. Examples include solar cells [2-3], optical sensors [4], hygienic products [5] and extensive environmental cleanup for both air pollutants [6-7] and wastewater [8-9], which is often referred to as Light Cleaning [10]. In particular, among the possible photocatalytic semiconductor materials, nanocrystalline TiO$_2$ has drawn enormous attention because it is photosensitive, inexpensive, non-toxic and chemically stable [11-14].

Photocatalysis occurs when a photocatalyst such as titanium dioxide, also known as titania, is exposed to photons with at least as much energy as the band gap energy of the photocatalyst. When the band gap energy is exceeded, the material forms electron-hole pairs, which are sets of negatively charged electrons and positively charged vacancies, where the electrons used to be. In general, the holes react with H$_2$O to form hydroxyl (OH$^-$) radicals, which lead to an oxidation reaction of a variety of contaminants, such as environmental pollutants and microorganisms. In other words, the oxidizing power of these radicals is the means by which organic chemicals are degraded during photocatalysis, whether in aqueous and gaseous media.

As an effective means of decomposing organic compounds as well as microorganisms, TiO$_2$ photocatalyst makes possible an innovative novel paper product, which is called photocatalytic paper [15], for toxin passivation, deodorizing and disinfection. Photocatalytic papers may also be able to be
more emphasized for environmental purifications. Moreover, as the time for staying indoors increases more and more nowadays, indoor air quality has become a concern and it is important that it be kept as clean as possible. It is well known that volatile organic compounds (VOCs) are representative of indoor air pollutants and, according to the EPA, VOCs are known to cause negative health effects, with multiple symptoms such as headache, nausea, conjunctiva irritation, dyspnea, allergic skin and emesis, etc. In particular, a large number of hazardous chemicals and the high risk for exposure to those chemicals in new houses and new buildings are the main causes of the serious sick building syndrome (SBS), which is commonly used to demonstrate that any uncomfortable symptoms pose a threat of occupants' health.

As one of promising technologies for VOC removal, there have been numerous studies on photocatalytic oxidation with different TiO₂ system and different chemicals, as already reviewed by S. Wang et al [17]. Despite many studies reported, few publications and patents have been found regarding photocatalytic paper for VOC removal [15]. H. Tanaka et al [18-20] have successfully prepared different types of photocatalytic paper composites with a dual polymeric retention system, using TiO₂ supported on the ceramic fiber matrix. These were found to remove hazardous chemicals both bisphenol A in wastewater and indoor air pollutants such as acetaldehyde and toluene. In addition, the void structure effect has recently been investigated and a kinetic study of TiO₂ containing paper on the VOC decomposition with photocatalytic activity [21-22] has been reported.

In the present study, nanosized TiO₂ photocatalytic paper was
successfully prepared by a natural zeolite microparticulate system based on the factorial experimental design and the ability of VOC removal was investigated with as-fabricated photocatalytic handsheets. For this purpose, retention of TiO$_2$ nanoparticles was tested primarily with the dynamic drainage jar (Britt Jar™) and the effect of natural zeolite in terms of retention was confirmed. Factors influencing retention of TiO$_2$ nanoparticles will be discussed via statistical analysis tools. TiO$_2$ nanoparticles used in this study were characterized by TEM and XRD and photocatalytic performance was carried out by toluene decomposition with a gas chromatograph.

Experimental

Materials

The pulps used for the retention were bleached hardwood and softwood northern kraft pulp and softwood bleached kraft pulp. These were also used for producing the photocatalytic handsheets. All of the pulps were refined to a Canadian Standard Freeness (CSF) of approximately 430 ml according to Technical Association of the Pulp and Paper Industry (TAPPI) test methods T 227[23] and T 248[24]. Nanosized bicrystalline TiO$_2$ (Degussa P25, 22 nm, 50 m$^2$/g, 70% anatase and 30% rutile), which is the most commonly discussed photocatalytic material, was employed as the photocatalytic agent. Natural zeolite (clinoptilolite, ZOBRITETM), provided by ZO mineral partners, was used for a TiO$_2$ supporter and retention aid as well. Cationic starch and cationic polyacrylamide (C-PAM, Core Shell 61607; NALCO) were used as flocculants in natural zeolite microparticle retention systems.
Characterization of TiO$_2$ nanoparticles

The X-ray diffraction (XRD) analysis was performed with a Diano X-ray Diffractometer at room temperature using 20 Kw Cu-K$_\alpha$ radiation ($\lambda$=0.15418 nm) to investigate the crystal structure and approximate particle size of TiO$_2$ nanoparticles. The morphology and accurate size of TiO$_2$ particles was obtained with transmission electron microscope (TEM, JEOL JEM-1230). The samples for TEM imaging were prepared by dropping a tiny amount of TiO$_2$ dispersed in 2-propanol on a Formvar/carbon-coated copper grid (01814F, Ted Pella). Three typical regions of each sample were imaged at 300,000X magnification.

Retention of TiO$_2$

A dynamic drainage device, typically called a Britt Jar (Electrocraft, Motomatic II), was used to simulate the main and interactive factors in microparticle retention systems involving cationic starch and polyacrylamide and to determine the effect of natural zeolite for the TiO$_2$ retention in the fiber matrix. As indicated in TAPPI test method T261 [25], paper stock was prepared with 500 mL of 0.5% pulp consistency and filler retention was tested at 750 rpm repetitively at each Britt Jar run with varying dosing levels of retention aids based on the $2^3$ factorial experimental design. The amount of TiO$_2$ loaded to paper stock was fixed at 10% of pulp consistency. The TiO$_2$ filler retention was determined by following formula [26];

$$R_{TiO_2}(\%) = \left(1-\frac{M_w}{M_H}\right) \times 100 \quad (7.1)$$
where $R_{\text{TiO}_2}$ is the retention rate of TiO$_2$ nanoparticles, $M_w$ is the solid weight of filtrate in the drainage and $M_H$ is the original solid weight of the pulp slurry stock, respectively. Main effect and interaction factors were analyzed to identify the most significant factors influencing TiO$_2$ retention in the pulp using MINITAB 14 software (Minitab Institute, USA).

Preparation of photocatalytic paper

Determined optimum levels of each retention aid, from the Britt Jar experiments, and pulp stock for the handsheet were blended with 10% nano TiO$_2$, 0.5% cationic starch, 0.1% C-PAM and 2% natural zeolite in that order. A 0.3% pulp consistency slurry was applied for stock preparation and at last 5 photocatalytic handsheets of approximate 100g/m$^2$ of base weight were obtained according to TAPPI test method T 205 [27]. All handsheets were dried under standard conditions given in TAPPI T 402 [28] for at least 24hrs prior to perform photocatalysis.

Evaluation of photocatalysis

To investigate VOC removal with handmade photocatalytic paper, toluene was chosen for this study as a model compound among various indoor VOC chemicals. Photocatalytic decomposition of gas-phase toluene was carried out in a 1L glass photoreactor under UV light irradiation (EIKO blacklight lamp, 4W, $\lambda=365$nm) with circular TiO$_2$ handsheet (11.29cm in diameter). For the quantitative analysis of toluene concentration, during the irradiation, gas samples were withdrawn from a sampling port attached to the reactor and injected into the Gas Chromatograph (GC, SRI 8610C)
equipped with a Flame Ionization Detector (FID) and a 30m x 0.25 mm fused silica capillary column (Quadrex Corp.).

Results and Discussion

TiO$_2$ photocatalyst characterization

Figure 7.1 shows XRD pattern of the P25 TiO$_2$ nanoparticles used for this study. Diffraction peaks obviously correspond to a reference pattern (ICDD 21-2172) of crystalline titanium dioxide. It is evident that P25 has bicrystalline structure comprising of anatase and rutile phases. The primary single particle size was estimated at about 22 nm from the X-ray line broadening technique using the Scherrer equation [29].

![XRD pattern of Degussa P25 TiO$_2$ powder.](image)

Figure 7.1. XRD pattern of Degussa P25 TiO$_2$ powder.

Figure 7.2 gives representative TEM images of the P25 TiO$_2$ powder.
As seen in Figure 7.2, two different sizes of grains are observed in their agglomerations among the particles. The smaller particles appear to be approximately 20 nm as shown more clearly in Figure 7.2(B) and the larger particles estimated to be about 50 nm in diameter. Since the anatase phase is predominant in the XRD pattern of Figure 7.1, it may be concluded that the smaller particles are anatase, while the larger particles are rutile, which is quite compatible with other observations [30]. It also should be noted that two phases in P25 TiO₂ exist separately in highly close proximity, for this phenomenon, photocatalytic activity of P25 TiO₂ may mainly be contributed to the anatase phase.

Figure 7.2. Representative TEM images of P25 TiO₂ nanoparticles; scale bar=50nm.

TiO₂ retention

A factorial experiment is quite effective to determine the most significant factors and reasonable to illustrate the main effects and
interactions of factors, because all levels of given factors correlated with every other factor in the experiments and all data are used in computing for both effects [31]. The $2^3$ factorial model was designed in this study and variables and levels are listed in Table 7.1. In a typical microparticulate retention system [32], the level of dosing of additives, cationic compounds and silica or bentonite clay, may affect retention of filler and fines and thus, it is necessary for the statistical experimental design to choose all of contents as operating variables, cationic starch, cationic PAM and natural zeolite, which is substituted for silica and bentonite clay.

Table 7.1. Factors and Levels for the $2^3$ Factorial Experimental Design

<table>
<thead>
<tr>
<th>Factor</th>
<th>Symbol</th>
<th>Variable*</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>Natural Zeolite (%)</td>
<td>- 0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Cationic Starch (%)</td>
<td>0 0.5</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Cationic Polymers (%)</td>
<td>0 0.1</td>
</tr>
</tbody>
</table>

* weigh percent versus 0.3% pulp contents
* Basis on 10% TiO$_2$ addition level

A set of 8 experiments were carried out and the results are shown in Figure 7.3. As fundamental of microparticle effects in fiber matrix, it was observed that there are significant differences in TiO$_2$ retention between with and without natural zeolite, and therefore, it is obvious and confirmed that natural zeolite definitely improves the TiO$_2$ retention with other cationic aids. The microparticle system readily makes it possible to achieve high retention and good formation because of decreased fiber-to-fiber flocculation resulting
from presenting microparticles between fiber and fiber. Natural zeolite microparticle retention aid has already been patented [33] by C.P. Klass and M.D. Sikora and has, in part, inspired this study. Conspicuously, as notated within Figure 7.3, it is interestingly revealed that natural zeolite may fairly act as a supporting substrate for TiO₂, because retention values are relatively higher than those for the presence of cationic additives with no natural zeolite. In the end, dosing levels of retention additives were determined for further preparation of photocatalytic paper.

Figure 7.3. TiO₂ retention values in bleached softwood pulp with varying retention aids; CSF=430 ml, 750rpm

Figure 7.4 shows main factor effects and interactions of the experimental variables. As expected in Figure 7.3, it was verified that natural
zeolite decisively affects the retention of TiO₂ nanoparticles and C-PAM is also notable for retaining TiO₂ in the pulp. For the interaction plot, natural zeolite interacted sensitively with the different levels of addition of two other variables and is as distinct from that of other factors, while cationic starch shows insignificant interaction effects, implying just little contribution on the TiO₂ retention made by cationic starch without natural zeolite and C-PAM. Natural zeolite, therefore, proved to play an important role not only in microparticle retention system, but as a means of supporting titania.

Figure 7.4. Main effect and interaction plot for TiO₂ retention (%) in natural zeolite microparticle system.
Photocatalytic activity

Figure 7.5 illustrates the toluene removal of photocatalytic paper prepared using a natural zeolite microparticle retention system. The concentration of gaseous toluene was 73.1 ppm and the photocatalytic test was performed under UV irradiation for 5 hrs after an initial stabilization time of 1hr. Prior to assessment of photocatalytic activity, blank tests were conducted with pure paper sheets, which had no TiO$_2$ and zeolite to exclude toluene oxidation in bulk by UV. In parallel with this, the variation of toluene concentration caused by both absorption and adsorption was also examined with 10% TiO$_2$ photocatalytic paper without UV.

As seen in Figure 7.5, toluene adsorbed steadily for almost 4hrs by natural zeolite followed by a period of stabilization of residual toluene. The last adsorption efficiency was about 25% of initial toluene and it seems reasonable to assume that it may happen largely because of zeolite pores and will effectively contribute to assisting the photocatalytic reaction. On the photocatalytic handsheets, toluene was decomposed continuously during the entire UV irradiation time in both samples having different contents of TiO$_2$. Residual toluene decreases progressively with slow decomposition rate in the 10% TiO$_2$ sheet, while toluene was removed more effectively for the 20% TiO$_2$ sheet and the efficiency achieved was almost 87%, which is probably due to the repetition of adsorption and photodecomposition of adsorbate between zeolite and TiO$_2$ nanoparticles when the photocatalytic sheets were under UV irradiation. In consequence, it is concluded that photocatalytic paper has became more influential in its potential of photocatalytic performance through the desired intent that natural zeolite takes effect not only as a
retention aid for the TiO$_2$ nanoparticles via both binder and supporter itself in the microparticle system, but also as adsorbent material being performance enhancing in photocatalytic decomposition as well.

![Graph showing photodecomposition of gaseous toluene by nano TiO$_2$ photocatalytic sheets.](image)

**Figure 7.5.** Photodecomposition of gaseous toluene by nano TiO$_2$ photocatalytic sheets.

**Conclusion**

Photocatalytic paper from nanosized TiO$_2$ was prepared using a natural zeolite microparticle retention system in papermaking and was investigated for VOC removal by prototype photocatalytic sheets. The retention of TiO$_2$ nanoparticles was outstandingly improved by addition of natural zeolite and, according to analysis of factorial experimental design, natural zeolite was shown to be the primary main effect factor affecting retention in paper stock and is vigorously interactive with sequential
additives of C-PAM and cationic starch. With the latent capability to adsorb contaminant due to natural zeolite, as-prepared photocatalytic papers were very effective in removing gaseous toluene, which is one of main indoor pollutants, and its ultimate removal efficiency was about 87%. Therefore, it should be pointed out that natural zeolite makes possible improving the retention of TiO$_2$ nanoparticles as both a microparticle retention aid and supporter, as well as enhancing the photocatalytic performance resulting from capturing the pollutant temporarily and photodecomposition under UV. In conclusion, the TiO$_2$ photocatalytic paper can be effectively fabricated with natural zeolite and it possesses high photodecomposition ability for organic contaminants.

References


[23] TAPPI test method T 227 om-99, Freeness of pulp (Canadian Standard Method)

[24] TAPPI test method T 248 sp-00, Laboratory beating of pulp (PFI mill method)

[25] TAPPI test method T 261 cm-00, Fines fraction by weight of paper stock by wet screening


[27] TAPPI test method T 205 sp-02, Forming handsheets for physical tests of pulp

[28] TAPPI test method T402 sp-98, Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products


Appendices

A. The Effect of TiO₂ and Natural Zeolite Contents on Retention Rate

![Retention Rate Graph]

- Hard Wood
- Soft Wood

<table>
<thead>
<tr>
<th>TiO₂ &amp; Natural Zeolite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ 10% Zeolite 2%</td>
</tr>
<tr>
<td>TiO₂ 10% Zeolite 5%</td>
</tr>
<tr>
<td>TiO₂ 10% Zeolite 10%</td>
</tr>
<tr>
<td>TiO₂ 5% Zeolite 10%</td>
</tr>
<tr>
<td>TiO₂ 2% Zeolite 10%</td>
</tr>
</tbody>
</table>

Pulp: 0.35% consistency
Cationic Starch: 0.5%
Cationic Polyacrylamide: 0.1%
B. The Effect of Cationic Starch Contents on TiO$_2$ Retention Rate

![Retention Rate Graph]

- Pulp 0.35%
- TiO$_2$ 10%
- Natural Zeolite 2%
- Synthetic Polymer 0.1%

Retention Rate (%) vs. Cationic Starch Contents (%):

- No Starch
- Starch 0.25%
- Starch 0.5%
C. The Effect of Cationic Polymer (C-PAM) on TiO$_2$ Retention Rate

![Bar chart showing the effect of different cationic retention aids on TiO$_2$ retention rate.](chart.png)
CHAPTER VIII

NATURAL ZEOLITE-BASED NANO TiO$_2$ PHOTOCATALYTIC PAPER: PREPARATION, CHARACTERIZATION AND PHOTOCATALYSIS ASSESSMENT

Seonghyuk Ko, Pnina Ari-Gur, Margaret Joyce and Paul D. Fleming
Department of Paper Engineering, Chemical Engineering and Imaging
Western Michigan University, Kalamazoo MI 49008, USA

A novel paper with high photocatalytic performance was successfully fabricated, using natural zeolite (clinoptilolite)-based nanosized TiO$_2$. Photocatalytic materials, from sol-gel derived TiO$_2$ colloids, incorporated into zeolite, have been designed, prepared and characterized. Resultant prematured anatase TiO$_2$ on zeolite particles were readily used in photocatalytic paper, which revealed zeolite-TiO$_2$ particles dispersed on a dense network of fibers with microvoids. Zeolite-based TiO$_2$ paper presented here decomposed gaseous toluene very effectively with UV irradiation and the removal efficiency was more competent than that of a group of comparisons with Degussa P25 TiO$_2$ paper and commercially available photocatalytic paper. It indeed is reasonably worthwhile that the outstanding findings provide us an in-depth view of the possibility of innovative photocatalytic paper being used for breaking down toxins and possibly microorganisms as well.

Keywords: natural zeolite, clinoptilolite, nanosized TiO$_2$, photocatalytic paper, photocatalysis
Introduction

Titanium dioxide (TiO₂) has been largely used for an opacifying pigment and photocatalytic agent [1]. Due to unique optical properties of a high refractive index and whiteness, TiO₂ has long been engaged in such applications requiring high opacity and brightness as coatings, paints, plastics, ink and paper [2]. In particular, since an epoch-making discovery of TiO₂ photoelectrochemical water splitting and hydrogen production using light in 1972 [3], as it is called Fujishima-Honda effect, there have been huge breakthroughs, both scientifically and practically, in various applications of semiconductor photocatalysis, for example, solar cells [4-5], optical sensors [6], hygienic products [7] and extensive environmental cleanup for both air pollutants [8-9] and wastewater [10-11], which is often referred to as “Light Cleaning” [1]. For these wide applications, nanocrystalline TiO₂ has been unchallenged among other semiconductor materials because of its photosensitivity, low cost, non-toxicity and chemical stability [12-15].

Encouraging as an effective means of decomposing organic compounds, as well as microorganisms, TiO₂ photocatalyst makes it possible to design an innovative novel paper product, which is called photocatalytic paper for toxin passivation, deodorizing and disinfection. Photocatalytic paper can be defined as smart paper that has light-activated catalytic function to decompose organic pollutants and kill pathogens and would be also specifically emphasized on two possible applications, antimicrobial active and VOC removable paper [16]. In recent years, food-borne microbial outbreaks have promoted developing the next generation of materials that incorporates anti-bacterial properties in active food packaging [17]. This is an
advanced packaging system functionalized by an interacting package component with a food product to satisfy desired demands for fresh-like foods, safe from pathogens [18]. More recently, a new bioactive paper and its packaging has been designed and developed to detect and deactivate any pathogens, such as E. coli and salmonella, borne by food, air and water [19].

In addition, as the time for staying indoors increases more and more these days, indoor air quality has become a bigger concern and it is more important for it to be kept as clean as possible. It is well known that volatile organic compounds (VOCs) are representative of indoor air pollutants and, according to the EPA, VOCs are known to cause negative health effects with such multiple symptoms as headache, nausea, conjunctiva irritation, dyspnea, allergic skin and emesis, etc. Among promising technologies for VOCs removal, there have been numerous studies on photocatalytic oxidation with different TiO\textsubscript{2} system and different chemicals were already reviewed by S. Wang et al [20]. Despite lots of studies reported, however, only a few publications and patents have been found regarding photocatalytic paper for VOC removal [16]. H. Tanaka et al [21-23] have successfully prepared different types of photocatalytic paper composites with a dual polymeric retention system, using TiO\textsubscript{2} supported on the inorganic fibers. These were found to remove hazardous chemicals both bisphenol A in wastewater and indoor air pollutants, such as acetaldehyde and toluene. In addition, the void structure effect has recently been investigated and a kinetic study of TiO\textsubscript{2} containing paper on the VOC decomposition with photocatalytic activity [24-25] has been reported.

As is often the case, it is of particular interest to immobilize nanosized
TiO$_2$ particles on such supporting or anchoring materials as silica [26-27], glass bead [28], alumina [29], fiberglass [30], clay [31] or zeolite [32-33], with the ultimate aim of intact photoactivity and further into the enhancement of photocatalytic efficiency. Of various supports, zeolites have been more favorable to be used in supporting TiO$_2$, due to their unique crystal structures and uniform pores and channels, which lead to large surface area and induce synergetic adsorption affects of organic matters in turn. A great deal of previous works has been performed in synthetic zeolites, for instance, HZSM-5 [34], Y zeolite [35] and MCM-41 zeolite [36], because of relatively larger surface area and supercages in infrastructure enabling entrapment of TiO$_2$ nanoparticles.

As distinct from synthetic zeolites, however, natural zeolite provides significant advantages of cost effectiveness, natural abundance and easier accessibility. Surprisingly, though, relatively few studies have been devoted to an anchoring and incorporation of TiO$_2$ on the natural zeolite. Moreover, our previous study revealed that natural zeolite plays important roles between fibers and TiO$_2$ particles not only as an effective microparticle retention aid, but as photocatalytic activity enhancer as well in photocatalytic paper [37]. It is worthwhile, thus, to investigate the integration of natural zeolite and nanosized TiO$_2$ and to evaluate the photocatalytic activity of photocatalytic paper containing as-prepared natural zeolite-based nano TiO$_2$. Such studies have not, so far, been noticed, nor, to our knowledge, have they been researched in detail in the area of photocatalytic paper.

The present study aims to synthesize, to characterize nano TiO$_2$-natural zeolite hybrid material from sol-gel derived nano titania colloids [38]
and to develop novel photocatalytic paper using natural zeolite-based TiO₂ nanoparticles retention system in papermaking. Photocatalytic activity on VOC decomposition was assessed with gaseous toluene, and to compare photocatalytic activity, two different types of photocatalytic papers were also tested, a commercial photocatalytic non-woven paper and representative sample paper prepared in the lab, using Degussa P25 TiO₂, which is the most referred for photocatalysis. In the end, the phenomenon of improving photocatalytic property will be discussed along with the photodegradation efficiency. The physical properties of both as-prepared zeolite-based TiO₂ nanoparticles and its photocatalytic paper will also be reported.

Experimental

Materials
Titanium tetra-isopropoxide (TTIP 99%), ACS reagent grade 2-propanol and hydrochloric acid (HCl) were used as received from Aldrich in the preparation of sol-gel derived TiO₂ colloids. Natural zeolite (clinoptilolite, ZOBRITE™) was favorably presented by ZO mineral partners [39]. The pulp used for the photocatalytic paper was bleached softwood northern kraft pulp and as retention aids in papermaking, cationic starch and cationic polyacrylamide (C-PAM, Core Shell 61607; NALCO) were used in a natural zeolite microparticle system. Nanosized P25 TiO₂ (Degussa, 22 nm, 50 m²/g, 70% anatase and 30% rutile), which is the most commonly referred photocatalytic material, was employed in comparative specimen as a photocatalysis agent. Non-woven photocatalytic paper was purchased from Ahlstrom (France, BR 1048-075, 75g/m²).
Combination of TiO$_2$ and natural zeolite

A few nanometers size of TiO$_2$ colloidal nanoparticles were prepared thorough a sol-gel synthetic route in which acid catalyzed hydrolysis of titanium tetra-isopropoxide dissolved in 2-propanol was carried out. Briefly, in a typical synthesis of zeolite-based TiO$_2$ photocatalyst [38], 10 ml of 0.5 M TTIP solution in 2-propanol was added slowly dropwise to 2 ml of 0.1M HCl in 88 ml of 2-propanol under vigorous stirring at 0°C and kept stirring for 4-6 hrs to further peptization, thereby obtained particle size in a transparent TiO$_2$ sol was 2-3 nm on an average (Figure 5.1(A)). Natural zeolite was subsequently mixed thoroughly with as-prepared titania sol by stirring. The solvent was removed completely by evaporation. TiO$_2$ impregnated natural zeolite was then collected and dried at 110°C followed by post-calcination at 300°C to 800°C to induce the crystallinity of TiO$_2$ on zeolite. TiO$_2$ contents in the final forms were adjusted to be in the same ratio of when zeolite is used in microparticle filler retention system in the papermaking technique [37]. Specifically, its corresponding ratio was 5TiO$_2$/1Natural Zeolite, designated here afterwards 5T/NZ, 3T/NZ and 1T/NZ were additionally prepared for comparison.

Preparation of photocatalytic paper

Photocatalytic papers of varied TiO$_2$ photocatalyst with approximate 100 g/m$^2$ of basis weight were prepared according to Technical Association of the Pulp and Paper Industry (TAPPI) test methods T 205 [40]. The pulp was mechanically refined to a Canadian Standard Freeness (CSF) of approximately 430 ml according to TAPPI test methods T 227 [41] and T 248
prior to blending with other materials. As-prepared zeolite-based TiO$_2$ was added to the pulp suspension with stirring followed by adding cationic starch and cationic polyacrylamide (C-PAM) as retention aids. In the event of P25 containing paper, natural zeolite was combined with the pulp suspension at the last step of dosing. The addition level of each retention aid was 10% photocatalyst, 0.5% cationic starch, 0.1% C-PAM and in case of need, 2% natural zeolite in that order versus 0.3% pulp consistency (3 g dry pulp/L). All handsheets were uniformly formed on a 200 wire mesh in a standard handsheet forming machine and dried under standard conditions given in TAPPI T 402 [43] for at least 24 hrs before it was used for the photocatalysis.

Characterization

Photocatalytic materials and their handsheets prepared in this study were meticulously characterized with an X-ray diffractometer (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM). The X-ray diffraction (XRD) analyses was carried out using a Diano X-ray Diffractometer at room temperature using 20 Kw Cu-K$_\alpha$ radiation ($\lambda=0.15418$ nm) to survey the crystal structures and integrity of raw natural zeolite and TiO$_2$ nanoparticles. All peaks were identified using MDI Jade 5.0 software (Materials Data Inc. USA). The morphology and accurate size of TiO$_2$ loaded natural zeolite was obtained with TEM (JEOL JEM-1230) and three typical regions of each sample were taken. The surface morphology of zeolite-based TiO$_2$ paper was observed by SEM (Akashi ISI-DS 130) after gold sputtering on the specimen.
Evaluation of photocatalytic activity

To assess the photocatalytic performance of the handmade photocatalytic papers, toluene was chosen for this study as a model compound among various indoor VOC chemicals. Photocatalytic decomposition of gas-phase toluene was carried out in a 1L glass photoreactor under UV light irradiation (EIKO blacklight lamp, 4W, λ=365nm) with a circular photocatalyst handsheet (11.29cm in diameter). For the quantitative analysis of varying toluene concentration through the entire experimental time, regardless of UV irradiation, gas samples were withdrawn from a sampling port attached to the reactor and injected into the Gas Chromatograph (GC, SRI 8610C) equipped with a Flame Ionization Detector (FID) and a 30m x 0.25 mm fused silica capillary column (Quadrex Corp.). All samples were tested three times to verify the photodegradation effect and the results were within 5% of standard deviations.

Results and Discussion

Characterization of zeolite-based TiO₂

Figure 8.1 shows the XRD patterns of TiO₂-supported natural zeolite annealed at different temperatures ranging from 300°C to 800°C in order to investigate crystal structural changes. Diffraction peaks were identified apparently using XRD patterns processing software and it is obviously observed that the TiO₂ crystalline phase is maintained clearly through annealing temperatures, without phase transition from anatase to rutile, even after heating to 800°C. One of the outstanding features observed in XRD results is that zeolite structure had not been damaged and isolated from TiO₂
crystallization indicating that as-prepared colloidal TiO\textsubscript{2} nanoparticles were effectively loaded to natural zeolite and well-combined into thermally stable zeolite-based TiO\textsubscript{2}. The crystal size of anatase TiO\textsubscript{2} over natural zeolite was estimated to 13nm based on the FWHM (full width at half maximum intensity).

Figure 8.2 gives the TEM images of zeolite-based TiO\textsubscript{2} nanoparticles. Three different samples were imaged at 300,000~500,000X magnification. As seen in Figure 8.2(A), a myriad of colloidal nanoparticles were loaded onto a mostly zeolite surface due to its smaller pore size than TiO\textsubscript{2} colloids, namely, natural zeolite has generally 0.4-0.7 nm of pore size [44] while as-prepared TiO\textsubscript{2} colloidal nanoparticles were about 2-3 nm. Figure 8.2(B) and (C) displays distinctly different sizes of grains as the form of zeolite surrounded by TiO\textsubscript{2} implying TiO\textsubscript{2} nanoparticles were gradually evolved from amorphous TiO\textsubscript{2} on the surface of zeolite. It is also observed that TiO\textsubscript{2} particles crystallized on zeolite are decidedly different in their size; specifically it appears to be approximately 10 nm at 600°C calcination in Figure 8.2(B), where as the larger particles shown in Figure 8.2(C) are estimated to be about 15 nm in diameter, which is consistent with the single particle size calculated from X-ray diffraction peaks in Figure 8.1. It is, therefore, evident that zeolite provides sufficient support, not only to hold tightly TiO\textsubscript{2} nanoparticles, but also to function as adsorption sites enabling an increase in photodegradation efficiency for organic materials.
Figure 8.1. XRD patterns of natural zeolite-based TiO$_2$ with varying calcination temperature.
Figure 8.2. Representative TEM images of TiO$_2$ nanoparticles on natural zeolite at different calcination temperature; (A) no calcination, (B) 600 °C and (C) 800 °C, scale bar = 50nm.
Morphology of photocatalytic paper

The surface morphology of photocatalytic papers was observed by scanning electron microscopy (SEM) and images are shown in Figure 8.3. One commercial and two lab-made photocatalytic papers using P25 TiO₂ and zeolite-based TiO₂ were tested with a blank sample, which contains neither TiO₂ nor zeolite. Fine particles were well-dispersed over the fibers and the pulps, except for the Ahlstrom sample shown in Figure 8.3(D), form highly dense fiber network structures, resulting from well-fibrillated internally and flexible fibers. Zeolite-based TiO₂ paper presents the most uniformly arranged microvoids in the fiber matrix, whereas the Ahlstrom sample has a somewhat loose configuration and it was found to contain many large pores between its non-woven fibers.

The upper images in each photograph in Figure 8.3 were to identify particles retained on the fibers within the microvoids. Although seen in partial agglomerates of particles, it is apparent that TiO₂-based particles are fairly attached to the inner microvoid fibers. In considering that the performance of TiO₂ paper is positively affected by the void structure [25], it makes possible the better photocatalytic performance in the zeolite-based TiO₂ paper, which is composed of properly distributed microvoids and confined zeolite-TiO₂ powders inside of voids.
Figure 8.3. SEM images of photocatalytic papers; (A) blank sheet, (B) P25 TiO$_2$/natural zeolite sheet, (C) natural zeolite-based nano TiO$_2$ paper and (D) Ahlstrom sample.
Evaluation of photocatalytic activity

Figure 8.4 illustrates the photodecomposition performance of photocatalytic papers prepared using zeolite-based TiO$_2$ synthesized with varying TiO$_2$ weight contents in a typical microparticle retention system. The concentration of gaseous toluene was 73.1 ppm and a constant specific time was given to allow initial adsorption, which occurred commonly after injection of toluene into the reactor. After it leveled off, photocatalysis was subsequently performed under UV irradiation for 5 hrs. To exclude the effect of adsorption without UV and oxidation in bulk by UV, both of blank and adsorption test were carried out prior to photocatalytic activity and the results are shown with photocatalysis in Figure 8.4.

As seen in the adsorption profile, toluene adsorbed steadily for almost 4hrs by natural zeolite followed by a period of stabilization of residual toluene. The last adsorption efficiency was about 30% of initial toluene and it seems reasonable to assume that it may happen mostly by zeolite pores in the layered fiber matrix and will effectively contribute to assist the photocatalytic reaction. On the photocatalytic handsheets, toluene was decomposed continuously during the entire UV irradiation time in both samples made from different contents of TiO$_2$ over zeolite. Residual toluene is decreasing progressively with a slow decomposition rate in 1TiO$_2$/natural zeolite sheet, while toluene is removed more rapidly at both 3TiO$_2$/NZ and 5TiO$_2$/NZ with small gap between those TiO$_2$ sheets and efficiency achieved was almost 95%, which is seen due to the repetition of adsorption by zeolite and photodecomposition of adsorbate by TiO$_2$ nanoparticles when the photocatalytic sheets were under UV irradiation.
As a comparison, one commercial and one hand made photocatalytic paper using Degussa P25 TiO₂ were evaluated for photodecomposition of toluene and the results are shown in Figure 8.5. It is observed that the immediate decrease in residual toluene with the Ahlstrom sample at the first point of examination. This phenomenon is caused probably by the mutual effect of its highly spotted macrovoids, as seen in Figure 8.3, and high adsorption capacity of SiO₂ used in this photocatalytic paper as a binder with TiO₂ and non-woven fibers. In spite of a striking adsorption property, however, it showed quite poor photocatalytic performance with regard to only photodegradation effect under UV, to be exact, only about 20% of toluene that disappeared totally was by photocatalysis activated by UV. As for photocatalysis itself, it also was interesting to observe that the other
samples made using a different type of TiO$_2$ exhibited a better capability to photodecompose the toluene, ostensibly, even though the commercial one shows higher removal efficiency than that of P25 TiO$_2$ paper. However, a remarkable fact is that zeolite-based TiO$_2$ papers display steep removal profiles, indicating conspicuously high photocatalytic activity and, in this regard, pre-loaded TiO$_2$ on zeolite is much more effective than when TiO$_2$ is used separately in papermaking with zeolite. These results are presumably attributed to multiple synergy effects with proper microvoids made in fiber-fiber connections, anatase-crystallized TiO$_2$ and zeolite, more exactly, paper detains the contaminants within the microvoids and zeolite subsequently traps the organic materials and also suppress the recombination of electron-hole pairs on the TiO$_2$ surface [45], thereby enhancing the photocatalytic activity.

![Figure 8.5](image.png)

Figure 8.5. Comparison of toluene photodegradation by different types of photocatalytic papers.
Conclusion

Nanosized TiO$_2$-supported natural zeolite photocatalytic papers were prepared using a microparticle retention system, with cationic starch and cationic polyacrylamide in papermaking. TiO$_2$ loaded on zeolite was well-matured from sol-gel derived colloids to about 10-13 nm size of anatase crystalline phase at the surface of zeolite. Fibers formed a closely-packed network, creating microvoids, and zeolite-based TiO$_2$ particles were attached on the web of fibers. As with the photocatalytic performance, photocatalytic paper using pre-synthesized zeolite-nano TiO$_2$ was definitely superior to the others in toluene removal, which were employed for a comparison including Degussa P25 TiO$_2$ and Ahlstrom photocatalytic paper as representative selections of current commercially available active TiO$_2$ and photocatalytic paper, respectively. It was noteworthy that photocatalytic paper, based on zeolite-TiO$_2$ hybrid materials, achieves the desired impact of robust photocatalytic efficiency, due to the reciprocal effect with order of confinement of organic contaminant in microvoids between fiber networks, its further adsorption on zeolite and subsequent photodecomposition of adsorbate by TiO$_2$ nanoparticles. Notably, the results presented in this study have offered unique insights into the novel photocatalytic paper, which has sufficient photocatalytic potential to completely remove toxins, and microorganism as well.

References


[39] ZO Minerals Partners, LTD, San Antonio, Texas 78205

[40] TAPPI test method T 205 sp-02, Forming handsheets for physical tests of pulp

[41] TAPPI test method T 227 om-99, Freeness of pulp (Canadian Standard Method)

[42] TAPPI test method T 248 sp-00, Laboratory beating of pulp (PFI mill method)

[43] TAPPI test method T402 sp-98, Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products


CHAPTER IX

CONCLUSION

Paper I: The synthetic characteristics of nanosized TiO$_2$ have been studied from sol-gel derived colloidal nanoparticles prepared through the experimental design approach. A few nanometer size of colloidal samples, which are in the range of 2.5 nm to 14.3 nm, determined predominantly by media temperature, were synthesized followed by annealing at varied temperatures. The evolution of crystalline phases and growth showed different-behavior sequences with different primary size of colloidal nanoparticles and it was confirmed that varying primitive properties of TiO$_2$ colloidal particles has an impact on the behavior of the crystalline phase transition and coarsening mechanisms as well. The photocatalytic activity of the selected as-prepared TiO$_2$ nanoparticles, which are comprised of only anatase phase, was more potent compared to that of Degussa P25 TiO$_2$ in toluene decomposition on a paper substrate.

Paper II: We present here the results of measurements of optical properties and photocatalytic activity that allow us to optimize the effect of polycrystalline phases of TiO$_2$ nanoparticles from the point of view of principal crystal structures, anatase and rutile. Six different fractions of crystal structure of TiO$_2$, which are in the range of 0.7 anatase: 0.3 rutile to only rutile phase, were prepared from P25 Degussa TiO$_2$ by means of heat treatment at 500$^\circ$C-800$^\circ$C. For the optical properties, opacity, brightness and CIEL*a*b* values were tested and 0.71 rutile/0.29 anatase phase composition
of TiO₂ was definitely superior to the others, even though pure rutile has the higher refractive index. The photocatalytic activity of the as-modulated TiO₂ nanoparticles was gradually decreased along with decreasing contents of anatase phase and photoactivity dropped largely from beyond 0.48 rutile ratio in toluene decomposition. Accordingly, it is obviously shown that there is an optimal range of anatase and rutile crystalline phases that possesses both better optical properties and photocatalytic activity. Consequently, it makes practically possible an optimal range of TiO₂ phase fraction in the range of 0.48 rutile:0.52 anatase and 0.71 rutile:0.29 anatase.

Paper III: Photocatalytic paper from nanosized TiO₂ was prepared using a natural zeolite microparticle retention system in papermaking and was investigated for VOC removal by prototype photocatalytic sheets. The retention of TiO₂ nanoparticles was outstandingly improved by addition of natural zeolite and, according to analysis of the factorial experimental design, natural zeolite was shown to be the primary main effect factor affecting retention in paper stock and is vigorously interactive with sequential additives of C-PAM and cationic starch. With the latent capability to adsorb contaminant due to natural zeolite, as-prepared photocatalytic papers were very effective in removing gaseous toluene, which is one of main indoor pollutants, and its ultimate removal efficiency was about 87%. Therefore, it should be pointed out that natural zeolite makes possible improving the retention of TiO₂ nanoparticles as both a microparticle retention aid and supporter, as well as enhancing the photocatalytic performance resulting from capturing the pollutant temporarily and photodecomposition under UV.
In conclusion, the TiO$_2$ photocatalytic paper can be effectively fabricated with natural zeolite and it possesses high photodecomposition ability for organic contaminants.

Paper IV: Nanosized TiO$_2$-supported natural zeolite photocatalytic papers were prepared using a microparticle retention system, with cationic starch and cationic polyacrylamide in papermaking. TiO$_2$ loaded on zeolite was well-matured from sol-gel derived colloids to about 10-13 nm size of anatase crystalline phase at the surface of zeolite. Fibers formed a closely-packed network, creating microvoids, and zeolite-based TiO$_2$ particles were attached dispersively on the web of fibers. As with the photocatalytic performance, photocatalytic paper using pre-synthesized zeolite-nano TiO$_2$ was definitely superior to the others in toluene removal, which were employed for a comparison including Degussa P25 TiO$_2$ and Ahlstrom photocatalytic paper as representative selections of currently commercially available active TiO$_2$ and photocatalytic paper, respectively. It was noteworthy that photocatalytic paper, based on zeolite-TiO$_2$ hybrid materials, achieves the desired impact of robust photocatalytic efficiency, due to the reciprocal effect with order of confinement of organic contaminant in microvoids between fiber networks, its further adsorption on zeolite and subsequent photodecomposition of adsorbate by TiO$_2$ nanoparticles. Notably, the results presented in this study have offered unique insights into the novel photocatalytic paper, which has sufficient photocatalytic potential to remove completely toxins, and favorably, microorganism as well.